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DENSITY FUNCTIONAL THEORY BASED INVESTIGATION OF NANOMATERIALS FOR THE DETECTION OF TOXIC GASES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY
by

ANURAG BHANDARI
(2K19/PHDAP/502)

Under the Supervision of

PROF. RISHU CHAUJAR

Professor

Department of Applied Physics
Delhi Technological University

PROF. NITIN K. PURI

Professor

Department of Applied Physics
Delhi Technological University



Department of Applied Physics

DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)

Shahabad Daulatpur, Main Bawana Road, Delhi-110042, India

MARCH, 2026

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Dedication

This dissertation is dedicated to my family and supervisors.

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First and foremost, I express my sincere gratitude to the Almighty for granting me the strength, patience, and perseverance to complete my thesis. I would like to sincerely thank my supervisors, **Prof. Rishu Chaujar** and **Prof. Nitin K. Puri**, as well as my research collaborator **Dr Piyush Dua**, for their constant guidance, encouragement, and support throughout my research. Their valuable suggestions, constructive feedback, and continuous motivation have played a significant role in shaping this thesis and bringing it to completion. I am truly grateful for their mentorship. I am also thankful to **Prof. Prateek Sharma**, Hon'ble Vice-Chancellor of DTU, for providing a supportive research environment and necessary facilities. I would also like to extend my gratitude to **Prof. Rinku Sharma**, Dean (Academic-PG), and **Prof. Vinod Singh**, Head of the Department of Applied Physics, as well as to all the faculty and staff members, for their cooperation and support during my research tenure. I would like to acknowledge my seniors, **Dr. Kamal Arora**, **Dr. Kanika Sharma**, **Dr. Ritika Khatri**, **Dr. Nikita Jain**, **Dr. Saroj Kumar Jha**, and **Mr. Sandeep Sarpal** as well as my fellow research lab mates **Mrs. Kajal Sharma**, **Mrs. Ayushi Lamba**, **Mrs. Shikha Singh**, **Mrs. Anshul**, **Mrs. Shubhda**, **Mrs. Anu**, **Dr. Yash Pathak**, **Dr. Sunil Kumar**, **Mr. Ashish Chopra**, **Mr. Bipin Misra**, **Mr. Laxmikant**, **Mr. Vishwas Kumar**, **Mr. Abhishek Kumar** and **Mr. Hemant Arora**, for their guidance, encouragement, cooperation, helpful discussions, and support throughout this journey. I would also like to express my deep respect and gratitude to my parents, **Mr G.S. Bhandari** and **Mrs. Vijna Bhandari**, whose love, sacrifices, and blessings have always guided me during the challenging. I am also thankful to my brothers, **Er. Abhishek Bhandari**, **Dr. Akshay Kumar Panwar**, **Er. Anand Panwar**, and **Er. Alok Panwar** for their constant support, encouragement, and belief in me. Lastly, I thank my nephews, **Aarav and Aayansh** as well as my niece **Aviyaa and Ananta**, whose presence brought joy and positivity during this journey.

Anurag Bhandari

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I, **Mr. Anurag Bhandari (2K19/PHDAP/502)**, hereby declare that the work which is being presented in the thesis entitled **"Density Functional Theory based investigation of nanomaterials for the detection of Toxic Gases"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy, submitted in the Department of Applied Physics, Delhi Technological University is an authentic record of my own work carried out during the period from **January 2020 to March 2026** under the supervision of **Prof. Rishu Chaujar & Prof. Nitin K. Puri, Department of Applied Physics, Delhi Technological University**. The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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Prof. Rishu Chaujar

(Supervisor)

Professor

Department of Applied Physic

Delhi Technological University

Delhi-110042, India

Prof. Nitin K. Puri

(Joint-Supervisor)

Professor

Department of Applied Physics

Delhi Technological University

Delhi-110042, India

Prof. Vinod Singh

HOD &DRC Chairman

Professor

Department of Applied Physics

Delhi Technological University

Delhi-110042, India

Date:

ABSTRACT

Density Functional Theory-based investigation of nanomaterials for the detection of Toxic Gases

Air pollution caused by the release of hazardous toxic gases such as C_2H_4 , CH_4 , CO_2 , CO , and H_2 during thermal runaway in lithium-ion batteries, along with industrial emissions like $COCl_2$ and $CNCl$, poses a significant threat to human health and environmental safety. The effective detection and monitoring of these gases require the development of highly sensitive, selective, and reliable gas sensing technologies capable of real-time operation. In this work, a comprehensive investigation of chemoresistive gas sensors is presented, with a particular focus on two-dimensional (2D) materials as promising candidates for next-generation sensing applications. These materials exhibit unique advantages, including a high surface-to-volume ratio, tunable electronic properties, and abundant active sites, which enhance gas adsorption and sensing performance. The study begins with an overview of the fundamental working principles of chemoresistive gas sensors, which rely on gas adsorption, charge transfer, and modulation of electrical conductivity in n-type and p-type semiconductors. Various 2D materials, including graphene, transition metal dichalcogenides, $g-C_3N_4$, MXenes, and hexagonal boron nitride (hBN), are systematically analysed in terms of their sensing mechanisms, advantages, and limitations. Strategies such as elemental doping, surface functionalization, and substrate engineering are highlighted as effective approaches to improve sensitivity, selectivity, and response dynamics. To gain atomistic insights into gas-surface interactions, Density Functional Theory (DFT) is employed as the primary computational framework. The theoretical foundation of DFT, based on the Hohenberg-Kohn theorems and the Kohn-Sham formalism, enables accurate modelling of many-electron systems using electron density as the central variable. The role of exchange-correlation functionals and their limitations, particularly in predicting band gaps, are also discussed, establishing the basis for first-principles calculations carried out in this work. Subsequently, DFT-based investigations are conducted to study the adsorption behaviour of toxic gases on pristine and Cu-modified hBN systems. For $COCl_2$ detection, pristine hBN exhibits weak physisorption with low adsorption energy and poor recovery characteristics. However, Cu incorporation through substitutional doping and surface adsorption significantly enhances gas interaction, leading to chemisorption and improved sensing performance. Electronic structure analyses, including Density of States (DOS), Hirshfeld charge, charge density difference, Electron Localization

Function (ELF), and Reduced Density Gradient (RDG), confirm strong charge transfer, band gap reduction, and enhanced conductivity. Similarly, for CNCl gas, Cu decoration improves adsorption strength and induces notable changes in electronic properties, including a significant work function variation of 31.54%, indicating high sensor sensitivity. Furthermore, the adsorption of lithium-ion battery thermal runaway gases (C_2H_4 , CO, CO_2 , H_2 , and CH_4) is investigated. While pristine hBN shows weak physisorption, Cu-doped hBN exhibits strong chemisorption, enhanced charge transfer, and significant band gap modulation, confirming its superior sensing performance. RDG analysis reveals the transition from weak van der Waals interactions in pristine systems to strong attractive interactions in Cu-doped configurations. Recovery time analysis further supports the practical applicability of these materials. In addition, the electronic properties of Cu-doped and Cu-adsorbed MoS_2 nanowires are examined. Substitutional doping is found to induce significant charge redistribution, improve electrical conductivity, and enhance electron emission characteristics, as evidenced by work function variation and Bader charge analysis. These results demonstrate the effectiveness of doping in tailoring material properties for sensing and nanoelectronics applications. Overall, we conclude from our present research work that Cu-functionalized 2D materials, particularly hBN and MoS_2 -based systems, as highly promising candidates for efficient, low-cost, and high-performance gas sensors. The integration of DFT-based insights with material engineering strategies provides a robust pathway for the design of advanced sensing devices aimed at environmental monitoring, industrial safety, and early detection of hazardous gases, contributing to improved public health and sustainable development.

LIST OF PUBLICATIONS

Publications included in this thesis:

1. Anurag Bhandari, Nitin K. Puri, and Piyush Dua. "Adsorption of Cyanogen Chloride Gas Onto the Pristine and Copper-Decorated hBN Monolayer: A Comparative DFT Study." *IEEE Sensors Journal* (2025).[Impact factor-4.5]
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LIST OF INTERNATIONAL CONFERENCES

Conference Contributions-Poster:

- 1) Presented a Poster paper entitled "Adsorption of Cyanogen chloride onto pristine hBN and Cudecorated hBN: A DFT study" in the International Conference On Atomic, Molecular, Material, Nano and Optical Physics with Applications (ICAMNOP) organized by the Department of Applied Physics, Delhi Technological University, Delhi, India from 20th-22th Dec,2023.
- 2) Presented a Poster paper entitled "Exploring Cu-decorated hBN as a multifunctional gas sensor with optical and magnetic sensing capabilities: A DFT study" in the 3rd International Conference On Advances in Nanomaterials and Devices for Energy and Environment(CANDEE-2024) organized by the Department of Engineering Sciences, Atal Bihari Vajpayee Indian Institute of Information Technology and Management Gwalior from 3-5 Dec,2024.

- 3) Oral presentation entitled **“Investigating the interaction of phosgene gas with pristine and Cu functionalized hBN : A DFT approach”** in the **International Conference On Digital Resilience For Ecological Advancement , Management and Sustainability(DREAMS-2025)** organized by DBS Global University, Dehradun from 22-23-Aug,2025.
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TABLE OF CONTENTS

Title	Page No.
Acknowledgement	4
Candidate's Declaration	5
Certificate by the Supervisor	6
Abstract	7-8
List of Publications	9
List of International Conferences	9
List of Figures	15
List of Tables	18
Chapter 1: Introduction	22
1.1 Introduction	23
1.1.1 Chemiresistor Gas Sensors and Sensing Mechanism	27
1.1.2 Adsorption of Oxygen Gas Molecules	27
1.1.3 Modulation of Schottky Barrier	29
1.2 2D Materials-Based Chemiresistive Gas Sensor	31
1.3 Different Types of 2D Based Chemiresistive Gas Sensor	34
1.3.1 Graphene-Based Chemiresistive Gas Sensor	34
1.3.2 Reduced Graphene Oxide (RGO) Based Chemiresistive Gas Sensor	35
1.4 Transition Metal Dichalcogenide (TMDs) Based Chemiresistive Gas Sensor	36
1.4.1 MoS ₂ Based Chemiresistive Gas Sensor	36
1.4.2 SnS ₂ Based Chemiresistive Gas Sensor	37
1.4.3 WS ₂ Based Chemiresistive Gas Sensor	37
1.4.4 Other TMDs Based Chemiresistive Gas Sensor	38
1.5 Other 2D Materials Based Chemiresistive Gas Sensor	38
1.5.1 Black Phosphorene Based Chemiresistive Gas Sensor	38
1.5.2 g-C ₃ N ₄ Based Chemiresistive Gas Sensor	39
1.5.3 MXenes Based Chemiresistive Gas Sensor	39
1.6 Hexagonal Boron Nitride	39
2.1 Sensing Mechanism of hBN-Based Gas Sensors	41
2.2 Strategies to Overcome Challenges Associated with hBN-Based Gas Sensors	43
2.4 Role of Density Functional Theory in the Field of Gas Sensing	45
3. Research Objectives	46
References	50
Chapter 2: Computational Methodology	62

2.1	Introduction.....	63
2.1.1	Hohenberg–Kohn Theorem	65
2.1.2	Summary of Hohenberg–Kohn Theorem.....	67
2.2	Thomas–Fermi Approximation.....	69
2.2.1	Derivation of the Kinetic Energy for the Thomas–Fermi Model	70
2.3	Exchange–Correlation Energy	71
2.3.1	Different Perspectives of Correlation Energy.....	72
2.4	Kohn–Sham Equation	74
2.4.1	Derivation of Kohn–Sham Equation.....	74
2.5	The Kohn–Sham Eigenvalues.....	76
2.5.1	Band Gap Problem.....	78
2.6	Hartree, Hartree–Fock and Dyson Equation.....	79
2.6.1	Basis Functions	80
2.7	Pseudopotential.....	83
2.8	Making DFT Practical: Approximations	85
2.9	Limitation of the DFT.....	90
	References.....	91

Chapter 3: Adsorption Mechanism of Phosgene Gas onto Pristine hBN and Cu-Decorated hBN Using DFT 96

3.1	Introduction.....	97
3.2	Computational Details	99
3.3	Results and Discussions.....	100
3.3.1	Electronic and Structural Properties Analysis of the Pristine hBN	100
3.3.2	Adsorption of COCl ₂ Gas onto the Pristine hBN Monolayer	101
3.3.3	Structural and Electronic Properties Analysis of the Cu-Doped hBN Monolayer	103
3.3.4	Adsorption of COCl ₂ onto the Cu-Doped hBN Monolayer.....	105
3.3.5	Structure and Electronic Properties Analysis of the Cu-hBN.....	107
3.3.6	Adsorption of COCl ₂ Gas onto the Cu-hBN.....	108
3.3.7	Comparison of the Adsorption Energies with Other Various Systems.....	110
3.3.8	Charge Density Difference and Hirshfeld Charge Analysis	110
3.3.9	Non-Covalent Interaction Analysis.....	112
3.3.10	Electron Localization Function Analysis (ELF).....	115
3.3.11	Frontier Molecular Orbital Analysis.....	116
3.3.12	Global Indices of Reactivity	118
3.3.13	Sensitivity Analysis	120
3.3.14	Recovery Time Analysis.....	122
	References.....	125

Chapter 4: Adsorption of Cyanogen Chloride Gas onto the Pristine and Copper-Decorated hBN Monolayer..... 131

4.1	Introduction.....	132
4.2	Results and Discussions.....	134
4.2.1	Adsorption of CNCl Gas onto Pristine hBN.....	134
4.2.2	Recovery Time Analysis for CNCl Gas Adsorbed onto hBN Monolayer.....	136
4.2.3	Adsorption of Cu Atom onto hBN Monolayer	137
4.2.4	Adsorption of CNCl Gas onto the Cu-Decorated hBN Monolayer	138
4.2.5	Electronic Properties Analysis of the Cu-Decorated hBN.....	140
4.2.6	Charge Density Difference Analysis	144
4.2.7	Electron Localization Function Analysis.....	145
4.2.8	Sensitivity Analysis	146
4.2.9	Work Function Analysis	147
4.2.10	Recovery Time Analysis.....	148
4.3	Conclusion	149
	References.....	150

Chapter 5: Adsorption Mechanism of Li-ion Battery Thermal Runaway Gases onto Cu-Decorated hBN Using DFT 154

5.1	Introduction.....	155
5.2	Results and Discussions.....	158
5.2.1	Adsorption of Thermal Runaway Gases onto Pristine hBN	158
5.2.2	Adsorption of Thermal Runaway Gases onto Cu-Doped hBN.....	162
5.2.3	Electronic Properties Analysis upon Adsorption onto Pristine hBN and Cu-Doped hBN	164
5.2.4	Charge Density Difference Analysis	169
5.2.5	Non-Covalent Interaction Analysis.....	172
5.2.6	Global Reactivity Descriptors.....	174
5.2.7	Sensitivity and Selectivity Analysis of hBN and Cu-Doped hBN.....	178
5.2.8	Recovery Time Analysis of Cu-Doped hBN	179
5.2.9	Comparison of Adsorption Energies, Band Gap, and Sensitivity.....	181
5.3	Conclusions.....	183
	References.....	185

Chapter 6: Effect of Substitutional Doping and Cu Adsorption on MoS₂ Nanowire 190

6.1	Introduction.....	191
6.2	Computational Details	193
6.3	Results and Discussions.....	194
6.3.1	Structure and Electronic Properties Analysis of MoS ₂ Monolayer and MoS ₂ NW	194

6.3.2 Adsorption of Cu Atom onto MoS ₂ NW	196
6.3.3 Comparison of the Calculated Adsorption Energies for Cu-MoS ₂ NW	199
6.3.4 Structure Analysis of the Cu-Doped MoS ₂ NW	199
6.3.5 Thermodynamic Stability of Cu-MoS ₂ NW and Cu-Doped MoS ₂ NW	201
6.3.6 Electron Localization Function (ELF) Analysis	202
6.3.7 Effect of Cu Adsorption on the Electronic Properties of MoS ₂ NW	204
6.3.8 Bader Charge and Electron Density Difference Analysis.....	206
6.3.9 Effect of Cu Adsorption on the Work Function of MoS ₂ NW.....	208
6.4 Conclusion	210
References.....	211
Chapter 7: Conclusions, Future Scope and Societal Impact.....	216
7.1 Summary of Research Work.....	217
7.2 Salient Features of the Thesis	220
7.3 Future Perspective.....	221
7.4 Societal Impact and Conclusions	223

LIST OF FIGURES

Figures No.	Page No.
1.1: Schematic diagram representing the components of the chemiresistive gas sensor.....	27
1.2: Schematic diagram illustrating the sensing mechanism of (a) and (d) N-type and P-type materials when exposed to air (b) and (e) when N and P-type materials are exposed to reducing gases (c) and (f) when N and P-type materials are exposed to reducing gases, respectively. ...	28
1.3: Schematic diagram representing the modulation of the Schottky barrier at (a)-(b) metal-N type interface (c) upon the exposure of the oxidizing gases (d) upon the exposure of the reducing gases at the metal-Ntype interface. Schematic diagram modulation of the Schottky barrier at (e)-(f) metal-P-type interface (g) upon the exposure of the oxidising gases (h) upon the exposure of the reducing gases at the metal-P-type interface, respectively.....	30-31
1.4: Schematic diagram illustrating various 2D materials to be used as a chemoresistive sensing material.	33
1.5: Plotted graph representing an exponential increase in the number of published hBN-based gas sensing papers over the years. This data is being taken from the Web of Science with the search keywords “hBN-based gas sensors”.	41
1.6: Plotted graph representing an exponential increase in the number of published DFT based gas sensing papers over the years. This data is being taken from the Web of Science with the search keywords “DFT based gas sensors”.	47
2.1: Schematic diagram illustrating the significance of understanding the microscopic interaction in the field of material science, modern advanced technology, biology and chemistry.....	65
2.2: Schematic diagram illustrating how the electron–electron interaction is replaced by an equivalent formulation based on electron density, which forms the central theme of DFT....	65
2.3: Schematic flow chart describing the iterative Self-Consistent Cycle (SCF) employed to solve the Kohn-Sham equations in the DFT	76
2.4: Schematic flow chart illustrating Kohn–Sham eigenvalues relation with observables	77
2.5: Schematic diagram representing the comparison of the all-electron wave function (solid line) with the pseudo wave function (black dotted line) in the Coulomb potential of the nucleus. It clearly shows that beyond cut off radius the pseudo wave function is in good agreement with the all-electron wave function.....	84
3.1: Convergence test for the (a) cut-off energy and (b) K points respectively.....	99
3.2: (a) Optimized structure of hBN monolayer with the red-coloured box representing the unit cell. The atoms in blue and pink correspond to the N and B atoms, (b) DOS, (c) PDOS, and (d) ELF plot. The red, blue, and green coloured areas correspond to high, low, and partially delocalized regions, respectively.	100
3.3: Top observation of the optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The arrows in black represent the distance from the hBN surface to the COCl ₂ gas. The red, black, and green atoms represent the O, C, and Cl elements respectively.....	102

3.4: Top observation of the optimized (a) Cu-VB-hBN and (b) Cu-VN-hBN doped systems. The atom in orange represents the Cu element.	103
3.5: (a) DOS and (b) PDOS plot upon substitutional doping of the Cu atom within the hBN respectively	105
3.6:(a) Lateral observation and (b) Top observation of the optimized C1 adsorption configuration and (c)Lateral observation and (d) Top observation of the optimized C2 adsorption configuration, respectively.....	106
3.7: (a) Lateral observation and (b) Top observation of the optimized structure upon Cu adsorption. (c)TDOS and (d) PDOS plot upon Cu adsorption onto hBN, respectively.	108
3.8: (a) Lateral observation and (b) Top observation of the optimized C1 adsorption configuration and (c)Lateral observation and (d) Top observation of the optimized C2 adsorption configuration, respectively.....	109
3.9: Charge density difference diagram for (a) A4, (b) B2, and (c) C2 configurations. The yellow and cyan colour in the CDD diagrams represents the electron accumulation and depletion regions, respectively (d) ESP map for the optimized COCl ₂ gas molecule. The blue and red colours represent the positive and negative charge sites.....	112
3.10: RDG scatter plot for the (a) A4, (c) Cu doped-hBN, (e) Cu-hBN, (g) B2, and (i) C2 adsorption configurations, respectively. Isosurfaces plot for the (b) A4, (d) Cu doped-hBN, (f) Cu-hBN, (h) B2, and (j) C2 adsorption configurations, respectively.	114-115
3.11: Bottom view of the ELF map for (a) A4, (b) B2 and (c) C2 adsorption configurations. Lateral view of the ELF map for (d) A4, (e) B2, and (f) C2 adsorption configurations, respectively.	116
3.12: HOMO and LUMO for (a) pristine hBN, (b) A4, (c) Cu-doped hBN, (d) Cu-hBN, (e) B2 and (f) C2 adsorption configurations, respectively	118
3.13: Plotted DOS for (a)A4, (b)B2, and (c) C2 adsorption configurations and plotted PDOS for (d)A4, (e)B2, and (f) C2 adsorption configurations, respectively	121
4.1: Side view of the different optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The pink, blue, black, and green atoms correspond to B, N, C, and Cl atoms.	136
4.2: (a) Optimized structures, (b) DOS and (c) PDOS of the Cu-hBN respectively.....	137
4.3: Side view of the different optimized structures (a) B1, (b) B2, and (c) B3, respectively. The orange colour corresponds to the Cu atom	139
4.4: (a) DOS and (b) PDOS plots for the CNCl-hBN system. (c) DOS and (d) PDOS plot for the CNCl-Cu-hBN system, respectively	140
4.5: RDG scatter plot for the (a) CNCl-hBN, (c)Cu-hBN, and (e) CNCl-Cu-hBN systems. Isosurfaces plot for the (b) CNCl-hBN, (d)Cu-hBN, and (f) CNCl-Cu-hBN systems, respectively	143
4.6: Charge Density difference plot (a) Top view for CNCl-hBN, (b) Top view for Cu-hBN, and (c) Side view for CNCl-hBN, (d) Side view for CNCl-Cu-hBN systems, respectively.....	144
4.7: ELF plot for (a) CNCl-hBN, (b) Cu-hBN, and (c) CNCl-Cu-hBN systems, respectively.....	145
5.1: Optimized different adsorption configurations of (a)-(d) C ₂ H ₄ , (e)-(f) CH ₄ , (g)-(j) CO, (k)-(m) CO ₂ , and (n)-(p) H ₂ gas molecules onto the pristine hBN, respectively.....	160-162

5.2: Optimized different (a)-(b) C ₂ H ₄ , (c)-(d) CO, (e)-(f) CO ₂ (g)-(h) H ₂ and (i) CH ₄ adsorption configurations onto the Cu-doped hBN respectively.....	163-165
5.3: DOS and PDOS for the (a)-(b) C ₂ H ₄ -hBN, (c)-(d) CH ₄ -hBN, (e)-(f) CO-hBN, (g)-(h) CO ₂ -hBN, (i)-(j) H ₂ -hBN, (k)-(l) C ₂ H ₄ -Cu-doped hBN, (m)-(n) CH ₄ -Cu-doped hBN, (o)-(p) CO-Cu-doped hBN, (q)-(r) CO ₂ -Cu-doped hBN, (s)-(t) H ₂ -Cu-doped hBN systems respectively.....	166-168
5.4: Charge density difference of (a) C ₂ H ₄ -hBN, (b) CH ₄ -hBN, (c) CO-hBN, (d) CO ₂ -hBN, (e) H ₂ -hBN, (f) Cu-doped hBN, (g) C ₂ H ₄ -Cu-doped hBN, (h) CH ₄ -Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO ₂ -Cu-doped hBN, (k) H ₂ -Cu-doped hBN respectively.....	171
5.5: Reduced density gradient plot for (a) C ₂ H ₄ -hBN, (b) CH ₄ -hBN, (c) CO-hBN, (d) CO ₂ -hBN, (e) H ₂ -hBN, (f) Cu-doped hBN, (g) C ₂ H ₄ -Cu-doped hBN, (h) CH ₄ -Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO ₂ -Cu-doped hBN, (k) H ₂ -Cu-doped hBN, respectively.....	173-174
5.6: Reduced density gradient isosurfaces plot corresponding to (a) C ₂ H ₄ -hBN, (b) CH ₄ -hBN, (c) CO-hBN, (d) CO ₂ -hBN, (e) H ₂ -hBN, (f) Cu-doped hBN, (g) C ₂ H ₄ -Cu-doped hBN, (h) CH ₄ -Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO ₂ -Cu-doped hBN, (k) H ₂ -Cu-doped hBN, respectively. The blue, red, and green colour schemes shown in the RDG isosurface correspond to attractive strong hydrogen bonding, repulsive steric effect, and weak vdW interaction.....	176-177
6.1: Optimized MoS ₂ monolayer and MoS ₂ NW struct Optimized (a) MoS ₂ monolayer and (b) MoS ₂ NW structure. The atoms in yellow and cyan colours represent the S and Mo atoms, respectively.....	195
6.2: Plotted (a) Band structure and (b) DOS for the MoS ₂ monolayer, respectively.....	195
6.3: DOS plot for the MoS ₂ NW. The black dotted line represents the fermi level set to zero for reference.....	195
6.4: The plotted red and blue curves represent the variation of the adsorption energy with adsorption heights for Cu adsorbed onto MoS ₂ NW at S and Mo sites, respectively.....	197
6.5: Top view of the different optimized adsorption configurations (a)-(k) at the S site and (l)-(s) at the Mo site, respectively.....	197-199
6.6: (a)Side view and (b) Top view of the optimized Cu-doped MoS ₂ NW structures.....	200
6.7: ELF plot for (a) Cu-MoS ₂ NW system and (b) Cu-doped MoS ₂ NW system, respectively. The ELF magnitude is given in a colour scheme in which red, blue, and green correspond to high electron density, low electron density, and free electrons, respectively.....	203
6.8: Calculated (a) DOS for the Cu adsorbed MoS ₂ NW. PDOS for (b) Cu, (c) Mo, and (d) S atoms, respectively. The black dotted line represents the Fermi level.....	205
6.9: Calculated (a) DOS for the Cu-doped-MoS ₂ NW. PDOS for (b) Cu, (c) S, and (d) Mo atoms, respectively.....	206
6.10: Electron density difference diagram for (a) Cu-MoS ₂ NW and (b) Cu-doped MoS ₂ NW systems. The red and blue regions indicate charge gain and charge loss regions, respectively.....	206
6.11: Calculated Bader charge distribution for the surface atoms of (a) Cu-MoS ₂ NW and (b) Cu-doped MoS ₂ NW, respectively. The red arrows represent the directions of electron transfer from the Cu atom to the MoS ₂ NW.....	208

LIST OF TABLES

Tables No.	Page No.
3.1: Calculated B-N bond lengths in Å, adsorption distances, and energies in Å and eV for the different optimized structures.	101
3.2: Calculated adsorption distance, energy, C=O, C-Cl and Cl-C bond lengths of the COCl ₂ gas for the different optimized adsorption configurations.....	105
3.3: Calculated adsorption distance, energy, C=O, C-Cl and Cl-C bond lengths of the COCl ₂ gas for the different optimized adsorption configurations.....	108
3.4: Adsorption energies reported previously for some of the various systems upon COCl ₂ adsorption.....	110
3.5: Calculated HUMO-LUMO energies, HOMO-LUMO gaps (E _g), Ionization potential (IP), electron affinity (EA), chemical potential (μ), electrophilicity (ω), chemical softness (S) and chemical hardness (η) respectively for the pristine hBN, A4, Cu-doped hBN, B2, Cu-hBN, and C2 systems respectively.....	120
3.6: Calculated recovery time for the Cu-doped hBN and Cu-hBN systems upon COCl ₂ adsorption at different temperatures under visible light and UV radiation	122
4.1: Calculated adsorption energies, heights and bond lengths for three different optimized adsorptions configurations.....	134
4.2: Calculated adsorption energies, heights, and bond lengths for three different optimized adsorption configurations.....	138
4.3: Calculated charge transfer for CNCl-hBN and CNCl-Cu-hBN adsorption configurations	145
4.4: Calculated electrical conductivity for CNCl-hBN and CNCl-Cu-hBN at different temperatures.....	146
4.5: Calculated recovery time at different temperatures for CNCl-Cu-hBN.....	148
5.1: The adsorption energy (E _{ads}), adsorption distances (D _{ads}), C-C, C-O, C-H, and H-H bond lengths upon the adsorption of C ₂ H ₄ , CH ₄ , CO, CO ₂ , and H ₂ gas molecules onto pristine hBN	160
5.2: The adsorption energy (E _{ads}), adsorption distances (D _{ads}), C-C, C-O, C-H, and H-H bond lengths upon the adsorption of C ₂ H ₄ , CH ₄ , CO, CO ₂ , and H ₂ gas molecules onto Cu-doped hBN	164
5.3: Calculated HOMO-LUMO energies, HOMO-LUMO gaps (E _g), ionization potential (IP), electron affinity (EA), chemical potential (μ), electrophilicity (ω), chemical softness (S), and chemical hardness (η) for the pristine hBN, C ₂ H ₄ -hBN, CH ₄ -hBN, CO-hBN, CO ₂ -hBN, and H ₂ -hBN, Cu-doped hBN, C ₂ H ₄ -Cu-doped hBN, CH ₄ -Cu-doped hBN, CO-Cu-doped hBN, CO ₂ -Cu-doped hBN, and H ₂ -Cu-doped hBN systems.....	177
5.4: Variation in the sensitivity of the C ₂ H ₄ -Cu-doped hBN, CH ₄ -Cu-doped hBN, CO-Cu-doped hBN, CO ₂ -Cu-doped hBN, and H ₂ -Cu-doped hBN at 300 K, 500 K, 700 K, and 900 K temperatures.....	178
5.5: Calculated recovery time for the adsorption of C ₂ H ₄ -Cu-doped hBN, CH ₄ -Cu-doped hBN, CO-Cu-doped hBN, CO ₂ -Cu-doped hBN, and H ₂ -Cu-doped hBN systems at different temperatures under visible light.....	181
5.6: Calculated recovery time for the adsorption of C ₂ H ₄ -Cu-doped hBN, CH ₄ -Cu-doped hBN, CO-Cu-doped hBN, CO ₂ -Cu-doped hBN, and H ₂ -Cu-doped hBN systems at different temperatures under UV radiation.....	181

5.7: Comparison of the adsorption energies, change in the band gap, and sensitivity at 300 K for the C ₂ H ₄ -Cu-doped hBN, CH ₄ -Cu-doped hBN, CO-Cu-doped hBN, CO ₂ -Cu-doped hBN, and H ₂ -Cu-doped hBN systems with respect to previously reported theoretical studies.....	182-183
6.1: The calculated adsorption energies and heights for the Cu atom adsorbed onto MoS ₂ NW at Mo and S sites	196
6.2: Comparison of the calculated adsorption energies for the Cu-MoS ₂ NW with previously reported adsorption energies for TM adsorbed onto various 2D materials	199
6.3: Reported cohesive energies for the various 2D materials and 1D materials along with MoS ₂ NW, Cu-doped MoS ₂ NW and Cu-MoS ₂ NW	201-202
6.4: Reported cohesive energies for the various 1D materials along with MoS ₂ NW, Cu-doped MoS ₂ NW and Cu-MoS ₂ NW.....	202

LIST OF ABBREVIATIONS

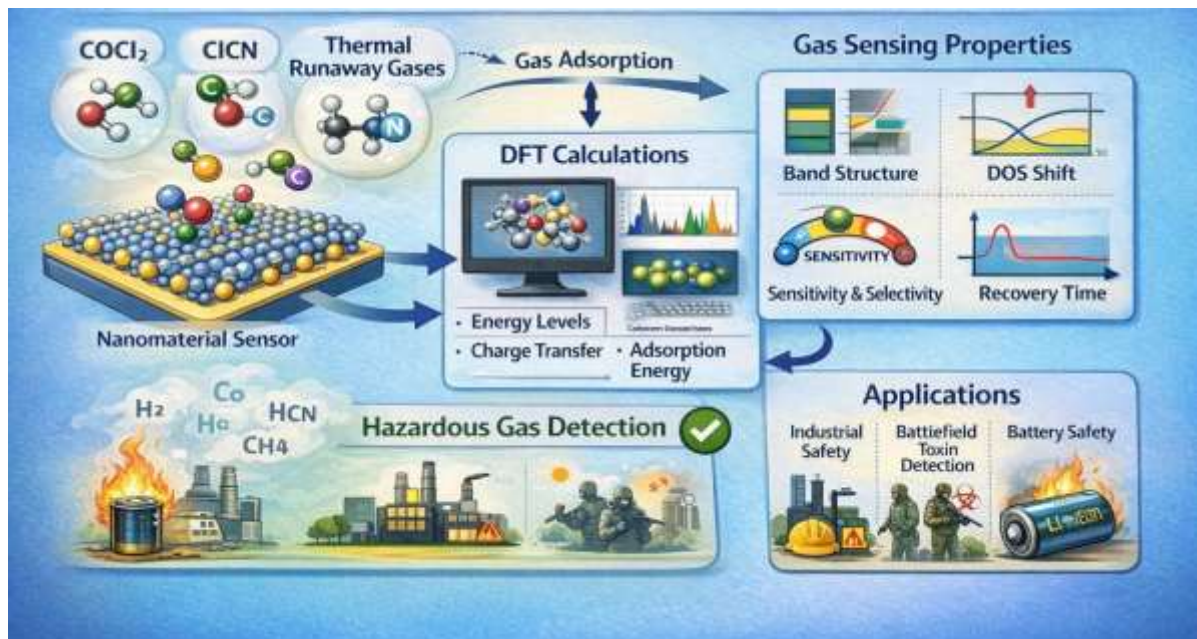
Abbreviation	Full Form
1D	One-Dimensional
2D	Two-Dimensional
BZ	Brillouin Zone
CBM	Conduction Band Minimum
CDD	Charge Density Difference
CNCl	Cyanogen Chloride
COCl ₂	Phosgene
CVD	Chemical Vapour Deposition
DFT	Density Functional Theory
DMC	Dimethyl Carbonate
DOS	Density of States
DZP	Double Zeta Polarized
EA	Electron Affinity
EC	Ethylene Carbonate
ELF	Electron Localization Function
FMO	Frontier Molecular Orbital
GEA	Gradient Exchange Approximation
GGA	Generalized Gradient Approximation
GO	Graphene Oxide
GTO	Gaussian Type Orbitals
hBN	Hexagonal Boron Nitride
HF	Hartree–Fock
HOMO	Highest Occupied Molecular Orbital
IOT	Internet of Things
IP	Ionization Potential
LCAO	Linear Combination of Atomic Orbitals
LCO	Lithium Cobalt Oxide
LDA	Local Density Approximation
LIB	Lithium-Ion Battery
LMO	Lithium Manganese Oxide
LUMO	Lowest Unoccupied Molecular Orbital
MoS ₂	Molybdenum Disulfide
NCM	Lithium Nickel Manganese Cobalt Oxide
NCI	Non-Covalent Interaction
NW	Nanowire
PAW	Projector Augmented Wave
PBE	Perdew–Burke–Ernzerhof

PC	Propylene Carbonate
PDOS	Partial Density of States
PVDF	Polyvinylidene Fluoride
QMC	Quantum Monte Carlo
RDG	Reduced Density Gradient
RGO	Reduced Graphene Oxide
SCF	Self-Consistent Field
SEI	Solid Electrolyte Interphase
SnS₂	Tin Disulfide
STM	Scanning Tunneling Microscopy
STO	Slater Type Orbitals
TDOS	Total Density of States
TM	Transition Metal
TMDs	Transition Metal Dichalcogenides
UV	Ultraviolet
VASP	Vienna Ab initio Simulation Package
VBM	Valence Band Maximum
vdW	van der Waals
WS₂	Tungsten Disulfide
XC	Exchange–Correlation

 58

Chapter1

Introduction



Air pollution due to the release of hazardous toxic gases such as C_2H_4 , CH_4 , CO_2 , CO , H_2 during the thermal runaway condition in Li-ion batteries, $COCl_2$ and $CNCl$ from the industrial activities has posed a serious threat to human health and the environment. Effective mitigation of this problem requires the development of highly sensitive, selective, and reliable gas-sensing technologies capable of real-time monitoring. This chapter provides a comprehensive overview of chemoresistive gas sensors, emphasising their working principles based on gas adsorption, charge transfer, and conductivity modulation in n-type and p-type semiconductors. Special attention is given to two-dimensional (2D) materials, due to their large surface-to-volume ratio, tunable electronic properties, and abundant active sites, which make them promising candidates for next-generation gas sensors. The sensing mechanisms, advantages, and limitations of various 2D materials—including graphene, reduced graphene oxide, transition metal dichalcogenides, black phosphorene, $g-C_3N_4$, MXene, metal–organic frameworks, and hexagonal boron nitride—are systematically discussed. Strategies such as elemental doping, surface functionalization, and substrate engineering are highlighted as effective routes to enhance sensor sensitivity, selectivity, and response dynamics. Finally, the chapter outlines research objectives that integrate with DFT calculations to elucidate gas adsorption mechanisms, optimize sensing performance, and guide the design of high-performance, stable, and practical gas sensors for the detection of toxic gases.

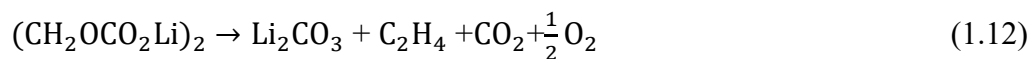
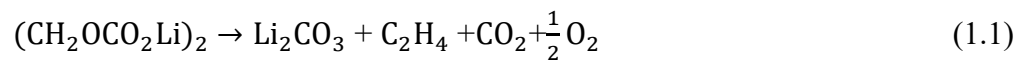
1. INTRODUCTION

With the rapid expansion of modern energy storage technologies, there has been a significant increase in the demand for efficient and reliable energy storage systems.[1-4] In this regard, Li-ion battery has emerged as a potential competitive energy solution for the highly growing sector like electric vehicles[5, 6], portable electronics[7, 8] and smart grids[9, 10] due to their high energy density[11-13], long cycling time[14, 15] and lack of memory effect[16-18]. Despite such remarkable advantages and the growing demand for high energy density, concerns regarding the safety issues associated with the Li-ion batteries are fire or even explosion due to thermal runaway conditions. There exists various reports in the past reporting the incidents associated with the thermal runaway condition in the Li-ion batteries. For example, according to a report issued by the China National Emergency Management Department, the risk of spontaneous combustion of electric vehicles in China is 0.26 per 10,000, indicating that, on average, nearly 7 electric vehicles catch fire per day. In 2022 alone, reports indicated that in China, around 18,000 e-bikes and 3,000 electric vehicles were destroyed due to thermal runaway in Li-ion batteries. In the last 5 years at the global level, at least 60 cases of thermal runaway conditions in Li-ion batteries have resulted in catastrophic. Thermal runaway is a situation in which the self-accelerating exothermic reactions cause the temperature of the battery to rise uncontrollably due to the successive decomposition of the battery components.

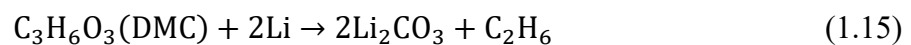
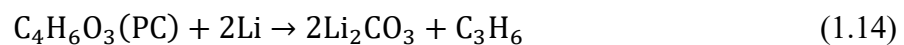
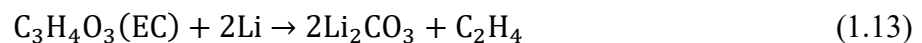
It is believed that mechanical damage[18-20], manufacturing defects[21, 22], overcharging[23, 24], faulty external wiring, internal short circuits[25, 26] and prolonged operation at high temperatures[26, 27] are the major reasons behind thermal runaway conditions in Li-ion batteries. Scientists have studied the thermal runaway condition in Li-ion batteries numerous times and found that it involves the following steps.

(A) Solid Electrolyte Interphase Decomposition reactions-Under normal working conditions, Li-ions dissolved in the electrolytic solution got transferred from the cathode to the anode. At this stage, the Li-ions present in the electrolytic solutions penetrate the surface of the anode. As a consequence, the surface of the anode undergoes a chemical reaction with the fraction of Li-ions and electrolyte molecule to form a thin passivating and highly ionic conducting film known as Solid Electrolyte Interphase (SEI)[28]. The formed SEI film acts as a protective barrier between the electrolyte-anode that prevents decomposition of the electrolyte while allowing Li-ions to pass through them. The SEI layer basically composed of organic stable substances, including ROLi (CH_2OLi),

ROCO₂Li (CH₂OCO₂Li), oxygenated polymer as well as steady state substances such as Li₂CO₃ and LiF. However, as the temperature reaches to 69⁰C, the formed SEI layer became unstable and beyond the 69⁰C, the formed SEI layer began to disintegrate into Li₂CO₃, hydrocarbons[29], thereby releasing CO₂ and O₂ [30] as shown in the equation (1.1) and (1.12)[31] below. The generated O₂ not only act as an oxidizing agent but also accelerates the decomposition reaction within the battery thereby endangering its performance and safety[32].



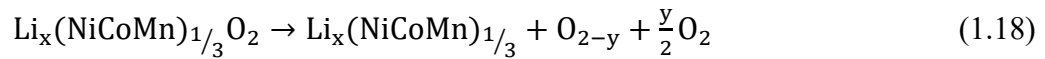
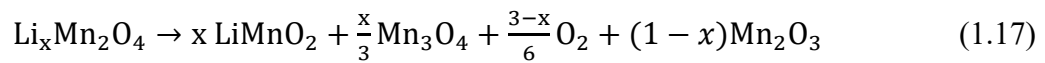
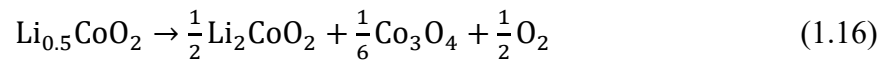
(B) Anode-electrolyte reactions- The decomposition of the SEI films causes direct exposure of the anode to the electrolyte.[33] As a result, the activation energy of the chemical process decreases, generating more and more heat due to the incorporation of more and more Li ions into the anode. At this stage, the organic electrolyte, such as EC(Ethylene Carbonate), PC(Polyethene carbonate), DMC (Dimethyl carbonate), reacts chemically with the intercalated Li-ions to generate Li₂CO₃ and hydrocarbons as shown in equations (1.13) to (1.15) respectively.



The generation of Li₂CO₃ leads to the formation of a new Solid Electrolytic Interphase(SEI) layer, a process commonly referred to as a SEI membrane regeneration reaction[34]. The regenerated SEI layer has a completely different structure from the SEI layer formed during charging. As a result, it no longer acts as a protective layer between the electrolytic solution and the lithium-ion embedded negative potential. Thus, the reaction between the electrolyte and the anode continues to increase the temperature.

(C) Decomposition of the Cathode-At this elevated temperature, the cathode materials, usually made up of Lithium Cobalt Oxide(LCO), Lithium Manganese Oxide (LMO) and Lithium Nickel Manganese Cobalt Oxide (NCM), undergo a decomposition reaction. During decomposition, the oxygen atoms bound to the crystal lattice are released as molecular oxygen or reactive oxygen species. The released oxygen is highly reactive and can react vigorously with organic electrolyte solvents such as EC, PC, and DMC, as shown melting point of the separator, which is typically made of polymer materials such as polyethene or polypropylene that separate the cathode from the anode, it begins to soften

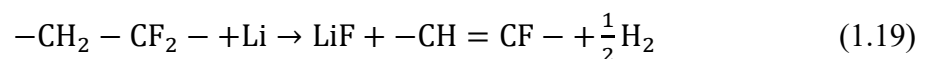
and eventually melts. This leads to internal short-circuiting, allowing faster electron flow between the cathode and anode and generating a large amount of heat in a very short time.



Decomposition of the Electrolyte- In a Li-ion battery, the electrolyte plays a very crucial role in the transportation of Li ions from the anode to the cathode. The most commonly used electrolyte solvents used in Li-ion batteries are EC, PC, and DMC, which are highly unstable at elevated temperatures.[37] As the temperature of the battery exceeds above 200°C These solvents undergo a decomposition reaction to produce a variety of volatile compounds. In addition to decomposition of electrolyte solvents, Lithium salts dissolved in the electrolyte are thermally unstable and begin to decompose. For example- The most widely used Lithium salt in Lithium-ion battery is Lithium Phosphorous Hexafluoride (LiPF_6)[38] which decomposes to Lithium Fluoride (LiF) and Phosphorous Pentafluoride (PF_5) which even under the presence of small amount of moisture undergoes a chemical reaction to form Hydrofluoric acid (HF) as mentioned in the equation (1.16)-(1.18) respectively.



(D) Anode-Binder reactions- In Li-ion batteries binder is a substance that is frequently used in the batteries to join the electrode materials, conductive agents and other components to form the electrode structure. As the temperature reaches beyond 260°C the anode material got directly exposed to the binder thereby creating gases such as fluoride and H_2 . For example- Polyvinylidene fluoride (PVDF), a binder for instance reacts quickly with lithium metal or LiC_6 at 350°C as shown below in the equation (1.19).[39, 40]



However, the problem of release of hazardous toxic gases such as C_2H_4 , CH_4 , CO_2 , CO and H_2 is associated with the Li-ion battery system alone. Besides, many industrial process and manufacturing operations involves the usage of various toxic gases such as phosgene (COCl_2)

Introduction

and Cyanogen Chloride (CNCl). Phosgene, which is itself a colourless toxic gas, was primarily used in the industries to produce polymeric isocyanate, carbamates, pharmaceuticals and pesticides. Exposure to its vapour even under low concentration has resulted in throat swelling, change in voice, pulmonary edema or pulmonary irritation. Similarly Cyanogen Chloride which is also a highly volatile and extremely poisonous gas was used in the manufacturing of rubber, plastics, fumigants and pesticides industries. Since all these gases are colourless and odourless as a consequence they are difficult to be detected by the human senses. Moreover accidental leakage of these gases in industries can pose a serious threat to the human health and environment. Therefore there is a need to develop an early warning system capable of identifying both the thermal runaway gases and highly industrial toxic gases has become an important issue in research. In this regard among the various existing gas sensing technologies such as optical[41, 42], electrochemical[43, 44], mass-based technologies[45, 46]. Chemoresistive gas sensor provides various advantages such as **cost-effectiveness, device miniaturization and ease of integration making them highly competitive for scalable and portable applications**. These sensors basically consists of a chemically sensitive material sandwiched between conducting electrodes as shown in the figure 1.1.[47] Chemiresistive gas sensor has gained enormous attention as an advanced gas detection technique due to its unique advantages. Firstly chemiresistive gas sensor exhibited remarkable sensitivity due to the usage of 2D materials having high surface to volume ratio thereby enabling the detection of these toxic gases at part per billion (ppb) level[48-50] which is very essential for applications such as environmental monitoring, medical diagnostics. In addition the selectivity of the gas sensor can be tailored via material modification, structural design which allow them to distinguish between different target gases and perform multicomponent gas analysis.[51, 52] Secondly they show rapid response behaviour often detecting gases within **a few seconds making them highly suitable for real time monitoring** particularly in critical **and** emergency situations. Moreover, the chemiresistive gas sensor typically consumes very low power and can operate at room temperature or with minimal heating, which makes them ideal for integration into Internet of Things (IOT) systems and wearable technologies. Finally, their ability to be miniaturised along with compatibility with advanced microfabrication techniques facilitates their incorporation into compact and portable devices for widespread sensing applications.

Introduction

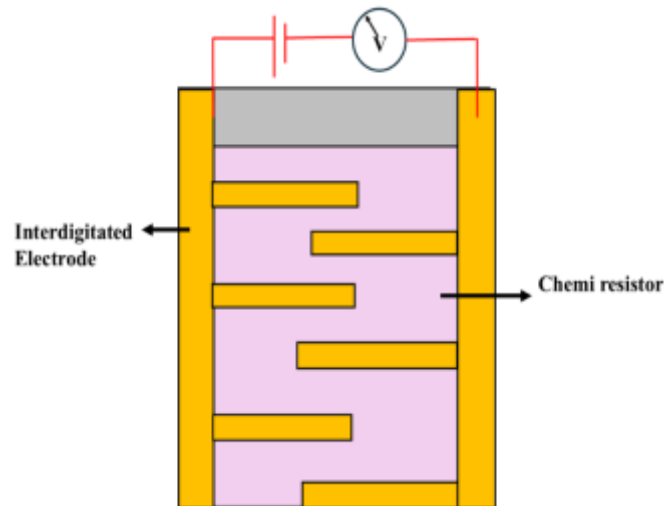


Figure 1.1: Schematic diagram representing the components of the chemiresistive gas sensor.

1.1 CHEMIRESISTOR GAS SENSORS AND SENSING MECHANISM

The sensing parameters, such as selectivity, sensitivity, sensing response and recovery time of the chemoresistive gas sensor, can only be effectively tuned if one has a deep understanding of the sensing mechanism, because a proper understanding of the sensing mechanism provides us a fundamental link between the material properties, surface chemistry and electrical responses. Therefore, in this section, we have discussed in detail how n-type and p-type semiconductor-based chemoresistive gas sensors change their electrical conductivity upon adsorption of oxidising and reducing gases, respectively.

1.1.1 ADSORPTION OF OXYGEN GAS MOLECULES

Whenever a P-type or N-type semiconducting material is exposed to the atmosphere, oxygen gas molecules are adsorbed onto the surface of the sensing materials, and they trap electrons from the conduction band to form O_2^- , O^- and O^{2-} ions depending on the operating temperature. This creates an electron-depletion layer and a hole-accumulation layer around the n-type and p-type semiconductors, as shown in Figure 1.2(a) and 1.2(d), respectively. For N-type materials, when a reducing gas is allowed to interact with the adsorbed oxygen species, it causes the adsorbed oxygen species to release the trapped electrons back to the conduction band, thereby reducing the electron depletion region, as shown in Figure 1.2(b). This results in a decrease in the electrical resistance of N-type materials as the concentration of their majority charge carriers, i.e., electrons, increases. In contrast, when the oxidising gases are allowed to interact with the N-type materials, it causes more trapping of electrons from the conduction

Introduction

band, thereby increasing the electron depletion region around the N-type materials, as shown in Figure 1.2(c). This causes an increase in the electrical resistance of the N-type materials due to the reduction in the concentration of the majority charge carriers, i.e., electrons in the N-type materials. For the P-type materials, when a reducing gas is allowed to interact with the adsorbed oxygen species it releases the trapped electrons which interacts with the holes in the Hole accumulation region thereby reducing the concentration of the majority charge carriers i.e. holes in the Hole accumulation region around the P-type materials as shown in Figure 1. (e). This causes increase in the electrical resistance of the P-type materials. On the other hand, the introduction of the oxidizing gases causes more and more trapping of electrons, this causes the width of the Hole accumulation layer to grow as shown in the Figure 1.2(f). Thus, the electrical resistance of the N-type and P-type sensing materials decreases for reducing and oxidizing gases whereas the electrical resistance of the P-type and N-type sensing materials increases for reducing and oxidizing gases respectively.

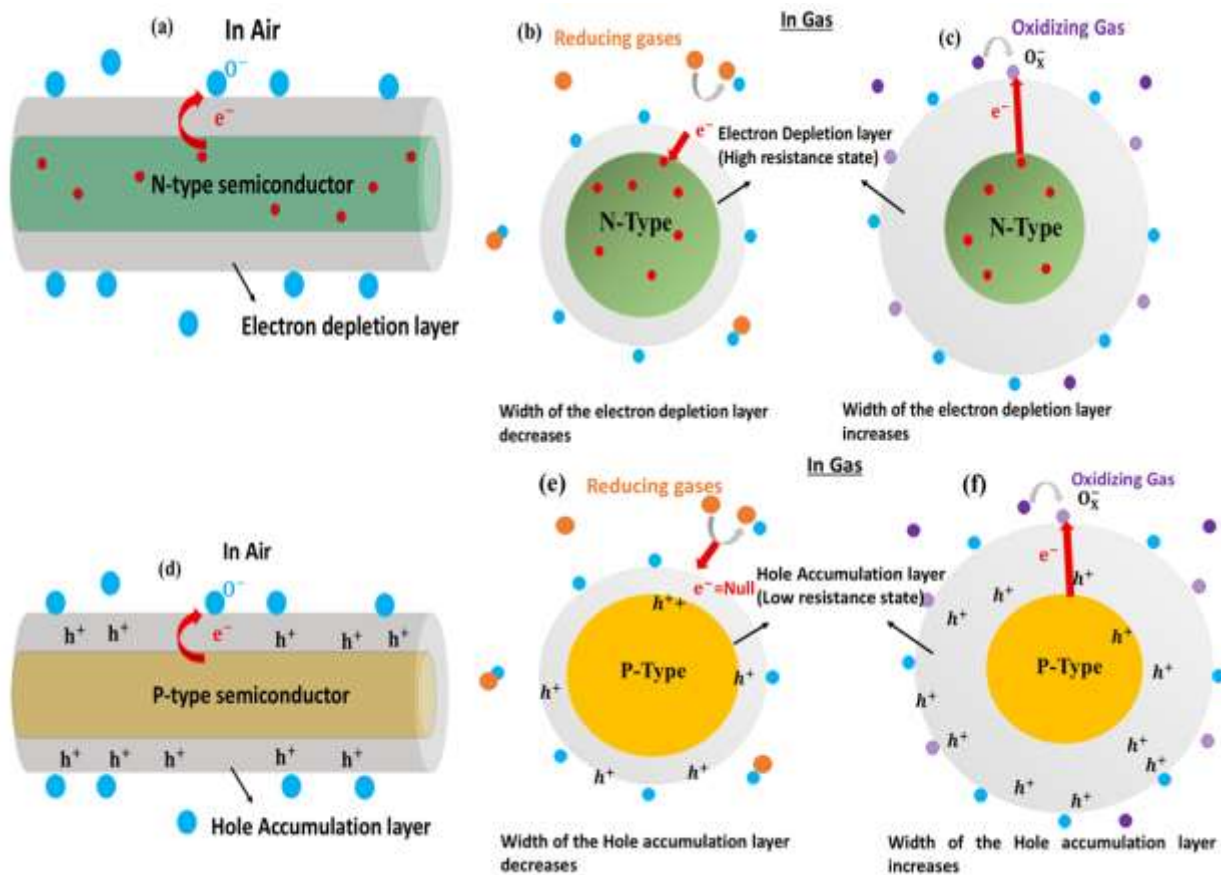


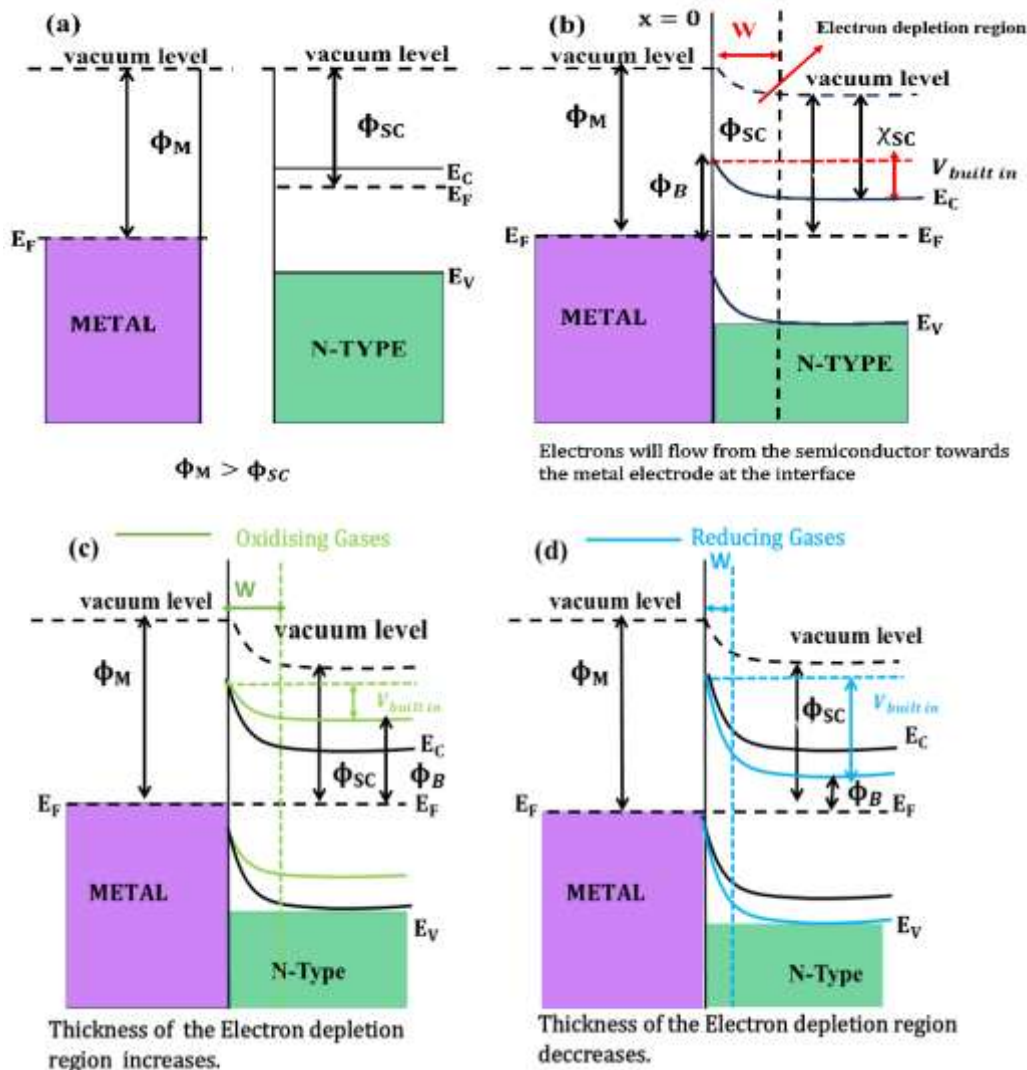
Figure 1.2: Schematic diagram illustrating the sensing mechanism of (a) and (d) N-type and P-type materials when exposed to air (b) and (e) when N and P-type materials are exposed to reducing gases (c) and (f) when N and P-type materials are exposed to oxidizing gases, respectively.

1.1.2 MODULATION OF SCHOTTKY BARRIER

Chemoresistive gas sensor basically relies on the change in electrical resistance caused due to the transfer of electrons between the sensing material- targeted gas molecule or between the metal contact-target gas molecule. These interactions strongly depend on various external factors such as relative humidity, operating temperature, pressure and presence of interfering gases. Whenever a semiconducting sensing material comes in contact with the metal electrode due to the difference in the Fermi level of the materials, the Fermi level of both the materials tried to lined up in order to attained equilibrium. The Fermi level basically describes the thermodynamical work required to add an electron to the solid-state body without considering the amount of work required to remove the electrons from a point within the solid-state body. It is the work function that determines the amount of work required to remove the electron from a point within the solid-state body. Generally, the Fermi level within a semiconductor basically lies within the band gap region and it is the difference between the Fermi level and vacuum defined the work function (ϕ). The nature of the interface formed between the metal and semiconductor at the interface depends on the difference in the work function. If the work function of the metal (ϕ_M) is greater than the work function of the semiconductor (ϕ_{SC}) as shown in the Figure 1.3(a) then the electrons from the conduction band of the semiconductor will flow towards the surface of the metal. This leaves behind the positively charged positive ions at the interface creating a region known as electron depletion layer. For a N-type semiconducting material where electrons are the majority charge carriers and the Fermi level (E_F) lies very close to the conduction band (E_C) this electron depletion region formed a potential barrier known as Schottky barrier(ϕ_B) which exhibits a rectifying behaviour as it allowed the current to flow in a particular direction similar to a diode as shown in Figure 1.3(b). In contrast if the work function of the semiconducting material (ϕ_{SC}) is greater than the work function of the metal electrode (ϕ_M), as shown in Figure 1.3(e) then for a P-type semiconductor material, at the interface Schottky barrier will be formed as shown in the Figure 1.3(f). For a P-type semiconducting material, the (E_F) lies very close to the valence band (E_V) where holes are the majority charge carriers as a consequence due the difference in the work function of the materials electron will flow from the surface of the metal towards the empty states in the (E_V) this creates an electron accumulation region/ hole depletion region at the interface as shown in Figure 1.3(f). Even in some cases, Ohmic contacts are also formed but are less significant for the use in chemiresistive gas sensors because they are very sensitive to

Introduction

the change in carrier concentration at the interface. The height of the Schottky barrier depends on the difference between the ϕ_M and electron affinity of the semiconductor (χ_{SC}) whereas the height of the built in potential ($V_{built\ in}$) depends on the difference between the work function of the metal and semiconductor. Adsorption of oxidising or reducing gases onto the surface of the sensing material has a chemical-doping effect that modifies the electronic properties of the semiconducting sensing layer. In case of the N-type material, the adsorbed oxidising gases, which are electron-withdrawing, reduce the ($V_{built\ in}$), increase the width of the electron depletion and Schottky barrier, resulting in an increase in the electrical resistance of the N-type materials, as shown in Figure 1.3 (c). In contrast the adsorbed reducing gases causes a shift in the (E_F) such that the width of the depletion region, height of the Schottky barrier decreases and increases the $V_{built\ in}$ thereby resulting an increase in the electrical resistance of the N-type materials as shown in Figure 1.3(d). The reverse to the N-type material happened in case of P-type materials upon the adsorption of oxidizing and reducing gases respectively as shown in Figure 1.3(g) and 1.3(h) respectively.



Introduction

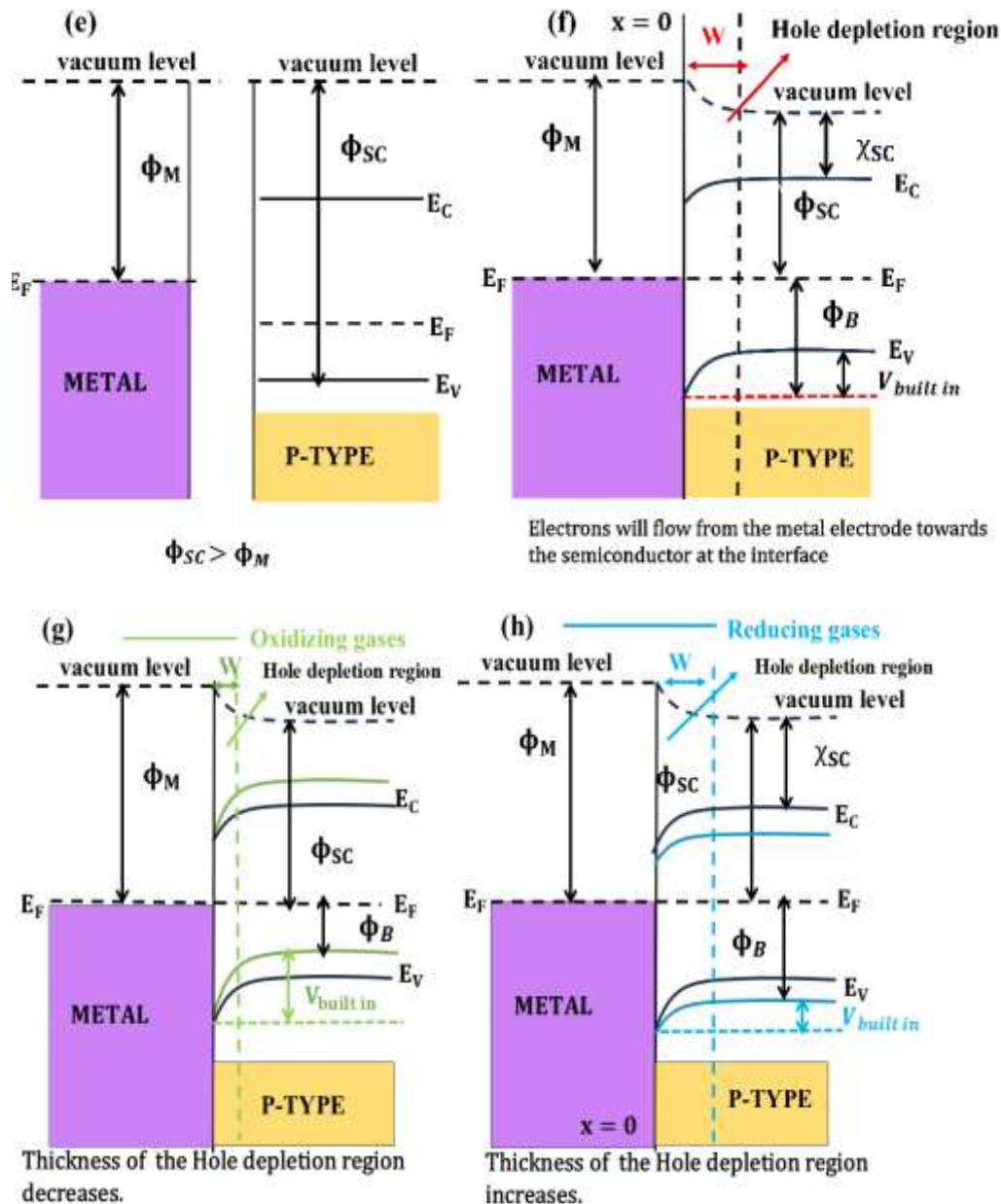


Figure 1.3: Schematic diagram representing the modulation of the Schottky barrier at (a)-(b) metal-N type interface (c) upon the exposure of the oxidizing gases (d) upon the exposure of the reducing gases at the metal-Ntype interface. Schematic diagram modulation of the Schottky barrier at (e)-(f) metal-P-type interface (g) upon the exposure of the oxidising gases (h) upon the exposure of the reducing gases at the metal-P-type interface, respectively.

1.2. 2D MATERIALS-BASED CHEMIRESENSITIVE GAS SENSOR

Two-dimensional materials have emerged as highly promising candidates for gas sensing applications due to their unique structural and electronic properties.[53] Among the various 2D material as shown in Figure (1.3), Graphene is one of the most extensively studied materials. In graphene's hexagonal honeycomb lattice, each carbon atom forms three σ -bonds with neighbouring carbon atoms, resulting in a stable planar structure with an in-plane bond length

Introduction

approximately 1.42 Å and an interlayer spacing of about 3.35 Å.[54, 55] Graphene exhibits exceptionally high carrier mobility ($\sim 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), high carrier density ($\sim 10^{12} \text{ cm}^{-2}$)[55], and a very large theoretical specific surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$)[56]. Due to its zero bandgap[57] in monolayer form, its electrical conductivity is highly sensitive to external perturbations, such as gas adsorption, making it an excellent candidate for room-temperature gas sensing[58]. The sensing mechanism of graphene is primarily governed by charge transfer interactions. When gas molecules adsorb onto its surface, they either donate or withdraw electrons, thereby altering the charge carrier concentration and resistance of the material. This high sensitivity of the graphene allowed it to detect even individual gas molecules. Additionally, its excellent mechanical flexibility and robustness make it suitable for integrating it into flexible and wearable sensing devices.[59] However, pristine graphene has limited selectivity and interaction strength with gas molecules. To address this limitation, derivatives such as Graphene oxide (GO) and reduced graphene oxide (RGO) have been developed. GO, typically synthesized using modified Hummers' method, contains abundant oxygen-containing functional groups (OCFGs) such as hydroxyl, epoxy, and carboxyl groups. These functional groups provide active sites for gas adsorption but significantly reduce electrical conductivity. To overcome this drawback, GO is reduced through thermal, chemical, or photonic treatments to form RGO, which restores conductivity while retaining a certain level of defects and functional groups. Compared to pristine graphene, RGO offers several advantages for gas sensing. First, as a p-type semiconductor, it facilitates strong charge transfer interactions with adsorbed gas molecules, often involving a transition from weak van der Waals interactions to stronger chemical bonding.[60] Second, the presence of defects, sp^2 -hybridized carbon domain and residual functional groups provides numerous active sites for gas adsorption.[61] Third, its surface can be easily functionalized, allowing tunable sensitivity and selectivity toward specific gases.[62] Building upon carbon-based 2D materials, transition metal dichalcogenides (TMDs) represent another important class of sensing materials. Compounds such as Molybdenum disulfide belong to the MX_2 family, where M is a transition metal and X is a chalcogen. These materials possess a layered structure with monolayer thicknesses of $\sim 6\text{--}7 \text{ Å}$ and tunable band gaps ranging from 1.0 to 2.2 eV depending on the number of layers.[63] Unlike graphene, TMDs exhibit intrinsic semiconducting behavior, which is advantageous for sensing applications. Their gas-sensing mechanism is also dominated by charge transfer processes, which have been validated through Density Functional Theory studies and experimental

techniques such as photoluminescence.[64] For instance, adsorption of electron-withdrawing gases, such as NO_2 , leads to electron depletion, while electron-donating gases, such as NH_3 , cause electron accumulation, thereby modulating the material's electrical properties. In addition to graphene-based materials and TMDs, other 2D materials further expand the scope of gas sensing. Black phosphorus (BP) exhibits a puckered layered structure with a tunable bandgap ranging from 0.3 to 2.0 eV depending on thickness.[65] Its high carrier mobility and large surface area, combined with abundant active sites due to its wrinkled structure, make it highly sensitive to gas adsorption.[66] Similarly, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), with its layered s-triazine-based structure and moderate bandgap ($\sim 2.5\text{--}2.8$ eV), shows strong affinity toward gas molecules due to interlayer van der Waals interactions and chemical bonding.[67] Another important class of materials is MXenes, which are derived from MAX phases by selectively etching the A-layer elements.[68] MXenes exhibit excellent electrical conductivity, tunable surface chemistry, and high thermal stability, making them highly suitable for room-temperature gas sensing applications.[68-70] Furthermore, two-dimensional conductive metal-organic frameworks (MOFs) offer unique advantages due to their ultrahigh porosity, large surface area, and tunable structures.[71] Their porous frameworks enhance gas adsorption and facilitate rapid diffusion, while their adjustable chemistry enables selective detection of specific gases. Overall, physical and chemical properties of the 2D materials as make them highly promising candidates for next-generation gas sensors, particularly for detecting hazardous gases released during thermal runaway in batteries as well as toxic industrial gases.

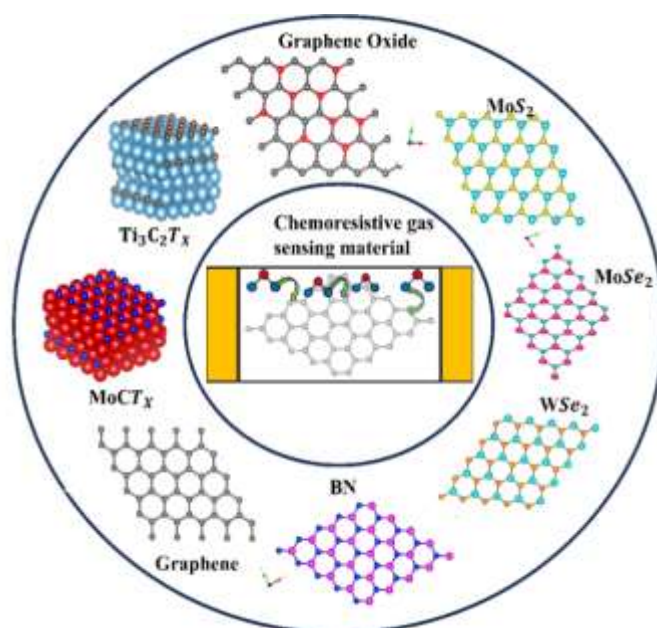


Figure 1.4: Schematic diagram illustrating various 2D materials to be used as a chemoresistive sensing material.

1.3. DIFFERENT TYPES OF 2D BASED CHEMIREISTIVE GAS SENSOR

1.3.1 GRAPHENE-BASED CHEMIREISTIVE GAS SENSOR

Graphene has attracted significant attention for gas sensing applications due to its exceptional properties, prompting extensive theoretical and experimental studies. A major breakthrough occurred in 2007 when Novoselov's team first showcased graphene's potential for gas sensing. They synthesized graphene single crystals, approximately 10 μm in size, on oxidized silicon substrates and fabricated graphene-based sensors by placing these crystals onto Au/Ti electrodes using electron beam lithography. Their sensor successfully detected multiple gases, including NO_2 , NH_3 , CO , and H_2O , at concentrations as low as 1 ppm. The sensing mechanism relies on variations in graphene's carrier concentration when gas molecules adsorb onto its surface, altering its electrical resistance. This pioneering research laid the foundation for future developments in graphene-based gas sensors. Further investigations, such as those by Leenaerts et al.[72] examined the adsorption behaviour of gases such as NO_2 , NH_3 , and CO on graphene nanosheets(NSs). Using density functional theory (DFT) calculations, they demonstrated that adsorbed gas molecules act as dopants, significantly modifying local carrier concentrations. However, because pristine graphene lacks dangling bonds, it exhibits weak chemisorption with gas molecules, leading to slow reaction rates and difficulties in returning to its original state after adsorption. As a result, gas sensors made from pristine graphene often suffer from prolonged response and recovery times. To enhance graphene's sensing capabilities, researchers have modified its surface properties. For instance, doping with elements like boron (B) and nitrogen (N) or introducing structural defects has been shown to significantly improve sensor performance. Zhang and his team demonstrated that such modifications greatly enhance graphene's gas response. Additionally, Bo et al.[73] studied the interaction of gases like NO_2 and H_2S with metal-decorated graphene, using metals such as Ni, Pd, and Pt. Their findings revealed that metal-functionalized graphene exhibits stronger chemisorption and higher sensitivity to NO_2 than its pristine counterpart. Other strategies for optimizing graphene-based gas sensors involve external stimuli such as heat treatment and ion beam irradiation. Kim et al.[74] developed a flexible, self-activating NO_2 sensor based on graphene, demonstrating that increasing the bias voltage and heating temperature improved its response and recovery times. Similarly, Yeo et al.[75] found that exposing graphene to Ar ion irradiation enhanced its sensitivity to NH_3 , NO_2 , and CO . In 2012, Chung et al.[76] introduced another promising approach by functionalizing graphene with oxygenated functional groups

Introduction

(OCFGs) using ozone treatment. This method significantly enhanced NO₂ sensing performance, with ozone-treated graphene (OTG) showing twice the response of pristine graphene and a much faster response time. These advancements highlight the potential of functionalized and modified graphene in the development of high-performance gas sensors for various applications.

1.3.2 REDUCED GRAPHENE OXIDE (RGO) BASED CHEMIRESENSITIVE GAS SENSOR

Pristine graphene's lack of a band gap limits its application in electronic devices. In order to overcome these challenges, graphene oxide (GO) has been synthesized using Hummers' method[77] and utilized in gas sensor fabrication. Unlike pristine graphene, GO contains abundant oxygenated functional groups (OCFGs) within its defect regions, which serve as active sites for gas adsorption. However, these OCFGs disrupt the conjugated electronic structure, leading to poor conductivity and restricting its effectiveness in electronic applications.[78] To enhance its conductivity, GO can be chemically reduced, resulting in reduced graphene oxide (RGO), which exhibits improved electrical conductivity. In gas sensors, the adsorption of gas molecules onto the surface of RGO leads to electron transfer, altering the carrier concentration and enabling gas detection. Based on this principle, extensive research has been conducted on RGO-based sensors operating at room temperature. In 2009, Professor Chen's research team developed a GO film by suspending GO on gold electrodes. After heat treatment in an argon atmosphere at temperatures between 100°C and 300°C, partial reduction occurred, allowing the material to detect NO₂. [79] The same team later reduced GO using hydrazine, creating an RGO-based field-effect transistor (FET) sensor, where RGO functioned as both the conductive channel and the gas-sensitive layer, with a silicon substrate serving as the gate. The hydrazine-reduced RGO sensor demonstrated a 360% enhancement in response to 100 ppm NO₂ compared to its thermally reduced counterpart.[80] Despite these advancements, RGO-based gas sensors still encounter challenges such as low sensitivity, sluggish response times, and incomplete recovery. To address these limitations, researchers have explored various modifications, including surface functionalization, heteroatom doping, incorporation of metal or metal oxide elements, conductive polymer composites, and laser irradiation. These strategies have shown significant improvements in the gas-sensing capabilities of RGO-based sensors.

1.4 TRANSITION METAL DICHALCOGENIDE (TMDs) BASED CHEMIREISTIVE GAS SENSOR

1.4.1 MoS₂ BASED CHEMIREISTIVE GAS SENSOR

MoS₂ is widely recognised for its gas-sensing capabilities due to its unique physical and chemical characteristics, such as its layered structure, high surface area, and strong adsorption properties. Structurally similar to graphene, MoS₂ consists of stacked layers bound by van der Waals forces (VDWFs), with each monolayer containing a hexagonal arrangement of molybdenum (Mo) atoms sandwiched between two sulfur (S) layers. Unlike metal oxides, the gas-sensing mechanism of MoS₂ involves charge-transfer interactions between the material and gas molecules, particularly with NO₂. Cho et al.[81] synthesized MoS₂ with atomic-scale thickness via chemical vapour deposition (CVD) and examined its NO₂ charge transfer mechanism using in-situ fluorescence spectroscopy. Donarelli et al.[82] employed liquid-phase exfoliation (LPE) to produce MoS₂ nanosheets, achieving NO₂ detection at temperatures between 150°C and 250°C. However, pure MoS₂ sensors have limitations, including low sensitivity and slow recovery times. To improve performance, various strategies have been implemented, including noble-metal nanoparticle (NP) doping and semiconductor integration. Zhang et al. [83] demonstrated that doping MoS₂ with noble metals like Cu, Pd, and Pt significantly enhanced hydrogen (H₂) sensing performance by lowering adsorption energy and strengthening interactions between the gas molecules and MoS₂. Moreover, the bandgap of MoS₂ increased upon H₂ adsorption, facilitating charge transfer. Xu et al.[84] used DFT calculations to show that Au and Pt significantly boosted adsorption energy on MoS₂ monolayers. Xiao et al.[85] investigated metal doping (Fe, Co, Ni, Cu) in MoS₂ and found that Fe doping notably improved NO₂ adsorption. Aneesh et al.[86] synthesized Ni- and Pd-functionalized MoS₂ through a hydrothermal process, with Pd-MoS₂ exhibiting a 700% sensitivity to 2 ppm NO and a detection limit of 0.1 ppm, while Ni-MoS₂ showed 80% sensitivity to 2 ppm H₂S. Hybrid structures have also been explored to enhance gas-sensing properties. Zhang et al.[87] developed MoS₂ /GO composites, finding that a sensor with a 3% GO-to-MoS₂ ratio exhibited a 75% response to 50 ppm triethylamine at 260°C. The crystallographic orientation of MoS₂ also plays a role in gas sensing. Cho et al. studied different alignments of MoS₂ films (HA-MoS₂, MHVA-MoS₂, and VA-MoS₂) and found that VA-MoS₂ exhibited the highest response to NO₂. Jung et al. confirmed that VA-MoS₂ had abundant edge sites and dangling bonds, enhancing gas adsorption. Additionally, Shi et al.[88] synthesized

3D nanosheets on mesoporous In_2O_3 , which improved NO_x detection. These findings underscore the potential of MoS_2 -based sensors, which can be optimized through surface modifications, hybrid structures, and tailored synthesis methods.

1.4.2 SnS_2 BASED CHEMIREISTIVE GAS SENSOR

SnS_2 has attracted interest in gas sensing due to its strong electronegativity, abundant adsorption sites, and excellent stability. Ma et al.[89] synthesized 2D SnS_2 via ultrasonic exfoliation from large single crystals, achieving high sensitivity to 5 ppm NH_3 . Tang et al.[90] developed an NO_2 sensor based on SnS_2 nanosheets, which demonstrated a response of 5.7 for 100 ppb NO_2 at 120°C . Despite its advantages, SnS_2 still faces limitations in sensitivity for broader gas sensing applications. Zeng et al.[91] synthesized SnS_2 nanosheets using chemical exfoliation and observed a response of 4.2 to 500 ppm NH_3 . Their study revealed that sulfur vacancies (S-vacancies) significantly enhance NH_3 adsorption. Further Zhao et al.[92] explored S-vacancy interactions with gas molecules in SnS_2 monolayers, suggesting that defect engineering could improve gas sensor performance. Additionally, Hayashi et al.[93] conducted theoretical calculations showing that natural sulfur vacancies in n-type SnS_2 facilitate p-type doping, aiding formaldehyde (HCHO) detection. Similar to MoS_2 , SnS_2 gas sensors can be further improved through quantum dot (QD) modification and light-assisted activation techniques.

1.4.3 WS_2 BASED CHEMIREISTIVE GAS SENSOR

WS_2 , which shares structural features with MoS_2 , has been widely investigated for gas-sensing applications. Colomer et al.[94] employed aerosol-assisted chemical vapor deposition (AA-CVD) to synthesize 2D WS_2 nanosheets, achieving ultra-sensitive detection of 5 ppb NO_2 . Xu et al.[95] fabricated ultra-thin WS_2 nanosheets with a 3D wall-like structure, which exhibited a 9.3% response to 100 ppb NO_2 at room temperature. To enhance WS_2 -based gas sensors, various strategies have been explored, including noble-metal nanoparticle (NP) doping, heterojunction formation, quantum-dot doping, and light irradiation. Kim et al.[96] designed a flexible CO sensor using Au- WS_2 nanofibers, which maintained stable performance even after 1000 bending cycles. UV irradiation further enhanced the response of Au- WS_2 sensors. Hybrid structures have also shown promise. Shi et al.[97] synthesized $\text{MoS}_2@\text{WS}_2$ heterojunctions, significantly boosting NO_2 response. Yang et al. developed a $\text{WS}_2\text{-ZnS}$ heterostructure achieving a response of 32.5 for 5 ppm NO_2 with a rapid 4-second detection

time at room temperature. Zhang et al.[98] created a highly sensitive formaldehyde (HCHO) sensor based on Ni-In₂O₃/WS₂, which exhibited a response 10 times higher than pure WS₂. Further improvements have been made using quantum dot decoration. Zeng et al.[99] incorporated Pt QDs into WS₂ nanosheets, increasing the NH₃ response by a factor of 10 for 250 ppm NH₃ compared to pristine WS₂. Qin et al.[100] utilized TiO₂ QDs to enhance NH₃ sensitivity in WS₂ sensors, resulting in a 17-fold improvement. Paolucci et al.[101] studied the impact of light exposure and temperature on WS₂-modified reduced graphene oxide (RGO) sensors, finding that purple-blue light and heat treatment significantly improved recovery and adsorption/desorption dynamics.

1.4.4. OTHER TMDs BASED CHEMRESISTIVE GAS SENSOR

Various transition-metal dichalcogenides (TMDs), including VS₂, MoTe₂, and WSe₂, have been explored for gas-sensing applications. Zhang et al.[102] fabricated a MoS₂/VS₂ heterostructure by assembling MoS₂ nanosheets onto porous VS₂, which demonstrated a stronger affinity for NH₃ compared to standalone MoS₂ or VS₂ sensors. MoTe₂, with a bandgap below 1.0 eV, has attracted interest in gas sensing. Feng's team enhanced the performance of MoTe₂ sensors by preparing MoTe₂ nanofibers and subjecting them to continuous UV exposure. Their findings revealed a 25-fold improvement in NH₃ detection when illuminated with 254 nm UV light. Similarly, Wu et al.[103] demonstrated that UV light also enhanced the sensitivity of MoTe₂ sensors for NO₂ detection. Additionally, DFT calculations by Panigrahi et al. indicated that substituting antimony (Sb) for tellurium (Te) in MoTe₂ increased the binding energy and altered the electronic properties, thereby improving its suitability for detecting gases such as NH₃, NO, and NO₂.

1.5 OTHER 2D MATERIALS BASED CHEMRESISTIVE GAS SENSOR

1.5.1 BLACK PHOSPHORENE BASED CHEMRESISTIVE GAS SENSOR

In 2014, Chen and colleagues employed first-principles calculations to investigate the adsorption of gases like carbon monoxide and nitrogen oxide on phosphorene monolayers, identifying specific adsorption sites for these molecules. Expanding on this, Yang et al.[104] examined phosphorene's interaction with gases such as SO₂ and H₂S, finding that SO₂ displayed stronger adsorption and greater electron transfer effects. Donarelli et al.[105] developed a BP-based gas sensor by chemically exfoliating BP flakes and depositing them onto Si₃N₄ substrates with Pt-interdigitated electrodes. While the BP sensor exhibited minimal response to CO and CO₂ at room temperature, it demonstrated stable H₂ sensitivity, with detection limits of 20 ppb for NO and 10 ppm for NH₃. That same year, Professor Cho's group compared BP, MoS₂, and graphene sensors for NO₂ detection, showing that the BP sensor had a significantly higher response (80%) to 1 ppm NO₂ and faster detection speeds than the other materials. Functionalizing BP with noble metals, particularly Pt, has been shown to enhance its gas-sensing capabilities. A Pt-modified BP sensor exhibited increased sensitivity and selectivity for low-concentration H₂ detection, outperforming pristine BP sensors. Additionally, research by Liang et al.[106] demonstrated that Pt-

functionalized BP hybrids showed improved responses to NO_x gases. Lei et al.[107] further explored the effects of noble-metal functionalization (Li, Na, and K) on phosphorene's gas-sensing performance, particularly on CO adsorption using DFT.

1.4.5 g-C₃N₄ BASED CHEMIREISTIVE GAS SENSOR

Graphitic carbon nitride (g-C₃N₄), characterized by its intrinsic porous structure and nitrogen atoms with lone pairs of electrons, has garnered considerable interest for gas sensing at room temperature (RT). Wang et al. [108] developed a g-C₃N₄ based gas sensor capable of detecting NO₂ at concentrations as low as 140 ppb under 65% relative humidity at RT. This high sensitivity was attributed to the strong interaction between NO₂ molecules and the pyridine nitrogen sites in g-C₃N₄. Another study, Srinivasan et al. [109] investigated the ethanol-sensing capabilities of g-C₃N₄ sensors, reporting a response of 182.4 when exposed to 50 ppm ethanol vapour and a detection limit of 500 ppb. The sensing efficiency of g-C₃N₄ can be further improved by integrating it with metal oxides. Zhang et al.[110] developed an α -Fe₂O₃/g-C₃N₄ ethanol sensor, where the formation of a heterojunction significantly enhanced its sensitivity. Additionally, Guo et al.[111] synthesized Ni-doped SnO₂/g-C₃N₄ composites for acetone detection, achieving a remarkable response of 142.5 at 10 ppm acetone, with a detection limit as low as 1.38 ppb.

1.4.6 MXenes BASED CHEMIREISTIVE GAS SENSOR

MXenes, known for their exceptional electrical and thermal conductivity as well as their tunable electronic and chemical properties, have emerged as promising materials for gas sensing applications. Using first-principles calculations, Yu et al.[112] examined the adsorption behavior of various gases, including NH₃, H₂, and CH₄, on MXene monolayers. Their findings indicated that NH₃ exhibited strong chemisorption on MXene nanosheets. Lee et al.[113] explored the gas sensing capabilities of Ti₃C₂T_x MXenes for detecting ethanol, methanol, acetone, and NH₃, concluding that the Ti₃C₂T_x sensor had the highest sensitivity to NH₃ at room temperature. Additionally, Guo and colleagues developed a Mo₂CT_x MXene-based sensor with excellent selectivity for toluene, recording a response of 2.81 at 140 ppm toluene, while showing significantly lower responses to benzene, ethanol, methanol, and acetone.[114]

2. HEXAGONAL BORON NITRIDE

In recent years, hexagonal boron nitride (hBN) has attracted considerable interest as a promising two-dimensional (2D) dielectric material.[115-117] Due to its structural resemblance to graphene, it is often referred to as "white graphene." [118] With a wide bandgap of around 6 eV, hBN serves as an excellent dielectric for high-performance 2D electronic [119] and optoelectronic [120] applications. Its chemical stability further enhances its suitability for

Introduction

transistors, where it functions as a gate dielectric and in electrical encapsulation. The atomic structure of hBN consists of boron and nitrogen atoms arranged in an alternating pattern, with strong covalent bonding within each layer, while weak van der Waals forces hold the layers together. This weak interlayer interaction allows for the easy exfoliation of thin hBN sheets from bulk crystals. In 2015, there were only 137 publications focused on 2D hBN, whereas by 2025, the number had surpassed 969, as shown in Figure 1.5. One of hBN's key advantages is its ability to enhance the performance of graphene-based devices. Graphene grown on conventional SiO₂ substrates often degrades its intrinsic properties. While suspended graphene retains its superior characteristics, the complexity of its device fabrication poses challenges. These limitations can be overcome by growing graphene on an atomically thin hBN substrate, which enables the exploration of new functionalities. For example, Giovannetti et al.[121] demonstrated that graphene placed on hBN acquires a bandgap of 53 meV, improving the performance of graphene-based field-effect transistors (FETs). As the only insulating member of the 2D materials family, hBN plays a critical role in applications such as high-quality dielectrics, atomically thin insulators, and ultra-thin tunneling devices. Several tunnelling devices utilising hBN's van der Waals interactions have been developed. Britnell et al.[122] introduced the first tunnelling device based on a graphene/hBN/graphene heterojunction, where hBN acted as the tunnelling barrier. In addition to its role in electronic devices, hBN exhibits outstanding optical, electrical, and mechanical properties, making it a promising material for next-generation technologies. Its exceptional thermal and mechanical stability makes it suitable for hydrophobic coatings, UV emitters, and oxidation-resistant layers. Beyond its dielectric applications, hBN's high thermal conductivity and stability make it an excellent candidate for gas sensing, particularly in extreme environments. Experimental and theoretical studies have explored the adsorption of gases such as NO₂, NO, NH₃, CO, CH₄, and H₂ on hBN surfaces. The alternating arrangement of boron and nitrogen atoms contributes to its reactivity with gas molecules, leading to changes in its electronic properties upon gas exposure, which is useful for sensor development. Its ultrathin nature provides a large surface area, enhancing gas adsorption and sensor sensitivity. Additionally, hBN can operate at high temperatures without significant performance degradation, making it well-suited for flexible and high-temperature gas sensing applications.

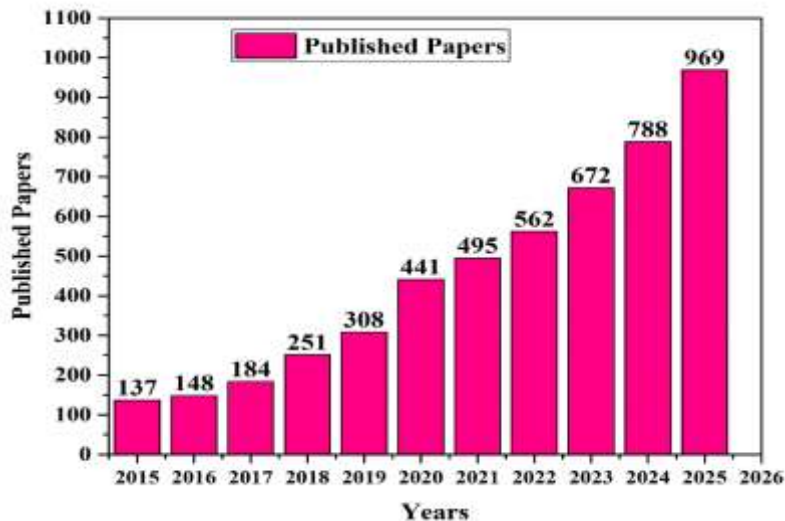


Figure 1.5: Plotted graph representing an exponential increase in the number of published hBN-based gas sensing papers over the years. This data is being taken from the Web of Science with the search keywords “hBN-based gas sensors”.

2.1 SENSING MECHANISM OF hBN-BASED GAS SENSORS

The ability of a material to withstand harsh environmental conditions is critical for its long-term effectiveness in gas-sensing applications. Graphene/hBN-based devices demonstrate exceptional stability even in humid environments, making them highly suitable for selectively detecting NO_x gases. De Souza et al.[123] investigated the performance of nanodevices exposed to NO, NO₂, NH₃, and CO₂, identifying 'CB' and 'CN' as primary adsorption sites. Their study found that NO₂ and NO exhibited the highest charge transfer values, leading to substantial electronic property modifications and enhanced sensitivity. The lowest adsorption energies were recorded for NO (1.00 eV) and NO₂ (2.02 eV), whereas CO₂ and NH₃ showed much lower values (0.33 eV). Similarly, charge transfer values were significantly higher for NO (0.1796 electrons) and NO₂ (0.7901 electrons), while CO₂ and NH₃ exhibited considerably lower charge transfers. The strong interaction of NO_x molecules with the graphene/ hBN surface, facilitated by shorter adsorption distances, contributed to the sensor's high selectivity for NO_x detection. MoS₂/hBN heterojunction-based sensors have also shown exceptional gas detection performance. Compared to MoS₂/SiO₂ devices, MoS₂/hBN sensors exhibited noticeable threshold voltage shifts when exposed to 25 ppb of NO_x, indicating strong charge transfer and heightened sensitivity. These findings further confirmed that graphene/hBN and MoS₂/hBN interfaces provide superior gas adsorption and charge transfer, making them highly effective for NO_x sensing. Additionally, hBN's excellent thermal conductivity and stability make it an attractive material for flexible electronics. Ayari et

Introduction

al.[124] developed an affordable, wearable NO₂ sensor by growing AlGa_{0.1}N/GaN on hBN and transferring it onto a flexible acrylic substrate. The 2D hBN facilitated this process, resulting in a twofold increase in sensitivity and a sixfold improvement in response time. The enhanced performance was attributed to self-heating within the acrylic layer, which boosted sensitivity. Computational studies by Beheshtian et al.[125] examined the adsorption energies of various gases on BN nanoclusters, reporting values of 6.07, 3.66, 1.35, and 1.06 kJ/mol for NO, N₂, H₂, and CH₄, respectively. The interaction of these gases with the nanocluster modified its electronic properties, thereby improving conductivity. Gautam et al.[126] developed hBN-based humidity and LPG sensors, explaining their mechanism through oxygen chemisorption. In this process, oxygen molecules extract electrons from the sensing layer, increasing resistance. Upon gas exposure, the electrons are released, reducing resistance and enhancing sensitivity. Similarly, Sajjad et al.[127] investigated resistance variations in BN nanosheet-based gas sensors, reporting sensitivities of 1.5 and 7.8 for oxygen and methane, respectively. Methane demonstrated higher adsorption due to its polarity. Lin et al.[128] synthesized hBN using a low-temperature solvothermal process and explored its gas-sensing properties. The sensitivity of the device increased with ethanol concentration, reaching a value of 4.5 at 100 ppm and 300°C. The sensing mechanism involved oxygen adsorption, which trapped free electrons and raised resistance. When ethanol was introduced, electrons were released, lowering resistance and improving detection performance. Generally, hBN functions as a chemiresistive or field-effect transistor (FET) gas sensor. For example, when methane interacts with boron nitride nanosheets, resistance increases, but once the gas desorbs in air or vacuum, resistance returns to its initial state. Although conventional metal oxide-based gas sensors are widely used, hBN exhibits high resistivity, which limits its direct application in gas sensing. However, this limitation can be addressed through doping, substitution, and functionalization, broadening its potential uses. hBN also offers distinct advantages over metal oxides, such as a larger surface-to-volume ratio, which provides more active adsorption sites and enhances sensing performance. Its ultra flat surface, exceptional stability, and reduced Coulomb scattering make it an excellent substrate for growing other materials. Additionally, hBN can function as a sacrificial layer in the fabrication of high-performance flexible and wearable sensors. One of hBN's key benefits is its thermal stability, which allows it to operate at temperatures up to 900°C without performance degradation. Its ultrathin structure also improves mechanical flexibility compared to metal oxide-based gas sensors. While metal oxide sensors typically require high temperatures due to surface-adsorbed oxygen ions (O₂⁻, O⁻, O₂²⁻), which increases power consumption and limits portability, hBN sensors rely on charge

transfer mechanisms. This allows them to function at lower temperatures with enhanced efficiency, making them a promising alternative for next-generation gas-sensing technologies.

2.2 STRATEGIES TO OVERCOME THE CHALLENGES ASSOCIATED WITH hBN-BASED GAS SENSORS

Hexagonal boron nitride-based gas sensors often face challenges such as slow response times, limited selectivity, and incomplete reversibility due to the material's chemically inert nature. Researchers have explored various strategies to enhance their sensing capabilities, including substrate engineering, surface modifications, and functionalization.

(a) Substrate Engineering: The gas-sensing performance of various two-dimensional materials is significantly affected by the selection of the substrate. Substrate engineering plays a crucial role in determining the efficiency of gas sensors. In recent years atomically thin, dangling bond-free surface of hBN facilitated high-quality graphene growth with reduced charge inhomogeneities. Decker et al.[129] reported that graphene grown on hBN exhibited a root mean square surface roughness of $2.3 \times 10^{10} \text{ cm}^2$, while graphene grown on SiO_2 showed a roughness of $8.2 \times 10^{10} \text{ cm}^2$. This lower surface roughness and minimized charge fluctuations make hBN an ideal substrate for fabricating high-performance 2D materials. Topographical and charge density comparisons between graphene grown on hBN and SiO_2 confirm the superior smoothness of graphene on hBN. Scanning tunneling microscopy (STM) images of cobalt phthalocyanine (CoPc) molecules deposited on graphene transferred onto SiO_2 and hBN substrates reveal that CoPc molecules on graphene/ SiO_2 exhibit displacement and disorder, whereas those on graphene/hBN retain an almost perfectly ordered structure. Furthermore, hBN can serve as a sacrificial layer to facilitate the defect-free, large-scale fabrication of sensing materials. These structures can then be transferred onto flexible substrates, paving the way for high-performance, wearable gas sensors. A recent study by Ali et al.[130] highlighted the outstanding NO_x detection capabilities of MoS_2/hBN heterostructure sensors. These MoS_2/hBN transistors demonstrated an exceptionally low detection limit of 6 ppb at room temperature, with the potential for further improvement through optimized synthesis and processing. A comparison between $\text{MoS}_2/\text{SiO}_2$ and MoS_2/hBN transistors revealed an increase in mobility from 0.25 to $1.16 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in MoS_2/hBN -based devices. This enhancement was attributed to a reduction in interfacial traps and disorder, leading to improved sensor performance. Cadore et al.[131] investigated different substrates for

Introduction

graphene-based NH_3 gas sensors and found that the interaction between graphene and gas molecules is not solely dependent on graphene's intrinsic properties but also on its proximity to the underlying substrate. Among the tested substrates, graphene/hBN exhibited the shortest separation due to the structural and lattice similarities between graphene and hBN. The gas-sensing response of graphene grown on various substrates under different NH_3 concentrations demonstrated that graphene/hBN sensors exhibited higher sensitivity and faster recovery times compared to their counterparts on other substrates.

(b) Surface Functionalization: It is also an effective approach for modifying the surface properties of hBN for gas-sensing. For instance- Wang et al.[132] demonstrated that surface-functionalized BN nanosheets with silver nanoparticles altered the thermal conductivity of pristine BN from $1.63 \text{ W m}^{-1} \text{ K}^{-1}$ to $3.06 \text{ W m}^{-1} \text{ K}^{-1}$. Similarly, Lin et al.[128] also enhanced the surface reactivity of hexagonal BN by introducing defects through a ball-milling process. He concluded that surface functionalization enhances the selectivity of Ag-hBN-based gas sensors toward specific molecules. Feng et al.[133] reported that Pt-hBN nanosheets effectively detected environmental pollutants, even in high-humidity conditions. When exposed to hydrogen and methane, the conductivity of the material increased significantly, leading to improved sensitivity. Notably, the sensor maintained stable performance at humidity levels of up to 75%. Surface modifications also improve sensor performance, especially in extreme environmental conditions, as confirmed by experimental and theoretical studies. For instance, He et al. designed a sulfate-modified hexagonal boron nitride sensor for nitrogen dioxide (NO_2) detection, which exhibited a remarkable sensitivity of 1.645 ppm^{-1} , surpassing pristine hBN and many other 2D materials. Furthermore, it had an impressively low detection limit of 20 ppb, well below the recommended NO_2 exposure threshold. Additionally, selectivity is a key factor in practical gas-sensing applications. While pristine hBN sensors tend to show similar responses to multiple gases, limiting their effectiveness, sulfate-modified hBN exhibited a strong preference for NO_2 due to the chemical interactions induced by sulfate groups. Even at a NO_2 concentration of 10 ppm, the modified sensor outperformed its response to 100 ppm of other gases. Lee et al.[134] also developed hydroxyl-functionalized BN nanoplatelets using an exfoliation technique, enabling their dissolution in various solvents for specialized applications.

Introduction

(b) Elemental Doping: Doping is a commonly employed strategy to modify the electrical and physical characteristics of two-dimensional materials, particularly to modify the catalytic properties. For instance- Sun et al.[135] investigated how magnesium (Mg) doping influences the electrical conductivity of hexagonal boron nitride (hBN). For this purpose Mg atom was substitutionally doped at the Boron site using CVD. This modification induces p-type behavior in hBN, leading to a hole density of $1.7 \times 10^{14} \text{ cm}^{-2}$ and a surface current of 12 mA. Unlike pristine hBN, which remains dielectric and shows negligible current flow under a voltage bias, Mg-doped hBN demonstrates a linear current increase with rising bias voltage, reaching 12 mA at 3V. Similarly, Azevedo et al. also explored how substitutional doping alters the electronic properties of hBN, reporting a 3.72 eV decrease in work function when carbon atoms were incorporated into the hBN lattice. Sajjad et al. fabricated wafer-scale BN nanosheets using pulsed laser deposition (PLD), ensuring uniform growth without thermal ablation. Carbon doping was introduced to enhance the sensing performance of these nanosheets for methane detection. The sensor's effectiveness was evaluated by monitoring variations in electrical resistance upon gas exposure. The results showed a stronger response to methane compared to oxygen. Furthermore, Fadlallah et al.[136] examined the NO₂ and SO₂ adsorption onto BN nanocones using first-principles calculations. Their DFT results demonstrated that pristine BN nanocone exhibited adsorption energies of 0.71 eV for NO₂ and 0.34 eV for SO₂. While the Al-doped BN nanocone increased these values to 3.00 eV and 2.22 eV respectively thereby improving the gas sensing performance. Additionally, Soltani et al.[137] investigated the sensing properties of Al and Ga-doped single-walled BN nanotubes. Their findings indicated that NH₃ got adsorbed with adsorption energy 1.82 eV and 1.66 eV onto Al-doped BN and Ga-doped BN. The higher adsorption energy was attributed to the robust interaction between the nitrogen p-orbital interaction between the Al-NH₃, thereby enhancing the chemical reactivity of the BN surface.

2.4 ROLE OF DENSITY FUNCTIONAL THEORY IN THE FIELD OF GAS SENSING

Density Functional Theory(DFT) has garnered significant attention from researchers working in the field of gas sensing. This can be inferred from the fact that in the recent 10 years, there has been an exponential rise in the number of published research papers using DFT to predict the gas-sensing behaviour of various 2D materials, as shown in Figure 1.6. The popularity and extensive implementation of the DFT lies in its theoretical framework, which has provided a

precise way to calculate adsorption energies, geometry optimisation, band structure and density of states, work function, diffusion coefficient upon the adsorption of targeted oxidizing/reducing gases onto various 2D materials such as graphene, TMDs, MXene, Metal oxides and Metal Organic Framework, etc. These DFT calculations revealed the most stable adsorption sites, strength of the interaction, nature of the bond (covalent, ionic) and adsorption process (chemisorption/physisorption), direction and magnitude of charge transfer between the gas molecule and the sensing surface. However, it is well known to researchers that through defect engineering and elemental doping, the sensing performance of various 2D materials can be improved significantly. But in reality, the creation of defects and elemental doping in the low-dimensional systems is very challenging and difficult because it involves the breaking of strong covalent bonds, which demands specialized expensive techniques such as ion-radiation and thermal annealing, which also create unwanted secondary defects, dislocations, and amorphization, thereby demanding a high level of precision to control dopants and defects. In response to all these issues, DFT-based software like Quantum ATK, Quantum Espresso, and VASP provides an intuitive way to model these structures using supercells and calculations to calculate formation energy, lattice distortion, and charge transition levels, thereby facilitating an easy way to optimise the various 2D materials with different morphologies without synthesising them. Furthermore, various experimental approaches pose serious limitations when assessing the sensing performance of 2D materials for multiple gases, including the need for a complex gas-sensing setup, extensive time, and a complicated fabrication process. Here, DFT allowed precise comparison of adsorption energies, charge transfer, diffusion barrier, modulation in the band gap and work function for various 2D materials upon the adsorption of multiple gases. Thus, enabling rapid screening of potential nanomaterials with superior sensing capabilities.

RESEARCH OBJECTIVES

1. Exploration of the sensing capabilities of 2D material as a sensing material for the detection of toxic gases under harsh environment conditions.
2. Analysis of the adsorption mechanism by which toxic gas got adsorbed onto the surface of the sensing material utilizing DFT.
3. Analysis of the improvisation in the sensing performance, adsorption capability and stability of the sensing material towards toxic gases upon surface

functionalization.

4. Investigation of the adsorption phenomena and sensing performance of the Nanowire towards the detection of toxic gases using DFT.

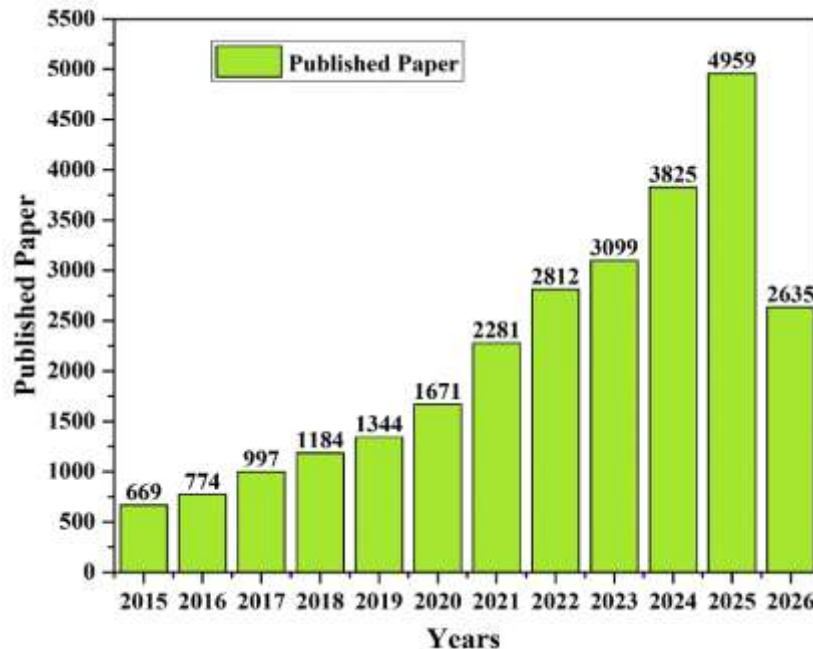


Figure 1.6: Plotted graph representing an exponential increase in the number of published DFT based gas sensing papers over the years. This data is being taken from the Web of Science with the search keywords “DFT based gas sensors”.

3.1 Organisation of the Thesis

This thesis is organised into seven chapters, each contributing to a comprehensive understanding of Cu-decorated hexagonal boron nitride and MoS₂-based gas sensing materials investigated through first-principles calculations.

Chapter 1 introduces the broader context of air pollution and its associated health and environmental hazards. It provides a detailed overview of chemoresistive gas sensing technologies, with particular emphasis on the working principles of n-type and p-type semiconductor-based sensors. The chapter systematically reviews two-dimensional materials—including graphene, reduced graphene oxide, transition metal dichalcogenides, black phosphorene, g-C₃N₄, MXene, metal–organic frameworks, and hexagonal boron nitride—as promising candidates for next-generation gas sensors. Enhancement strategies such

Introduction

as doping, defect engineering, heterostructure formation, and light-assisted activation are discussed, culminating in the statement of the research objectives.

Chapter 2 presents the theoretical background underpinning all computational investigations in this thesis. It covers the foundational principles of Density Functional Theory (DFT), beginning with the Hohenberg–Kohn theorems and the variational principle, and progressing through the Kohn–Sham formulation, exchange–correlation approximations, and the origin of the band-gap problem. A comparative discussion of the Kohn–Sham, Hartree, Hartree–Fock, and Dyson equations is also provided to situate DFT within the broader framework of many-body theory.

Chapter 3 investigates the adsorption behaviour of phosgene (COCl_2) on pristine hBN, Cu-doped hBN, and Cu-decorated hBN (Cu-hBN) monolayers using DFT. The chapter demonstrates that Cu incorporation significantly strengthens adsorption through chemisorptive interactions, reduces the band gap, and enhances electrical conductivity by up to 72.25%. Charge transfer analyses via Hirshfeld charges, charge density differences, ELF, and RDG calculations confirm the role of Cu atoms as electron donors. Recovery time under visible light irradiation at elevated temperatures is also evaluated.

Chapter 4 examines the adsorption of cyanogen chloride (CNCl) on pristine and Cu-decorated hBN. While pristine hBN exhibits physisorption with a poor recovery time, Cu decoration markedly enhances the adsorption energy and modifies the electronic structure. The chapter highlights a 31.54% variation in work function upon CNCl adsorption on Cu-hBN, indicative of high sensitivity. Recovery time calculations at 300 K, 400 K, and 500 K are reported, and RDG analysis confirms the non-covalent nature of the Cu-hBN– CNCl interaction.

Chapter 5 addresses the detection of thermal runaway gases (C_2H_4 , CO , CO_2 , H_2 , and CH_4) released during lithium-ion battery failure. The adsorption of these gases on pristine and Cu-doped hBN is systematically studied using DFT. Substitutional Cu doping at a boron vacancy site is found to convert physisorption into chemisorption, substantially improving sensitivity, selectivity, charge transfer, and recovery time. DOS and RDG analyses confirm chemoresistive behaviour and strong attractive non-covalent interactions, establishing Cu-doped hBN as a viable sensing material for battery safety monitoring.

Chapter 6 investigates the influence of Cu substitutional doping and surface adsorption on the electronic properties of MoS₂ nanowires (NW). ELF and Bader charge analyses reveal that Cu adsorption leads to covalent bonding, while substitutional doping induces ionic bonding with significant charge redistribution. Work function calculations demonstrate an enhanced electron emission capability in Cu-doped MoS₂NW. Thermodynamic stability is confirmed through cohesive energy calculations, and the results highlight the potential of Cu-doped MoS₂NW for field emission and nanoelectronics applications.

Chapter 7 presents the overall conclusions drawn from the research investigations reported in the preceding chapters. It summarises the key findings related to the sensitivity, selectivity, and sensing performance of Cu-decorated and Cu-doped hBN-based gas sensors, and contextualises their significance in the detection of hazardous gases in industrial, automotive, and urban environments. The chapter also outlines the broader societal implications of the work and proposes directions for future research aimed at advancing the development of efficient, low-power, and cost-effective gas sensing technologies.

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Chapter 2

Computational Methodology



In this chapter, the theoretical foundations and practical realisation of Density Functional Theory (DFT) are taught as a powerful framework for studying many-electron systems. It explains how the Hohenberg-Kohn theorems establish the electron density as the central quantity that uniquely determines the ground-state wave function, the total energy, the external potential, and all observables, thereby reducing the complexity of the many-body Schrödinger equation. The chapter shows how the variational principle leads to an energy functional whose minimum corresponds to the actual ground state, while also highlighting why early approaches like the Thomas-Fermi model are inadequate due to their neglect of exchange and correlation effects and their inability to describe molecular stability. A key learning outcome is the introduction of exchange-correlation energy, which accounts for both Pauli exclusion (exchange) and electron-electron interactions (correlation), and the recognition that its exact form is unknown and must be approximated. The Kohn-Sham formulation is considered the most practical implementation of DFT, replacing the interacting many-body problem with an auxiliary non-interacting system that reproduces the correct electron density through a self-consistent cycle, which forms the basis of modern first-principles calculations. The chapter also clarifies the interpretation and limitations of Kohn-Sham eigenvalues, the origin of the band-gap problem due to derivative discontinuities in the exchange-correlation functional, and why local and semi-local approximations such as LDA and GGA often underestimate band gaps. Finally, by comparing the Kohn-Sham, Hartree, Hartree-Fock, and Dyson equations, the

chapter provides insight into how DFT connects to many-body theory, emphasising both its computational efficiency and the ongoing need for improved functionals to accurately describe strongly correlated systems.

2.1 INTRODUCTION

All the matter around us, whether solids, liquids, gases or even biological systems, is composed of atoms and molecules, which are the building blocks of matter.[1] Therefore, a proper understanding of the behaviour of atoms and molecules is necessary, as macroscopic properties of matter, such as mechanical strength, electrical conductivity, optical absorption, and biological functionality, depend on microscopic interactions, including electron-electron and electron-nucleus interactions as shown in figure (2.1).[2] Historically, classical theories have provided computationally efficient and highly effective methods for studying larger complex systems over meaningful time scales. For example, the most effective computational approach for bridging the relationship between microscopic interactions and macroscopic behaviour was molecular dynamics[3-5], which is based solely on classical concepts. In molecular dynamics, the atoms are treated as classical particles having well-defined initial positions and velocities.

The time evolution of the positions and velocities was determined by solving Newton's second law of motion through numerical integration techniques. It is the time-ordered records of positions and velocities that contain all the microscopic information needed to compute macroscopic properties such as diffusion, temperature, pressure, etc., through Statistical Mechanics.[6] Despite such success, molecular dynamics failed to explain phenomena arising from quantum effects, such as superconductivity, electron tunnelling, the discretization of energy levels, and the breaking and formation of bonds. The reason behind the failure of Molecular dynamics lies in its mathematical formalism, which is based on classical concepts. On the other hand, Quantum Theory was able to overcome this limitation by considering the wave nature of microscopic particles, such as electrons, through the Schrödinger equation[7]. For a single electron system having a mass(m) moving under the influence of an external potential $V(r)$ the non-relativistic Schrodinger equation is written as shown below in the equation (2.10)

$$\left[\frac{-\hbar^2 \nabla^2}{2m} + V(r) \right] \psi(r) = E\psi(r) \quad (2.10)$$

Where $-\frac{\hbar^2 \nabla^2}{2m}$ represents the Kinetic energy. The wave function $\psi(r)$ for a single electron system has a dependence on the position coordinates (x, y, z) as a result, this reduces the non-relativistic Schrodinger equation to a three-dimensional problem, which can be solved exactly

for a Coulomb potential i.e. $V(r) = -\frac{Ze^2}{4\pi\epsilon r}$ analytically through the variable separable method. In contrast, for a system having more than one electron, the non-relativistic Schrodinger's equation can be written as shown below in equation (2.11).

$$\left[\left[\sum_{i=1}^N \frac{-\hbar^2 \nabla^2}{2m} + V(r_i) \right] + \sum_{i<j} U(r_i, r_j) \right] \psi(r_1, r_2, r_3 \dots r_N) = E \psi(r_1, r_2, r_3 \dots r_N) \quad (2.11)$$

Where N is the number of electrons, $\sum_{i<j} U(r_i, r_j)$ is the interaction energy term for a Coulomb system having electron-electron repulsion, the interaction energy operator ($\hat{U}$) can be written as $\sum_{i<j} \frac{q^2}{|r_i - r_j|}$. The wavefunction $\psi(r_1, r_2, r_3 \dots r_N)$ for a multielectron system, the dependence will be on the particle's position coordinate. This reduces the non-relativistic Schrodinger equation for a multielectron system to a 3N-dimensional problem, which is very difficult for a normal human being to solve analytically or numerically. It is by comparing equations (2.10) and (2.11) that we found that, as the number of particles in a system increases from a single particle to multiple electrons, the interaction energy term becomes significant, making the problem extremely complex. This is known as the many-body problem[8]. For decades, many powerful methods have been developed to solve Schrödinger's equation for many-body problems. In Physics, for example, there exist various effective approaches, such as diagrammatic Perturbation theory[9], which is based on the systematic expansion in a Slater determinant[10]. The major issue with all these approaches is that they demand high computational resources; as a result, it is impossible to apply them efficiently to a larger and more complex system. This can be inferred from the fact that till now nobody has ever calculated the chemical properties for a system having 100 atom/ molecule and electronic properties for a real semiconductor without using Green's function.[11]. It is here where DFT[12, 13] provides a more versatile but less accurate approach to solving many-body problems by reformulating the many-body problem in terms of electron density, which depends on the position vector regardless of the number of electrons. As a consequence, DFT systematically mapped the many-body problem with $\hat{U}$ onto a single body problem without $\hat{U}$ as shown in Figure 2.2. This approach provided the basis for the electronic structure, magnetic, and structural properties of an extended system. The extent to which DFT has contributed to the science of molecules can be inferred from the fact that, in 1998, the Nobel Prize in Chemistry was awarded to Walter Kohn and John Pople for founding DFT and implementing it in computational chemistry. Hence, the main objective of the current chapter is to provide an overview of DFT by presenting many interesting, detailed proofs of the

theorems, illustrative application and exciting development which might be useful to the undergraduate, post-graduate students who have completed a first course in Quantum Mechanics as well as to the researchers interested in exploring the structural, magnetic, electronic, optical properties in low dimensional systems[14], relativistic effects in heavy elements[15] and various biological processes such as enzyme catalysis[16], metal ion coordination[17], and drug–target interactions[18].

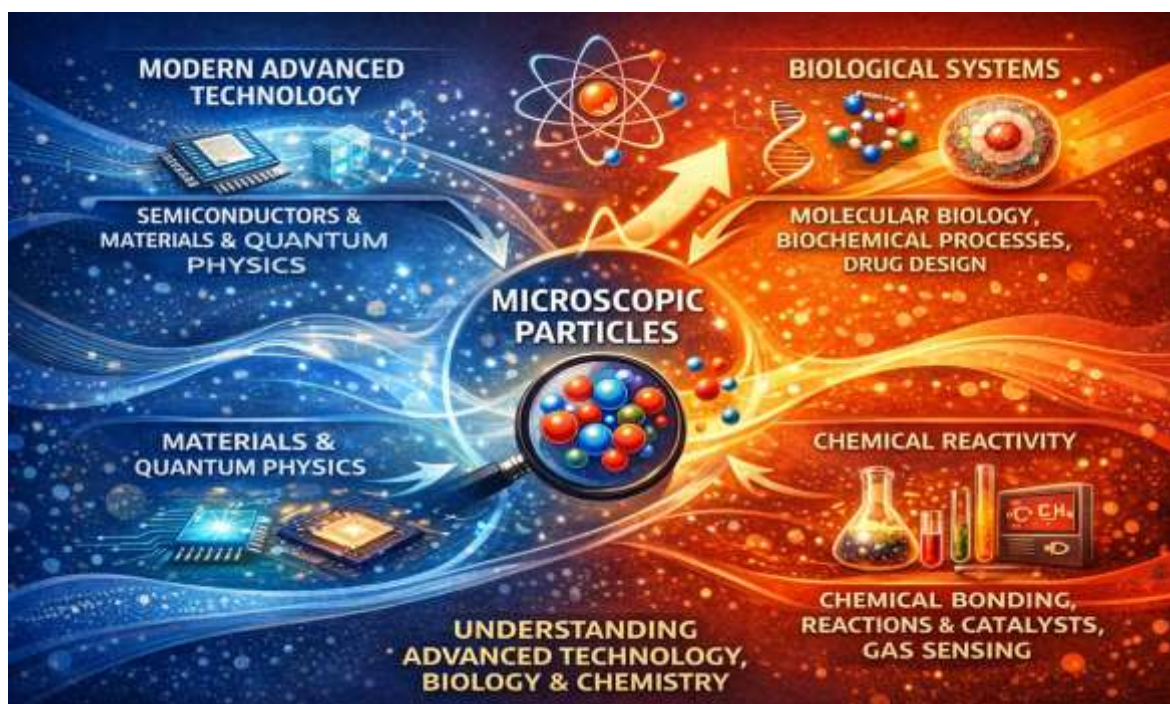


Figure 2.1 Schematic diagram illustrating the significance of understanding the microscopic interaction in the field of material science, modern advanced technology, biology and chemistry.

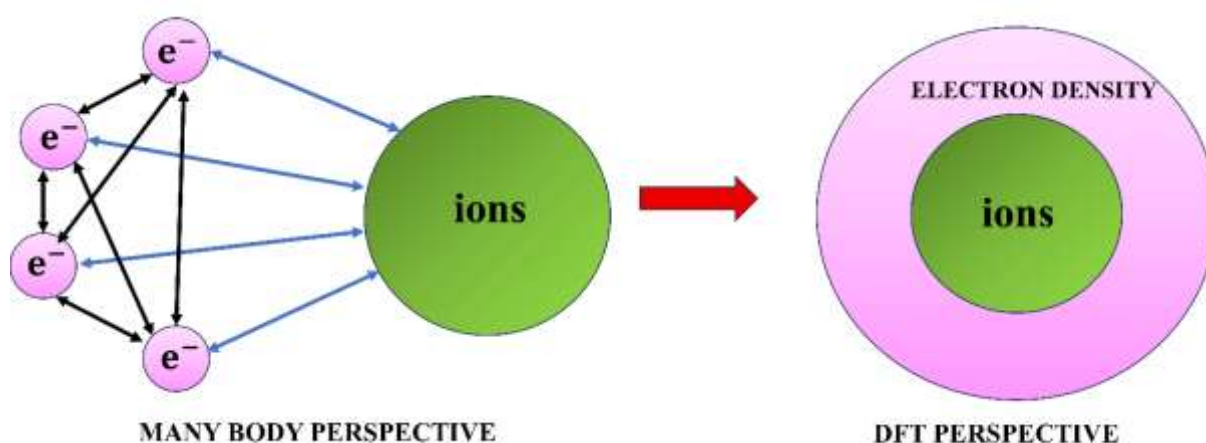


Figure 2.2 Schematic diagram illustrating how the electron–electron interaction is replaced by an equivalent formulation based on electron density, which forms the central theme of DFT.

2.2 HOHENBERG-KOHN THEOREM

At the heart of the DFT is the Hohenberg-Kohn theorem[19, 20]. According to the Hohenberg-Kohn theorem, for a given ground state density $n_0(\mathbf{r})$, it is possible to calculate the corresponding ground state wave function $\psi(r_1, r_2, r_3, r_4, \dots, r_n)$. This means that ψ_0 is a functional of $n_0(\mathbf{r})$. As a consequence, all observables are functions of $n_0(\mathbf{r})$ as well. If (ψ_0) can be calculated from $n_0(\mathbf{r})$ and $n_0(\mathbf{r})$ can be calculated from $\psi_0(\mathbf{r})$, this implies that both the functions are equivalent and contain the same information. It seems impossible that how can electron density ($n_0(\mathbf{r})$), which is a function of one variable, i.e. position vector ($\vec{r}$), be equivalent to a wavefunction ψ_0 , which is itself a function of N variables $r_1, r_2, r_3, r_4, \dots, r_n$? The answer to this question lies in the fact that the knowledge of $n_0(\mathbf{r})$ implies an implicit understanding of much more than that of an arbitrary function $f(\mathbf{r})$. The ground-state wave function ψ_0 is the one that not only reproduces the ground-state electron density $n_0(\mathbf{r})$ but also minimizes the system's energy. For a given ground-state electron density, this can be written as in equation (2.12)

$$E_{v,o} = \min_{\psi-n_0} \langle \psi | \hat{T} + \hat{U} + \hat{V} | \psi \rangle \quad (2.12)$$

Where $E_{v,o}$ denotes the ground state energy in a potential $V(\mathbf{r})$. The above equation tells us that, for a given electron density $n_0(\mathbf{r})$, not only does $n_0(\mathbf{r})$ reproduce the ground-state electron density $n_0(\mathbf{r})$, but it also minimizes the system's energy. For any arbitrary density $n(\mathbf{r})$, we can write the energy functional $E_v[n]$ as given in equation (2.13).

$$E_v[n] = \min_{\psi-n} \langle \psi | \hat{T} + \hat{U} + \hat{V} | \psi \rangle \quad (2.13)$$

If $n(\mathbf{r})$ is an electron density which is different from the ground state electron density $n_0(\mathbf{r})$ in a potential $V(\mathbf{r})$, then the $\psi(r_1, r_2, r_3, r_4, \dots, r_n)$ wave function generated from the $n(\mathbf{r})$ is different from the ψ_0 generated from $n_0(\mathbf{r})$. According to the variational principle, the minimum value of $E_v[n]$ will be either higher than or equal to the ground state energy $E_{v,o} = E_v[n_o]$. This indicates that the functional $E_v[n_o]$ can be minimized for $n(\mathbf{r}) = n_0(\mathbf{r})$ and its minimum value will be $E_{v,o}$. The total energy functional can be written as shown in the equation (2.14) below.

$$E_v[n] = \min_{\psi-n} \langle \psi | \hat{T} + \hat{U} | \psi \rangle + \int d^3r n(\mathbf{r})v(\mathbf{r}) = F[n] + V[n] \quad (2.14)$$

Where $F[n] = \min_{\psi-n} \langle \psi | \hat{T} + \hat{U} | \psi \rangle$ is the internal energy function $F[n]$ which is clearly independent of the $v(\mathbf{r})$ and can only be determined by the structural form of $\hat{T}[n]$ and $\hat{U}[n]$. The universality of the internal energy function enables us to define the ground state wave

function ψ_0 as an antisymmetric N-particle function that yields the minimum of $F[n]$ and reproduces $n_0(r)$. The strong form of the Hohenberg-Kohn theorem is based on the inequality[21-23].

$$\int d^3r \Delta n(r) \Delta v(r) < 0 \quad (2.15)$$

Here $\Delta n(r)$ and $\Delta v(r)$ represent a change in the electron density and potential. According to equation (2.15), if $\Delta v(r) \neq 0$ then $\Delta n(r) \neq 0$, this means that any change in the potential would lead to a change in the electron density. This leads to the conclusion that there can't be two local potentials corresponding to the same ground-state charge density. Moreover, equation (2.15) also establishes a relation between the signs of $\Delta n(r)$ and $\Delta v(r)$ if $\Delta v(r)$ is mostly positive then $\Delta n(r)$ must be negative. On the other hand, for a Coulomb potential, the electron density will have a cusp at the position of the nuclei where it must satisfy the condition given by the equation (2.15).[24, 25]

$$Z_k = \frac{-a_0}{2n(r)} \frac{dn(r)}{dr} \Big|_{r=R_k} \quad (2.16)$$

where R_k denotes the position of the nuclei, Z_k their atomic number and $a_0 = \hbar^2/me^2$ is the Bohr radius. For a Coulomb system it is through the information of the electron density ($n(r)$) one can thus completely specify the Hamiltonian of the system the integral over $n(r)$ yields the total particle number (N), the position of the cusps of $n(r)$ are the position of the nuclei (R_k) and the derivatives of $n(r)$ at these positions yields Z_k by means of equation (2.16). But in practice, it is tough for one to know the density distribution sufficiently well in order to search for the cusp and calculate the local derivatives. But Kato's theorem provides a vivid illustration of how, from the knowledge of electron density, one can completely specify a non-trivial Hamiltonian.

2.1.1 SUMMARY OF HOHENBERG KOHN THEOREM

1. The non-degenerate ground state (GS) wave function is a unique function of the ground state electron density ($n_0(r)$). This is the core of the Hohenberg-Kohn theorem. It is due to this theorem that any observable ($\hat{O}$) will also be a functional of electron density too.

$$O_0 = O[n_0] = \langle \psi[n_0] | \hat{O} | \psi[n_0] \rangle \quad (2.17)$$

The most critical observable is the ground-state energy, which is given by equation (2.17) below. For any non-trivial wave function ψ' which is not the ground state wave function ψ_0 ,

ψ' will never have an energy value below the true ground-state energy. Similarly, in exact DFT, if $E[n]$ is the total energy evaluated for any system having an external potential $v(r)_{ext}$ and if $n(r)$ is the non-trivial electron density, which is not the actual ground-state electron density $n_0(r)$, then $n(r)$ will never have a total energy below the true ground-state energy.

$$E_v[n_0] = \langle \psi[n_0] | \hat{H} | \psi[n_0] \rangle \quad (2.18)$$

$$E_v[n_0] \leq E_v[n'] \quad (2.19)$$

$$E_{v,0} = E_v[\psi_0] = \langle \psi_0 | \hat{H} | \psi_0 \rangle \leq \langle \psi' | \hat{H} | \psi' \rangle = E_v[\psi'] \quad (2.20)$$

While performing the minimization of $E_v[n]$ there is a constraint that the integral of the total particle number N is an integer, which is taken into account by means of a Lagrange multiplier, thereby replacing the constrained minimization of $E_v[n]$ by an unconstrained one of $E_v[n] - \mu N$. Thus, energy minimization leads to the relation for calculating chemical potential.

$$\frac{\delta E_v[n]}{\delta n(r)} = \mu = \frac{\partial E}{\partial N} \quad (2.21)$$

2. For any non-relativistic Coulombic system, the energy functional $E_v[n]$ can be written as

$$E_v[n] = T[n] + V[n] + U[n] = F[n] + V[n] \quad (2.22)$$

where $T[n]$ and $U[n]$ are universal functions independent of the $v(r)$, on the other hand, the potential energy for any system having potential $v(r)$ is just the expectation value of $v(r)$. Moreover, equation (2.23) also indicates that if the potential $v(r)$ for any system is well known then just from the knowledge of the electron density, one can calculate the functional $V[n]$ very easily.

$$V[n] = \int d^3r n(r) v(r) \quad (2.23)$$

3. There is a fourth sub statement to the Hohenberg-Kohn theorem, which shows that if $v(r)$ is not held fixed, then the functional $V[n]$ becomes universal. This means that the ground-state electron density not only determines the ground-state wave function but also the potential $V = V[n_0]$ up to an additive constant. This can be proved from Schrodinger's equation as the potential operator $\hat{V}$ can be written as in the equation (2.24)

$$\hat{V} = \sum_i^N v(r_i) = E_k \frac{(\hat{T} + \hat{U})\psi_k}{\psi_k} \quad (2.24)$$

The above equation (2.24) indicates that any eigenstate ψ_k determines the potential operator $\hat{V}$ up to an additive constant corresponding to the energy eigenvalue. As a result, the explicit

reference to the potential v in the energy functional $E_v[n]$ is not necessary, and one can rewrite the ground state energy as in equation (2.25).

$$E_o = E[n_o] = \langle \psi[n_o] | \hat{T} + \hat{U} + \hat{V}[n_o] | \psi[n_o] \rangle \quad (2.25)$$

Also, we found from equation (2.25) that n_o now does determine not only the ground state wave function but the complete Hamiltonian and thus all excited states too:

$$\Psi(r_1, r_2, r_3, r_4, \dots, r_n) = \psi_k[n_o] \quad (2.26)$$

where k labels the entire spectrum of the many-body Hamiltonian $\hat{H}$ in the equation (2.26).

2.3 THOMAS FERMI APPROXIMATION

According to the Hohenberg–Kohn theorem it is possible to calculate the observables once the knowledge of the electron density is known because they are all functionals of the electron density $n(r)$. But in practice, using the Hohenberg-Kohn theorem, we can calculate only those observables that are explicit functions of $n(r)$ like total number of electrons, external potential energy and classical electrostatic energy, whereas it doesn't tell us how to compute those observables that are implicit functions of electron density $n(r)$ like optical properties, band gap, transport properties and excitation energies. Also, the energy minimization is a tough numerical problem. To overcome this problem, Llewellyn Thomas and Enrico Fermi proposed a model known as the Thomson-Fermi Model, which treats a large number of electrons within atoms and molecules as a uniform, non-interacting Fermi gas moving in an effective electrostatic potential. As a consequence, the full interaction energy, which was approximated by the Hartree energy as written in equation (2.27). On the other hand, the kinetic energy functional can be approximated as written in the equation (2.28).

$$U[n] = U_H[n] = \frac{q^2}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} \quad (2.27)$$

$$T[n] \approx T^{LDA}[n] = \int d^3r n(r) t_{Homo} \quad (2.28)$$

Where t_{Homo} represents the kinetic energy of the homogeneous interacting system with a fixed electron density $n(r)$. For any interacting system, the nature of the t_{Homo} is not known explicitly as a function of (r) ; therefore, its determination requires further approximation. Initially, the local density approximation (LDA) was used to determine the function of t_{Homo} . According to this approximation, one can imagine the real inhomogeneous system to be decomposed into small cells having $n(r)$ and $v(r)$ as the electron density and potential, respectively, which are approximately constant. The per-volume energy of each cell contributes

to the real inhomogeneous one. For any interacting system, the nature of the t_{Homo} is well known explicitly as a function of $n(r)$, which can be inferred from equation (2.29), but further, this was also approximated using LDA as a result, the kinetic energy functional for the non-interacting system can be written as mentioned in the equation (2.30).

$$t_s^{homo}(n) = \frac{3\hbar^2}{40m_e} \frac{3^{2/3}}{\pi^{2/3}} n(r)^{5/3} \quad (2.29)$$

$$T[n] \approx T_s^{LDA}[n] = \int d^3r n(r) t_s^{homo} \quad (2.30)$$

Where $T_s^{LDA}[n]$ is the local density approximation to the kinetic energy of the non-interacting electrons of density $n(r)$. Combining equations (2.27) and (2.30), the total energy functional using the Thomas-Fermi approximation can be written as

$$E[n] = T[n] + U[n] + V[n] \approx E^{TF}[n] = T_s^{LDA}[n] + U_H[n] + V[n] \quad (2.31)$$

The biggest limitation of the Thomas-Fermi model is that it cannot explain the molecule's stability, as the approximation implies that the molecule's energy is greater than the sum of its constituent atoms' energies.[26, 27] This type of limitation and inaccuracy is a consequence of the neglect of the correlation in the $U_H[n]$ and usage of local density approximation in the $T[n]$, thereby limiting the practical implementation of the Thomas-Fermi model in DFT.

(A) DERIVATION OF THE KINETIC ENERGY FOR THE THOMAS-FERMI MODEL

Let us consider a small volume element (ΔV) in real space at $T=0K$. The electrons are in their ground state and can occupy momentum states from $p=0$ to the maximum $p=p_F$ in momentum space. Thereby filling the spherical volume in the momentum space up to V_F , whose value is given by equation (2.32)

$$V_F = \frac{4}{3} \pi p_F^3(\vec{r}) \quad (2.32)$$

Where $\vec{r}$ is the position vector of a point in ΔV . Since each point in the phase space corresponds to an allowed state. Therefore, the corresponding real space volume (ΔV) in the phase space will be ∇V_{ph} which is given as in equation (2.33)

$$\Delta V_{ph} = \frac{4}{3} \pi p_F^3(\vec{r}) \Delta V \quad (2.33)$$

But according to the Heisenberg uncertainty principle, the uncertainty in position and momentum coordinates in two dimensions ($x-p_x$) is connected as $\Delta x \Delta p_x \geq \hbar$. Similarly $\Delta y \Delta p_y \geq \hbar$ and $\Delta z \Delta p_z \geq \hbar$. As a result, the minimum volume that can be occupied in phase

space is $\hbar^3$. Also, according to the Pauli exclusion principle, only electrons having different spins can occupy the same states. As a result, the number of electrons that can be allowed to occupy a particular state is 2. The number of electrons available in the phase space volume ΔV_{ph} is ΔN_{ph} given by the equation (2.34).

$$\frac{2}{\hbar^3} \Delta V_{ph} = \frac{2}{\hbar^3} \left(\frac{4}{3} \pi p_F^3(\vec{r}) \Delta V \right) = \frac{8}{3} \pi p_F^3(\vec{r}) \Delta V \quad (2.34)$$

Where the quantity $\frac{2}{\hbar^3}$ is the density of electrons in the phase space. In real space, the electron density $n(r)$ will be the ratio of ΔN_{ph} to ΔV .

$$n(r) = \frac{\Delta N_{ph}}{\Delta V} = \frac{8}{3} \pi p_F^3(\vec{r}) \quad (2.35)$$

$$p_F = \frac{[3 n(r) \hbar^3]^{1/3}}{[8\pi]^{1/3}} \quad (2.36)$$

The fractions of electrons at a position $\vec{r}$ having momentum between $\vec{p}$ and $\vec{p} + d\vec{p}$ is given by the distribution function ($f_r(p)dp$) which is defined as in equation (2.37)

$$f_r(p)dp = \begin{cases} \frac{4\pi p^2}{\frac{4\pi p_F^3}{3}}, & \text{if } p \leq p_F \\ 0, & \text{otherwise} \end{cases} \quad (2.37)$$

Using the classical expression for the kinetic energies, the kinetic energy for a non-interacting electron having mass (m_e) and electron density $n(r)$ is given below in equation (2.38) -(2.40).

$$T_S[n] = \int_0^{p_F} \frac{p^2}{2m_e} f_r(p) n(r) dp \quad (2.38)$$

$$T_S[n] = \int_0^{p_F} \frac{p^2}{2m_e} \frac{4\pi p^2}{\frac{4\pi p_F^3}{3}} n(r) dp = \int_0^{p_F} \frac{3p^4}{2m_e} n(r) dp = \frac{3p_F^2}{2m_e} n(r) \quad (2.39)$$

$$T_S[n] = \frac{3n(r)}{2m_e} \left[\frac{(3\hbar^3 n(r))^{2/3}}{(8\pi)^{2/3}} \right] = \frac{3\hbar^2}{40m_e} \left[\frac{(3)^{2/3} (n(r))^{5/3}}{(\pi)^{2/3}} \right] \quad (2.40)$$

2.4 EXCHANGE CORRELATION ENERGY

As discussed in the section on the usage of the Local density approximation, the $T[n]$ resulted in inaccuracy. Therefore, to overcome this issue, a more accurate method was developed to account for the kinetic energy of the interacting electrons. Under this scheme, the $T[n]$ is decomposed into $T_s[n]$ and $T_c[n]$, where $T_s[n]$ is the kinetic energy of the non-interacting particles of electron density $n(r)$ and $T_c[n]$ is the kinetic energy of the correlated electrons.

$$T[n] = T_s[n] + T_c[n] \quad (2.41)$$

Here in the above equation (2.41) $T_s[n]$ is an unknown function of the electron density $n(r)$ but can be easily expressed in terms of the single particle orbitals $\varphi_i(r)$ of a non-interacting system with electron density $n(r)$ as shown below in the equation (2.42).

$$T_s[n] = \frac{-\hbar^2}{2m} \sum_i^N \int d^3r \varphi_i^*(r) \nabla^2 \varphi_i(r) \quad (2.42)$$

This is because for non-interacting particles, the total kinetic energy is just the sum of the individual kinetic energies. Moreover, the single-particle orbitals $\varphi_i(r)$ is itself a functional of electron density $n(r)$; as a result, the kinetic energy of the single particle $T_s[n]$ becomes an explicit function of single-particle orbitals $\varphi_i(r)$, but on the other hand, it is an explicit function of electron density $n(r)$. As a consequence, we can rewrite the exact energy functional as in the equation (2.43)

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\varphi_i[n]\}] + U_H[n] + V[n] + E_{XC}[n] \quad (2.43)$$

On comparing equation (2.43) with equation (2.31), we found that the energy functional is formally exact but E_{xc} is unknown, although the Hohenberg-Kohn theorem guarantees that it is also a function of electron density $n(r)$. This function is called the exchange correlation energy, [28, 29], which is basically the difference between (T_c) and $(U-U_H)$. The exchange correlation energy itself can be decomposed into E_X and E_C as $E_{XC} = E_X + E_C$. Where E_X is the exchange energy and E_C is the correlation energy. The exchange energy is due to the Pauli Principle, and E_C is due to correlations. The exchange energy (E_X) can be written explicitly in terms of the single-particle orbitals as written below in equation (2.44).

$$E_X[\{\varphi_i[n]\}] = \frac{q^2}{2} \sum_{jk} \int d^3r \int d^3r' \frac{\varphi_j^*(r) \varphi_k^*(r') \varphi_j(r') \varphi_k(r)}{|r-r'|} \quad (2.44)$$

The above equation (2.44) is known as the Fock term, but no general exact expression in terms of electron density is known.

(A) DIFFERENT PERSPECTIVES OF CORRELATION ENERGY

PROBABILISTIC APPROACH-In quantum mechanics for a system having (N) number of electrons, the probability of finding these electrons at any position (r) is just the amplitude of the many-body wave function. But if the existence of any electron doesn't affect the existence of other electrons, then the amplitude of the wave function of the many-electron system can be written as the amplitude of the wave function of the individual electrons. In reality, due to Coulomb repulsion, electrons repel each other; as a result, the probability of finding an electron

in the vicinity of another electron decreases. This mutual repulsion between the electrons causes the lowering of the total energy because the repulsion energy is dependent on the joint probability of finding an electron in the vicinity of another electron. For a system that is highly correlated, the correlation energy will be higher or comparable to the kinetic energy of the single particle, whereas for a weakly correlated system, the correlation energy will be lower than the kinetic energy of the single particle [Ts].

MEAN FIELD THEORY—Let us consider an alternative form of the Coulomb interaction represented by the operator $\hat{U}$ defined below by the equation (2.45)

$$\hat{U} = \frac{q^2}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} - \frac{q^2}{2} \int d^3r \int d^3r' \frac{n(r)\delta(r-r')}{|r-r'|} \quad (2.45)$$

The term $\frac{q^2}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|}$ and $\frac{q^2}{2} \int d^3r \int d^3r' \frac{n(r)\delta(r-r')}{|r-r'|}$ in the equation (2.45) represents the Hartree energy term whereas the second term represents the interaction of the electron with itself. The expectation value of the operator $\hat{U}$ will involve the expectation value of the product of the density operator, i.e. $\langle n(r)n(r') \rangle$. In order to understand how mean field theory deal with the expectation value of the product of the density operator we need to recall that the quantum correlation between the interacting particles give rise to quantum fluctuation. Therefore, rewriting the electron density operator by incorporating the fluctuation operator the resulting electron density operator is given by equation (2.46) and (2.47)

$$\hat{n}(r) = n(r) + \delta\hat{n}(r)_{\text{fluctuation}} \quad (2.46)$$

$$\hat{n}(r') = n(r') + \delta\hat{n}(r')_{\text{fluctuation}} \quad (2.47)$$

Substituting the value of the $\hat{n}(r)$ and $\hat{n}(r')$ in the expectation value of the product of the density operator, i.e. $\langle n(r)n(r') \rangle$ we get

$$\langle n(r)n(r') \rangle = \langle (n(r) + \delta\hat{n}(r)_{\text{fluctuation}})(n(r') + \delta\hat{n}(r')_{\text{fluctuation}}) \rangle$$

$$\begin{aligned} & \langle n(r)n(r') \rangle + \langle (n(r)(\delta\hat{n}(r')_{\text{fluctuation}})) \rangle + \langle (\delta\hat{n}(r)_{\text{fluctuation}})(\delta\hat{n}(r')_{\text{fluctuation}}) \rangle \\ & + \langle (\delta\hat{n}(r)_{\text{fluctuation}})(n(r')) \rangle \end{aligned}$$

$$\begin{aligned} & \langle n(r) \rangle \langle n(r') \rangle + \langle (n(r)) \rangle \langle \delta\hat{n}(r')_{\text{fluctuation}} \rangle + \langle (n(r')) \rangle \langle \delta\hat{n}(r)_{\text{fluctuation}} \rangle \\ & + \langle (\delta\hat{n}(r)_{\text{fluctuation}}) \rangle \langle (\delta\hat{n}(r')_{\text{fluctuation}}) \rangle \end{aligned}$$

If we neglect the quantum fluctuation this implies that $\langle (\delta\hat{n}(r)_{\text{fluctuation}}) \rangle = \langle (\delta\hat{n}(r')_{\text{fluctuation}}) \rangle = 0$ then the expectation value of the product of the density operator

becomes equal to the product of the expectation value of the individual electron density, i.e. $\langle n(r)n(r') \rangle = \langle n(r) \rangle \langle n(r') \rangle$ in the case of mean field theory.

2.5 KOHAN SHAM EQUATION

DFT can be implemented in various ways, as discussed in the previous section; one is the minimization of the energy functional, which is not an efficient method. In response to this issue, the Kohan Sham equation[30, 31] is considered the most widely accepted approach for implementing the DFT method. The success and popularity of the Kohan Sham can be attributed to the fact that it replaces the difficult interacting many body systems in the Hamilton equation (2.11) with different auxiliary system that can be solved more easily. As a consequence, the many body system appears to be a single body system. Therefore, in the section (A) we have tried to derived the Kohan Sham equation in order to understand the formalism.

(A) DERIVATION OF KOHAN SHAM EQUATION

In the previous section (2.4), we observed that the kinetic energy of non-interacting electrons depends on the orbitals. Therefore, one cannot directly minimize the energy functional directly with respect to electron density $n(r)$. With respect to this issue, Kohan Sham provides an indirect method of minimizing the energy functional as follows in equation (2.48).

$$0 = \frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V[n]}{\delta n(r)} + \frac{\delta U_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} \quad (2.48)$$

$$\frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + v(r) + v_H(r) + v_{xc}(r) \quad (2.49)$$

Since the derivative of $E_{xc}[n]$ with respect to $n(r)$ can only be calculated if one has the knowledge of the approximation used for $E_{xc}[n]$. Therefore, we have assumed $v_{xc}[n]$ is equal to the derivative of $E_{xc}[n]$ with respect to $n(r)$. According to the Sham-Schulter equation, it is related to the irreducible self-energy. For a system having non-interacting electrons moving under the influence of the potential $V_s(r)$ The energy minimisation condition is simply given by equation (2.50).

$$0 = \frac{\delta E_s[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V_s[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + v_s(r) \quad (2.50)$$

The above equation (2.50) suggests that, for a system of non-interacting electrons, the v_H and v_{xc} terms are absent. Let $n(r)$ and $n_s(r)$ be the electron density satisfying the energy minimization condition given by the equations (2.49) and (2.50) respectively. Comparing equation (2.49) with equation (2.50) we found that both the energy minimization conditions

can have the same solution, i.e. $n_s(r) = n(r)$ if $v_s(r)$ satisfies the condition given by the equation (2.51).

$$v_s(r) = v(r) + v_H(r) + v_{xc}(r) \quad (2.51)$$

As a consequence, one can calculate the density of the interacting system having the potential $v(r)$ just by solving the Schrodinger equation for a system of non-interacting particles having the potential $v_s(r)$. In particular, the Schrodinger equation for an auxiliary system mentioned in equation (2.52) yields an orbital ($\varphi_i(r)$) capable of reproducing the original electron density for the system through a relation given by equation (2.53)

$$\left[\frac{-\hbar^2 \nabla^2}{2m} + v_s(r) \right] \varphi_i(r) = \epsilon \varphi_i(r) \quad (2.52)$$

$$n_s(r) = n(r) = \sum_{i=1}^N f_i |\varphi_i(r)|^2 \quad (2.53)$$

Where f_i is the occupied i^{th} orbital. The above-mentioned equation from (2.51) to (2.53) is known as the Sham equations. Thus, Kohan Sham replaces the problem of solving many-body systems by solving the Schrödinger equation for a system of non-interacting particles. The flow chart shown in Figure (2.3) represents the algorithm of solving the Kohan Sham equation, which is utilized by various DFT-based software like VASP, Quantum Espresso, Gaussian, Wien-2K, etc. The usual way of solving the Kohan Sham equation is by starting with an initial guess for the electron density $n(r)$, followed by the calculation of $v_s(r)$ and then the solution of the auxiliary differential equation given by the equation (2.52) for the orbitals $\varphi_i(r)$. After evaluating the orbitals $\varphi_i(r)$ one can calculate the new electron density using the equation (2.53). If the calculated electron density converges with the initial electron density, then this process step otherwise continues; this process is called “Self-Consistent Cycle”. Different convergence criteria such as convergence in the energy, density or some observable calculated from these and various convergence accelerating algorithms such as mixing of old and new effective potential are also used. In practice, it requires a dozen iterations to achieve convergence, whereas if the convergence seems unattainable, a self-consistent solution of the Kohn-Sham equation can't be found. If ($n_0(r)$) is the converged solution, then one can calculate the total energy in an alternative form is given by the equation (2.54).

$$E_0 = \sum_{i=1}^N E_i - \frac{q^2}{2} \int d^3r \int d^3r' \frac{n_0(r)n_0(r')}{|r-r'|} - \int d^3r n_0(r) V_{exc}(r) + E_{xc}[n_0] \quad (2.54)$$

Equation (2.54) follows from writing $V[n]$ in (2.43) by means of (2.51) as shown in the equation (2.55).

$$\begin{aligned}
 V[n] &= \int d^3r v(r)n(r) = \int d^3r [V_s(r) - V_H(r) - V_{xc}(r)]n(r) \\
 &= \int d^3r V_s n(r) - \int d^3r [V_H(r) + V_{xc}(r)]n(r)
 \end{aligned}
 \quad (2.55)$$

Thus, the total energy of the non-interacting system as $E_s = \sum_i^N E_i = T_s + V_s$.

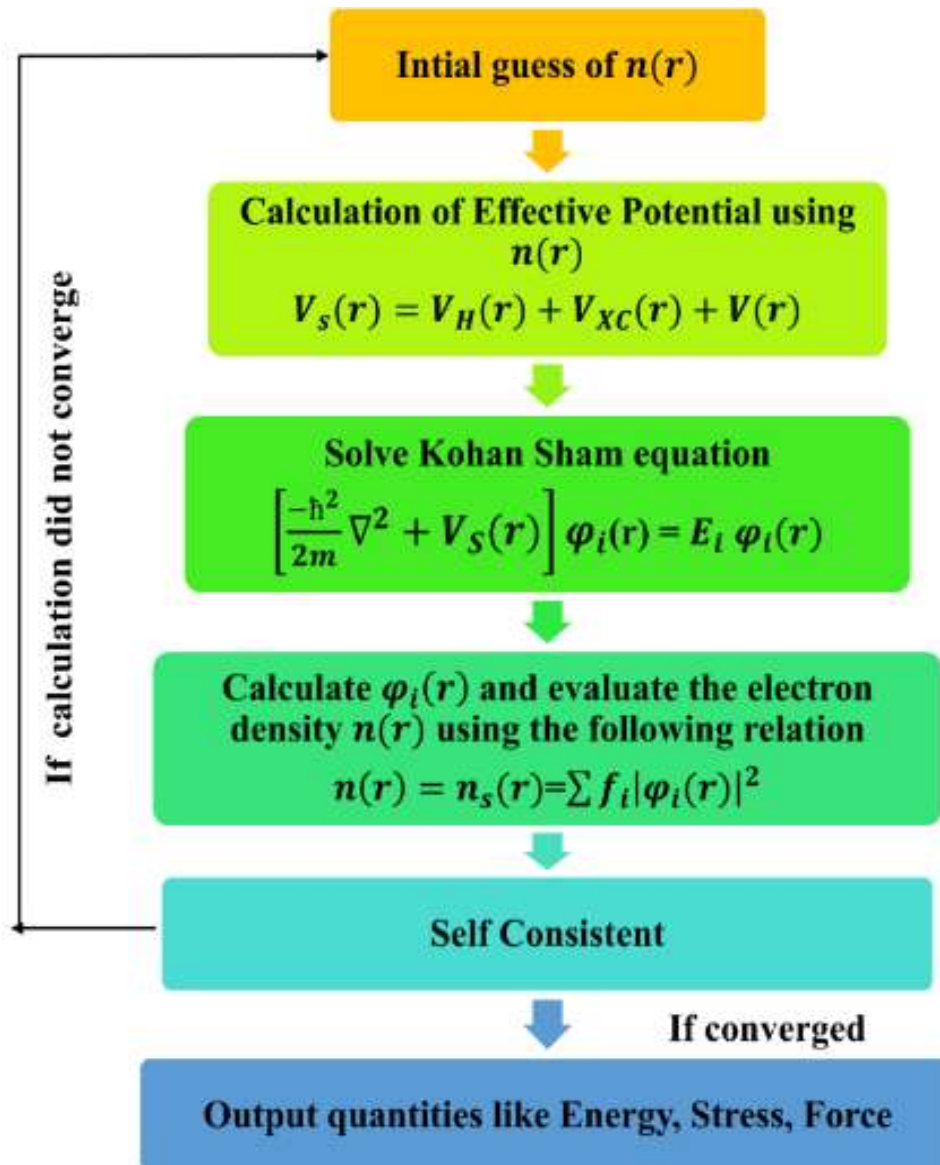


Figure 2.3: Schematic flow chart describing the iterative Self-Consistent Cycle (SCF) employed to solve the Kohn-Sham equations in the DFT.

(B) THE KOHAN SHAM EIGENVALUES

In the previous section we have observed while deriving the Kohn Sham equation that (E_i) has been treated as artificial objects because they are the eigenvalues corresponding to the eigenfunction $\varphi_i(r)$ orbitals capable of yielding the correct density. It is this electron density that has a strict meaning to the Kohn Sham. The calculated Kohn Sham eigenvalues was found to bear a semi quantitatively approach to the true energy spectrum[32], thereby

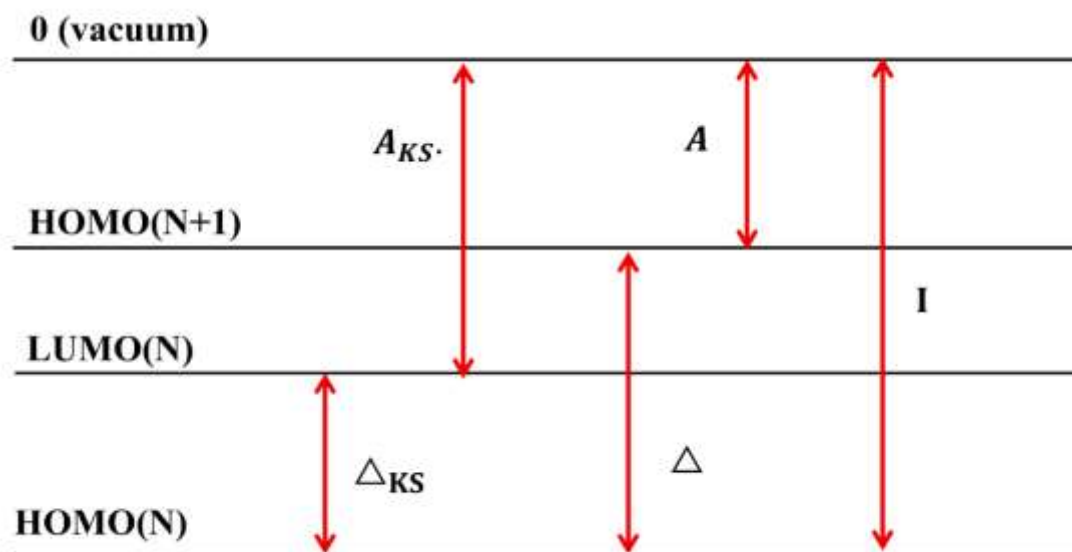


Figure 2.4: Schematic flow chart illustrating how the Kohan-Sham eigenvalues are related with some observables.

indicating that they cannot be trusted quantitatively. The major exception to this rule is the highest occupied Kohan Sham eigenvalues. Let $E_N(M)$ denotes the N^{th} eigenvalues having M electrons. It has been proven through rigorous calculation that $E_N(N) = -I$ and $E_{N+1}(N+1) = -A$

where I and A are the first ionization energies and electron affinity of the system having N electrons.[32, 33] These results hold good for exact functional but when calculated using local density approximation and Generalized Gradient approximation, the calculated highest Kohan Sham eigenvalues don't provide good approximation to the experimental I and A . In order to obtained better results for these observables they were calculated using the energy difference like $E_0(N-1) - E_0(N) = I$ and $E_0(N+1) - E_0(N) = A$ where $E_0(N)$ is the ground state energy of the N body system. Alternatively self-interaction correction was also used to improve the ionization energies and electron affinity from the Kohan Sham eigenvalue.[34].

Figure (2.4) represents the role played by the highest and lowest Kohan Sham eigenvalues and their relation with observable. For a molecule HOMO(N) and LUMO(N) is the highest and lowest occupied molecular orbital for a system having N electrons. In case of a solid having a gap, the HOMO and LUMO become the top and bottom of the valence and conduction band, respectively, whereas in the case of a metal, they both lie at the Fermi level. The vertical line in Figure (2.4) indicates the Kohan Sham gap (Δ_{KS}), the fundamental gap (Δ), and the derivative discontinuity in the XC function interacting electron system. Here $I(N) = -E_N(N)$, $A(N) = -E_{N+1}(N+1)$ is the electron affinity and the Kohan Sham electron affinity $A_{KS}(N) = -E_{N+1}(N)$. For a system that is characterized by fermionic quasi particles and the absence of

correlation, it is a surprise that the Kohan Sham eigenvalues (E_i) do provide a reasonable first approximation to the actual energy level of an extended system. This approximation to the Kohan Sham eigenvalues does provide a useful and successful method of calculating the band structure in solid state physics. But on the other hand, one must remember that in the Kohan Sham equation, we are literally treating the auxiliary single-body equation as an approximation to the many-body Schrodinger equation. As a consequence, DFT is practical in this mode and no longer serves as a many-body theory but rather as a mean-field theory. Moreover, the neglect of the derivative discontinuity (Δ_{XC}) by the standard local and semi-local XC function leads to an underestimation of the band gap. This problem, known as the band-gap problem, is the most commonly observed in transition-metal oxides and other strongly correlated systems. Self-interaction correction also provides a partial remedy to this problem.[35, 36]

(C) BAND GAP PROBLEM

The most intriguing property of the exact exchange correlation part is the derivative discontinuity of the exchange correlation function with respect to the total number of particles given by equation (2.56)[37-39].

$$\frac{\delta E_{xc}[n]}{\delta n(r)} \Big|_{N+\delta} - \frac{\delta E_{xc}[n]}{\delta n(r)} \Big|_{N-\delta} = v_{exc}^+ - v_{exc}^- = \Delta_{XC} \quad (2.56)$$

Where δ is the infinitesimal shift in the electron number (N) and Δ_{XC} is system-dependent but $\vec{r}$ is the independent shift of the exchange potential ($V_{XC}(\vec{r})$) as it passes from the electron-poor to the electron-rich side of integer N. As a consequence, the exact functional cannot be described by local (LDA) or semi-local (GGA or meta-GGA) approximations. This is because the exact function is highly non-local, meaning that it depends on the electron density over a region of space rather than just at a point ($\vec{r}$) whereas the LDA and GGA /meta GGA approximation depend on the electron density and a few local derivatives at a position ($\vec{r}$). Similarly, the Kinetic energy functional exhibits a discontinuity, as expressed below.

$$\frac{\delta T_s[n]}{\delta n(r)} \Big|_{N+\delta} - \frac{\delta T_s[n]}{\delta n(r)} \Big|_{N-\delta} = E_{N+1} - E_N = \Delta_{KS} \quad (2.57)$$

Where E_{N+1} and E_N are the highest and lowest Kohan-Sham eigenvalues in the equation (2.57). In chemistry, the highest and lowest Kohan Sham eigenvalues are called HOMO and LUMO.

The discontinuity in the derivative of the kinetic energy functional with respect to particle number gives rise to the Kohan Sham single particle gap Δ_{KS} . The true fundamental gap $\Delta = E(N+1) + E(N-1) - 2E(N)$ is the discontinuity of the total ground state energy function.

Differentiating the energy functional $E[n]$ given by equation (2.58) with respect to the particle number.

$$E[n] = T_s[n] + V[n] + U_H[n] + E_{xc}[n] \quad (2.58)$$

$$\frac{\delta E[n]}{\delta n(r)}|_{N+\delta} - \frac{\delta E[n]}{\delta n(r)}|_{N-\delta} = \frac{\delta T_s[n]}{\delta n(r)}|_{N+\delta} - \frac{\delta T_s[n]}{\delta n(r)}|_{N-\delta} + \frac{\delta V[n]}{\delta n(r)}|_{N+\delta} - \frac{\delta V[n]}{\delta n(r)}|_{N-\delta} + \frac{\delta U_H[n]}{\delta n(r)}|_{N+\delta} - \frac{\delta U_H[n]}{\delta n(r)}|_{N-\delta} + \frac{\delta E_{xc}[n]}{\delta n(r)}|_{N+\delta} - \frac{\delta E_{xc}[n]}{\delta n(r)}|_{N-\delta} = \Delta_{KS} + \Delta_{XC} \quad (2.59)$$

Since the rest of the terms in the exact energy functional don't have derivative discontinuity with respect to particle number which means they are continuous except the kinetic energy functional and the exchange correlation functional. As a consequence, the fundamental gap which is the sum of derivative discontinuity in the kinetic energy functional and exchange correlation functional with respect to the particle number, but standard approximation functionals like LDA or GGA predicted $\Delta_{XC}=0$ as a result, it underestimated the band gap. Thus, giving rise to the so-called "Band Gap problem".[40-42]

(D) HATREE, HATREE FOCK AND DYSON EQUATION

In this section, we will see how the Kohan Sham eigenvalues can serve as a starting point for the calculation of the quasi-static particle energy, i.e. the total energy required to remove any electron or add an electron to a many-body system, just by comparing the Kohan Sham equation with the self-consistent equation for many-body physics. Among the many self-consistent equations for many-body physics, the Hartree-Fock and Dyson equations are some of the equations.

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) + v_H(r) \right] \phi_i^H(r) = E_i^H \phi_i^H(r) \quad (2.60)$$

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) + v_H(r) \right] \phi_i^{HF}(r) - q^2 \int d^3r' \frac{Y(r,r')}{|r-r'|} \phi_i^{HF}(r) = E_i^{HF} \phi_i^{HF}(r) \quad (2.61)$$

Where $Y(r,r')$ is the density matrices in the equation (2.61). According to Koopman's theorem[43, 44], the Hartree-Fock eigenvalues can be interpreted as the energy required to remove the unrelaxed electrons, whereas in the case of density functional Theory (DFT), the highest Kohn-Sham eigenvalues can be interpreted as the energy required to remove an electron for a many-body system. Here, unrelaxed electrons mean an electron whose presence or absence is treated without allowing the orbitals to adjust self-consistently. The Kohan Sham equation includes both exchange and correlation via a multiplicative operator, $\text{cap}V_{\text{exc}}$, as anormal approximation in DFT. On the other hand, the Hartree-Fock equation takes into

account the exchange exactly through the integral operator containing $Y(r, r')$, but completely ignores the correlation. In practice, the result obtained using DFT Kohn Sham eigenvalues is as good as the one obtained using Hartree Fock and often comparable for the more sophisticated correlated methods. Also, Kohn Sham equations are much more easily solvable compared to the Hartree-Fock equation. All the three equations, Hartree, Hartree-Fock Fock and Kohn-Sham equations, can also be interpreted as approximations to the Dyson equation, which can be rewritten as mentioned below.

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + v(r) \right] \psi_K(r) + \int d^3 r' \Sigma(r, r', E_K) \psi_K(r') = E_K \psi_K(r) \quad (2.62)$$

Where Σ is the irreducible self-energy in the equation (2.62). The calculated E_K appearing in the above equation (2.62) is essentially the true energy required to add or remove an electron from the many-body system. There is no doubt that the rewritten equation (2.62) is more complicated and difficult to solve than the Koopmans-Suhm equation or the Hartree-Fock equation. Moreover, it is also harder to find a useful approximation to the irreducible self-energy than for V_{XC} . Thus, on comparing the equation (2.60) with equation (2.62) we found that the Kohn Sham equation involves a local, energy-independent potential in place of a non-local, energy-dependent operator Σ . Whenever this is a good approximation then the energy eigenvalue (E_i) calculated in case of Kohn Sham are also a good approximation to E_K . Thus, the interpretation of the Kohn Sham equation as an approximation to the rewritten Dyson equation is suggestive and useful, but it is not necessarily sufficient for DFT to work. If the Kohn Sham equation is used to obtain the electron density, and observables, such as total energies, depend on it, then the Kohn Sham equation is not an approximation at all but simply a very useful mathematical tool.

2.6 BASIS FUNCTIONS

In practice the numerical solution of the Kohn Sham equation typically proceeds by expanding the Kohn Sham orbitals as a combination of well-known suitable basis sets. This in turns convert the original Kohn Sham partial differential equation into a secular equation whose eigenvalues is basically the solution. This approach is very useful in practice because it avoids direct solving of complicated partial differential equations in 3D, works effectively for atoms, molecules, and periodic solids, and controls both the accuracy and computational costs. The understanding regarding the construction of suitable basis sets doesn't begin with the introduction of DFT rather it was well known to the physicists from the time they had been

dealing with the band structure and electronic calculations using the other theoretical frameworks like Free electron model, Tight band method, Hartree and Hartree Fock calculations. It is through these theoretical frameworks that researchers have gained extensive experience in choosing the basis functions that represent the crystal symmetry and periodicity, describing both localised (core) and non-localised (valence) electrons. In physics, there are two conceptually distinct ways to choose a basis function.

1. Fixed basis sets that don't depend on energy.

2. Energy depended basis sets.

Some of the common examples of the fixed basis sets that don't depend on energy are Plane Wave expansion, Tight binding, LCAO (Linear Combination of Atomic Orbitals)[45], OPW (Orthogonalized Plane Wave) methods[46, 47], whereas example of the energy dependent basis sets is APW (Augmented Plane Wave)[48], KKR (Koringa Kohn Rostoker)[49] approaches. There exists a fundamental separation between the working of fixed basis set that don't depend on energy the Kohan Sham orbitals are written as a combination of basis functions that are energy independent as a result the chosen basis functions can be used for all the energy states thereby reducing the Kohan Sham equation to a linear generalized eigenvalue problem which can be easily solved using standard Linear Algebra method like diagonalization of matrices. On the other hand, in the case of energy-dependent basis sets, the chosen basis functions are explicitly dependent on the energy, as a result, the Kohn-Sham, when expressed as a combination of these basis functions. This reduces the Kohan Sham differential equations to a non-linear eigenvalue equation which require complex solving method like ire complex solving method like Iterative Linearization / Self Consistent, Newton Raphson/Secant method, energy grid/ scanning methods. The major advantage of the fixed basis sets that don't depend on energy over those that do depend on energy is that it is easy to solve computationally, whereas on the other hand, the accuracy per basis function is moderate for fixed basis sets that don't depend on energy, and higher in the case of energy-dependent basis sets. The most widely used method to solve the Kohn-Sham equation in solid state physics is LMTO (Linear Muffin Tin Orbital)[50] and LAPW (linear Augmented Plane Wave)[51]. Similar situation exists in chemistry where quantum chemists have learned the art of constructing chemical basis sets suitable for molecules by spending many decades doing Hartree-Fock and Configuration interactions calculation. The chemical basis sets have been classified as Slater Type Orbitals (STO)[52] and Gaussian Type Orbitals (GTO)[53] based on how the radial function varies with

the distance from the nucleus. The mathematical formalism of the Slater Type Orbital consists of a radial function is of the form $r^{n-1}e^{-\xi r}$ and the angular part is determined by the spherical harmonics $Y_l^m(\theta, \phi)$.

$$\psi(r, \theta, \phi) = N r^{n-1} e^{-\xi r} Y_l^m(\theta, \phi). \quad (2.63)$$

Where (r) is the distance from the nucleus, N is the Normalization constant, and (ξ) is the orbital exponent which controls the orbital size, and l respectively in the equation (2.63). The mathematical formalism of the Gaussian Type orbitals is of the form

$$\psi(r, \theta, \phi) = N e^{-\alpha r^2} x^l y^m z^n. \quad (2.64)$$

Where (x, y, z) are the Cartesian coordinates, (n, l, m) are the quantum numbers, and α is a parameter controlling radial decay, respectively in the equation (2.64). In practice, Slater Type Orbitals are capable of resembling the true behaviour of the atomic wave function, effectively compared to the Gaussian Type Orbitals. The answer to this statement lies in their mathematical formalism. Let us try to understand how their mathematical formalism approximates the behaviour of atomic wavefunctions.

- 1) In atoms, the electron feels a strong attraction as the electron approaches the nucleus due to the strong Coulomb interaction between the electron and the nucleus. It is because of this strong interaction electron density around the nucleus increases. This causes the wave functions to change sharply, which is possible if and only if there exist a non-zero derivative wave functions with respect to radial distance as $\vec{r}$ tends to zero. This creates a condition known as the electron-nucleus cusp. It is quite clear from Figure (2.4) that in the case of Gaussian-type orbitals, the wave function is flat at $\vec{r}=0$, indicating that the electron density doesn't change sharply near the nucleus whereas in the case of Slater Type Orbitals, the wave function has a sharp edge at $\vec{r}=0$, indicating that the electron density changes sharply near the nucleus. As a result, for Slater Type Orbital $\frac{d\psi_{slater}}{dr}|_{r=0} \neq 0$ whereas $\frac{d\psi_{slater}}{dr}|_{r=0} = 0$.
- 2) Moreover, at a larger distance from the nucleus, real atomic orbitals decay exponentially reflecting the binding energy of the electron. Slater Type Orbitals reproduces this type of behaviour because of the term $e^{-\xi r}$ whereas Gaussian type orbitals decay at a much faster rate due to the term $e^{-\alpha r^2}$ as a result it underestimates the electron density in the outer region.

- 3) Also, the orbital exponent (ξ) factor represents an effective nuclear charge and allows Slater Type Orbitals to account for electron shielding in multielectron atoms, making them flexible enough to model realistic electron densities. Additionally, the presence of spherical harmonics in the angular part of the Slater Type Orbitals produces the correct orbital shapes and angular nodes of the atomic orbitals as suggested by the real atomic orbitals. The main advantage of practicing Gaussian Type Orbital is that they are computationally efficient because they are easier to handle numerically as the product of two Gaussian Type Orbitals located at different atoms is another Gaussian Type Orbitals located somewhere between the two atoms. On the contrary in case of Slater Type Orbital, the product of two Slater Type Orbitals is not a Slater Type Orbitals, the so called “contracted Basis functions” are utilized to solve Kohan Sham equations. In this type of basis functions, the Slater type orbitals are expressed in a small number of Gaussian Type Orbitals basis functions. This is the most common method used in quantum chemistry for solving the Kohan Sham equation.

2.7 PSEUDOPOTENTIAL

In all the quantum mechanical calculations for a many-electron system, the most fundamental problem is the treatment of the core electron-nucleus interaction in Schrodinger's equation. This is because all the electron wave functions oscillate very rapidly near the nucleus due to the strong Coulomb interaction. Therefore, an accurate description of these rapid oscillations in the Plane wave basis methods requires a very high cut-off energy and extremely large basis sets, which make the calculations very expensive. However, considering the core electrons in calculations of molecular properties such as chemical bonding, elastic, phonon, and optical properties, create computational inefficiencies, as significant effort is spent describing electrons that barely affect the chemistry. To overcome these limitations, the combined effect of the nucleus and core electrons on the valence electrons is replaced by an effective potential, known as a pseudopotential, which acts only on the valence states. Within the core region, this pseudopotential is significantly weaker and smoother than the bare, singular Coulomb potential of the nucleus. As a result, the corresponding pseudo-wavefunctions are smooth, free of rapid oscillations near the nucleus, and contain no nodes in the core region, while matching the true all-electron valence wavefunctions outside the cut-off. radius as shown in the figure. This smoothing of the pseudo-wavefunctions greatly reduces the basis-set requirements and makes quantum-mechanical calculations significantly more efficient without compromising

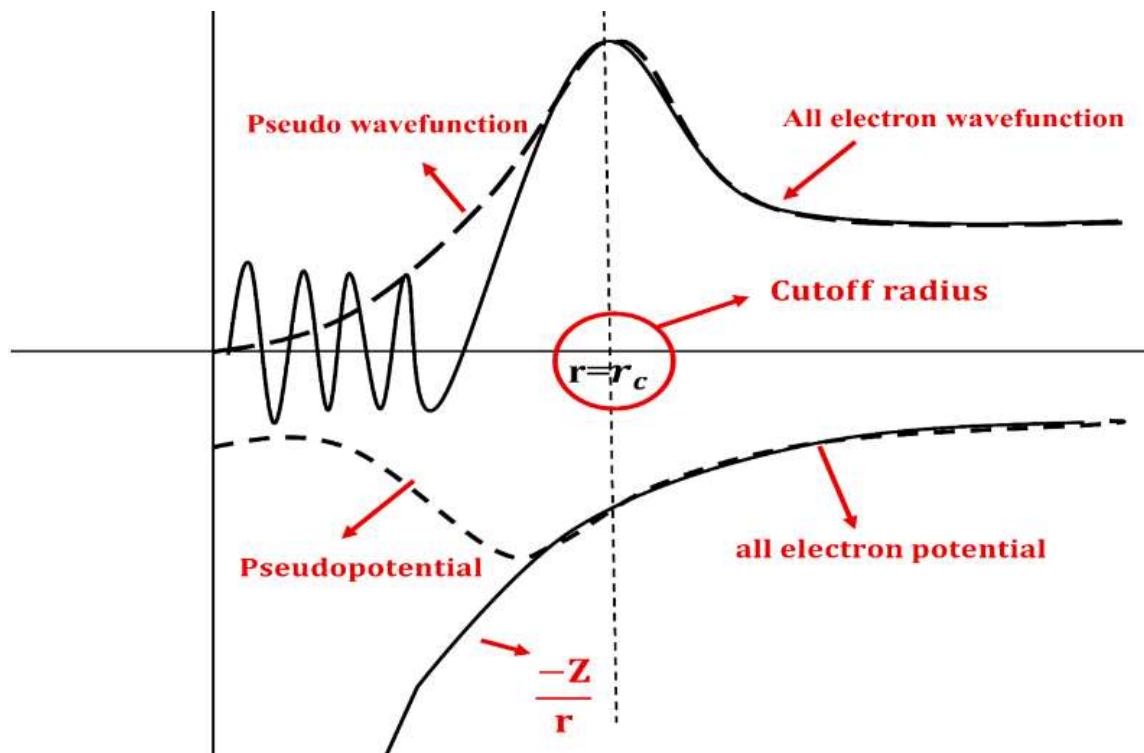


Figure 2.5: Schematic diagram representing the comparison of the **all-electron wave function (solid line)** with the **pseudo wave function (black dotted line)** in the **Coulomb potential** of the nucleus. It clearly shows that beyond cut off radius the pseudo wave function is in good agreement with the all-electron wave function.

the accuracy of valence-electron properties. Let us try to understand how a pseudopotential can be generated using an atomic calculation. In the original Kohan Sahm equation, the effective potential for a non-interacting electron can be defined as $V_s[n] = V_{\text{ext}} + V_H[n] + V_{\text{XC}}[n]$ is actually determined from the knowledge of the electron density ($n(r) = n_c(\vec{r}) + n_v(\vec{r})$) which contained the information of the core electron density ($n_c(\vec{r})$) and valence electron density ($n_v(\vec{r})$) in it. In the pseudopotential approach, the Hartree (V_H) and the exchange energy (V_{XC}) terms are solely determined from the n_v and the core electron densities are accounted for by replacing the external potential (V_{ext}) with a pseudopotential ($V_{\text{ext}}^{\text{PP}}$). Hence, the effective potential for a non-interacting (single-body) system in the pseudopotential approach can be redefined as below in the equation (2.65).

$$V_s^{\text{PP}}[n] = V_{\text{ext}}^{\text{PP}} + V_H^{\text{PP}}[n] + V_{\text{XC}}^{\text{PP}}[n] \quad (2.65)$$

The external pseudopotential can be determined in two steps. Firstly, through an auxiliary atomic calculation, the V_s^{PP} for the reference atomic configuration will be the one for which the single particle orbitals beyond a cut off radius separating the core and the valence region matches exactly with the valence orbitals obtained on solving all the electron Kohan Sham

equation for the same atomic configuration. As a consequence, this causes the calculated valence electron densities for the atomic Kohn Sham equation, and the pseudopotential approach are same. Next one can subtract the atomic -valence contributions. Next one can subtract the atomic-valence contributions $V_H[n_V^{at}]$ and $V_H[n_V^{at}]$ from $V_H[n_V^{at}]$ to obtain the external pseudopotential $V_H[n_V^{at}]$ which is then used in solids or molecular state calculation with $V_H[n_V]$ and $V_H[n_V]$ taken at the proper valence densities for these systems. The way V_s^{PP} is generated using atomic calculation is a very common approach known to the researchers. Some of the popular pseudopotentials generated using atomic calculations are Troullier Martins[54], ultrasoft pseudopotentials[55], Vanderbilt [56], and PAW (Projected Augmented Wave)[57, 58]. Thus, the pseudo potential approach in DFT calculations is used because it reduces the number of electrons treated explicitly, making DFT calculations feasible for systems with tens of thousands of electrons.

2.8 MAKING DFT PRACTICAL: APPROXIMATIONS

In the standard DFT, there exist basically three types of approximations. In the first type of approximations, we are primarily concerned with the interpretation of the Kohn-Sham eigenvalues and orbitals as physical energies and wave functions. The second type of approximations involves numerical modelling for solving the Schrodinger equations for an auxiliary system. The third type of approximations involves the construction of an expression for the unknown exchange correlation function $E_{xc}[n]$ which contains all the many-body quantum effects, such as how electrons with the same spins tend to avoid each other, formation of the exchange hole and how the motion of an electron affects the motion of other electrons due to Coulomb repulsion. Among the different types of approximations discussed above, it is the third type of approximation we are primarily interested in. For this purpose, we have reported and discussed local functions such as Local Density Approximations (LDA)[59], semi-local functions such as Gradient exchange approximations (GEA), Generalized Gradient Approximations (GGA)[60] and non-local functions such as hybrid orbital functions, such as meta-GGA[61] and SIC[62], their feature are discussed in this section.

A) Local Density Approximation-Historically the most important type of approximation in the DFT is the local density approximation. In order to understand the concept of LDA there is a need to recall how the kinetic energy functional have dependent on the electron density. According to the Thomas-Fermi approximation for a homogeneous non-interacting system ($n(r) = \text{constant}$) the kinetic energy was expressed in the equation (2.29). On the other side, the kinetic energy for an inhomogeneous system ($n(r) \neq \text{constant}$) can be

written just by replacing the electron density term with $n(r)$ in the equation (2.29) we get the following equation (2.66).

$$t_s(r) = t_s^{homo}[n(r)] = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n(r)^{5/3} \quad (2.66)$$

$$T_s(n) = \int d^3r t_s^{homo}[n(r)] = \int \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n(r)^{5/3} d^3r \quad (2.67)$$

The total kinetic energy can be obtained just by integrating it all over the space volume. In the above equation (2.67), we found that the kinetic energy has become highly local because it has dependence on the electron density ($n(r)$) at any position ($\vec{r}$), independent of the gradient electron density (∇n). This has led to the inferior treatment of kinetic energy in orbitals, as in Koopmans' theorem. But the concept of LDA has been extremely useful in approximating the exchange energy term present in the energy functional. For a homogeneous interacting system, the exchange energy per unit volume can be expressed as mentioned in the equation (2.68).

$$E_{xc}[n] = \frac{-3q^2}{4} \left(\frac{3}{\pi}\right)^{1/3} n^{4/3} \quad (2.68)$$

Whereas for a non-homogeneous interacting system, the exchange energy per unit volume can be expressed as in the equation (2.69)

$$E_{xc}^{LDA}[n] = \frac{-3q^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n(r)^{4/3} d^3r \quad (2.69)$$

On the other hand, for the correlation energy $E_c[n]$ present in the energy functional, the situation is more complicated because the exact form of the expression for the correlation energy is still unknown for the homogeneous interacting system, which is itself a many-body problem. To approximate the correlation energy, perturbation theory was initially used. Later, these approximations became outdated with the introduction of highly precise Quantum Monte Carlo (QMC) calculations for the electron liquid by Ceperley and Alder, whereas modern expressions for the correlation energy are just parameterizations of these data. These modern expressions are implemented in most standard DFT packages and, in typical applications, give nearly identical results. It is based on comparison that the earlier parameterization based on perturbation theory was found to deviate substantially from the Quantum Monte Carlo ones; therefore, they are generally avoided. Therefore, in the case of Local Density Approximation, the exchange correlation energy can be approximated independently of the parameterization as described below in the equation (2.70)

$$E_{xc}[n] = E_{xc}^{LDA}[n] = \int e_{xc}^{homo} n(r) d^3r \quad (2.70)$$

Where $e_{xc}^{homo} = e_x^{homo} + e_c^{homo}$. The corresponding XC potential is simply the derivative of the exchange of correlation energy with respect to electron density as in equation (2.71).

$$V_{xc}^{LDA} = \frac{\partial e_{xc}^{homo}(n)}{\partial n(r)} \quad (2.71)$$

The way $E_{xc}[n]$ has been approximated in the local density approximation has been very successful even for system that are quite different from the electron liquid which forms a reference system in the LDA. The real reason behind such success can be attributed to the fact that the LDA underestimates the correlation energy (E_c) but overestimates the E_x , resulting in the expectedly good values of E_{xc} . This error cancellation is known as systematic error, which is caused by the fact that for any electron density, the LDA XC hole satisfies the correct sum rule $\int n_{xc}^{LDA}(r, r') d^3r = -1$, which is possible if and only if the integrated error in the n_x^{LDA} cancels with those of n_c^{LDA} . For many decades, the LDA has been used by physicists to calculate band structures and total energies in solid-state physics. In Quantum chemistry, LDA failed to yield results accurate enough for a quantitative discussion of the chemical bond in a molecule. This is known as “chemical accuracy” which requires calculation with an error of not more than 1 Kcal/mole = 0.04338 eV/particle. Initially, the way local density approximations in the DFT deal with the inhomogeneous interacting many-body system, like atoms and molecules, is by decomposing it into two simpler problems. Firstly, the solution for a spatially homogeneous interacting system yielding uniform exchange energy. Secondly, the solution of an inhomogeneous non-interacting system yields the particle density. Finally, it is through the local density potential that the XC energy of the uniform interacting system enters into the equation for the inhomogeneous non-interacting system. The particular way in which the inhomogeneous many-body problem is decomposed and the various possible improvements on the LDA are behind the success of DFT in practical applications of Quantum Mechanics to real materials.

B) Semi-local GGA, GEA and beyond- In the previous section, we observed that the LDA approximated the exchange correlation energy functional by assuming that the electron density at each point in a real system remained uniform. But in reality, the electron density at each point in a real system varies. Therefore, there is an inevitable need to include the information on how rapidly the electron density varies with the position in the exchange energy functional. In this regard, the first initial attempt made by the researchers was so-called the “Gradient Expansion Approximation” (GEA). In this type of approximation, one tries to systematically incorporate the gradient corrections of the form $|\nabla n(r)|$, $|\nabla n(r)|^2$ and $\nabla^2 n(r)$ etc by expanding the exchange correlation function as a

power series. A famous example to the lowest order gradient corrections to the Thomas-Fermi approximation for $T_s[n]$ as mentioned in the equation (2.72)

$$T_s[n] \approx T_s^W[n] = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} \int n(r)^{5/3} d^3r + \frac{\hbar^2}{5m} \int \frac{|\nabla n(r)|^2}{n(r)} d^3r \quad (2.72)$$

The second term on the right-hand side is called Weizsacker term. Similarly, applying the lowest order gradient correction to the exchange energy function can be approximated in case of LDA we get in the equation (2.73)

$$E_x[n] \approx E_x^{GEA}[n] = -\frac{3q^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n(r)^{4/3} d^3r - \frac{10q^2}{432\pi(3\pi^2)^{1/3}} \int \frac{|\nabla n(r)|^2}{n(r)^{4/3}} d^3r \quad (2.73)$$

where $E_x[n] = -\frac{3q^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int n(r)^{4/3} d^3r$. The second term on the right-hand side of the equation (2.73) is the lowest order gradient correction to $E_x^{LDA}[n]$. In Practice the incorporation of the lower order gradient correction to the LDA don't significantly improve it but worsen it also.

This is because the lower order gradient correction work very well for all those systems in which the electron density $n(r)$ varies very slowly i.e. $|\vec{\nabla} n(r)| \ll n(r)K_F$ but in real systems electron density varies rapidly near the nucleus, bonding region. As a result, higher order gradient correction of the form $|\nabla n(r)|$, $|\nabla n(r)|^2$ and $\nabla^2 n(r)$ etc. becomes highly significant which are difficult to calculate while approximating the exchange correlation energy. To overcome this entire situation, it was realized in the early eighties that instead of expanding the exchange correlation function as a power series containing gradient corrections one can represent exchange correlation functional as a function of $n(r)$ and $\vec{\nabla} n(r)$ as mentioned in the equation (2.74) whose numerical integral over the volume gives numerical value.

$$E_{xc}^{GGA}[n] = \int f(n(r), \vec{\nabla} n(r)) d^3r \quad (2.74)$$

The above equation (2.74) is known as Generalized Gradient function. It is based on the method employed in constructing the functional $f(n(r), \vec{\nabla} n(r))$ there exists various type of GGA. For example, in Quantum chemistry GGA are developed by fitting parameters to the tests of selected molecules whereas in condensed matter physics the GGA are developed based on the extent they can satisfy the constraints. Currently the most widely used and trusted GGA are PBE (denoting the functional proposed in 1996 by Perdew Burke and Ernzerhof) in physics and BLYP[63] (denoting the combination of Becke's 1988 exchange functional with the 1988 correlation functional of Lee, Yang and Parr in chemistry. In general, GGA provides very reliable results while calculating magnetic moments, lattice constants, Bulk modulus etc.

However, both the LDA and GGA failed to describe the Vander Waals interaction existing in the layered structure materials. In order to describe the Vander Waals interaction dispersion corrections such as Grimme DFT-D2[64], Grimme DFT-D3[65, 66] are available in DFT. Finally, it is due to the extensive implementation of GGA in the DFT calculations by the researchers working in the domain of physics and chemistry has led to the major improvement in the GGA functional compared to LDA, although chemical accuracy has not been yet fully achieved but is of great research interest in future.

C) **Orbital functional and other non-local approximations hybrids, Meta-GGA, SIC, OEP-** In spite of such advancement the quest for more accurate exchange correlation beyond GGA functional exists both in physics and chemistry. In this regard hybrid exchange correlation function proved to be a very useful and viable option. The construction of hybrid functional involves a certain amount of empiricism in mixing of Hartree Fock exchange functional into DFT exchange functional. However, this approach appeared to be a drawback but in practice this approach has proved to be very successful. For example- B3 which is the most successful exchange functional when mixed with LYP GGA for correlation (E_C) resulted in the most popular exchange correlation in quantum chemistry which is B3LYP[63]. Another recent beyond GGA development is the emergence of so called Meta-GGA. In Meta-GGA, the exchange correlation function depends on electron density, gradient of the electron density and Kohan Sham kinetic energy density $\Gamma(r)$ as written in the equation (2.74).

$$\Gamma(r) = \frac{-\hbar^2}{2m} \sum_i |\nabla \phi_i|^2 \quad (2.74)$$

We have seen in the section (2.74) that the Kohan-Sham kinetic energy functional is known as orbital function because they are explicit function of single particle orbital but an implicit function of electron density. Similarly, here Meta-GGA functional are also known as orbital functions because they have a direct dependence on Kohan Sham kinetic energy functional which is itself explicit function of single particles orbitals. The major advantage of including the Kohan sham kinetic energy density as the additional degree of freedom besides electron density, gradient electron density is to satisfy some additional constraints such as finite exchange potential at the nucleus, self-interaction correction to the correlation function (E_C). As a result, in various tests, Meta-GGA have provided better accuracy while calculating atomic energies, structural properties and bond lengths as compared to Generalized Gradient Approximations (GGA).

2.9 LIMITATION OF THE DFT

Although DFT has provided a strong theoretical framework to the researchers working in the field of condensed matter physics, quantum chemistry, surface and catalysis, nanotechnology, material science, biophysics and drug design. Despite its various advantages offered by DFT as a theoretical framework to predict and calculate the physical and chemical properties of various low-dimensional systems, DFT faces some serious limitations in comparison to experimental approaches which are listed as below:

- 1) Experimental approaches analyse the sensor sensing performance under realistic conditions, such as operating temperature, pressure, relative humidity and presence of interfering gases, whereas DFT calculations are performed under idealistic conditions, such as $T=0K$, perfect vacuum conditions, defect-free surfaces, etc.
- 2) In reality, low-dimensional systems consist of grain boundaries, surface roughness, and defects, which significantly influence the sensing behaviour of the low-dimensional
- 3) systems, but in DFT, it is practically very tough to model these structures precisely before performing quantum mechanical calculations on them.
- 4) DFT calculations are computationally expensive, as a result, they are typically restricted to hundreds or a few thousand atoms, whereas real fabricated devices contain billions of atoms, thus making full device-scale simulation impractical.
- 5) DFT calculations also include a potential source of error despite their remarkable predictive properties because they are based on certain assumptions and approximations. These include the choice of exchange correlation function, treatment of vanderwaal correction, consideration of spin-orbit coupling. In addition, the level of accuracy of DFT calculations varies as it depends on the system and level of theory employed.

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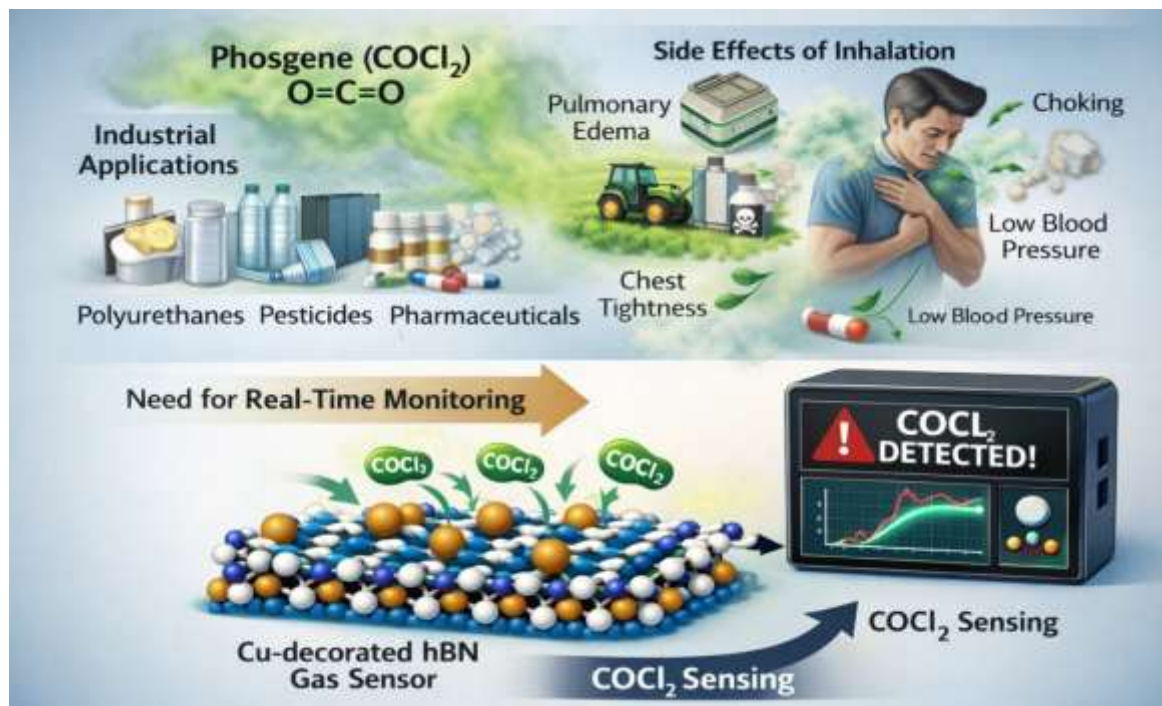
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Chapter 3

Adsorption mechanism of Phosgene gas onto the pristine hBN and Cu-decorated hBN using DFT



The adsorption behaviour of pristine hBN monolayer and Cu-decorated hBN monolayer towards the detection of toxic gases, such as COCl₂, was explored using first-principles calculations based on Density Functional Theory (DFT). The calculated low adsorption energy for the A4 configurations suggests that the interaction of COCl₂ gas with pristine hBN was weak, resulting in a poor recovery time. Therefore, to enhance the adsorption affinity of hBN, the Cu atom was adsorbed onto the surface of hBN (Cu-hBN) and substitutionally doped (Cu-doped hBN). It was based on energy minimization, and B2 and C2 configurations were the most stable configurations among the different adsorption configurations. The adsorption study revealed that a strong chemical interaction exists, and the adsorption of COCl₂ gas onto Cu-hBN and Cu-doped hBN was a chemisorption. Further, various calculations such as DOS, Hirshfeld atomic charge, charge density differences, ELF, and RDG were calculated for the most stable configurations. The resulting DOS plot revealed that the COCl₂ adsorption enhances the electrical conductivity due to the 72.25% and 54.13% reduction in the band gap. Hirshfeld and ELF analysis revealed that substantial charge transfer occurs in the case of B2 and C2 compared to the A4 configuration. ELF analysis revealed that the Cu atom loses electrons to the COCl₂, confirming the behavior of adsorbates as electron donors and COCl₂ as

electron acceptors. Furthermore, RDG analysis revealed vdW interaction in the case of A4, whereas strong, attractive interaction exists in the case of B2 and C2 adsorption configurations. Finally, the calculated recovery time for B2 and C2 adsorption configurations at elevated temperatures under visible light suggests that Cu-doped hBN and Cu-hBN systems can be utilized as a sensing material in gas sensors to detect COCl_2 gas at high temperatures.

3.1 INTRODUCTION

Toxic carbonyl compounds such as phosgene[1] (COCl_2), a colourless gas, are primarily used in industries to produce polymeric isocyanates, carbamates, pharmaceuticals, and pesticides. It has also been used as a chemical warfare agent during World War I[2]. Exposure to its vapor resulted in throat swelling, change in voice, pulmonary irritation, or pulmonary edema.[3, 4]. Recently, accidental exposure to the COCl_2 gas due to the derailment of a freight train carrying vinyl chloride resulted in an environmental hazard near East Palestine, Ohio.[5]. Therefore, considering the industrial utility and the adverse effects of COCl_2 gas on the environment and human health, there is an inevitable need to detect and monitor COCl_2 gas under the permissible limit of 0.1 ppm in the air for the safety of human civilization and a cleaner environment. In this regard, robust gas sensors capable of exhibiting better selectivity, sensitivity, and fast recovery time in harsh environments are required. A wide range of research is ongoing in the search for optimal gas-sensing materials capable of detecting hazardous and toxic gas molecules. At present researchers have extensively explored as a gas sensing material diverse range of layered two-dimensional materials (2D) such as graphene[6], black phosphorene[7], germanene[8], silicene[9], transitional metal chalcogenides (TMCs)[10], transitional metal dichalcogenides (TMDs)[11, 12], Aluminium Nitride (AlN)[13], indium Nitride(InN)[14] and MXene[15] due to their high surface area to volume ratio, a large number of active sites, tunable band gap, and optical properties, good compatibility with the device integration[16]. Despite such unique properties, these materials exhibit poor selectivity and sensitivity at high temperatures, which hinders the practical implementation of these materials as gas-sensing materials to detect toxic and hazardous gas molecules in harsh environments[17]. Therefore, sensing materials capable of exhibiting good sensitivity and selectivity in harsh environments are required. In this regard, atomically thin hexagonal boron nitride (hBN), known as “white graphene,” can be considered a promising sensing material in harsh environments due to its exceptional properties, such as wide band gap, high thermal conductivity, better temperature stability, resistance to oxidation, and excellent chemical inertness[18, 19]. However, numerous

studies exist reporting the usage of hBN monolayer as a gas sensor and biosensor[20, 21]. On the other hand, these studies have also reported the sluggish response, poor selectivity, and instantaneous recovery time of the hBN-based gas sensor due to the weak interaction between the gas and hBN [22-24]. Therefore, to counter the problem of weak gas adsorption capability of the sensing material, researchers have adopted the technique of surface functionalization through elemental doping[25-27], substrate engineering[28, 29], and defect engineering[30-32]. It has been well proven that doping Transition metal (TM) onto 2D materials significantly enhances the adsorption capability of 2D materials. For example, Liu et al. investigated the gas sensing capability of TM (Fe, Pd, Co) doped MoTeSe monolayer in detecting thermal runaway gases of lithium-ion batteries. He concluded that adding TM dopants enhances the conductivity and adsorption capability of the MoTeSe monolayer[33]. N Yuskel et al. examined the gas-sensing capability of both Pt and Pd-doped graphene sheets in detecting propylene oxide (PO). His findings indicate that Pt and Pd-doped graphene sheets can effectively adsorb PO. In another study, Wang et al. discovered that the adsorption of four greenhouse gases such as CH₄, N₂O, CO₂, and SF₆, onto pristine GeSe monolayer was physisorption. However, after modifying it with a Pd atom, he observed better adsorption affinity and sensitivity in the Pd-GeSe monolayer for N₂O and SF₆ gas molecules[34]. Despite such advances, numerous kinds of literature exist reporting the utilization of various morphologies of hBN as a gas sensor to detect COCl₂ gas. For example- Mohammadi et al. reported that the adsorption of H₂S, Cl₂, NH₃, and COCl₂ gas onto B₁₂C₆N₆ was physisorption. However, Li-decorated B₁₂C₆N₆ exhibits excellent sensitivity towards Cl₂ and COCl₂ gas molecules[35]. Hussain et al. studied the adsorption of COCl₂ onto Cu-decorated B₁₂N₁₂ nanocage. His finding indicates that Cu atom decoration onto B₁₂N₁₂ nanocage enhances the adsorption strength, stability, and chemical reactivity of B₁₂N₁₂, and Cu-decorated B₁₂N₁₂ nanocage can be used as an efficient gas sensor for the detection of COCl₂ gas molecule[36]. Behesstain et al. emphasized that Sc-doped boron nitride nanotube (BNNT) can be utilized as an electronic sensor to detect COCl₂ gas molecules. This can be attributed to the significant enhancement in the adsorption strength and electrical conductivity of Sc-BNNT[37]. However, from the above literature survey, we found that there have been no reports regarding the adsorption behavior of Cu-decorated hBN towards COCl₂. This lack of prior research led us to investigate the adsorption behavior of Cu-decorated hBN towards COCl₂ gas. For this purpose, we have decorated Cu atoms onto hBN via (a) substitutional doping[38, 39] and (b) surface charge transfer doping[40, 41]. Therefore, in the present study, we have investigated the adsorption of COCl₂ onto substitutionally doped Cu

atoms and adsorbed Cu atoms using DFT. Here, the adsorption energy and distances were calculated to determine the interaction strength upon COCl_2 adsorption onto the hBN, substitutionally doped Cu atom, and surface-adsorbed Cu atom. Further, to analyze the effect of COCl_2 gas adsorption, we have calculated DOS and PDOS for various adsorption configurations, respectively. For the quantitative and qualitative analysis of the charge transfer during the interaction of COCl_2 with the adsorbents, we calculated the charge density difference and Hirshfield atomic charge. Further, RDG and ELF analyses were performed to examine any non-covalent interaction and electron density distribution around the interacting atoms. Finally, the recovery time and sensitivity were calculated to examine the performance of the Cu-doped hBN, Cu-hBN, and pristine hBN systems upon COCl_2 adsorption.

3.2 COMPUTATIONAL DETAILS

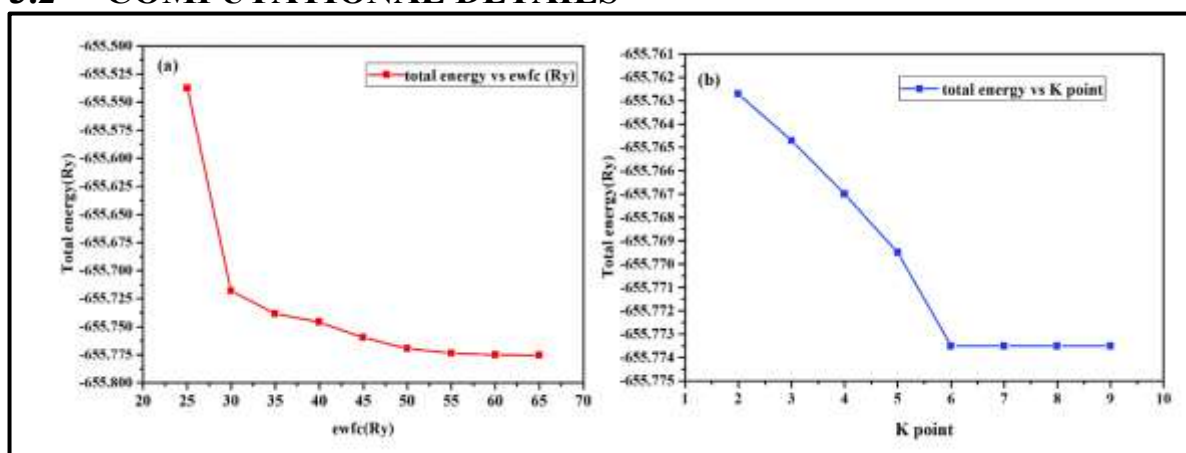


Figure 3.1: Convergence test for the (a) cut-off energy and (b) K points respectively.

All the computational calculations were carried out within the framework of DFT using the QUANTUM ESPRESSO software package.[42]. To describe the correlation between the electrons, we have used Generalized Gradient Approximation (GGA)[43]with Perdew Burke-Ernzerhof (PBE)[44]as an exchange-correlation (XC) function. A Plane wave basis within the framework of the projector augmented wave (PAW)[45] was implemented with ultrasoft pseudopotential to represent the electron-ion interaction. For the proper convergence of the self-consistent field (SCF) calculation, we have performed a convergence test to determine the optimized cut-off energy and K points. The convergence test results shown in Figure 3.1(a) and 3.1(b)respectively illustrate that 55Ry and 7x7x1 are the optimized cut-off energy and K points. To simulate, the hBN monolayer 5X5 supercell was created by repeating the unit cell 5 times along the X and Y axes. Further, a vacuum layer of 20Å was applied along the z-axis to obstruct the interaction between the periodic replicas. We have implemented the “Grimme

DFT-D2.”[46] method to consider the weak vanderwaal (vdW) interaction accurately in the layered structure. All the geometries were completely optimized until the energy, pressure, and force convergence were less than 10^{-4} Ry, 0.5 kbar, and 10^{-3} Ry/Bohr, respectively, using the Boryden- Fletcher- Goldfarb- Shanno (BFGS) scheme. VESTA software was utilized to calculate the adsorption distance and bond angle and visualize the charge density difference diagram for various optimized adsorption configurations. In addition, Multiwin and VMD software were also utilized to visualize the RDG scatter and RDG isosurface plots.

3.3 RESULTS AND DISCUSSIONS

3.3.1 ELECTRONIC AND STRUCTURAL PROPERTIES ANALYSIS OF THE PRISTINE hBN

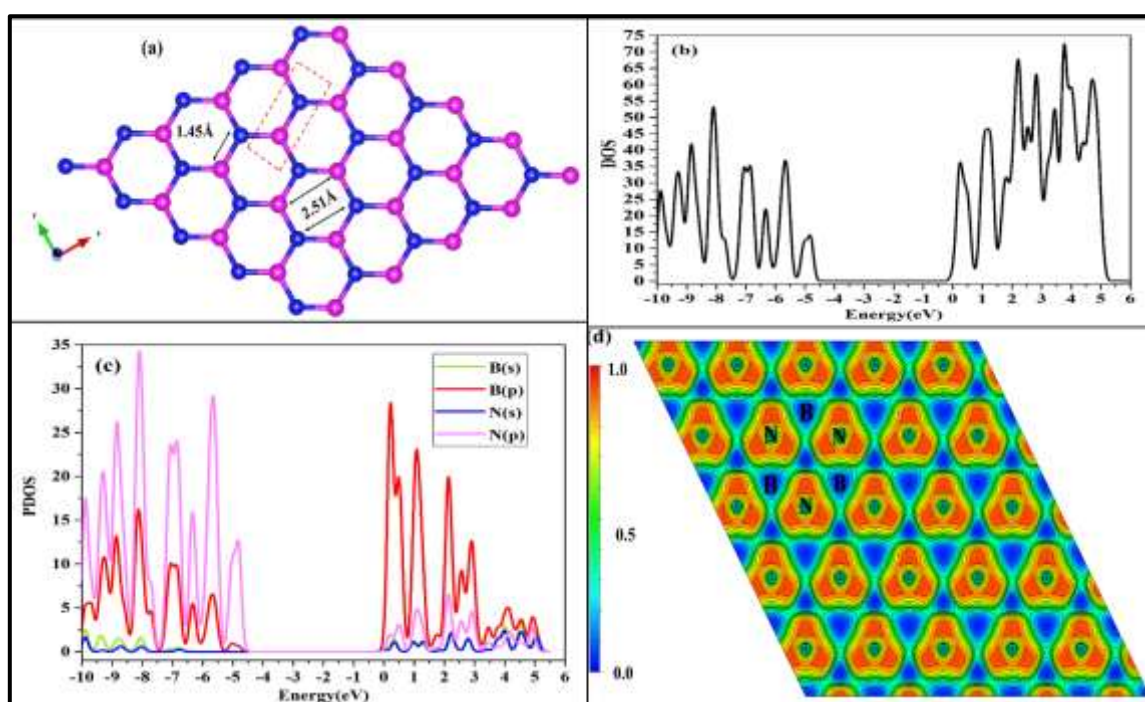


Figure 3.2: (a) Optimized structure of hBN monolayer with the red-colored box representing the unit cell. The atoms in blue and pink correspond to the N and B atoms, (b) DOS, (c) PDOS, and (d) ELF plot. The red, blue, and green colored areas correspond to high, low, and partially delocalized regions, respectively.

In the present section, the electronic and structural properties of the pristine hBN were investigated to differentiate the electronic and structural properties modification pristine hBN undergoes upon Cu decoration and COCl_2 adsorption. Therefore, we have optimized the geometry and found that the resulting optimized structure exhibits an alternate periodic arrangement of N and B atoms bonded to nearby three B and N atoms, giving rise to sp^2 hybridized honeycomb-like planar structure shown in Fig.2(a). Moreover, the optimized B-N bond length, the bond angle between B-N-B, and the nearest distance between the B-B or N-N atoms were found to be 1.45 Å, 120° , and 2.51 Å, respectively.[47-49]. These findings were

consistent with the experimental results reported by various authors. Further, we have performed a DOS calculation to investigate the electronic properties of the optimized structure. The DOS plot shown in Figure 3.2(b) revealed that the optimized structure behaved as an insulator with an energy band gap of about 4.29eV, consistent with the band gap (4.30eV) calculated by Kim et al.[50]. Therefore, the agreement of our calculated band gap with the previously theoretical result validates the reliability of our DFT calculation. We have performed PDOS calculations to study the contribution from the individual atomic orbitals to the TDOS. The resulting PDOS plot in Figure 3.2(c) revealed that the contributions to the valence band (VB) and conduction band (CB) were primarily from the 2p orbitals of the N and B atoms, respectively. We have utilized the Electron Localization Function (ELF) to visualize the electron density around the atoms. The ELF plot in Figure 3.2(d) illustrated a region of high and low electron densities around the N and B atoms identified by the red and blue-colored regions, respectively. The observed variation in the electron densities can be attributed to the difference in the electronegativity. Being highly electronegative, the N atom withdraws electrons from the B atom, making the N and B sites electron-rich and electron-deficient sites, respectively. This confirmed the behavior of N and B atoms as an electron donor and acceptors, respectively. Hence, the structural and electronic properties analysis suggest that the resulting optimized structure behaved as an hBN monolayer.

3.3.2 Adsorption of COCl_2 gas onto the pristine hBN monolayer

Table 3.1 Calculated B-N bond lengths in Å, adsorption distance, and energies in Å and eV for the different optimized structures.

Optimized structures	Adsorption distance (Å)	Adsorption Energy (eV)	B-N bond length (Å)
A1	3.572	-0.501	1.451
A2	3.320	-0.439	1.449
A3	3.340	-0.435	1.449
A4	3.527	-0.533	1.450

To explore the interaction of the COCl_2 gas with the pristine hBN monolayer, we have considered the B site (top of the B atom) and N site (top of the N atom) as the most preferential adsorption sites because B and N sites are electron-deficient and rich sites, suggested by our ELF calculation in the previous section. Hence, they served as active sites for the COCl_2 gas adsorption onto the hBN. Therefore, we have considered various possible orientations of the gas at the B and N sites as the input geometries for optimization. Upon optimization, we

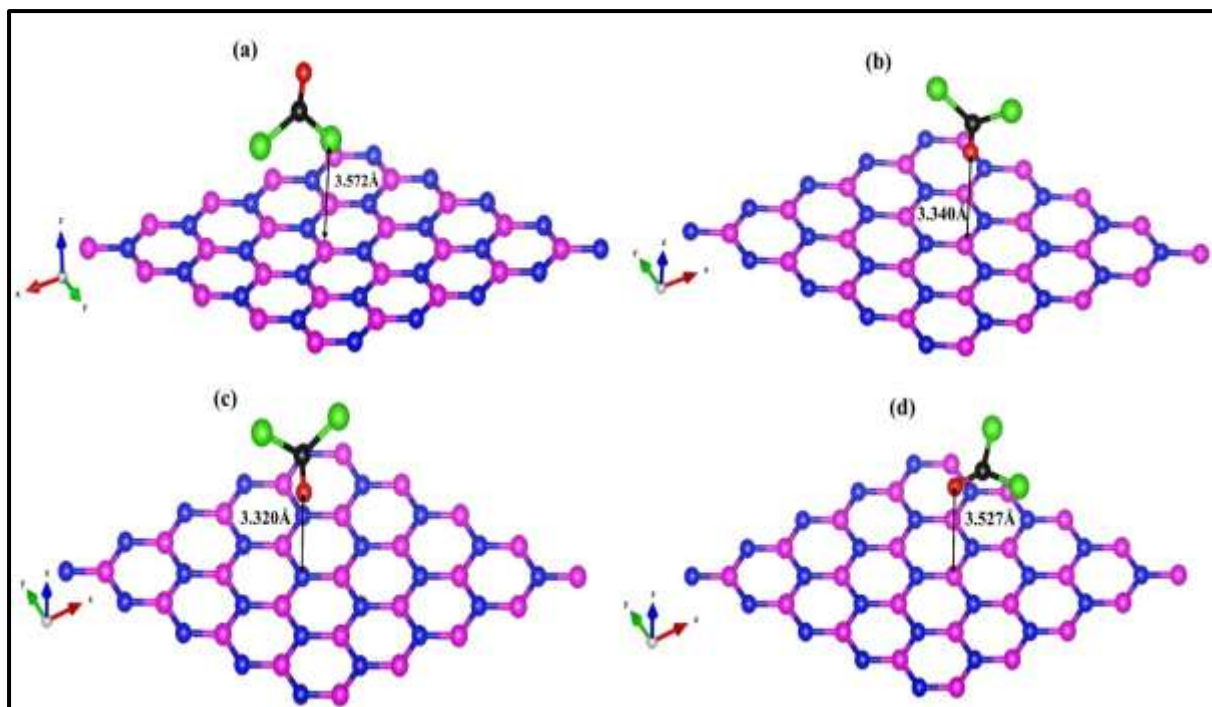


Figure 3.3: Top observation of the optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The arrows in black represent the distance from the hBN surface to the COCl_2 gas. The red, black, and green atoms represent the O, C, and Cl elements respectively.

obtained four different optimized structures abbreviated as A1, A2, A3, and A4. The resulting optimized structures shown in Fig.3 revealed that the N-B, C=O, and C-Cl bond lengths did not vary too much from that of the N-B bond length in pristine hBN and C=O, C-Cl bond lengths in isolated COCl_2 molecules. This can be attributed to the weak interaction between the COCl_2 and pristine hBN. From Figure 3.3(a) and Figure 3.3(d), we observed that in the case of A1 and A4 adsorption configurations, the COCl_2 gas orients itself parallel and perpendicular to the z-axis and got adsorbed at a distance of 3.572Å and 3.527Å with the Cl and O atoms facing toward the B site. In contrast, for the A2 and A3 adsorption configurations, we observed that the COCl_2 gas orients itself along the z-direction and got adsorbed at a distance of 3.340Å and 3.320Å with the O atoms facing toward the B and N sites, as shown in Fig.3(b) and 3(c), respectively. From Table 3.1, we found that the adsorption distances for all the optimized structures lie within the range of 3.320Å-3.572Å, which is greater than the sum of

the atomic radius of O, C, Cl, B, and N atoms, indicating that the adsorption of COCl_2 gas onto hBN was physisorption. Further, to determine the interaction strength and most stable adsorption configuration among the different optimized structures, we have calculated the adsorption energies for all the optimized structures using equation (3.1).

$$E_{\text{ads}} = E_{\text{hBN+gas}} - (E_{\text{hBN}} + E_{\text{gas}}) \quad (3.1)$$

where $E_{\text{hBN+gas}}$, E_{hBN} and E_{gas} represents the total energies of the pristine hBN upon gas

adsorption, pristine hBN, and isolated COCl_2 gas molecule, respectively. According to the equation (3.1), the calculated adsorption energies for the A1, A2, A3, and A4 adsorption configurations were found to be -0.501eV , -0.439eV , -0.435eV , and -0.533eV , respectively. The reported negative value of the adsorption energies in Table 3.1 validates that the adsorption of COCl_2 onto pristine hBN was physisorption, spontaneous, and exothermic. It was based on the comparison of the reported adsorption energies in Table 3.1, we found the A4 adsorption configuration to be the most stable adsorption configuration among the different adsorption configurations due to its lowest adsorption energy. Therefore, we have considered A4 as the final structure for the rest of the study. Hence, based on the results from the adsorption study, we found that the pristine hBN exhibits weak adsorption affinity towards the COCl_2 gas.

3.3.3 Structural and electronic properties analysis of the Cu-doped hBN monolayer

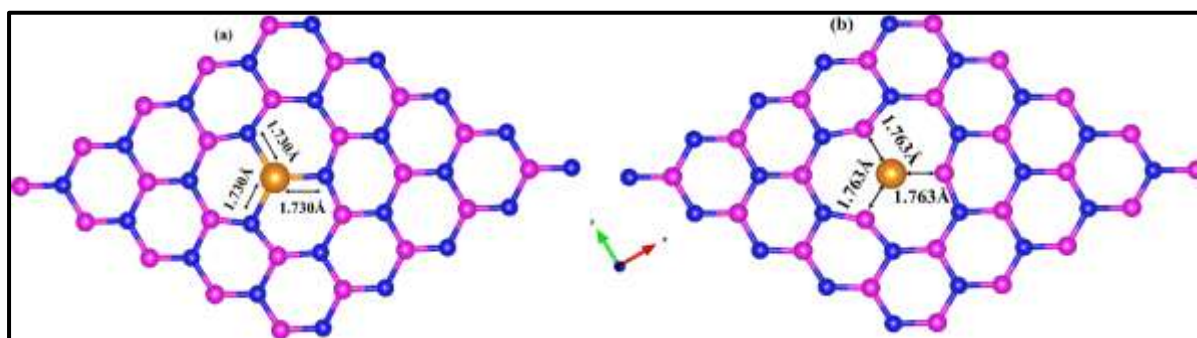


Figure 3.4: Top observation of the optimized (a) Cu- V_B -hBN and (b) Cu- V_N -hBN doped systems. The atom in orange represents the Cu element.

In the previous section, we observed that hBN exhibits poor gas adsorption affinity towards COCl_2 gas molecules. It is well known that doping 2D materials with Transition metal (TM) atoms effectively enhances the gas adsorption ability of 2D materials[51]. Among the various Transition Metal (TM) atoms, we have selected the Cu atom as the dopant because it is cost-effective, readily available, surplus in nature, and does not get poisoned by the analyte. Therefore, in this section, we have investigated the effect of substitutional doping the Cu atom on the structural and electronic properties of hBN. For this purpose, we have created the B and N vacancies by ejecting a single B and N atom from the hexagonal lattice. After creating the vacancy, the Cu atom embedded at the B and N vacancies was allowed to relax. Upon relaxation, we obtained two doped structures abbreviated as ‘Cu- V_B -hBN’ (Cu-doped at B vacancy) and ‘Cu- V_N -hBN’ (Cu-doped at N vacancy), respectively. The resulting relaxed doped structure revealed that the hexagonal B-N ring no longer remained intact and underwent distortion. It was due to the large atomic radius of the Cu ($1.28\text{\AA}$) atom compared to the B ($0.85\text{\AA}$) and N ($0.65\text{\AA}$) atoms that the hexagonal B-N ring underwent an expansion to

accommodate the substitutional doped Cu atom within the hexagonal lattice. From Figure 3.4(a) and 3.4(b), we observed that in the case of 'Cu-V_B-hBN' and Cu-V_N-hBN doped structures, the Cu atom got bonded with the adjacent three N and B atoms respectively. The atomic distance between the Cu atom with the adjacent three N and B atoms was 1.739 Å and 1.763 Å, which is comparable with the Cu-B (1.87 Å) and Cu-N (2.10 Å) bond lengths reported by Balkani et al. in their studies[52]. The differences in the calculated bond lengths were due to the usage of different basis sets in the SCF. In the comparison, we found that the calculated Cu-B and Cu-N bond lengths were longer than the B-N bond lengths in pristine hBN. This indicates that the doped Cu atom bulges slightly outward from the surface, making it a highly preferred adsorption site for the gas molecule. Also, the averaged B-N bond lengths in the case of Cu-V_B-hBN and Cu-V_N-hBN doped structures were 1.439 Å and 1.445 Å, smaller than the B-N bond lengths of the pristine hBN. This indicates that the doped Cu atom causes the overall structure to be somewhat corrugated. Further, to determine the bonding strength of the Cu atom with the hBN monolayer and the stability of the doped structures, we have calculated the binding energy (E_b) and formation energy (E_f) using equations (3.2) and (3.3) for the Cu-V_B-hBN and Cu-V_N-hBN configurations, respectively.

$$E_b = E_{\text{Cu-hBN+gas}} - (E_V + E_{\text{Cu}}) \quad (3.2)$$

$$E_f = E_{\text{Cu+hBN}} - E_{\text{hBN}} - \mu_{\text{Cu}} + \mu_X \quad (3.3)$$

where $E_{\text{Cu+hBN}}$, E_V , E_{Cu} , μ_{Cu} and μ_X represents the total energies of the substitutional doped Cu atom into hBN, total energies of the defected hBN, total energies of the isolated Cu atom, and chemical potentials of the isolated Cu and ejected atoms from the hexagonal lattice, respectively. According to equations (3.2) and (3.3), the binding and formation energies for the Cu-V_B-hBN were -5.048 eV and 5.379 eV, whereas for the Cu-V_N-hBN were 1.31 eV and 9.42 eV, respectively. The calculated formation energy suggests that the Cu atom can be doped easily at the B vacancy compared to the N vacancy due to the low formation energy of the Cu-V_B-hBN. This result is consistent with the theoretical studies in which it was proved that doping TM metal atoms at the B vacancy is energetically more favourable than N vacancy[53, 54]. Further, Cu-V_B-hBN has the lowest binding and formation energies compared to Cu-V_N-hBN. These findings suggest that Cu-V_B-hBN was the most stable configuration among the Cu-V_B-hBN and Cu-V_N-hBN doped structures. Therefore, in the subsequent section, we have selected the Cu-V_B-hBN as the final doped structure to study the interaction with the COCl₂ gas and referred to Cu-V_B-hBN as 'Cu-doped hBN' for the rest of the study. In addition, the DOS plot in Figure 3.5(a) revealed that substitutional doping of the Cu atom introduces a new impurity

state at -4eV, reducing the energy band gap from 4.29eV to 3.10eV. Consequently, there was an enhancement in the peak intensity of the conduction band, indicating an increment in the conductivity of the hBN. In addition, the PDOS plot in Figure 3.5(b) illustrated there exists multiple overlapping between the 3d-Cu and 2p-N atomic orbitals within the energy range from -4eV to -10eV, indicating strong hybridization between the atomic orbitals to form molecular orbitals involved in the bond formation. These findings indicates that strong chemical(ionic/covalent) interaction exists between the substitutionally doped Cu atom and the nearby neighbouring N atom. Hence, the structural and electronic properties analysis suggests that the substitutional doped Cu atom induces distortion in the structure and modifies the electronic properties of the hBN.

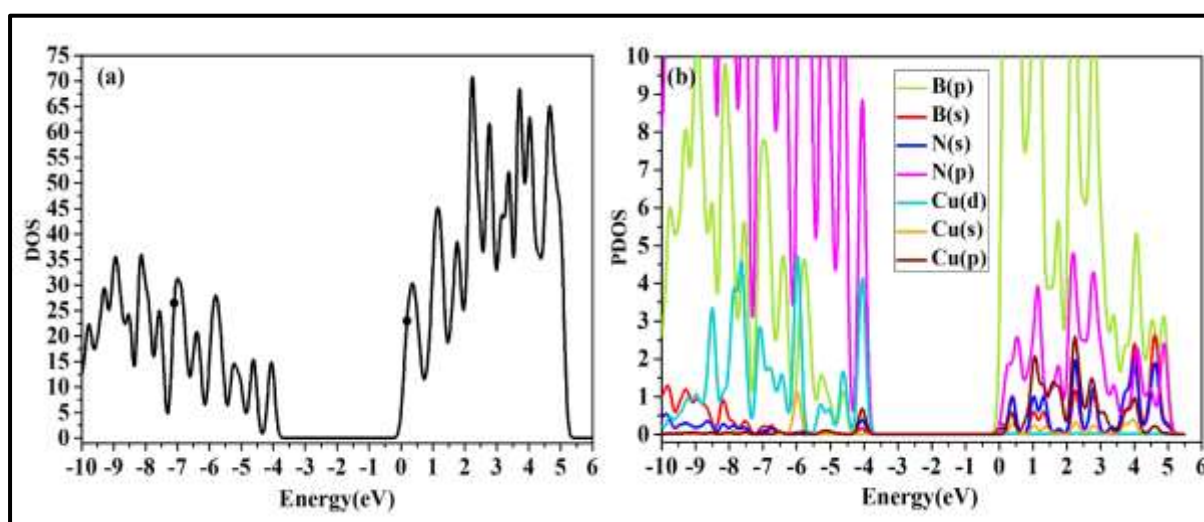


Figure 3.5: (a) DOS and (b) PDOS plot upon substitutional doping of the Cu atom within the hBN respectively.

3.3.4 Adsorption of COCl_2 onto the Cu-doped hBN monolayer

Table 3.2 Calculated adsorption distance, energy, C=O, C-Cl, and Cl-C bond lengths of the COCl_2 gas for the different optimized adsorption configurations.

Optimized structures	Adsorption distance (Å)	Adsorption energy(eV)	C=O bond length (Å)	C-Cl bond lengths (Å)
B1	2.236Å	-1.851eV	1.203Å	1.732-1.733Å
B2	2.198Å	-1.939eV	1.207Å	1.727-1.731Å

To analyze the interaction of COCl_2 gas with the Cu-doped hBN systems, we have considered the dopant site as the most preferential adsorption site because of the protrusion the COCl_2 gas can easily interact with the Cu atom. Therefore, different orientations of the COCl_2 gas above the doped Cu atom were considered the input geometries for optimization. After optimization, we obtained two adsorption configurations abbreviated as B1 and B2. For the B1 and B2 that

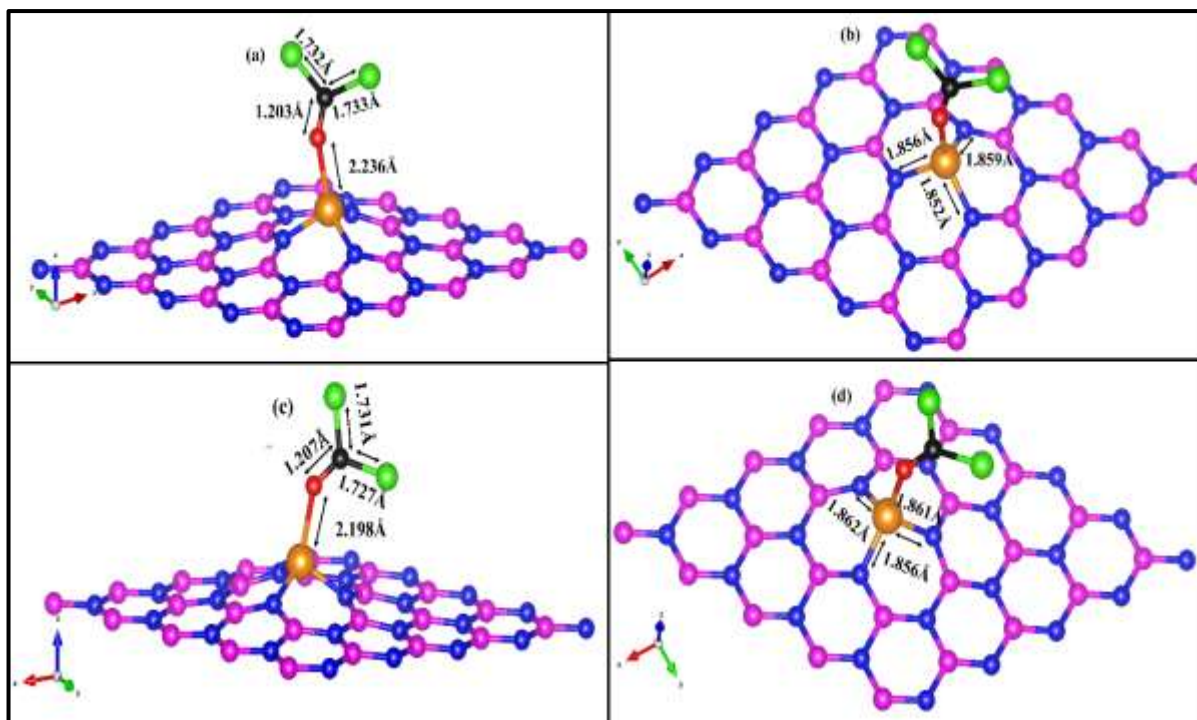


Figure 3.6: (a) Lateral observation and (b) Top observation of the optimized structure upon Cu adsorption. (c)TDOS and (d) PDOS plot upon Cu adsorption onto hBN, respectively.

the C=O (1.180 Å) and C-Cl (1.720 Å) bond lengths of the isolated COCl₂ gas molecules. In addition, for the B1 adsorption configuration, we observed that the three Cu-N bond lengths got elongated from 1.730 Å to 1.852 Å, 1.856 Å and 1.859 Å upon COCl₂ gas adsorption. In contrast, for the B2 adsorption configuration, we observed that the three Cu-N bond lengths got elongated from 1.730 Å to 1.856 Å, 1.861 Å, and 1.862 Å upon COCl₂ gas adsorption. The observed elongation in the C=O, C-Cl, and Cu-N bond lengths might be due to the attractive electrostatic interaction between the COCl₂ gas and Cu-doped hBN. Further, to determine the strength of the interaction between the COCl₂ gas and Cu-doped hBN, we have calculated the adsorption energies for the B1 and B2 adsorption configurations using equation (3.4).

$$E_{\text{ads}} = E_{\text{Cu-doped-hBN+gas}} - (E_{\text{Cu-doped-hBN}} + E_{\text{gas}}) \quad (3.4)$$

where $E_{\text{Cu-doped-hBN+gas}}$, $E_{\text{Cu-doped-hBN}}$ and E_{gas} represent the total energy of the Cu-doped hBN system upon COCl₂ adsorption, the total energy of the Cu-doped hBN without COCl₂, and the total energy of the isolated COCl₂ gas. According to equation (4), the adsorption energies for the B1 and B2 adsorption configurations were found to be -1.851 eV and -1.939 eV, respectively. The high adsorption energy and short adsorption distances for the B1 and B2 adsorption configurations suggest that the adsorption process was chemisorption. This finding indicates that COCl₂ binds strongly with the Cu-doped hBN. Based on the comparison of adsorption energies, we found that the B2 adsorption configuration was the most

stable among the B1 and B2 configurations, due to its lowest adsorption energy. Therefore, we have selected the B2 adsorption configurations for the recovery time and sensitivity analysis in the subsequent section of the present study. Hence, our adsorption study confirms that substitutional doping of the Cu atom effectively enhances hBN adsorption capacity for COCl₂.

3.3.5 Structure and Electronic properties analysis of the Cu-hBN

To analyze the effect Cu adsorption had on the structure and electronic properties of hBN. For this purpose, we have considered the N site the most preferential adsorption site for the Cu atom based on the previous theoretical studies[55]. Therefore, in this study, we have optimized the Cu atom adsorbed above the N sites and abbreviated the resulting optimized structure as 'Cu-hBN'. The resulting optimized structure shown in Figure 3.7(a) and 3.7(b) revealed that the Cu atom adsorbed at 2.207Å from the surface, and the B-N bond length elongated from 1.450 Å to 1.468Å. The observed elongation in the B-N bond lengths indicates that the monolayer undergoes expansion to increase the available space for the adsorption of the Cu atom onto the surface. Further, to determine the thermodynamic stability of the structure and strength of the interaction between the adsorbed Cu atom and hBN, we have calculated the cohesive energy/atom ($E_{coh}/atom$) and adsorption energy (E_{ads}) for the Cu-hBN using equations (3.5) and (3.6), respectively.

$$E_{coh} = \frac{E_{(hBN-Cu)} - [x \cdot E_{(B)} + y \cdot E_{(N)} + E_{(Cu)}]}{N} \quad (3.5)$$

$$E_{ads} = E_{(hBN-Cu)} - [E_{(hBN)} + E_{(Cu)}] \quad (3.6)$$

where $E_{(hBN-Cu)}$, $E_{(hBN)}$, $E_{(B)}$, $E_{(N)}$ and $E_{(Cu)}$ represents the total energies of the adsorbed Cu atom onto hBN, pristine hBN, isolated B, N, and Cu atoms, whereas x , y , and N represent the number of B, N, and total atoms within the unit cell, respectively. According to equations (3.6) the adsorption energy for the Cu-hBN was -0.33eV. In contrast, the cohesive energy/atom for the Cu-hBN using equation (3.5) was found to be -1.40eV/atom. The calculated low value of the adsorption energy suggests that the adsorbed Cu atom binds weakly with the hBN, and the adsorption of the Cu atom onto the hBN was physisorption. The calculated negative value of the cohesive energy suggests that the Cu-hBN configurations remained thermodynamically stable. From Figure 3.7(c), we observed an impurity state in the energy range from -4eV to -3eV, reducing the energy gap from 4.29eV to 2.42eV. It was revealed by the PDOS plot in Figure 3.7(d) that the impurity state was due to the contribution from the 4s-Cu and 2p-N atomic orbitals, and there exists weak interaction between the atoms due to weak hybridization between the atomic orbitals. This result was consistent with our findings that the Cu atom binds

weakly with the hBN. Hence, our DOS, PDOS and adsorption results are in agreement with each other.

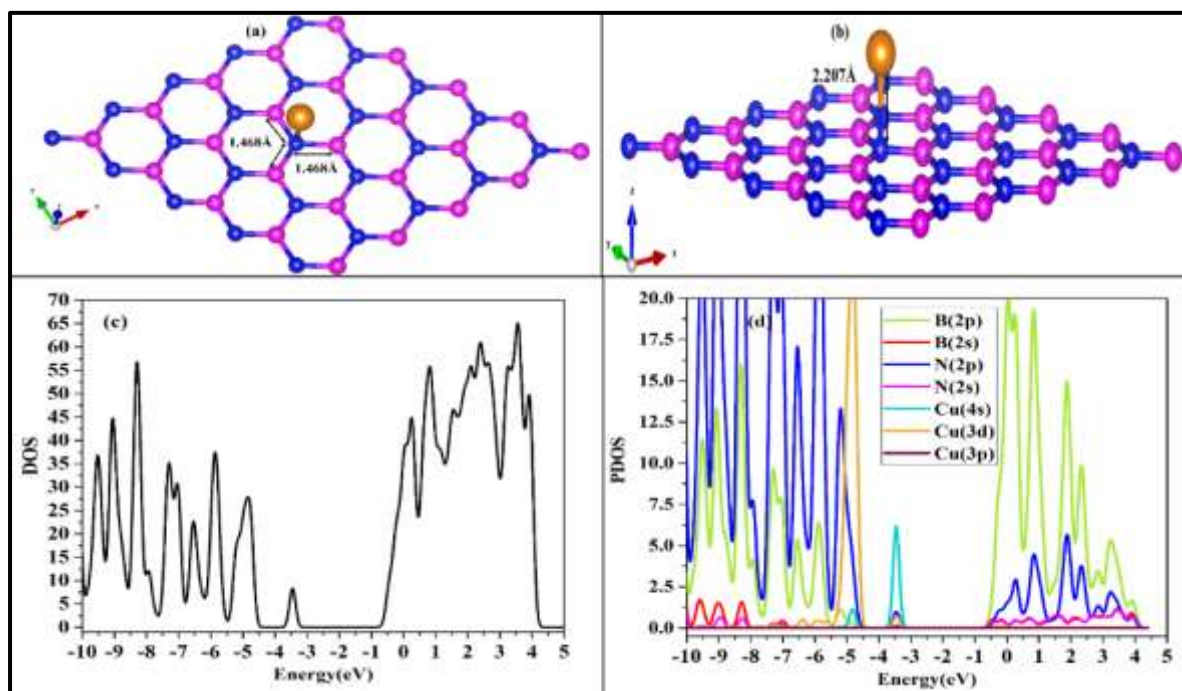


Figure 3.7: (a) Lateral observation and (b) Top observation of the optimized structure upon Cu adsorption. (c) TDOS and (d) PDOS plot upon Cu adsorption onto hBN, respectively.

3.3.5 Adsorption of COCl_2 gas onto the Cu-hBN

Table 3.3 Calculated adsorption distance, energy, C-O, C-Cl, and Cl-C bond lengths of the COCl_2 gas for the different optimized adsorption configurations.

Optimized structures	Adsorption distance (Å)	Adsorption energy(eV)	C=O bond length (Å)	C-Cl bond lengths (Å)
C1	1.840Å	-1.101eV	1.265Å	1.782Å
C2	1.841Å	-1.155eV	1.271Å	1.791Å

To analyze the interaction of COCl_2 gas with the Cu-hBN, we have considered different orientations of the COCl_2 gas above the adsorbed Cu atom as the input geometries for the optimization. After optimization, we obtained two adsorption configurations abbreviated as C1 and C2. For the C1 and C2 adsorption configurations, we observed that the COCl_2 gas orients itself perpendicular and parallel to the z-axis and got adsorbed at a distance of 1.840Å and 1.841Å with the O atom of COCl_2 gas facing toward the Cu atom, as shown in Figure 3.8(a) and Figure 3.8(c). From the reported data in Table 3.3, we found that upon COCl_2 adsorption, there was a variation in the B-N, C=O, and C-Cl bond lengths. As the C=O and C-Cl bond lengths for the C1 adsorption configuration increase from 1.180Å to 1.268Å and from 1.720Å to 1.782Å. In contrast, for the C2 adsorption configuration, the C=O and C-Cl bond lengths increase from 1.180Å to 1.271Å and from 1.720Å to 1.791Å. In addition, the B-N bond lengths

vary from 1.481Å-1.482Å and 1.481Å-1.485Å in the case of C1 and C2 adsorption configurations, as shown in Figure 3.8(b) and 3.8(d), respectively. The observed elongation in the B-N, C=O, and C-Cl bond lengths might be due to the strong attractive electrostatic interaction between the COCl_2 gas and Cu-hBN. Therefore, to determine the strength of the interaction, we have calculated adsorption energies using equation (3.7) for the C1 and C2 adsorption configurations.

$$E_{\text{ads}} = E_{\text{hBN-Cu-COCl}_2} - (E_{\text{hBN-Cu}} + E_{\text{COCl}_2}) \quad (3.7)$$

where $E_{\text{hBN-Cu-COCl}_2}$, $E_{\text{hBN-Cu}}$ and E_{COCl_2} represents the total energies of the Cu-hBN upon COCl_2 adsorption, Cu-hBN without gas molecule, and isolated COCl_2 gas, respectively. Using equation (3.7), the calculated adsorption energies for the C1 and C2 adsorption configurations were -1.101eV and -1.155eV, respectively. The calculated high value of the adsorption energies for the C1 and C2 adsorption configurations suggests that the adsorption of COCl_2 gas onto Cu-hBN was chemisorption, confirming the existence of ionic/covalent interaction between the COCl_2 gas and Cu-hBN. Hence, these findings suggest that COCl_2 gas binds strongly with the Cu-hBN systems. Further, a comparison of the reported adsorption energies for the different adsorption configurations in Table 3.3 suggests that C2 was the most stable adsorption configuration among the different adsorption configurations due to its lowest adsorption energy. Therefore, we have also selected the C2 adsorption configuration for the recovery time and sensitivity analysis in the subsequent section of the present study.

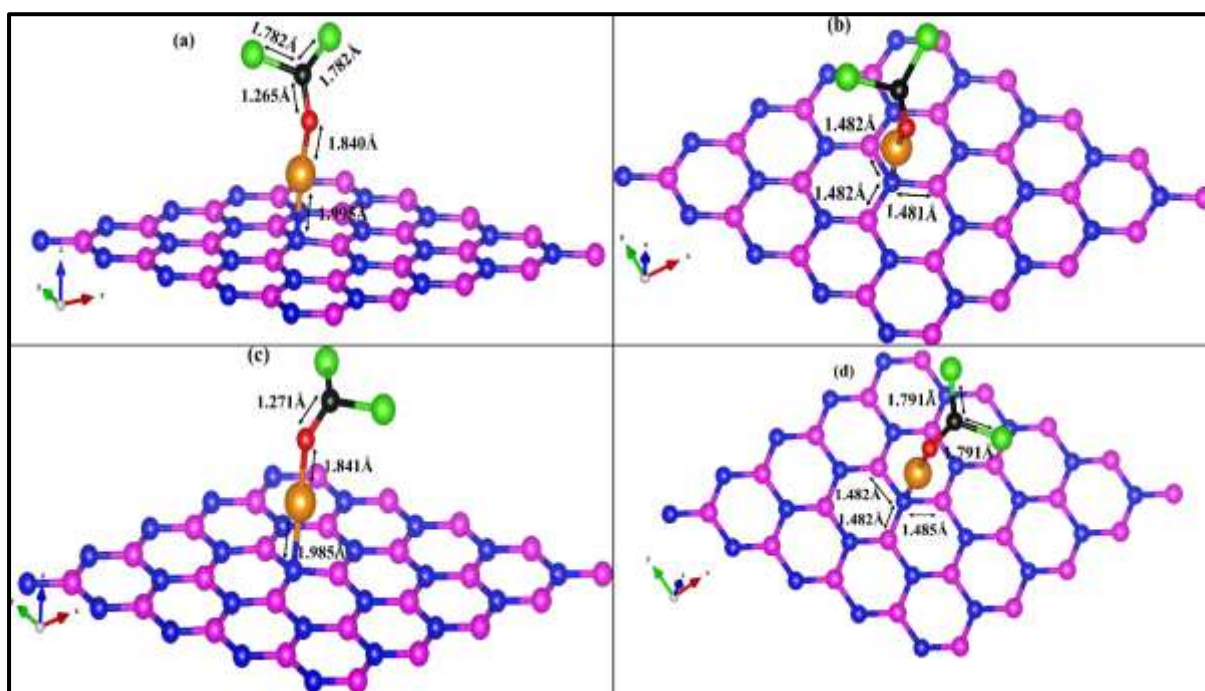


Figure 3.8: (a) Lateral observation and (b) Top observation of the optimized C1 adsorption configuration and (c) Lateral observation and (d) Top observation of the optimized C2 adsorption configuration, respectively.

3.3.7 Comparison of the adsorption energies with other various systems

Table 3.4 Adsorption energies reported previously for some of the various systems upon COCl_2 adsorption.

Systems	Adsorption energy(eV)	Reference
$\text{B}_{12}\text{N}_{12}$ nanocage	-0.097	[36]
Cu-decorated $\text{B}_{12}\text{N}_{12}$ nanocage	-0.175	
$\text{B}_{12}\text{P}_{12}$	-0.271	[56]
Cu-decorated $\text{B}_{12}\text{P}_{12}$	-1.233	
BN nanotubes	-0.043	[37]
Sc-doped BN nanotubes	-0.182	
Li-decorated $\text{B}_{12}\text{C}_6\text{N}_6$ nanocage	-0.790	[35]
Cr-graphene	-0.719	[57]
BN nanoflake	-0.141	[58]
$\text{B}_{24}\text{N}_{24}$ nanocage	-0.043	[59]
Al- $\text{B}_{24}\text{N}_{24}$ nanocage	-0.236	
BN nanocones	-0.254	[60]

In this section, we have compared the adsorption energies of the B2 and C2 adsorption configurations with the various systems from the literature, specifically regarding the sensing of COCl_2 gas molecules as shown in in Table3.4. However based on the literature survey in terms of sensing COCl_2 , a wide range of various systems such as $\text{B}_{12}\text{N}_{12}$ nanocage, $\text{B}_{12}\text{P}_{12}$, Cu- $\text{B}_{12}\text{N}_{12}$ nanocage, Cu- $\text{B}_{12}\text{P}_{12}$, BN nanotubes, Sc-doped BN nanotubes, Li- $\text{B}_{12}\text{C}_6\text{N}_6$, Cr-graphene, BN nanoflake, BN nanocones, $\text{B}_{24}\text{N}_{24}$ nanocage and Al- $\text{B}_{24}\text{N}_{24}$ nanocage exhibited adsorption energy values of -0.097eV, -0.175eV, -1.233eV, -0.043eV, -0.182eV, -0.79eV, -0.719eV, -0.141eV, -0.254eV, -0.043eV and -0.920eV, respectively. The B2 adsorption configuration demonstrates better adsorption energy, whereas the C2 adsorption configuration also demonstrates better adsorption energy than all reported systems in Table 3.4 except Cu- $\text{B}_{12}\text{P}_{12}$. Hence, the comparison results confirmed that both B2 and C2 adsorption configurations have efficient adsorption ability towards COCl_2 adsorption.

3.3.8 Charge Density Difference and Hirshfield Charge Analysis

To gain an understanding of the charge transfer process upon COCl_2 adsorption onto pristine hBN, Cu-doped hBN, and Cu-hBN, we have analyzed the charge transfers quantitatively and

qualitatively using the Hirshfield and charge density difference (CDD) methods for the A4, B2, and C2 adsorption configurations, respectively. The charge density difference ($\Delta\rho$) for all these adsorption configurations was calculated using the following equation (3.8).

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B \quad (3.8)$$

where ρ_{AB} , ρ_A , and ρ_B represent the charge densities of the complexes with gas molecules, the charge densities of the complexes without gas molecules, and the charge densities of the isolated gas molecules, respectively. The yellow and cyan-colored in the charge density difference diagrams represent the electron accumulation and depletion regions. From Fig.9(a), we observed that upon COCl_2 adsorption onto hBN, a small yellow-colored region exists around the O atom, and large blue and yellow-colored regions exist between the B and N atoms. These findings indicate that B and N atoms primarily interact with each other, resulting in weak charge transfer between hBN and COCl_2 . As a consequence, there exists a weak interaction between the hBN and COCl_2 . In addition, we also observed a large cyan and a yellow-colored region around the Cu and O atoms, indicating a strong charge transferred from the Cu atom to the COCl_2 . These findings confirmed the nature of the Cu atom and COCl_2 as an electron donor and acceptors, respectively. Further, we calculated the electrostatic potential (ESP) for the COCl_2 to gain additional insights into the charge transfer mechanism, as shown in Figure 3.9(d). The red and blue colour in the ESP map corresponds to positive and charge distribution. From Figure 3.9(d), we found that a negative charge distribution exists around the O atom, identified by the red color, whereas a positive charge distribution exists around the C and Cl atoms, identified by the blue color, respectively. The observed charge distribution can be attributed to the difference in the electronegativity between the atoms. O atom, being highly electronegative compared to the C atom, withdraws electrons from it. As a consequence, the electron density around the O atom increases, making it an electron-rich and C atom electron-deficient species. These findings indicate that the strong electrostatic attraction between the Cu atom and COCl_2 was responsible for the orientation of the COCl_2 with the O atom facing toward the Cu atom upon optimization and strong charge transfer in the case of B2 and C2 adsorption configurations. The Hirshfield charge analysis validate that a weak charge transfer of $-0.162e$ takes place in the case of A4 adsorption configuration compared to strong electron transfer of $-0.457e$ and $-0.292e$ in the case of B2 and C2 configurations. This finding is in support of the results from the charge density difference calculations. Hence the results of our Hirshfield and charge density difference calculations are in good agreement with each other.

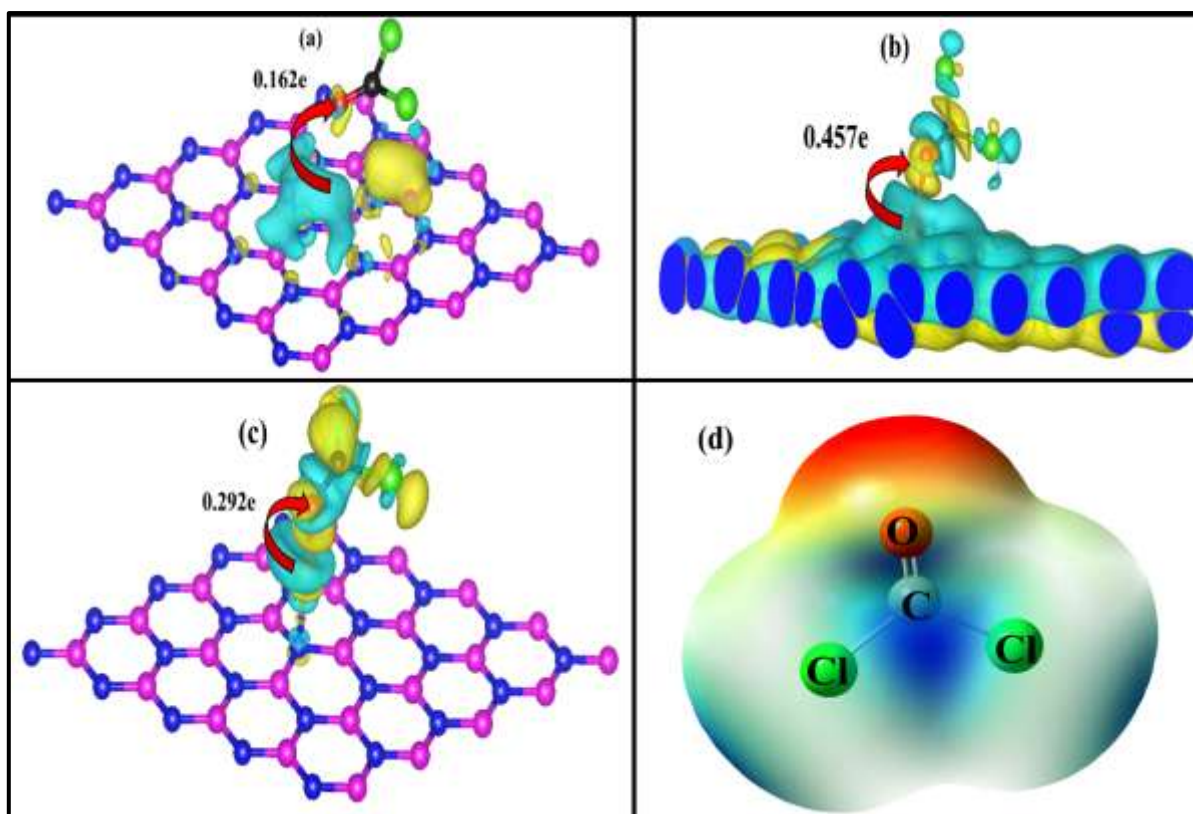


Figure 3.9: Charge density difference diagram for (a) A4, (b) B2, and (c) C2 configurations. The yellow and cyan color in the CDD diagrams represents the electron accumulation and depletion regions, respectively (d) ESP map for the optimized COCl₂ gas molecule. The blue and red colors represent the positive and negative charge sites.

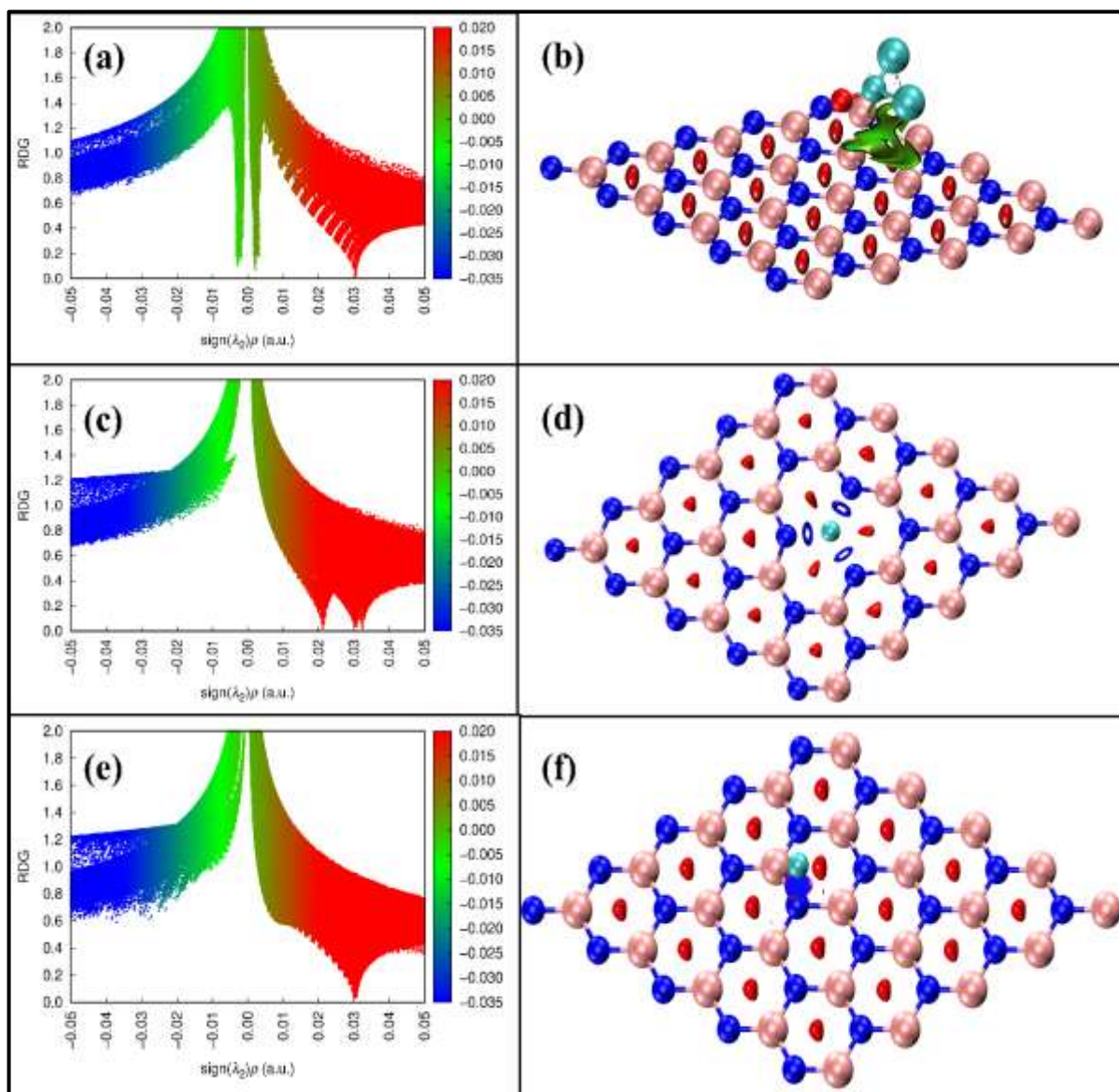
3.3.9 Non-Covalent Interaction Analysis

Noncovalent interactions (NCIs) are of great importance in gas sensing since they play a vital role in the adsorption of the gas, thereby influencing the adsorption energy and the recovery time of the sensing materials. Therefore, to analyze the existence of any non-covalent interaction between pristine hBN, Cu-doped hBN, Cu-hBN, and COCl₂, we have calculated the variation in the value of the reduced density gradient (RDG) function[61] with $\text{sign}(\lambda_2) \rho(r)$ for the A4, B2, and C2 adsorption configurations. Further, we have utilized the RDG scatter plot and RDG isosurfaces for all these adsorption configurations to visualize the variation in the RDG function. Here, the RDG function ($s(r)$) defined in equation (3.9) represents a relation between the electron density($\rho(r)$) and its gradient ($\nabla\rho(r)$). The quantity $\text{sign}(\lambda_2) \rho(r)$ is of great significance as it describes the fluctuation in the electron density near the critical points, which is helpful in determining the nature of the non-covalent interactions. If $\text{sign}(\lambda_2) \rho(r) < 0$, $\text{sign}(\lambda_2) \rho(r) \approx 0$, and $\text{sign}(\lambda_2) \rho(r) > 0$, it indicates attractive strong hydrogen bonding, van der Waals interaction (vdW), and repulsive strong steric effects.

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla p|}{[p(r)]^{4/3}} \quad (3.9)$$

The blue, red, and green color schemes shown in the RDG isosurface correspond to attractive strong hydrogen bonding, repulsive steric effect, and weak vdW interactions. We observed that the RDG scatter plots underwent a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) > 0$ for all the adsorption configurations, as shown in Figure 3.10. This confirmed the existence of a strong repulsive steric effect. Further, the corresponding RDG isosurfaces revealed that strong steric effects exist between the B and N atoms of the hBN layer. The observed steric effect arose due to the strong electrostatic repulsion between the positively charged Cl and B atoms as the COCl_2 gas approached. From Figure 3.10(a), we observed a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) \approx 0$ in the case of A4 adsorption configuration. The corresponding RDG isosurface shown in Figure 3.10(b) verified that weak vdW interaction exists between the COCl_2 gas and hBN identified by the green patches. This confirmed that weak vdW interaction was responsible for the physisorption of the COCl_2 gas onto hBN. However, upon substitutional doping of the Cu atom and Cu adsorption, we observed from the RDG scatter plot in Figure 3.10(c) and Figure 3.10(e) a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$. The RDG isosurface plot revealed that strong attractive H bonding exists between the Cu atom and the nearby neighbouring N atom identified by blue patches as shown in Figure 3.10(d) and Fig.10(f), respectively. This can be attributed to the electrons transfer from the positively

charged Cu atom to the nearby negatively charged N atom, creating a strong, attractive interaction between the oppositely charged species. These findings confirmed that the doped Cu atom in the case of Cu-doped hBN and Cu-hBN systems interacts electrostatically with the hBN. In contrast, upon COCl_2 adsorption, we found from the RDG scatter plot that there is a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$ for the B2 and C2 adsorption configurations, as shown in Figure 3.10(g) and Figure 3.10(i), respectively. These results indicate a strong, attractive electrostatic interaction between the Cu atom and COCl_2 identified by the blue patches, as shown in Fig3.10(h) and Figure 3.10(j). These findings validated that it was due to the strong electrostatic interaction that COCl_2 binds strongly to the Cu-doped hBN and Cu-hBN systems, resulting in high adsorption energy. Hence, our RDG results are in good agreement with those of our adsorption study.



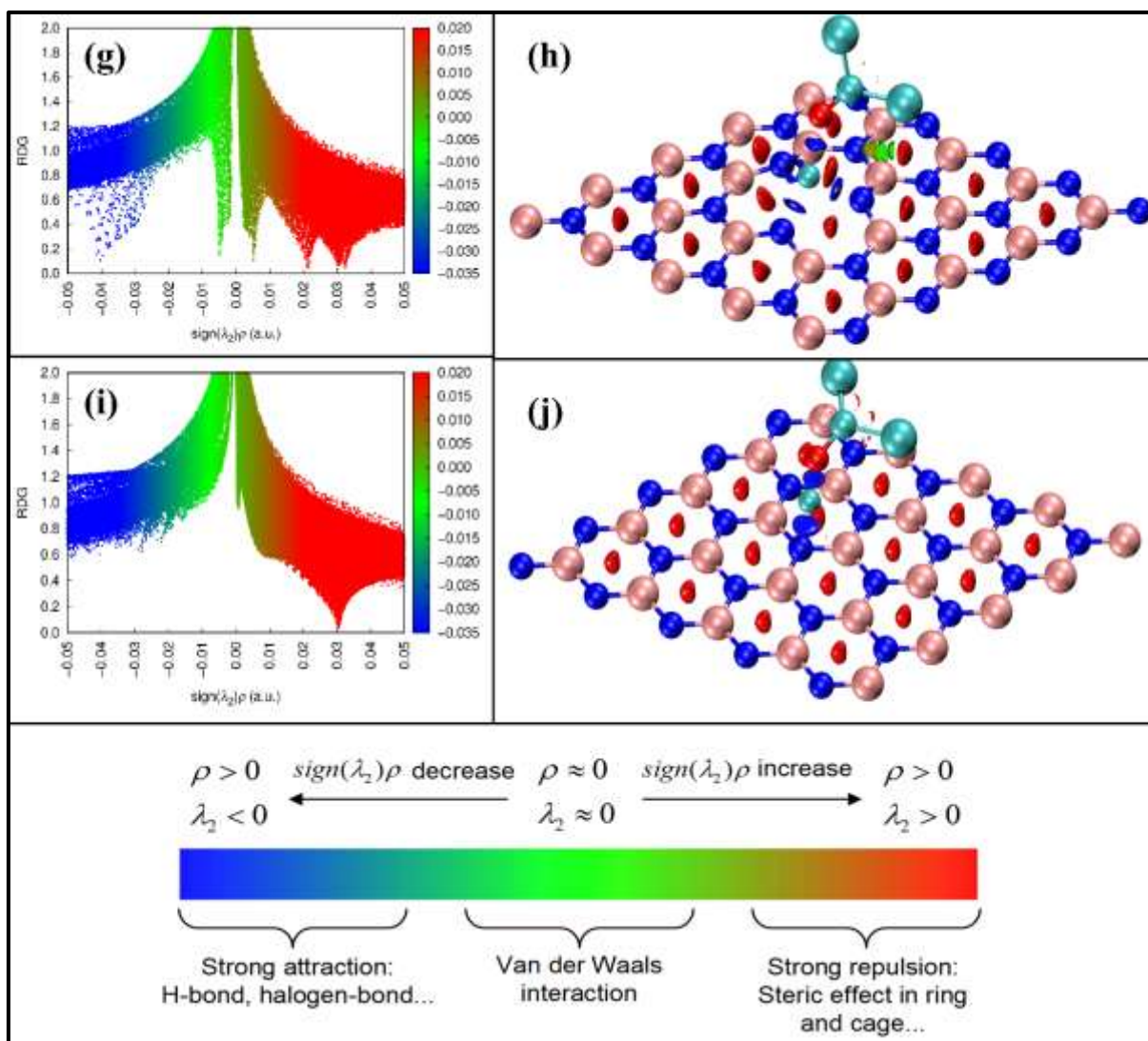


Figure 3.10: RDG scatter plot for the (a) A4, (c) Cu doped-hBN, (e) Cu-hBN, (g) B2, and (i) C2 adsorption configurations, respectively. Isosurface plot for the (b) A4, (d) Cu doped-hBN, (f) Cu-hBN, (h) B2, and (j) C2 adsorption configurations, respectively.

3.3.10 Electron Localization Function Analysis (ELF)

To analyze how the electrons are distributed around the interacting atoms upon COCl_2 adsorption onto hBN, Cu-doped hBN, and Cu-hBN, we have utilized the ELF to visualize the distributions of electrons in the A4, B2, and C2 adsorption configurations. The corresponding ELF plot for all these configurations is shown in Figure 3.11. From Figure 3.11(d), we observed that upon COCl_2 adsorption onto pristine hBN, there exists an intense red-colored region around the O and Cl atoms, indicating that electrons are strongly localized to the COCl_2 gas. There also exists a large region of low electron density exists in between the COCl_2 gas and the hBN monolayer, which is identified by the blue-colored region. These findings suggest a weak interaction exists between the COCl_2 gas and the hBN monolayer. Further, to validate our findings, we have plotted the bottom view of the ELF plot for the A4 configuration, as

shown in Figure 3.11(a). Due to the weak interaction, we found that electron density distribution around the monolayer upon COCl_2 adsorption was identical to that without COCl_2 gas. But, for the B2 and C2 adsorption configurations, we found there was a decrement in the intensity of the red color around the Cu atom and an increment in the intensity of the red color around the O atom, as shown in Figure 3.11(e) and Figure 3.11(f) respectively. These results indicate that electrons are transferred from the Cu atom to the COCl_2 gas during COCl_2 gas adsorption. However, the Cu atom intensity in the C2 configuration was higher than in the case of the B2 configuration, indicating a stronger charge transfer took place from Cu-doped hBN than Cu-hBN to COCl_2 , which is consistent with our Hirshfeld analysis. The bottom view of the ELF plot for the C2 configuration shown in Figure 3.11(c) revealed that the electron density distribution around the atoms remained unaltered upon COCl_2 adsorption onto Cu-hBN. Similarly, the bottom view of the ELF plot for the B2 configuration shown in Figure 3.11(b) revealed that the electron density distribution around the atoms remained unaltered upon COCl_2 adsorption onto Cu-doped hBN and a low electron density at the doping site. Hence, these findings suggest that the Cu atom was the primary active site for the adsorption of the COCl_2 gas onto Cu-doped hBN and Cu-hBN systems, respectively. This is because of the strong electrostatic interaction COCl_2 primarily interacts with the Cu atom. As a consequence, the interaction of the COCl_2 with the hBN becomes weak during the COCl_2 adsorption.

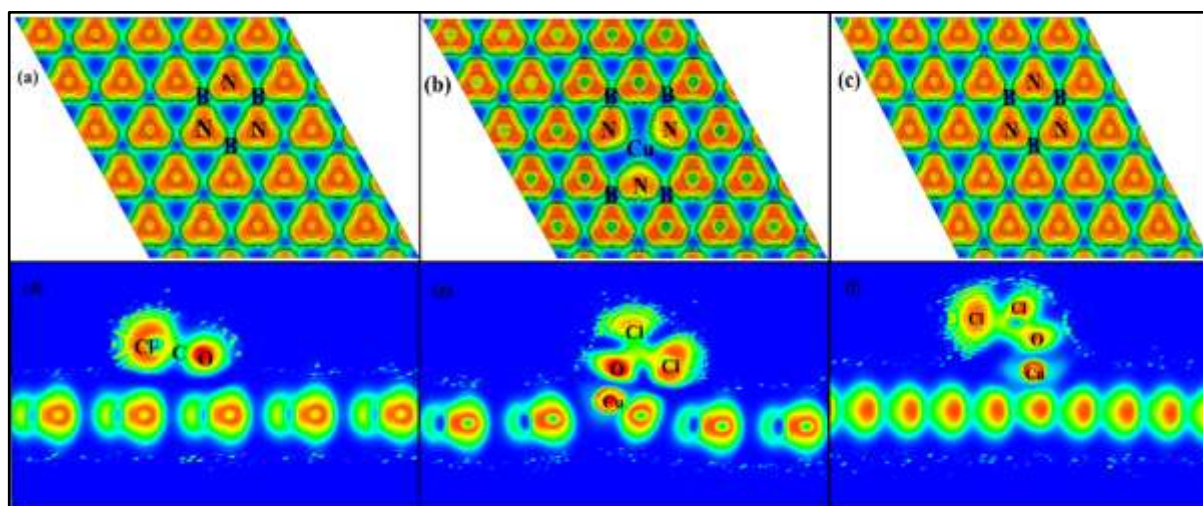


Figure 3.11: Bottom view of the ELF map for (a) A4, (b) B2 and (c) C2 adsorption configurations. Lateral view of the ELF map for (d) A4, (e) B2, and (f) C2 adsorption configurations, respectively.

3.3.11 Frontier Molecular Orbital Analysis

The Frontier Molecular Orbitals (FMO) include the Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO), which provide useful

information regarding the alteration in the electronic properties upon the adsorption of the specified gas molecule on the adsorbent. Therefore, we have calculated the HOMO-LUMO energies for the various adsorption configurations. The data presented in Table 3.5 indicate that hBN exhibits insulating behavior with a HOMO-LUMO energy gap of 4.29eV. In the pristine hBN, the HOMO and LUMO energy levels lie at -4.51eV and -0.22eV, respectively. However, upon substitutional doping, it was observed that the HOMO energy level shifts from -4.51eV to -3.60eV, and the LUMO energy level shift from -0.22eV to -0.50eV. Similarly, upon adsorption of the Cu atom, it was observed that the HOMO energy level shift from -4.51eV to -3.17eV, and the LUMO energy level shift from -0.22eV to -0.75eV, respectively. These changes in the position of HOMO and LUMO reduce the energy band gap by 27.74% and 43.58% for the Cu-doped hBN and Cu-hBN systems, respectively. Furthermore, the adsorption of COCl_2 onto hBN shifts the HOMO from -4.51eV to -4.35eV and the LUMO from -0.22eV to -1.73eV, thereby reducing the band gap to 2.62eV. For the B2 and C2 adsorption configurations, the HOMO shifts to -3.14eV and -2.09eV, whereas the LUMO shifts to -2.28eV and -0.98eV. Here the shifts in the position of HOMO and LUMO narrows the band gap from 3.10eV to 0.86eV and from 2.42eV to 1.11eV for the B2 and C2 adsorption configurations respectively. The reduction in the band gap indicates that doping of Cu atom favours the adsorption of the COCl_2 . We also found on comparison that the B2 and C2 configuration exhibits excellent conductivity than A4 configurations. The observed reduction in the energy gap, as well as changes in the position of the HOMO and LUMO, can be attributed to the destabilization and stabilization of the HOMO and LUMO, respectively. Further, we have analyzed the distribution of HOMO-LUMO orbitals for all these configurations to justify the observed variation in the HOMO-LUMO energies. From Figure 3.12(a), we observed that the HOMO-LUMO orbitals are concentrated around the N and B atoms indicating that in case of hBN both N and B atoms are involved in charge transfer process. But upon substitutional doping and Cu adsorption, we observed that the HOMO orbitals got concentrated around the Cu atom, and LUMO orbitals got concentrated around the nearby neighbouring N atoms, as shown in Figure 3.12(c) and 3.12(d), respectively. This happens because the Cu atom causes a redistribution of electrons in the hBN by losing excessive electrons to the nearby highly electronegative N atom. On the other side, for the B2 and C2 adsorption configurations, we observed that upon COCl_2 adsorption, the HOMO remained distributed around the Cu atom, whereas the LUMO orbitals got distributed around the COCl_2 as shown in Figure 3.12(e) and

Figure 3.12(f). It was due to the charge transfer from the Cu atom to COCl_2 we observed a shift in the LUMO around the COCl_2 . Hence the HOMO-LUMO analysis suggests that COCl_2 adsorption modifies the electronic properties of Cu-doped hBN and Cu-hBN by reducing the band gap making them a promising candidate to be utilized as an electronic sensor.

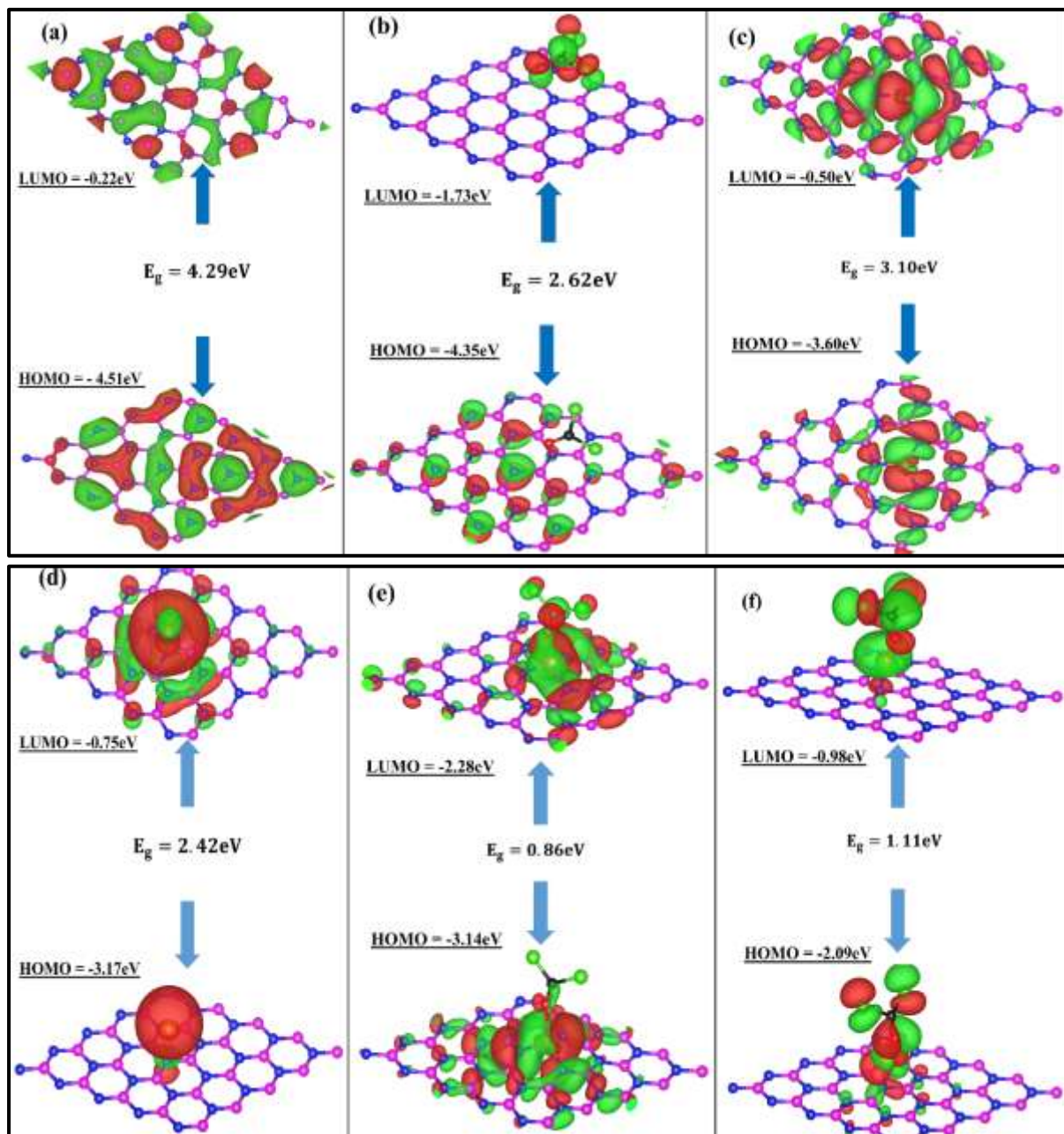


Figure 3.12: HOMO and LUMO for (a) pristine hBN, (b) A4, (c) Cu-doped hBN, (d) Cu-hBN, (e) B2 and (f) C2 adsorption configurations, respectively

3.3.12 Global Indices of Reactivity

To determine the chemical reactivity, sensing ability and performance of the surface sensing materials, we have calculated various quantum descriptors such as Ionization potential (IP), HOMO-LUMO gaps (E_g), electron affinity (EA), chemical potential(μ), electrophilicity (ω),

chemical softness(S), and hardness(η). These quantum descriptors were reported in Table (3.5) and calculated using the below equation (3.9) -(3.13).

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (3.9)$$

$$\mu = \frac{-E_{\text{HOMO}} - E_{\text{LUMO}}}{2} \quad (3.10)$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (3.11)$$

$$S = \frac{1}{2\eta} \quad (3.12)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (3.13)$$

The negative value of the HOMO and LUMO energies represent the ionization potential and electron affinity in Table 5. The reported value in Table 5 indicates that hBN has the highest ionization potential(4.52eV) and lowest electron affinity(0.22eV) among the various adsorption configurations. It was due to the chemically inert nature of the hBN layer. In contrast, upon substitutional doping of the Cu atom we found that the ionization potential decreases to 3.60eV and the electron affinity increases to 0.50eV. Similarly, upon Cu adsorption onto hBN, we found that the ionization potential decreases to 3.17eV, and the electron affinity increases to 0.75eV. Further, we found that COCl_2 adsorption onto hBN decreases the ionization potential to 4.35eV and increases the electron affinity to 1.73eV. For the B2 adsorption configuration, the adsorption of the COCl_2 decreases the ionization potential to 3.14eV and increases the electron affinity to 2.28eV, whereas, for the C2 adsorption configuration, the COCl_2 adsorption lowers the ionization potential to 2.09eV and increases the electron affinity to 0.98 eV. These results implies that efficient charge transfer took place in case of B2 and C2 configurations respectively. Furthermore, to examine the chemical reactivity of the surface sensing material, we have calculated electrophilicity which describes the electron-accepting tendency of the adsorbent. From Table 5, we found that pristine hBN has the lowest electrophilicity value of about 1.31eV, and this property increases by 3.81% and 21.37% upon substitutional doping and Cu adsorption respectively. These findings imply that the incorporation of the Cu atom enhances the electrophilicity character in Cu-doped hBN and Cu-hBN systems by losing electrons to the nearby highly electronegative N atoms. However, upon COCl_2 adsorption, we found that the B2 (8.54eV) configuration exhibits the highest electrophilicity among the various configurations. In addition, to determine the chemical stability, we have calculated the chemical hardness and softness factor for all these adsorption configurations because it describes the resistance and willingness of the material to undergo any change in its electronic properties. The chemical hardness factor for the pristine hBN, Cu

doped hBN, and Cu-hBN systems was found to be 2.15eV, 1.55eV, and 1.21eV, whereas the corresponding chemical softness factor was found to be 0.23eV, 0.32eV, and 0.41eV, respectively. We found that Cu-doped hBN has a high hardness and a low softness compared to Cu-hBN. These findings suggest that Cu-hBN would exhibit significant variation in the energy gap upon incorporating Cu atom onto hBN, consistent with our HOMO-LUMO gap results. We also observed that upon COCl_2 adsorption, there was a 39.47 % increase in softness and a 39.06 % decrease in hardness factor for the A4 adsorption configuration. In contrast, for the B2 and C2 adsorption configurations, there was a 72.41% and 54.44% increment in the softness factor, whereas 72.25% and 53.71% decrement in the hardness factor, respectively. The observed high softness and low hardness imply that both B2 and C2 configurations are more likely to undergo significant variations in the electronic properties. Hence, the above-discussed quantum descriptors suggest that Cu-doped hBN and Cu-hBN exhibit excellent chemical reactivity towards COCl_2 compared to pristine hBN.

Table3.5 Calculated HUMO-LUMO energies, HOMO-LUMO gaps (E_g), Ionization potential (IP), electron affinity (EA), chemical potential(μ), electrophilicity (ω), chemical softness(S) and chemical hardness(η) respectively for the pristine hBN, A4, Cu-doped hBN, B2, Cu-hBN, and C2 systems respectively. All the reported values are in eV.

Adsorption Configurations	HOMO	LUMO	E_g	μ	IP	EA	S	η	ω
Pristine hBN	-4.51	-0.22	4.29	-2.37	4.51	0.22	0.23	2.15	1.31
A4	-4.35	-1.73	2.62	-3.04	4.35	1.73	0.38	1.31	3.53
Cu-doped hBN	-3.60	-0.50	3.10	-2.05	3.60	0.50	0.32	1.55	1.36
B2	-3.14	-2.28	0.86	-2.71	3.14	2.28	1.16	0.43	8.54
Cu-hBN	-3.17	-0.75	2.42	-1.96	3.17	0.75	0.41	1.21	1.59
C2	-2.09	-0.98	1.11	-1.54	2.09	0.98	0.90	0.56	2.14

3.3.13 Sensitivity analysis of the pristine hBN, Cu-doped hBN and Cu-hBN

Sensitivity is considered an important parameter in determining the sensing performance of chemical gas sensors, and it is primarily judged by the variation in electrical conductivity upon gas adsorption. According to equation (14), the electrical conductivity of the sensing material depends exponentially on the negative of the band gap at a certain temperature. This implies that a reduction in the band gap leads to an enhancement in the electrical conductivity of the sensing material. Therefore, to analyze the sensitivity of the A4, B2, and C2 adsorption configurations, we have utilized DOS to calculate the changes the band gap underwent upon COCl_2 adsorption.

Adsorption mechanism of Phosgene

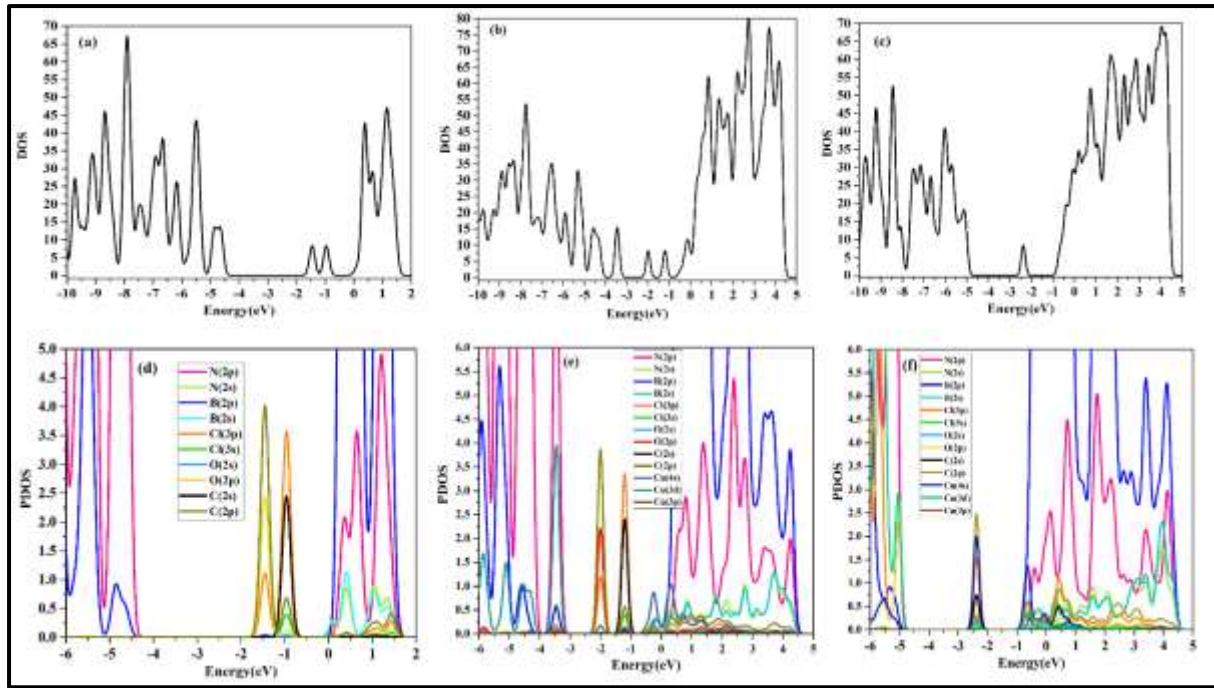


Figure 3.13: Plotted DOS for (a)A4, (b)B2, and (c) C2 adsorption configurations and plotted PDOS for (d)A4, (e)B2, and (f) C2 adsorption configurations, respectively.

$$\sigma = Ae^{\left(\frac{-E_g}{2K_B T}\right)} \quad (14)$$

where σ is electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and K_B is the Boltzmann constant in eV/K. The resulting DOS plot shown in Figure 3.13 (a) revealed that the COCl_2 adsorption onto hBN introduces an impurity state near the conduction band, reducing the band gap from 4.29 eV to 2.62 eV. In contrast, COCl_2 adsorption onto the Cu-doped hBN and Cu-hBN creates an impurity state in the energy range -2 to -1 eV and -3 to -2 eV reduces the band gap from 3.10 eV to 0.86 eV, and from 2.42 eV to 1.11 eV as shown in Figure 3.13(b) and Figure 3.13(c) respectively. The calculated band gap indicates that the B2 and C2 configurations exhibit better electrical conductivity than the A4 configuration due to the 72.25% and 54.13% reduction in the energy gap. Further, to gain additional insights regarding the contribution of the different atomic orbitals to the impurity state, we have calculated PDOS for all these configurations. The resulting PDOS plot in Figure 3.13(d) revealed that the impurity states in case of A4 configurations were due to the contribution from the 2p-B, 2p-C, 2p-O, 3p-Cl atomic orbitals. However, the contribution from the 2p-B atomic orbital was weak, resulting in weak hybridization between the B and O atoms, accounting for the weak interaction between the COCl_2 gas and hBN. Conversely, the PDOS plot in Figure 3.13(e) revealed that the impurity states in the case of A4 configurations were due to the contribution from the 2p-C, 2p-O, 3p-Cl, 2s-C, and 3d-Cu atomic orbitals. Similarly, for the

C2 configuration, 3d-Cu and 2p-C atomic orbitals contribute to the impurity states lying in the energy range from -3eV to -2eV, as shown in Figure 3.13(f). These findings suggest that impurity states lying very close to the conduction band facilitate easy pathways for the charge transfer during the interaction of the COCl₂ with the sensing material. Therefore, it was due to the reduction in the band gap, there was a strong charge transfer in the case of B2 and C2 configurations, which is responsible for the observed enhancement in the electrical conductivity of the Cu-doped hBN and Cu-hBN upon COCl₂ adsorption. Hence our findings suggest that both the Cu-doped-hBN and Cu-hBN systems exhibit better sensitivity than pristine hBN, making them a promising sensing material to detect COCl₂ gas molecules.

3.3.14 Recovery time analysis of the hBN, Cu-doped hBN and Cu-hBN systems

Table 3.6 Calculated the recovery time for the Cu-doped hBN and Cu-hBN systems upon COCl₂ adsorption at different temperatures under visible light and UV radiation

B2			C2	
Temperature(K)	recovery time visible light	recovery time UV	recovery time visible light	recovery time UV
300 K	3.661 x10 ²⁰ sec	3.661 x10 ¹⁷ sec	2.495x10 ⁷ sec	2.495x10 ⁴ sec
400K	2.647 x10 ¹² sec	2.647 x10 ⁹ sec	3.530x10 ² sec	3.530x10 ⁻¹ sec
500K	3.453 x10 ⁷ sec	3.453 x10 ⁴ sec	4.347x10 ⁻¹ sec	4.347x10 ⁻⁴ sec
600K	1.913x 10 ⁴ sec	1.913x 10 ¹ sec	4.995x10 ⁻³ sec	4.995x10 ⁻⁶ sec
700K	9.033 x 10 ¹ sec	9.033 x 10 ⁻² sec	2.056x 10 ⁻⁴ sec	2.056x 10 ⁻⁷ sec
800K	1.626 x 10 ⁰ sec	1.626 x 10 ⁻³ sec	1.879x10 ⁻⁵ sec	1.879x10 ⁻⁸ sec
900K	7.154x 10 ⁻² sec	7.154x 10 ⁻⁵ sec	2.992x10 ⁻⁶ sec	2.992x10 ⁻⁹ sec
1000K	5.876 x 10 ⁻³ sec	5.876 x 10 ⁻⁶ sec	6.593x10 ⁻⁷ sec	6.593x10 ⁻¹⁰ sec

To analyze the reusability of the gas sensor, we have calculated the recovery time (τ) using equation (15) for the A4, B2, and C2 adsorption configurations, respectively.

$$\tau = v^{-1} e^{\left(\frac{-E_{bp}}{K_B T}\right)} \quad (3.15)$$

where T is the testing temperature measured in Kelvin (K), and K_B is the Boltzmann constant whose value is 8.62×10^{-5} eV/K. E_{bp} is the potential barrier for the desorption of gas molecules, which can be substituted with adsorption energy (E_{ads}) because adsorption and desorption are reverse processes to each other, and v represents the attempt frequency, which is 10^{12} Hz for the visible radiation. The recovery time calculated for the A4, B2, and C2 adsorption configurations at 300K under visible light was found to be 8.937×10^{-4} sec, 3.661×10^{20} sec, and 2.495×10^7 sec, respectively. The reported too-high recovery time for the B2 and C2 adsorption configurations can be attributed to the calculated high adsorption energy for these configuration

This result implies that the too-high recovery time limits the reusability of both the Cu-doped hBN and Cu-hBN systems as gas sensing material in a chemical gas sensor to detect COCl_2 gas at room temperature. According to equation (3.15), we can improve the recovery time either by increasing the temperature, the attempt frequency, or both if the adsorption energy is kept constant. Recently, Li et al. also validated that ultraviolet (UV) radiation assists quick recovery time of the gas sensor[62]. Therefore, to examine the effect that UV radiation and increased temperature had on the recovery time of the B2 and C2 configurations. We have calculated the recovery time value at different temperatures under visible and UV light exposures for these configurations. The reported value in Table 3.6 suggests that the recovery time for the B2 and C2 configurations reduces from 3.661×10^{17} sec to 5.876×10^{-6} sec and from 2.495×10^4 sec to 6.593×10^{-10} sec, respectively, as the temperature increases from 300K to 1000K under UV radiation. This happened because both high temperatures and UV radiation facilitate additional high input energies required for the desorption of the COCl_2 gas from the surface of Cu-doped hBN and Cu-hBN. These findings suggest that annealing at high temperatures under UV radiation effectively improves the recovery time of the Cu-doped hBN and Cu-hBN systems. Hence, the recovery time analysis validates that Cu-doped hBN and Cu-hBN systems can be used as a sensing material at elevated temperatures to detect COCl_2 gas.

4. Conclusion

In the present work, we have systematically investigated the adsorption behavior of COCl_2 gas onto the pristine hBN and Cu-decorated hBN using first principle calculations. The adsorption of COCl_2 onto pristine hBN was a physisorption due to their small adsorption energy. The physisorption of COCl_2 onto pristine hBN resulted in poor sensitivity and recovery time. Therefore, the Cu atom was adsorbed onto hBN and substitutional doped into hBN at N and B vacancy. The formation and binding energy suggest that the Cu atom doped at B vacancy is the most stable configuration. On the other side, the Cu atom adsorbed at the N site was the most stable configuration. Further, the adsorption energy upon COCl_2 adsorption onto Cu-doped hBN and Cu-hBN was found to be high, indicating that the adsorption process was a chemisorption and there exists strong chemical interaction between the COCl_2 and Cu-doped hBN and Cu-hBN. The RDG analysis revealed that there exists a weak vdW interaction between the COCl_2 and pristine hBN. In contrast, for the B2 and C2 adsorption configurations, it was the electrostatic interaction that caused the COCl_2 to orient with the O atom facing toward the Cu atom. This resulted in the strong electron transfer from the Cu atom to the COCl_2 , as verified by the Hirshfeld and charge density difference methods. As a consequence, there

was a shift in the impurity state towards the conduction band and a reduction in the band gap upon COCl_2 adsorption, indicating an enhancement in the sensitivity of the B2 and C2 adsorption configurations. The corresponding PDOS plot revealed that strong hybridization exists between the 3d-Cu atom and the 2p-O atom, accounting for the strong interaction between the gas and the adsorbate. Furthermore, the calculated recovery time for the B2 and C2 adsorption configurations at 300K was found to be too high. Therefore, annealing at high temperatures under UV exposure improves the recovery time of the B2 and C2 adsorption configurations. Hence, the improved recovery time, better sensitivity, adsorption energy, and enhanced electrical conductivity upon COCl_2 adsorption validate that Cu-doped hBN and Cu-hBN are promising sensing materials at elevated temperatures for sensing COCl_2 .

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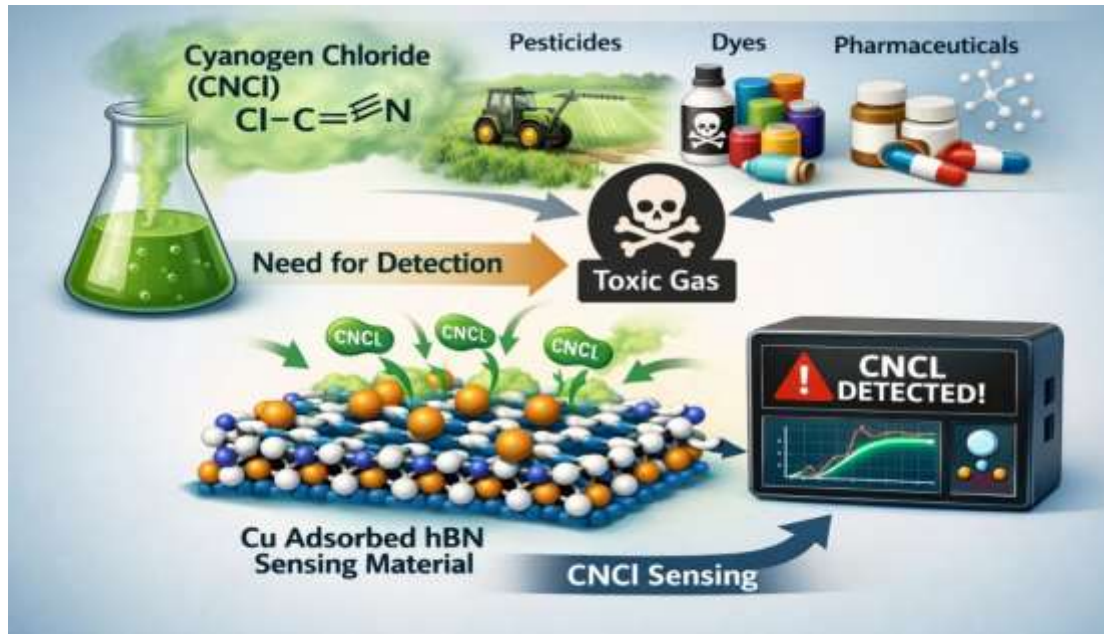
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Chapter 4

Adsorption of Cyanogen Chloride Gas onto the Pristine and Copper-Decorated hBN Monolayer: A Comparative DFT Study



The adsorption of toxic gas such as Cyanogen Chloride (CNCl) onto the pristine and Cu-decorated hexagonal boron nitride (hBN) was investigated using Density Functional Theory (DFT). The adsorption of CNCl gas molecules onto pristine hBN was a physisorption, resulting in a poor recovery time. However, Cu decoration onto hBN modifies the electronic properties of hBN. Further CNCl adsorption onto Cu-hBN resulted in three structures abbreviated as B1, B2, and B3. The calculated adsorption energies suggest that the adsorption of CNCl gas onto Cu-hBN was physisorption with enhanced adsorption energy, and B3 was the most stable configuration. Further, various parameters such as DOS, charge density differences, and ELF were calculated for the most stable adsorption configuration. The DOS result revealed that CNCl adsorption enhances the conductivity by reducing the band gap. It was due to the charge transfer from CNCl gas to the Cu-hBN, verified from the charge density difference. The reduction in the band gap resulted in a 31.54% variation in the work function, indicating highly sensitive behaviour of the Cu-hBN system. Additionally, RDG

analysis suggests that the non-covalent interaction between CNCl and Cu-hBN was responsible for the physisorption. Finally, the recovery time for CNCl adsorbed onto Cu-hBN was found to be 1.596×10^{-5} sec, 2.525×10^{-7} sec, and 2.098×10^{-8} sec at 300K, 400K, and 500K, respectively. Hence, based on our DFT results, the Cu-hBN system can be used as a practical sensor to detect CNCl gas at 300K.

4.1 Introduction

CNCl[1], being a colourless gas, volatilizes into a toxic gas upon exposure to air, and is primarily used in the rubber, plastic, fumigants, and pesticides industries. Acute exposure to CNCl gas causes sleepiness, sore throat, cough, dizziness, and nausea[2]. In contrast, prolonged exposure causes respiratory failure, metabolic obstruction, and irreversible damage to the red blood cells and central nervous system[3]. Therefore, looking at the detrimental effects CNCl gas has on human health, there is a need to monitor, capture, and remove toxic gas for a safer and cleaner environment. In this regard, gas sensors that exhibit high selectivity, sensitivity, stability, and rapid recovery time in harsh environments are required. Two-dimensional (2D) materials such as graphene[4], black phosphorene[5], germanene[6], silicene, Aluminium nitride (AlN)[7], Indium nitride (InN)[8], and transitional metal dichalcogenides (TMDs)[9, 10] have been extensively explored as sensing materials due to their high surface-to-volume ratio, tunable optical and electronic properties, and structural diversities. However, due to certain limitations like the absence of a dangling group, zero band gap in graphene[11], and low carrier mobility in TMDs, hinder the practical application of these materials as a sensing material in gas sensors. Moreover, poor selectivity and sensitivity at elevated temperatures are also considered as bottleneck problems for these 2D materials[12]. Therefore, there is an inevitable need to explore alternative 2D materials capable of exhibiting high sensitivity, selectivity, fast recovery time, stability, and reliable operation at high temperatures[13, 14]. In

this regard, hBN, widely known as ‘white graphene,’ can be considered a suitable sensing material in harsh environments due to its unique properties, like high thermal conductivity and better structural stability at high temperatures. However, there have been numerous reports regarding the utilization of hBN as a sensor[15-17]. In contrast it was also concluded from the literature that pristine hBN-based gas sensors exhibit instantaneous recovery time, slower response, and poor selectivity[18]. This can be attributed to the weak adsorption ability of hBN due to its inherent chemical inertness. Therefore, to overcome the issue of weak adsorption ability and poor sensing performance of hBN, researchers have adopted the method of surface activation method by doping[19, 20] and substrate engineering[21, 22]. It has been well proven that metal atom decoration onto hBN enhance the adsorption ability and sensing performance of hBN[23]. Recently, Kalwar et al. studied the adsorption of harmful toxic gases such as CO₂, CO, H₂S, HF, and NO onto a Ti-doped hBN monolayer. Their study revealed that CO₂, CO, H₂S, HF, and NO got adsorbed onto Ti-doped hBN with adsorption energies - 1.32eV, -1.66eV, -1.20eV, -0.81eV and -1.82eV respectively. Additionally, Ti decoration onto hBN resulted transitions from semiconductor to narrow band semiconductor and metal upon CO₂, H₂S, NO, and CO, HF adsorption, respectively. The reported variation in the electronic properties and adsorption energy upon Ti decoration onto hBN lead to high sensitivity and better recovery time than pristine hBN. In another study Khan et al. reported that the adsorption of CO, COS, CH₂N₂, and CF₂O onto Fe-decorated hBN was chemisorption, whereas the adsorption of CO₂ and CH₄O onto Fe-decorated hBN was physisorption [24]. There exist various reports regarding the adsorption of CNCl gas onto metal-doped graphene quantum dots[25], Al and Ga-doped BN nanotubes[26], and phosphorene nanosheets[27]. However, there have been no reports regarding adsorption of CNCl gas onto Cu-decorated hBN monolayer has served as a motivation for this work. Therefore, in this work, we have investigated

the adsorption of CNCl gas onto Cu-decorated hBN monolayer using DFT. Adsorption energy and adsorption distances were calculated in order to determine the strength of interaction during the adsorption of CNCl gas onto hBN and Cu-decorated hBN system. Moreover, to analyze the effect Cu decoration on hBN and CNCl gas adsorption had on the electronic properties, DOS and PDOS were calculated, respectively. Charge transfer during the interaction was analyzed quantitatively and qualitatively using charge density difference and Hirshfield calculation. RDG and ELF calculations were also performed to determine the existence of any non-covalent interaction and distribution of electron density around the interacting atoms. Finally, the sensitivity and recovery time of the Cu-decorated hBN and pristine hBN upon CNCl adsorption were evaluated utilizing the work function and adsorption energy, respectively. The outcome of the DFT study provides a deep insight into the adsorption mechanism and sensing performance of hBN and Cu-decorated hBN towards CNCl gas detection, which would be helpful for the experimentalist to design Cu-decorated hBN-based gas sensors.

4.2 Results and Discussions

4.2.1 Adsorption of CNCl gas onto pristine hBN

Table 4.1 Calculated adsorption energies, heights and bond lengths for three different optimized adsorption configurations

systems	Adsorption heights (Å)	C-N bond length (Å)	C-Cl bond length (Å)	Adsorption Energy (eV)
B1	3.881	1.166	1.623	-0.204
B2	2.960	1.167	1.672	-0.126
B3	1.859	1.172	1.650	-0.411

To analyze the interaction of CNCl gas with the hBN monolayer, we have considered the B site (on top of the B atom) and the N site (on top of the N atom) as the adsorption sites. This is because the gas molecules can easily interact with the electron-deficient (B site) or electron-rich (N site) sites. For the adsorption study, we have considered different orientations of CNCl gas at N and B sites as the input geometries for optimization. Upon optimization, we obtained four

different optimized structures abbreviated as A1, A2, A3, and A4. As shown in Figure 4.1, the resulting optimized structures revealed that the C-Cl and C-N bond lengths underwent no significant variation upon adsorption. This indicates weak interaction between the CNCl gas and the hBN layer. In A1 and A2 geometries, the CNCl gas molecule got adsorbed at a distance of 3.739 Å and 3.490 Å in a direction perpendicular and parallel to the z-axis with the C and N atoms orientating towards the B sites, as shown in Figure 4.1(a) and 4.1(b), respectively. In A3 and A4 geometries, the CNCl gas molecule got adsorbed at a distance of 3.475 Å and 3.530 Å in a direction perpendicular to the z-axis with the Cl and N atoms orienting towards the N sites, as shown in Figure 4.1(c) and 4.1(d), respectively. Further adsorption energies (E_{ads}) for the optimized structures were calculated using equation (4.1) where $E_{hBN-CNCl}$, E_{hBN} , and E_{CNCl} represent the total energies of the CNCl gas adsorbed onto hBN complexes, pristine hBN, and isolated CNCl gas molecule, respectively.

$$E_{ads} = E_{hBN-CNCl} - (E_{hBN} + E_{CNCl}) \quad (4.1)$$

From Table 4.1, the adsorption energies for the A1, A2, A3, and A4 geometries were found to be -0.191eV, -0.141eV, -0.189eV and -0.094eV respectively. The negative value reported in Table 4.1 indicates that the adsorption process was exothermic. Based on energy minimization we found A1 to be the most stable among the various optimized structures[28]. We have referred A1 configuration as 'CNCl-hBN' for the rest of the study. The calculated adsorption energy suggests that the adsorption of the CNCl gas molecule onto the hBN monolayer was physisorption. Moreover, the reported adsorption distance in Table 4.1 was larger than the sum of the atomic radii of B, N, C, and Cl atoms, confirming a weak interaction between the CNCl gas molecule and the hBN layer. Hence, from the perspective of the adsorption study, we found that pristine hBN exhibits weak adsorption of CNCl gas molecules.

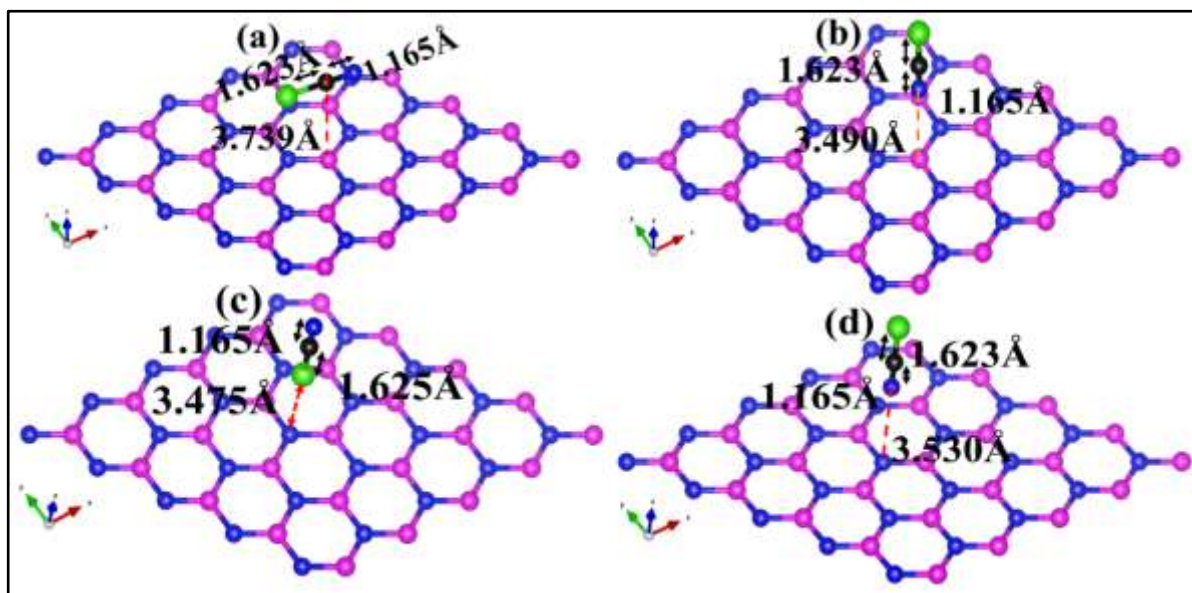


Figure 4.1: Side view of the different optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The pink, blue, black, and green atoms correspond to B, N, C, and Cl atoms

4.2.2 Analysis of the recovery time for the CNCl gas adsorbed onto hBN monolayer

To analyze the gas sensing performance of the CNCl-hBN, we have calculated recovery time (τ), defined as the time required by the gas molecule to desorb entirely from the surface of the sensing material using equation (4.2).

$$\tau = \nu^{-1} e^{\left(\frac{-E_{bp}}{K_B T}\right)} \quad (4.2)$$

Where T is the testing temperature measured in Kelvin (K), K_B is the Boltzmann constant whose value is 8.62×10^{-5} eV/K. E_{bp} is the potential barrier for desorption of gas molecules, which can be substituted with E_{ads} because adsorption and desorption are reverse processes to each other, and ν represents the attempt frequency, which is 10^{12} Hz [29] for the visible radiation. According to equation (4.2), the recovery time for the CNCl-hBN system was found to be 2.225×10^{-9} s under visible light exposure at 300K, which is too small to produce any variation in the electronic property of the hBN. Hence, based on the recovery time analysis, we found that the hBN sheet cannot be utilized as a gas sensor to detect CNCl gas at room temperature.

4.2.3 Adsorption of Cu atom onto hBN monolay

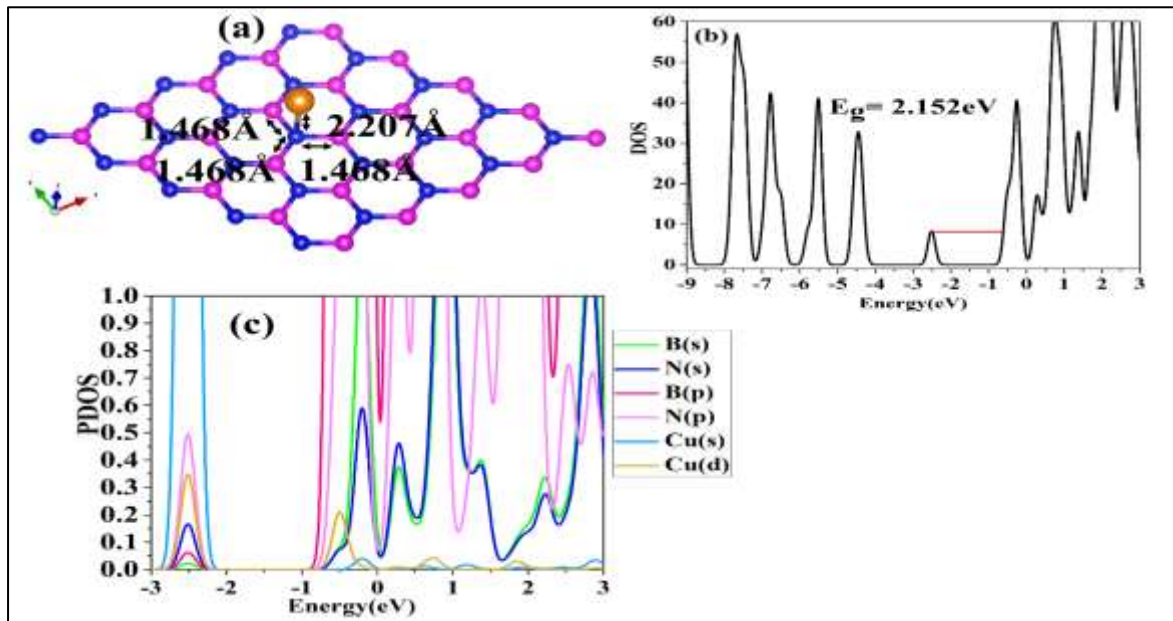


Figure 4.2 (a)Optimized structure, (b) DOS, and (c) PDOS of the Cu-hBN, respectively

In the previous section, we observed that pristine hBN exhibits poor gas adsorption ability and sensing performance towards CNCl gas. The decoration of Transition metal (TM) atoms onto 2D material enhances the gas adsorption capability of the 2D material. Therefore, we decorated the Cu atom on the hBN layer by placing the Cu atom above the N site. Among the various TM metal atoms, we have selected the Cu atom because it is inexpensive, abundant in nature, and does not get poisoned by the analyte[30]. Based on previous theoretical studies, we have selected the N site as the most preferential adsorption site for the Cu atom[31, 32]. Upon optimization, the resulting optimized structure as shown in Figure 4.2(a) is abbreviated as Cu-hBN. The optimized structure revealed that the B-N bond length increased from 1.450Å to 1.468Å, and the CNCl gas got adsorbed at a distance of 2.207Å with adsorption energy -0.33eV. The observed increment in the B-N length indicates that the B-N ring undergoes expansion to incorporate the Cu atom. Further, cohesive energy ($E_{coh}/atom$) was calculated using equation (4.3) to determine the thermodynamic stability of the Cu-hBN system.

$$E_{coh} = \frac{E_{hBN-Cu} - (x \cdot E_B + y \cdot E_N + E_{Cu})}{n} \quad (4.3)$$

where E_{hBN-Cu} , E_B , E_N , E_{Cu} x, y, and n represent the total energies of the Cu-hBN system, isolated B, N, and Cu atoms, the number of B, N, and total atoms within the unit cell, respectively. According to equation (4.3), the E_{coh} /atom for the Cu-hBN system was found to be -1.40eV/atom. The negative value of the E_{coh} /atom indicates that the structure remained thermodynamically stable, which is consistent with the other theoretical calculations[33-35]. Additionally, we have performed DOS calculations to investigate the electronic properties of the Cu-hBN system. From Figure 4.2 (b), we observed that the impurity state within the energy range -3 to -2eV reduces the band gap from 4.45eV to 2.152eV upon Cu decoration. It was confirmed from the PDOS study that the impurity state is a result of the hybridization between the 4s-Cu and 2p-N orbitals, as shown in Figure 4.2(c). The observed reduction in the band gap indicates an enhancement in the electrical conductivity of the hBN layer. This might occur due to the charge transfer from the Cu atom to the hBN layer. Hence, the observed structural and electronic properties suggest that Cu atom decoration onto hBN modifies the structural and electronic properties of the hBN layer.

4.2.4 Adsorption of CNCl gas onto the Cu-decorated hBN monolayer

Table 4.2 Calculated adsorption energies, heights and bond lengths for three different optimized adsorption configurations

systems	Adsorption heights (Å)	C-N bond length (Å)	C-Cl bond length (Å)	Adsorption Energy (eV)
B1	3.881	1.166	1.623	-0.204
B2	2.960	1.167	1.672	-0.126
B3	1.859	1.172	1.650	-0.411

To analyze the interaction of the CNCl gas with the Cu-hBN system, we have considered different orientations of the CNCl gas at the dopant site as the input geometry for optimization. The dopant site is selected as the adsorption site because the CNCl gas molecule can readily be adsorbed at the dopant site. After optimization, we got three optimized structures abbreviated as B1, B2, and B3, respectively as shown in Figure 4.3. The optimized structure shown in Figure 4.3(a),

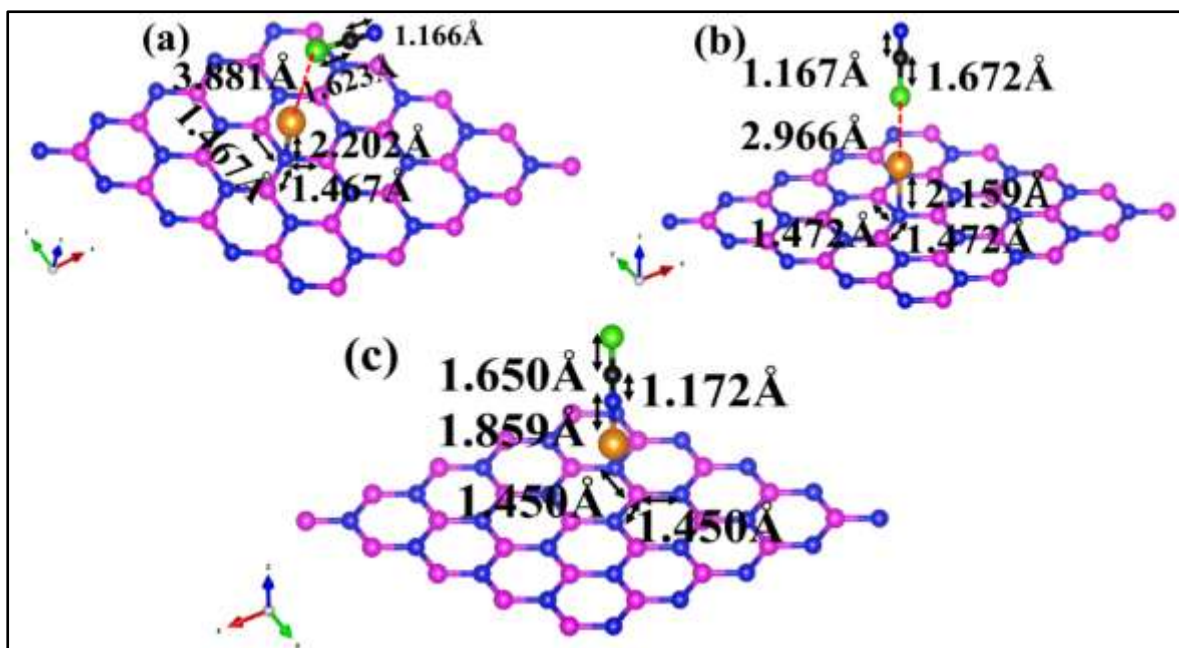


Figure 4.3: Side view of the different optimized structures (a) B1, (b) B2, and (c) B3, respectively. The orange colour corresponds to the Cu atom.

Fig.4.3(b) and Fig.4.3(c) suggests that the C-Cl bond lengths are 1.166 Å, 1.167 Å, and 1.172 Å for the B1, B2, and B3 configurations. In contrast, the C-N bond lengths are 1.623 Å, 1.672 Å, and 1.650 Å for the B1, B2, and B3 configurations. We found on the comparison that the C-Cl and C-N bond lengths of CNCl gas upon adsorption vary from those of the isolated CNCl molecule in all the optimized structures. The observed variation in the bond length was due to the catalytic effect of the Cu atom. Further, adsorption energies were calculated using equation (4.4) and reported in Table 4.2 to determine the interaction strength between the CNCl gas and Cu-decorated hBN monolayer.

$$E_{\text{ads}} = E_{\text{hBN-Cu-CNCl}} - (E_{\text{hBN-Cu}} + E_{\text{CNCl}}) \quad (4.4)$$

Where E_{CNCl} , $E_{\text{hBN-Cu-CNCl}}$ and $E_{\text{hBN-Cu}}$ represents the total energies of the isolated CNCl gas molecule, Cu-decorated hBN with and without CNCl gas molecule, respectively Table 4.2 shows that the adsorption energies for the B1, B2, and B3 structures were found to be -0.204 eV, -0.126 eV, and -0.411 eV, respectively. The negative value of the adsorption energies suggested that the adsorption process was exothermic. We found that the B3 structure was the most stable among the various optimized structures because of its lowest adsorption

energy. For the rest of the study, we have referred to B3 as “CNCl-Cu-hBN”. The reported adsorption energy in Table 4.2 suggests that the adsorption process was physisorption. Moreover, the reported adsorption energy in Table 4.2 was more enhanced than the adsorption energy in Table 4.2 on comparison. This indicates that the Cu-hBN system has better adsorption affinity than the pristine hBN for CNCl gas. Hence, the adsorption study suggests that the decoration of the Cu atom onto hBN is an effective way to enhance the gas adsorption ability of the hBN sheet towards CNCl gas

4.2.5 Electronic properties analysis of the Cu-decorated hBN

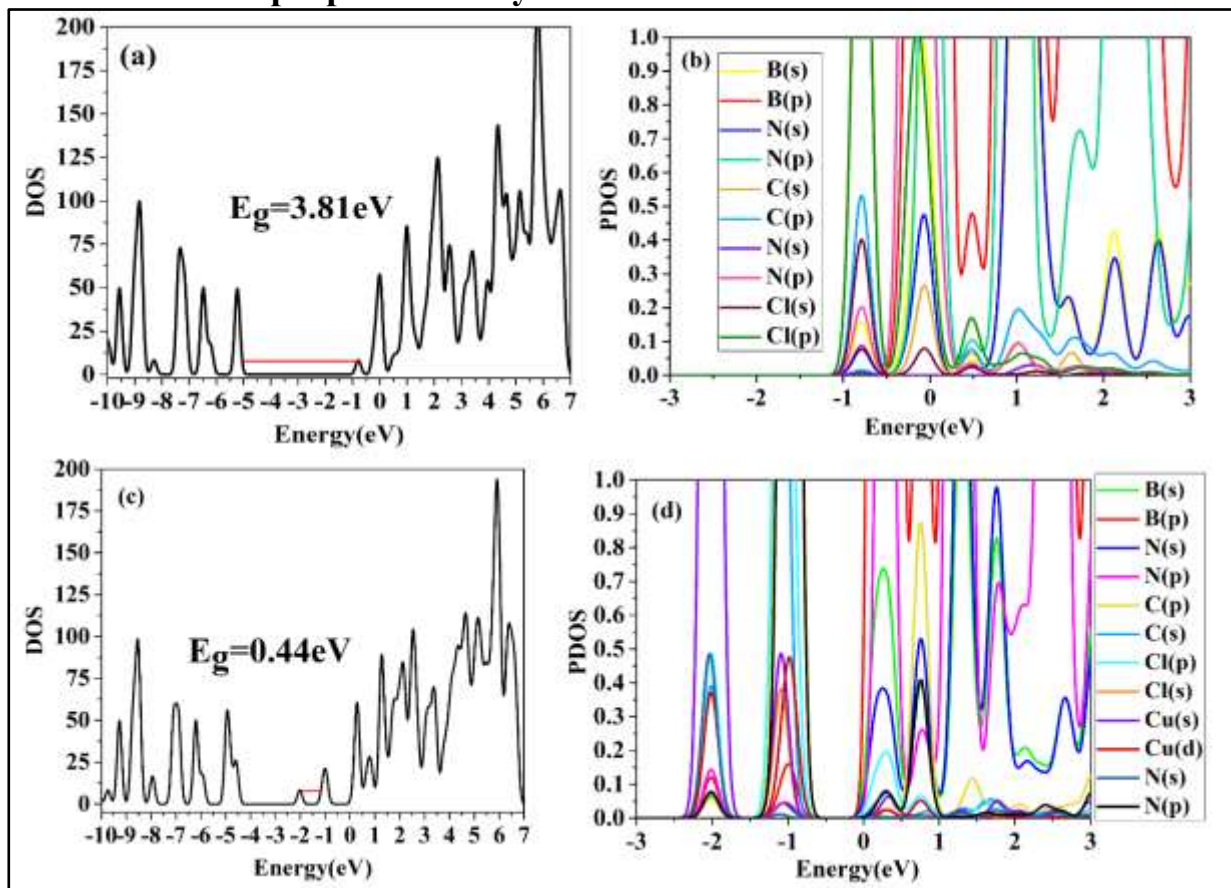


Figure 4.4: (a) DOS and (b) PDOS plots for the CNCl-hBN system. (c) DOS and (d) PDOS plot for the CNCl-Cu-hBN system, respectively.

To analyse the effect of CNCl gas had on the electronic properties of hBN and Cu-hBN systems, we have performed DOS and PDOS calculations for CNCl-hBN and CNCl-Cu-hBN systems, we have performed DOS and PDOS

calculations for CNCl-hBN and CNCl-Cu-hBN systems. The DOS results shown in Figure 4.4(a) revealed that CNCl gas introduces an impurity state in the energy range -1 to 0 eV, thereby reducing the band gap from 4.45 eV to 3.81 eV in the case of the CNCl-hBN system. In the case of the CNCl-Cu-hBN system, CNCl gas introduces a new impurity state at -1 eV adjacent to the impurity state created upon Cu decoration at -2 eV, as shown in Figure 4.4(c). The new impurity state facilitates easy charge transfer from the Cu atom to the CNCl gas during the interaction, reducing the band gap from 2.152 eV to 0.44 eV. Further, the PDOS plot in Figure 4.4(b) indicates hybridization between the 3p-N and 2p-C atomic orbitals of hBN and CNCl gas responsible for creating an impurity state in the energy range -1 to 0 eV. From Figure 4.4(d), we found that hybridization between the 3p-N and 4s-Cu atomic orbitals of CNCl and Cu-hBN was responsible for the observed impurity state in the energy range -2 to -1 eV. On comparison, we found that CNCl produces significant variation in the band gap of Cu-hBN, thereby enhancing the conductivity of the Cu-hBN system. This might be due to the significant charge transfer during the interaction. Hence, based on the observed variation in the electronic properties of CNCl-hBN and CNCl-Cu-hBN systems, we found that the Cu-hBN system can be used as an electronic sensor.

4.2.6 Non-Covalent Interaction

To determine the existence of non-covalent interaction between the CNCl gas molecules and the adsorbent, we have performed the reduced density gradient (RDG) analysis proposed by Johnson and co-workers. The results obtained from the RDG analysis were visualized using the RDG scatter plot and RDG isosurfaces, as shown in Figure 4.5. The RDG scatter plot represents the relationship between the RDG function $s(r)$ and $\text{sign}(\lambda_2) \rho(r)$, where λ_2 represents the second eigenvalues of the Hessian matrix interaction and $s(r)$ defines a relation between the electron ($\rho(r)$) and its gradient ($\nabla\rho(r)$) as follows:

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{[\rho(r)]^{4/3}} \quad (4.5)$$

The function $\text{sign}(\lambda_2) \rho(r)$ is of great significance as it provides information about the nature of the interaction. If $\text{sign}(\lambda_2) \rho(r) < 0$, $\text{sign}(\lambda_2) \rho(r) \approx 0$, and $\text{sign}(\lambda_2) \rho(r) > 0$, it indicates strong attractive hydrogen bonding, weak van der Waals (vdW) interaction, and strong repulsive steric effects. In Figure 4.5(a), the RDG scatter plot illustrates a sharp decline in the RDG function value around $\text{sign}(\lambda_2) \rho(r) \approx 0$ for the CNCl-hBN system. Further, the corresponding RDG isosurface plot in Figure 4.5(b) illustrates green patches between the CNCl gas and hBN layer, indicating vdW interaction between the CNCl gas and hBN monolayer. These findings confirmed that the adsorption of CNCl gas onto hBN was physisorption. The RDG scatter plot in Figure 4.5(c) illustrated a fluctuation in the RDG value around $\text{sign}(\lambda_2) \rho(r) > 0$ upon adsorption of Cu atom whereas the corresponding RDG isosurface plot as shown in Figure 4.5(d) illustrated blue patches between the Cu atom and hBN layer indicating that strong electrostatic interaction exists between the adsorbed Cu atom and hBN monolayer. Further the RDG scatter plot in Fig. 4.5(e) illustrated a fluctuation in the RDG value around $\text{sign}(\lambda_2) \rho(r) > 0$ and $\text{sign}(\lambda_2) \rho(r) \approx 0$ upon CNCl adsorption onto Cu-hBN systems. From Figure 4.5(f), the corresponding RDG isosurface plot illustrated blue patches between the CNCl gas and hBN layer and green patches between the Cu atom and hBN layer. The observed blue patches indicate that the interaction of CNCl gas with the Cu atom is purely electrostatic which is responsible for the observed enhancement in the adsorption energy. These findings suggest that Cu-hBN binds CNCl more effectively than pristine hBN. This proved that Cu-hBN system has better adsorption affinity for CNCl gas than pristine hBN. Hence, based on our RDG analysis, we found that non-covalent interaction exists, which strongly influences the adsorption of CNCl gas and sensitivity of the hBN and Cu-hBN systems.

Adsorption mechanism of Cyanogen Chloride

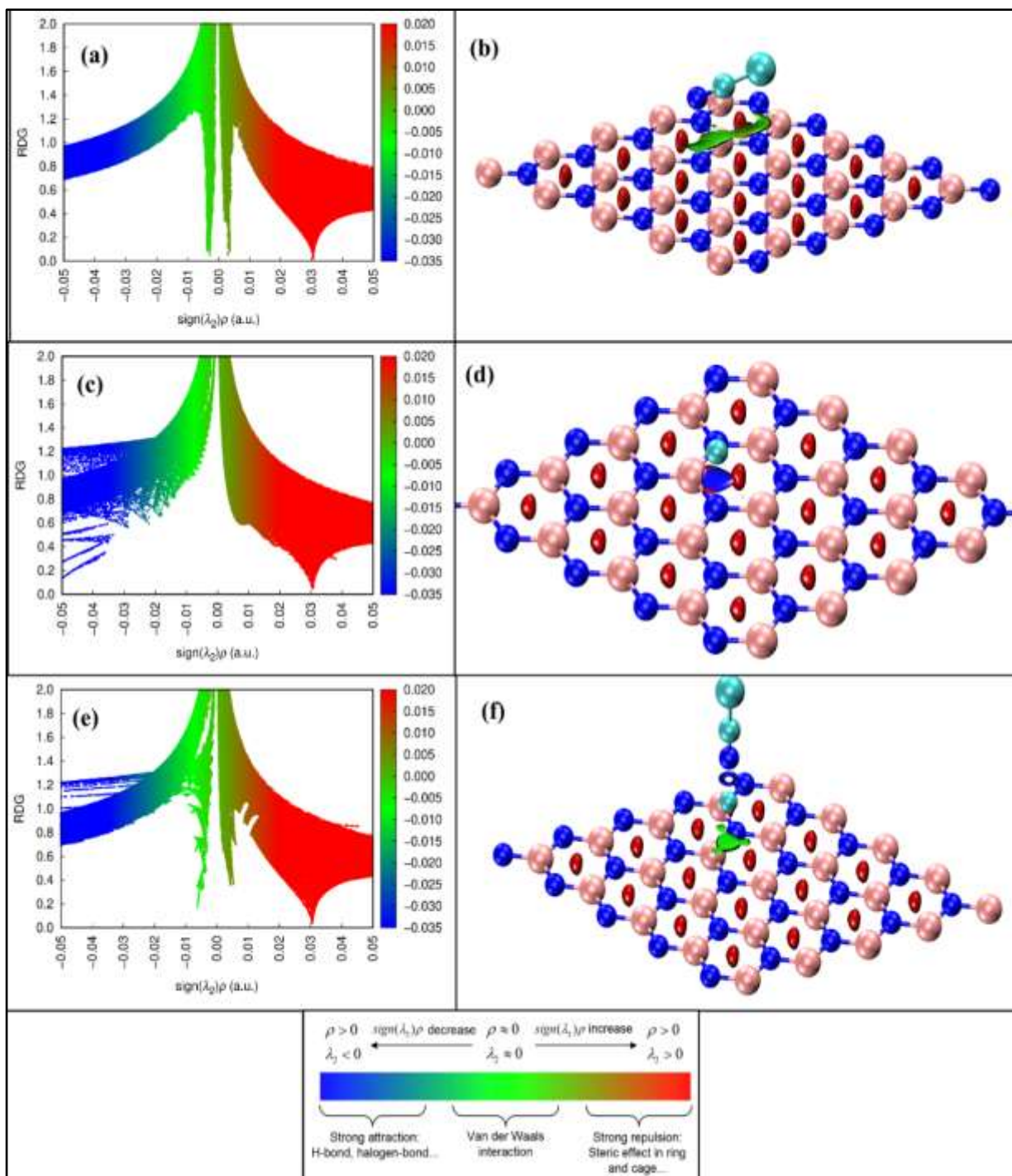


Figure 4.5: RDG scatter plot for the (a) CNCl-hBN, (c)Cu-hBN, and (e) CNCl-Cu-hBN systems. Isosurface plot for the (b) CNCl-hBN, (d)Cu-hBN, and (f) CNCl-Cu-hBN systems, respectively.

4.2.6 Charge Density Difference analysis

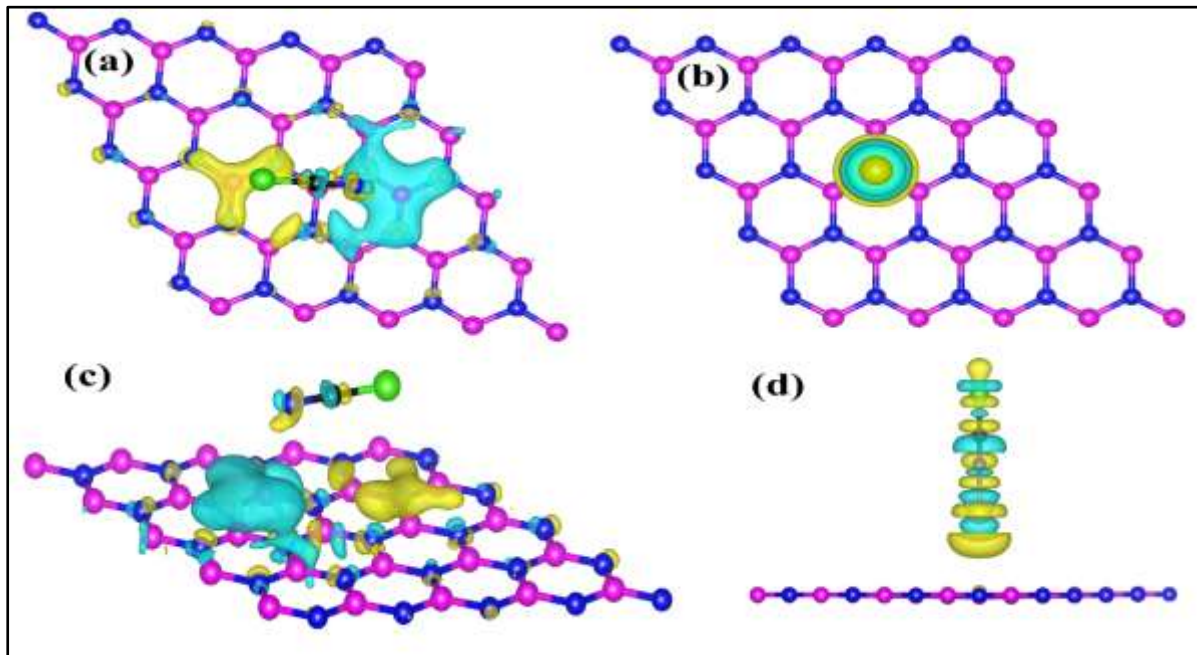


Figure 4.6: Charge Density difference plot (a) Top view for CNCl-hBN, (b) Top view for Cu-hBN, and (c) Side view for CNCl-hBN, (d) Side view for CNCl-Cu-hBN systems, respectively.

To investigate the charge transfer during the interaction of CNCl gas with the sensing material, we have utilized charge density difference and Hirshfield methods to visualize the charge transfer. From Hirshfield charge analysis, we found that $0.067e$ was transferred between CNCl and hBN, whereas $0.142e$ was transferred between CNCl and Cu-hBN. It was on comparison of the reported charge transfer in Table 4.3 we found that significant charge transfer took place in the case of CNCl-Cu-hBN. This was verified from the charge density difference diagram shown in Figure 4.6. From Figure 4.6(a) and 4.6(c), we observed a small region of charge loss and gain around the N and C atoms of the CNCl gas molecule, identified by the cyan and yellow colours, respectively. This indicates weak charge transfer from hBN to CNCl. Furthermore, Figure 4.6(b) and 4.6(d) illustrate significant charge loss and gain regions around the Cu and N atoms. This indicates that a significant charge was transferred from the Cu atom to the CNCl gas. The observed charge transfer can be attributed to the difference in the electronegativity between the Cu and N atoms. Being highly

electronegative, the N atom withdraws electrons from the highly electropositive Cu atom during the interaction. Hence our charge density difference results agreed with the Hirshfield charge analysis.

Table 4.3 Calculated charge transfer for CNCl -hBN, CNCl-Cu-hBN adsorption configurations.

Configuration	CNCl-hBN	CNCl-Cu-hBN
Charge transfer	0.067e	0.142e

4.2.7 Electron Localization Function analysis

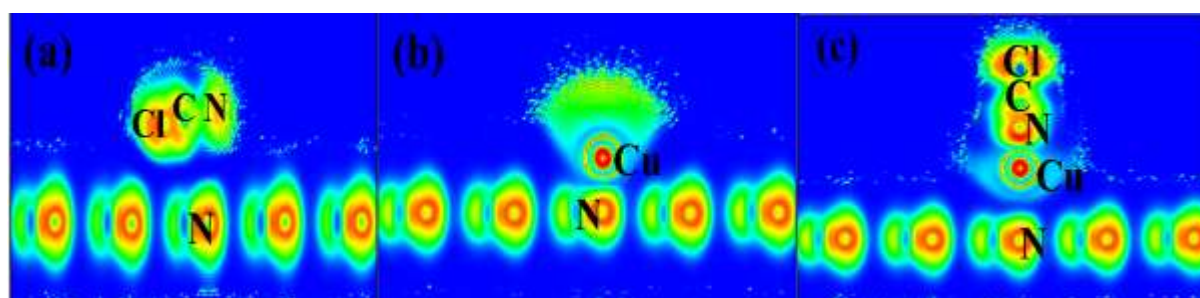


Figure 4.7: ELF plot for (a) CNCl-hBN, (b) Cu-hBN, and (c) CNCl-Cu-hBN systems, respectively

We have performed ELF calculations to analyze the distribution of electrons around the interacting atom during the adsorption of CNCl onto sensing material. The ELF plot shown in Figure 4.7(a) illustrates high electron density around N and Cl atoms, indicating the highly reactive sites of CNCl gas identified by red. Moreover, a large region of low electron density exists in the interacting region identified by the blue colour. This indicates a weak interaction between CNCl gas and the hBN layer. However, upon Cu decoration, we found a large red colour region around the N atom compared to the Cu atom, as shown in Figure 4.7(b). This happens due to the electron transfer from the Cu atom to the nearby N atom, making the Cu atom electropositive and the N atom electron-rich. Further upon CNCl adsorption, we observe a large red-coloured region around the CNCl gas compared to the Cu atom, as shown in Figure 4.7(c). This indicates that electrons were transferred from the Cu atom to the CNCl gas, confirming the interaction of CNCl gas with the Cu atom is purely electrostatic. These findings were consistent with our RDG result that a strong, attractive interaction exists between the CNCl

gas and Cu-hBN layer upon CNCl adsorption. Hence, our ELF results were in agreement with the RDG analysis.

4.2.8 Sensitivity analysis

Table 4.4 Calculated electrical conductivity for CNCl-hBN and CNCl-Cu-hBN at different temperatures

Configuration	σ ($\Omega^{-1} \text{ m}^{-1}$) at $T=300\text{K}$	σ ($\Omega^{-1} \text{ m}^{-1}$) at $T=400\text{K}$	σ ($\Omega^{-1} \text{ m}^{-1}$) at $T=500\text{K}$
CNCl-hBN	1.017×10^{-32}	1.012×10^{-24}	6.373×10^{-20}
CNCl-Cu-hBN	2.019×10^{-4}	1.694×10^{-3}	6.069×10^{-3}

The sensitivity of the semiconducting material is judged mainly by its electrical conductivity, which undergoes a variation with the adsorption of the gas molecule. Therefore, we utilized equation (4.7) to calculate the electrical conductivity of the CNCl-hBN and CNCl-Cu-hBN systems.

$$\sigma = Ae^{\left(\frac{-E_g}{2K_B T}\right)} \quad (4.7)$$

where σ is electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and K_B is the Boltzmann constant in eV/K. The calculated data in Table 4.4 indicates that the electrical conductivity of the CNCl-hBN and CNCl-Cu-hBN systems increases with temperature and upon CNCl adsorption. The observed increase in the electrical conductivity with temperature indicates the semiconductor behaviour of the CNCl-hBN and CNCl-Cu-hBN systems. On comparison, we found that the CNCl-Cu-hBN system exhibits better electrical conductivity than the CNCl-hBN system. This can be attributed to the large reduction in the band gap upon gas adsorption. The DOS calculation verified that the CNCl adsorption reduces the band gap by 14.38% and 79.58% in the case of CNCl-hBN and CNCl-Cu-hBN systems. Significant variation in the band gap of the CNCl-Cu-hBN system leads to efficient charge transfer between the interacting species, leading to measurable changes in the electrical signal. This indicates that the CNCl-Cu-hBN system exhibits sensor properties and can be used as an electronic sensor. Hence, all these findings suggest that Cu decoration onto hBN improves the sensitivity of the hBN layer toward CNCl gas.

4.2.9 Work function analysis

The sensitivity of the sensing material in a work function-based gas sensor is generally determined by the work function(ϕ). Since any variation in the work function ($\Delta\phi$) causes changes in the emitted electron current densities, this can be inferred from equation (4.8), which shows the exponential dependence of emitted electron current densities on ϕ .

$$j = AT^2 e^{\left(\frac{-\phi}{k_B T}\right)} \quad (4.8)$$

where j is the emitted electron current density (A/m^2), A is a Richardson constant ($A/m^2 K^2$), ϕ is the work function of the material in eV, T is the temperature in K, and K_B is the Boltzmann constant in eV/K respectively. Therefore, we have analyzed qualitatively the variation in the

work function ($\Delta\phi$) of hBN and Cu-hBN systems upon CNCl adsorption. For this purpose, the work function for these systems was calculated using equation (4.9).

$$\phi = E_{\text{inf}} - E_F \quad (4.9),$$

E_{inf} and E_F represent the electrostatic potential at infinity and the Fermi level energy. The electrostatic potential at infinity is assumed to be zero. In contrast, variation in the value of $\Delta\phi$ was calculated by subtracting the work function of the sensing material without gas molecules from that of the sensing material with gas molecules. The computed value of ϕ for the pristine hBN with and without gas molecules was found to be 2.44 eV and 2.12 eV, respectively. In contrast, for the Cu-hBN system, the value of ϕ with and without gas molecules was found to be 1.154 eV and 0.790 eV, respectively. Further, on comparison, we found a large negative variation in the work function of the Cu-decorated hBN sheet. The large negative variation can be attributed to the significant charge transfer between the CNCl and Cu-hBN, validated by our charge density difference calculations. Hence, from the perspective of work function analysis again, we

found that the Cu-hBN system exhibits better sensitivity towards CNCl gas than the pristine hBN.

4.2.10 Recovery time analysis

Table 4.5 Calculated recovery time at different temperatures for CNCl-Cu-hBN

Visible light exposure		Ultraviolet exposure	
Temperature	Recovery time	Temperature	Recovery time
300 K	1.596×10^{-5} sec	300K	1.596×10^{-8} sec
400K	2.525×10^{-7} sec	400K	2.525×10^{-10} sec
500K	2.098×10^{-8} sec	500K	2.098×10^{-11} sec

Recovery time is considered a key indicator in evaluating the reusability of a gas sensor. Therefore, we have calculated the recovery time for the CNCl-Cu-hBN system to investigate its practical utility as a gas sensor. The calculated recovery time for the CNCl-Cu-hBN system at 300K under visible light was found to be 1.596×10^{-5} sec, which is better than the reported recovery time for the CNCl-hBN system. This was due to the better adsorption affinity of the Cu-hBN system for CNCl gas. According to equation (4.2), increasing the temperature, attempt frequency, or both can reduce recovery time if adsorption energy is kept constant. Recently, Li et al. reported that ultraviolet (UV) radiation assists quick recovery time of the gas sensor[36]. Therefore, to analyze the effect that annealing and exposure to UV radiation had on the recovery time of the CNCl-Cu-hBN system. We have calculated and reported the recovery time in Table 4.5 at 400K and 500K under visible and UV light exposure. The reported data in Table 4.5 indicate that the recovery time reduces from 1.596×10^{-5} sec to 2.525×10^{-8} sec and 2.098×10^{-11} sec upon annealing and exposure to UV light at 400K and 500 K, respectively. Hence, the reported data suggest that annealing above 500K under UV radiation makes the recovery time too short to reuse as a gas sensor to detect CNCl gas.

4.3 CONCLUSION

In this study, we have systematically investigated the sensing performance of hBN and Cu-hBN systems towards CNCl gas using DFT. From the adsorption study, the adsorption of CNCl gas onto hBN was found to be physisorption, involving a weak vanderwaal interaction between them. However, upon Cu adsorption, the adatom creates new electronic states within the band gap region due to the strong hybridization between the 4s-Cu and 2p-N atomic orbitals, verified from the DOS and PDOS calculations. This facilitates the easy charge transfer from the adsorbed Cu atom to the nearby N atom. As a consequence, the Cu atom enhances the nucleophilic nature by becoming a highly electropositive atom, whereas the surrounding N atoms become an electron-rich species verified from the ELF calculation. This makes the Cu-decorated hBN surface highly reactive towards the adsorption of the gas molecule containing electrophilic species. Further, upon CNCl adsorption, as the CNCl gas approaches the adsorbed Cu atom, the adatom tries to orient the CNCl in such a way that the nucleophilic part of the CNCl gas faces toward the Cu atom to maximize the electrostatic interaction and charge transfer between. This causes an increase in the adsorption energy, thereby validating that Cu-decorated hBN binds CNCl gas more effectively than hBN due to the involvement of electrostatic interactions. Finally, the recovery time analysis revealed that the Cu-hBN system exhibits a better recovery time than pristine hBN, which can be further improved by annealing under UV radiation. Hence, based on our DFT results, we conclude that the Cu-hBN system can be used as a gas sensor to detect CNCl gas.

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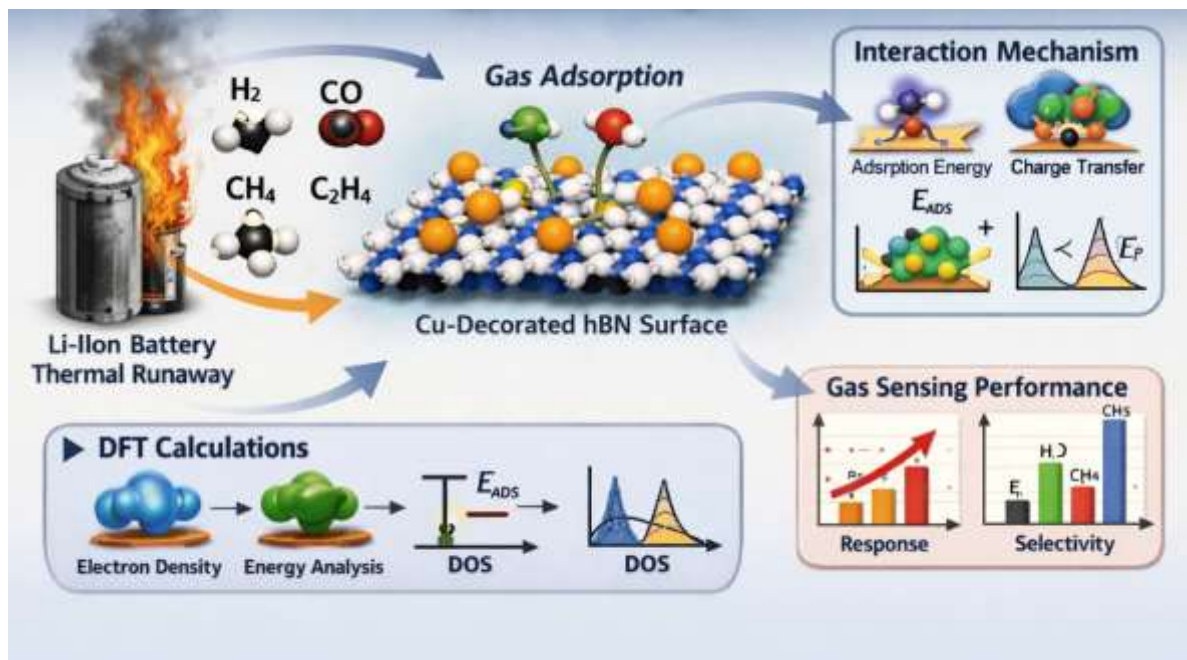
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Chapter 5

A deep insight into the adsorption mechanism of lithium-ion battery thermal runaway gases onto Cu-decorated hBN for gas sensing applications using DFT



Lithium-ion batteries, due to their environmental friendliness and high energy capacity, are extensively used in the field of transportation and energy storage. However, the problem of thermal runaway in lithium-ion batteries has become a serious threat to humans. Therefore, looking at these issues, we have investigated the adsorption mechanism of thermal runaway gases (C_2H_4 , CO , CO_2 , H_2 , and CH_4) onto pristine hBN and Cu-doped hBN using the Density Functional Theory (DFT). The adsorption of C_2H_4 , CO , CO_2 , H_2 , and CH_4 gas molecules onto pristine hBN was physisorption, resulting in poor recovery time, charge transfer, selectivity and sensitivity. However, substitutional doping of the Cu atom at the B vacancy causes thermal runaway gases to be adsorbed chemically. DOS calculation showed that the adsorption of C_2H_4 , CO , CO_2 , H_2 , and CH_4 gas molecules reduces the band gap of the Cu doped hBN, indicating chemoresistive behaviour of Cu-doped hBN. Further, various other calculations, such as charge density differences, showed that C_2H_4 , CH_4 , CO , CO_2 and H_2 gas act as electron donors and Cu-doped hBN as electron acceptors, whereas RDG calculation confirmed that weak vdW and strong attractive type of non-covalent interaction exist in the case of pristine hBN and Cu-doped hBN, respectively. Finally, our DFT results confirmed that Cu-doped hBN

exhibits enhanced sensitivity and recovery time towards thermal runaway gases, thereby making Cu-doped hBN a potential candidate to be utilized as a sensing material in gas sensors to detect thermal runaway gases

5.1 Introduction

Fossil fuels have been the primary source of energy in industrialisation, transportation, and domestic heating.[1-3] Due to globalisation, there has been a rapid increase in the consumption of fossil fuels, causing depletion of natural resources, a rise in environmental pollution, and global warming, which has become the most important issues human race is facing today.[4-6] Therefore, there is an inevitable need to develop clean and sustainable green energy, which is challenging without the help of energy storage technologies.[7] In response to these challenges, researchers are actively working towards the development of electrochemical energy storage systems. Among the various electrochemical energy storage systems such as lead-acid[8],lithium[9, 10],sodium-ion[11], and nickel-cadmium[12] batteries. It is the lithium-ion batteries that have attracted significant attention due to their high energy density, long cycling time, and lack of memory effects.[13, 14] As a consequence, they are finding their utility as an energy storage system in Electric vehicles (EVs),[15, 16] portable electronics,[17, 18] aerospace,[19] power grids, and other fields. However, due to electrical,[20] thermal and mechanical abuse,[21-23] lithium-ion batteries undergo thermal runaway conditions generating heat that doesn't get dissipated from the battery, thereby causing a rapid increase in the pressure and temperature, which accelerates the reaction rate, ruptures the cells, and releases highly flammable gases like C_2H_4 , CO_2 , CO , CH_4 and H_2 . The continuous production of these flammable gases causes lithium-ion batteries to explode, leading to major accidents. According to a report, a total of 357 incidents related to thermal runaway of lithium-ion batteries were reported from 2006 to 2022, and in the year 2020, over 100 cases of self-burning of electric vehicles were reported.[24] Since the thermal runaway condition in lithium-ion batteries is unavoidable. Therefore, there is a necessary and urgent need to monitor the thermal runaway gases in order to ensure the safety of the environment and human civilization. Currently, there exist various gas detection techniques such as gas chromatography, gas chromatography-mass spectrometer, but these kinds of detection techniques are expensive, time-consuming, and require a skilled operator for their operation[25] whereas techniques like infrared thermography and acoustic are also expensive, difficult to port in devices due to their large volume.[26] In reply to these issues, gas sensors can be considered as an optimal detection

technique because of their low cost, ease of operation and simple preparation methods.[27] For this purpose, researchers are extensively exploring various layered structures such as graphene, Transition Metal Dichalcogenides (TMDs),[28, 29] blue phosphorene,[30, 31] Transition metal chalcogenides (TMCs)[32, 33], Gallium nitride (GaN)[34, 35], Aluminium nitride (AlN),[36, 37],MXene[38] and metal oxides [39, 40] due to their high surface-to-volume ratio, tunable band gap, good compatibility with modern electronics.[41] Despite such unique properties, these materials in their pristine form are practically immature to meet the current requirement as a sensing materials. In order, to overcome these issues, researchers have adopted various methods such as surface functionalization through Transition metal (TM) doping[42-44], substrate engineering[45, 46], and defect engineering[47]. Previous studies have proved that doping TM atoms into 2D materials significantly improves the gas sensing characteristics. For example, Yu et al.[48] investigated the adsorption of CNCl, HCN, and NH₃ on metal-doped diamine. He observed that the introduction of the metal atom improves the adsorption capacity and sensitivity of the diamine. Mohammadi et al.[49] reported that the adsorption of H₂S, Cl₂, NH₃, and COCl₂ gas onto B₁₂C₆N₆ was physisorption, whereas Li-decorated B₁₂C₆N₆ exhibits excellent sensitivity towards Cl₂ and COCl₂ gas molecules. Hussain et al.[50] studied the adsorption of COCl₂ onto Cu-decorated B₁₂N₁₂ nanocage. His finding indicates that Cu atom decoration onto B₁₂N₁₂ nanocage enhances the adsorption strength, stability, and chemical reactivity of B₁₂N₁₂, and Cu-decorated B₁₂N₁₂ nanocage can be used as an efficient gas sensor for the detection of COCl₂ gas molecules. Xiao et al.[51] prepared Pt-BiVO₄ nanosheets via a two-phase method. He observed that the Pt-BiVO₄-based gas sensor exhibits high sensitivity, excellent stability, and a low detection limit towards acetone compared to BiVO₄.Beheshtian et al.[52] emphasised that doping of Sc atom into boron nitride nanotubes (BNNTs) enhances the adsorption capability and electrical conductivity of BNNT upon COCl₂ adsorption, thereby making Sc-doped BNNT a potential candidate to be utilised as an electronic sensor to detect COCl₂ gas molecules. There exists a plethora of literature reporting the utilisation of 2D materials as a sensing material to detect thermal runaway gases. Wu et al.[53] investigated the adsorption and gas sensing properties of Cu_n and Pd_n (n=1-3) clusters modified MoSe₂ for lithium-ion battery thermal runaway gases. Their results revealed that Cu_n-MoSe₂ and Pd_n-MoSe₂ have potential applications as a sensing material towards thermal runaway gases. Li et al.[54] also investigated the adsorption and gas sensing properties of Cu-embedded HfS₂ (Cu-HfS₂) and Cu-decorated HfS₂ (Cu@HfS₂) using DFT. Their studies revealed that Cu@HfS₂ has a strong adsorption capability towards CO, C₂H₄, and H₂, whereas Cu-HfS₂ has a strong

adsorption capability towards CH_4 and CO_2 . In another study, Xue et al.[55] studied the gas sensing properties of precious metal (Ag and Au) modified Janus MoSeTe for lithium-ion thermal runaway gases. His findings revealed that the introduction of Ag and Au significantly improved the adsorption capacity and charge transfer of Ag- MoTeSe_2 towards CH_4 . Recently, Qin et al.[56] investigated the adsorption capabilities of Pd_4/hBN , Rh_4/hBN , and Ru_4/hBN structures towards thermal runaway gases like CH_4 , CO_2 , CO , and H_2 using DFT. Their DFT results revealed that metal modification significantly enhances the adsorption capability of hBN towards all these gases. Hou et al. developed a Ce-doped MoS_2 -based gas sensor with high humidity resistance for detecting H_2 , which is generated during thermal runaway of lithium-ion batteries.[57] It exhibited excellent H_2 selectivity in the presence of CO , $\text{C}_3\text{H}_6\text{O}$, CH_4 , and $\text{C}_2\text{H}_6\text{O}$, maintaining its stability under high humidity conditions ranging from 30% to 85%, demonstrating a fast response to H_2 , making it ideal for monitoring H_2 levels during thermal runaway conditions. Chem et al. analysed the sensing characteristics of Ag-CdS, Pd-CdS, and Pt-CdS towards H_2 and CO_2 . [58] They found that Pd-CdS and Pt-CdS showed potential for room temperature H_2S sensing, while the CdS monolayer displays the potential for H_2 and CO_2 cleaning. The sensitivity of Pt-CdS and Pd-CdS towards H_2 at 300K is 78.61% and 98.17%, while their sensitivity towards CO_2 is 99.99%. Similarly, Zhou et al. studied the physicochemical properties of Rh-doped PdS_2 and Rh- PdS_2 and their sensing performance towards the thermal runaway gases in lithium-ion batteries.[59] He found that the adsorption of CO and C_2H_4 onto Rh-doped PdS_2 and Rh- PdS_2 was chemisorption, whereas the adsorption of H_2 , CO_2 , and CH_4 was physisorption. Further work function analysis suggested that both systems can be utilized as work function-based gas sensors with comparable performance. Yang et al. investigated the sensing performance of the BC_5 -based gas sensors for organic and inorganic gases using DFT.[60] Their DFT results indicated that the BC_5 is very sensitive to the adsorption of CO , NH , NO , NO_2 , C_2H_2 , C_2H_4 , and HCHO , thereby validating that the BC_5 monolayer can be used as a sensing material in gas sensors. Li et al. investigated the gas sensing capabilities of TM (Fe, Co, Pd) doped MoTeSe monolayer in detecting thermal runaway gases of lithium-ion batteries.[61] He reported that adding TM atom as a dopant enhances the electrical conductivity and adsorption capacity of MoTeSe , thereby confirming that the Pd- MoTeSe monolayer has the best sensing performance, followed by Co- MoTeSe and Fe- MoTeSe monolayers. However, it is to the best of the author's knowledge that there have been no previous reports regarding the study of the adsorption behaviour of the thermal runaway gases of lithium-ion batteries onto the Cu-doped hBN. This lack of prior

research findings motivated us to investigate the adsorption behaviour of the thermal runaway gases of lithium-ion batteries onto the pristine hBN and Cu-doped hBN. Therefore, in this study, we have used DFT as a tool to calculate the adsorption energy and distances of the thermal runaway gases onto the pristine hBN and Cu-doped hBN. In addition to analysing the effect of adsorption of thermal runaway gases on the electrical conductivity of the pristine hBN and Cu-doped hBN, we have calculated DOS and PDOS for these systems, respectively. For the quantitative analysis of the charge transfer during the interaction of thermal runaway gases with all these systems, we have calculated the charge density difference. Further, RDG analysis was performed to examine the existence of any type of non-covalent interaction between the adsorbate and adsorbent. Finally, the recovery time sensitivity and selectivity were also calculated to examine the performance of the Cu-doped hBN upon the adsorption of thermal runaway gases.

5.2 Results and Discussions

5.2.1 Adsorption of thermal runaway gases onto pristine hBN

To study the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules onto pristine hBN, we have considered B sites (on top of the B atom) and N sites (on top of the N atom) as the active sites for the adsorption of these gases molecules due to their electron deficient and electron rich behaviour which is also suggested by our ELF calculation. Therefore, we have considered different orientations of the thermal runaway gases at the B and N sites as the initial structure for optimization. It was upon geometry optimization we obtained sixteen different absorption configurations, abbreviated as A1, A2, A3, A4, B1, B2, C1, C2, C3, C4, D1, D2, D3, and E1, E2, E3 as shown in Figure 5.1(a)-5.1(p) respectively. For the A1, B1, D1 and E1 adsorption configurations, we observed that the C_2H_4 , CH_4 , CO_2 and H_2 gas molecules oriented themselves in a direction parallel to the Z axis at a distance of 4.285Å, 4.036Å, 3.330Å and 3.00Å from the B sites as shown in Figure 5.1(a), 5.1(e), 5.1(k) and 5.1(n) respectively whereas for the A2 and D2 adsorption configurations we observed that the C_2H_4 and CO_2 gas molecules got oriented themselves in a direction perpendicular to the Z axis at a distance of 4.055Å and 3.871Å, from the B sites as shown in Figure 5.1(b) and 5.1(l) respectively. In case of A3, B2 and E2 adsorption configurations, we observed that the C_2H_4 , CH_4 and H_2 gas molecules got oriented in a direction parallel to the Z axis at a distance of 4.275Å, 3.616Å and 2.998Å from the N sites as shown in Figure 5.1(c), 5.1(f) and 5.1(o) respectively. Similarly, in the case of C1, C2, and C3, C4 adsorption configurations, the CO gas molecules got adsorbed at a distance of 3.375Å, 3.534Å and 3.480Å, 3.656Å from the N sites in a direction parallel to the Z axis as

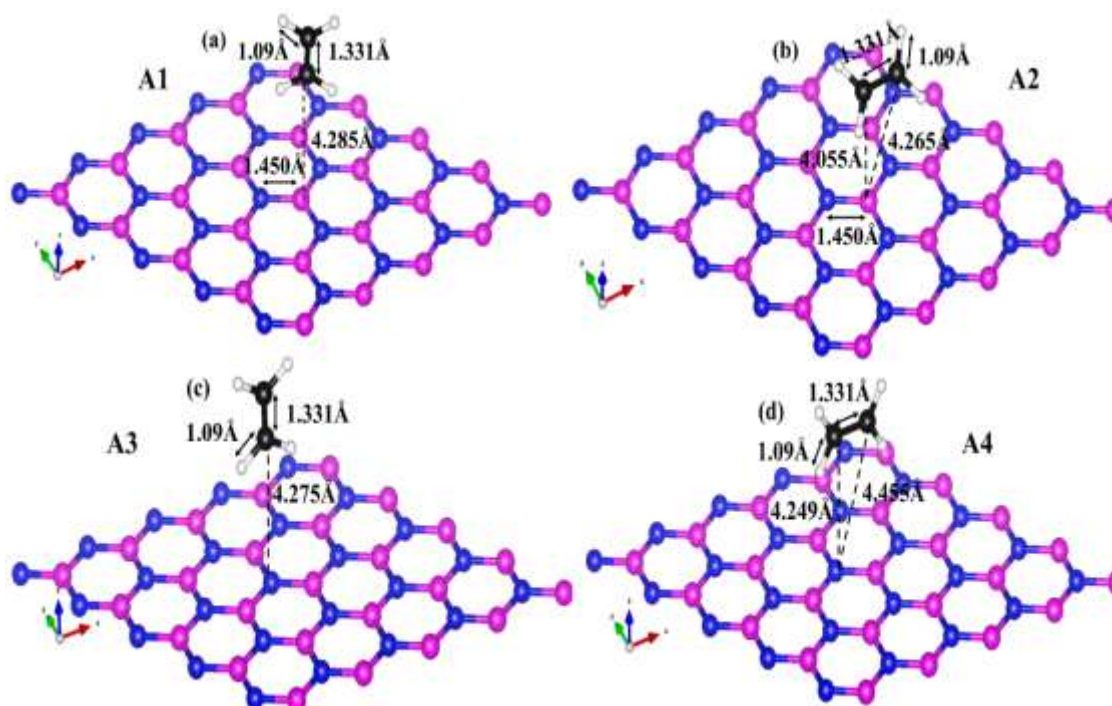
shown in Figure 5.1(g), 5.1(h) and 5.1(i), 5.1(j) respectively. We also observed that in the case of A4, D3 and E3 adsorption configurations, C₂H₄, CO₂ and H₂ gas molecules got adsorbed at a distance of 4.249Å, 3.600Å and 3.328Å from the N sites in a direction perpendicular to the Z axis as shown in Figure 5.1(d), 5.1(m) and 5.1(p), respectively. The reported B-N, C-H, C-C, C-O, and H-H bond lengths in Table 5.1 didn't vary too much from those of the bond lengths in the case of pristine hBN and isolated C₂H₄, CH₄, CO, CO₂, and H₂ gas molecules. These findings suggest that there exists weak interaction between thermal runaway gases and pristine hBN. Further to verify the above findings, we have calculated adsorption energy (E_{ads}) for all these adsorption configurations using equation (5.1) in order to determine the most stable adsorption configurations and the strength of the interaction between the gas molecule and hBN.

$$E_{ads} = E_{A/gas} - E_A - E_{gas} \quad (5.1)$$

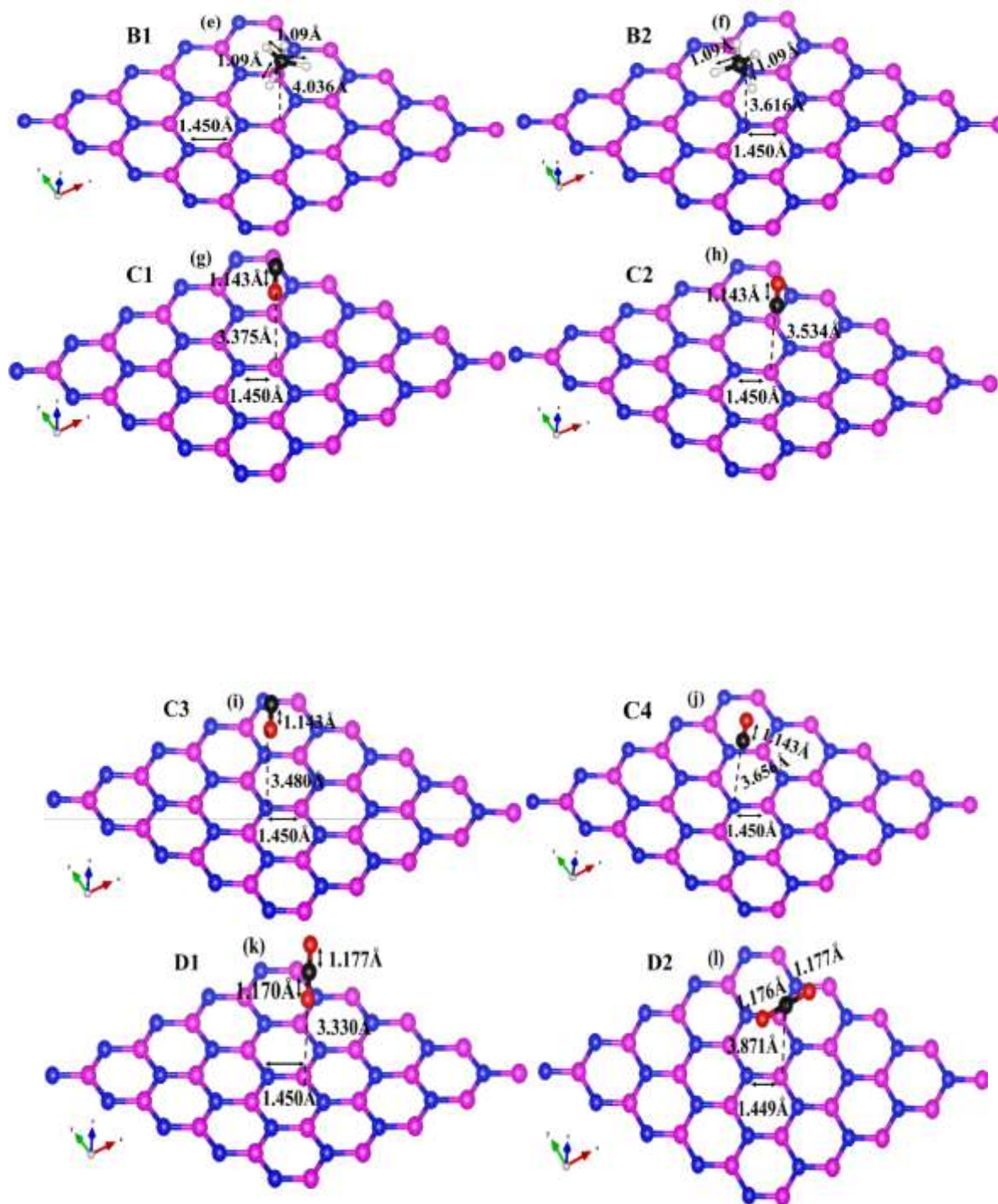
Where $E_{A/gas}$, E_A , and E_{gas} represent the total energy of the gas adsorbed onto the sensing material, energy of the pristine sensing material, and energy of the isolated gas molecules, respectively. The calculated adsorption energies for the A1, A2, A3, A4, B1, B2, C1, C2, C3, C4, D1, D2, D3 and E1, E2, E3 adsorption configurations were found to be -0.140eV, -0.191eV, -0.140eV, -0.184eV, -0.108eV, -0.134eV, -0.085eV, -0.089eV, -0.077eV, -0.077eV, -0.323eV, -0.357eV, -0.383eV and -0.054eV, -0.053eV and -0.049eV respectively. The above calculated too low value confirmed that the adsorption of thermal runaway gases onto pristine hBN was physisorption, and a weak interaction exists between C₂H₄, CH₄, CO, CO₂, and H₂ gases and hBN. It was based on the minimization of the adsorption energies, we found that A2, B2, C2, D3, and E2 were the most stable adsorption configurations among the different optimized C₂H₄, CH₄, CO, CO₂, and H₂ gas adsorbed onto hBN configurations. For the rest of the study, we have considered A2, B2, C3, D2, and E2 as the final adsorption configurations and referred to them as C₂H₄-hBN, CH₄-hBN, CO-hBN, CO₂-hBN, and H₂-hBN, respectively.

Table 5.1 The adsorption energy (E_{ads}), adsorption distances (D_{ads}), B-N and C-H bond lengths upon the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules adsorbed onto pristine hBN

System	$E_{ads}(eV)$	$D_{ads}(Å)$	B-N($Å$)	C-H($Å$)	C=C($Å$)	H-H($Å$)	C-O($Å$)
A1	-0.140	4.285	1.450	1.09	1.331	-	-
A2	-0.191	4.055-4.265	1.450	1.09	1.331	-	-
A3	-0.140	4.275	1.450	1.09	1.331	-	-
A4	-0.184	4.249-4.455	1.450	1.09	1.331	-	-
B1	-0.108	4.036	1.450	1.09	-	-	-
B2	-0.134	3.616	1.450	1.09	-	-	-
C1	-0.085	3.375	1.450	-	-	-	1.143
C2	-0.089	3.534	1.450	-	-	-	1.143
C3	-0.077	3.480	1.450	-	-	-	1.143
C4	-0.077	3.656	1.450	-	-	-	1.143
D1	-0.323	3.330	1.450	-	-	-	1.170-1.177
D2	-0.357	3.871	1.449	-	-	-	1.176-1.177
D3	-0.383	3.600	1.452	-	-	-	1.176-1.177
E1	-0.054	3.000	1.450	-	-	0.752	-
E2	-0.053	2.998	1.451	-	-	0.753	-
E3	-0.049	3.328-3.491	1.450	-	-	0.752	-



A deep insight into the adsorption



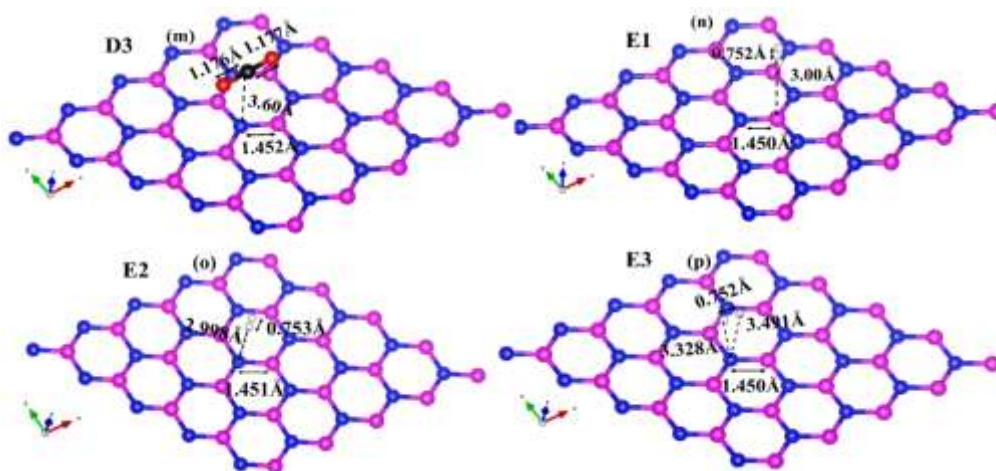
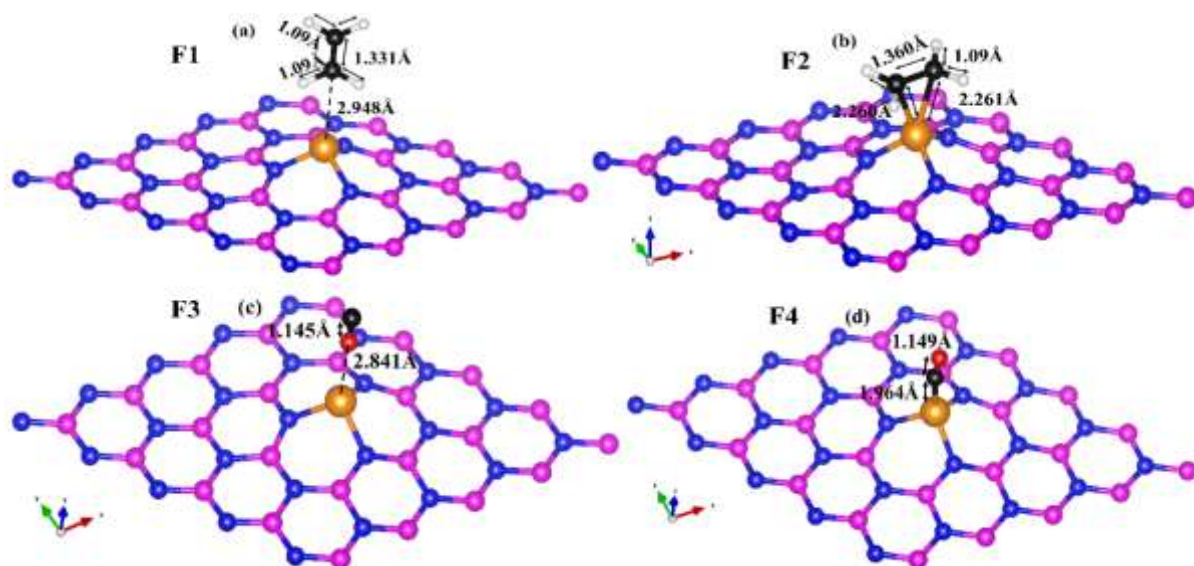


Figure 5.1 Optimized different adsorption configurations of (a)-(d) C_2H_4 , (e)-(f) CH_4 , (g)-(j) CO , (k)-(m) CO_2 , and (n)-(p) H_2 gas molecules onto the pristine hBN, respectively.

5.2.2 Adsorption of thermal runaway gases onto Cu-doped hBN

To investigate the adsorption of C_2H_4 , CO , CO_2 , CH_4 , and H_2 gas molecules onto Cu-doped hBN, we have considered the dopant sites as the most preferential adsorption sites because of the protrusion incoming gas molecules are more likely to interact with the dopant atom than atoms at the B and N sites. Therefore, we have considered different orientations of the thermal runaway gases at the dopant sites as the initial structure for optimization. It was upon optimization that we obtained two different optimized adsorption configurations each in the case of C_2H_4 , H_2 , CO , CO_2 gas molecule adsorbed onto Cu-doped hBN, abbreviated as F1, F2, F3, F4, F5, F6, F7, F8 and one different optimized adsorption configurations in case of CH_4 adsorbed onto Cu-doped hBN abbreviated as F9 as shown in Figure 5.2(a)-5.2(i) respectively. For the F1, F5, F7 and F9 adsorption configurations, we observed that the C_2H_4 , CO_2 , H_2 and CH_4 gas molecules oriented themselves in a direction parallel to the Z axis at a distance of 2.948 Å, 2.590 Å, 2.141 Å and 2.865 Å from the dopant sites as shown in Figure 5.2(a), 5.2(e), 5.2(g) and 5.2(i) respectively whereas for the F2, F6 and F8 adsorption configurations we observed that the C_2H_4 , CO_2 and H_2 gas molecules got oriented themselves in a direction perpendicular to the Z axis at a distance of 2.260 Å, 4.092 Å and 2.214 Å from the dopant sites as shown in Figure 5.2(b), 5.2(f) and 5.2(h) respectively. On the other side, in the case of F3 and F4 adsorption configurations, we observed that the CO gas molecules got adsorbed at a distance of 2.841 Å and 1.964 Å from the dopant sites in a direction parallel to the Z axis with C and O atoms facing towards the Cu atom, as shown in Figure 5.2(c) and 5.2(d), respectively. Furthermore, the reported C-H and C-C bond lengths in Table 5.2 in case of F1 and F2 adsorption configurations increases from 1.06 Å to 1.09 Å and from 1.20 Å to 1.331 Å and

Furthermore, the reported C-H and C-C bond lengths in Table 5.2 in cases of F1 and F2 adsorption configurations increases from 1.06Å to 1.09Å and from 1.20Å to 1.331Å and 1.360Å respectively whereas for the F7, F8 and F9 the H-H and C-H bond lengths increases from 0.751Å to 0.760Å, 0.767Å and from 1.09Å to 1.10Å respectively. For F3 and F4 adsorption configurations, we observed that the length of the triple-bonded C-O increases from 1.128 Å to 1.145 Å and 1.149 Å, respectively. On the other side, the length of the two double-bonded C-O increases from 1.160Å to 1.173Å and 1.179Å in the case of F5, whereas for the F6 systems, the C-O increases from 1.160Å to 1.177Å. The observed variation in the bond length upon the adsorption of the thermal runaway gases indicates weakening of the bond, resulting in activation of gas molecules towards bond formation with the doped Cu atom. These finding indicates the catalytic behaviour of the Cu atom. The calculated adsorption energies for the optimized F1, F2, F3, F4, F5, F6, F7, F8 and F9 adsorption configurations were found to be -1.429eV , -2.028eV, -1.341eV, -1.986eV, -1.625eV, -1.528eV, -1.386eV, -1.330eV, and -1.440eV, respectively. The above calculated high value of the adsorption energies suggested that the adsorption of C₂H₄, CH₄, CO, CO₂, and H₂ gas molecules onto Cu-doped hBN was chemisorption, verifying that a strong interaction exists between the adsorbed thermal runaway gases and Cu-doped hBN. It was based on the minimization of the adsorption energies; we found that F2, F4, F5, F7, and F9 were the most stable adsorption configurations. For the rest of the study, we have considered F2, F4, F5, F7, and F9 as the final adsorption configurations and referred to them as C₂H₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, H₂-Cu-doped hBN, and CH₄-Cu-doped hBN, respectively.



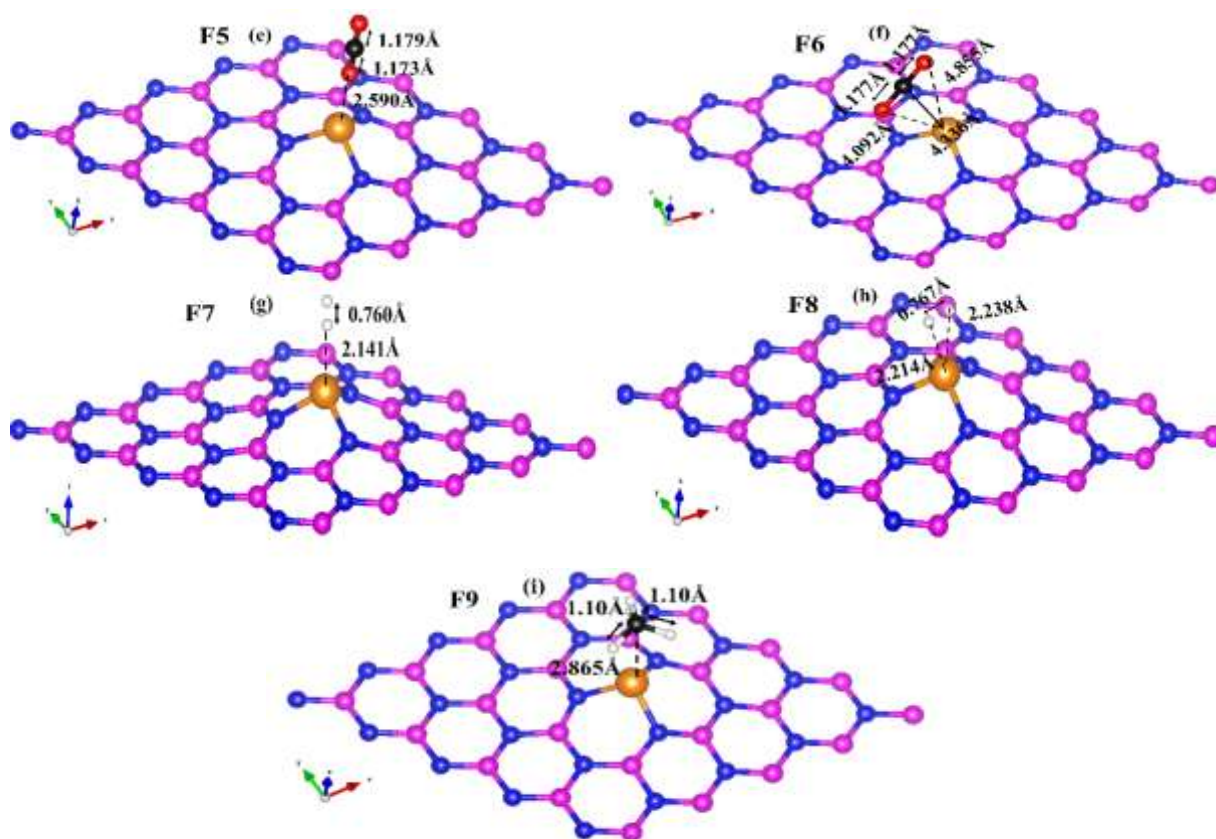


Figure 5.2: Optimized different (a)-(b) C₂H₄, (c)-(d) CO, (e)-(f) CO₂ (g)-(h) H₂ and (i) CH₄ adsorption configurations onto the Cu-doped hBN respectively.

Table 5.2: The adsorption energy (E_{ads}), adsorption distances (D_{ads}), C-C, C-O, C-H, and H-H bond lengths upon the adsorption of C₂H₄, CH₄, CO, CO₂, and H₂ gas molecules adsorbed onto Cu-doped hBN.

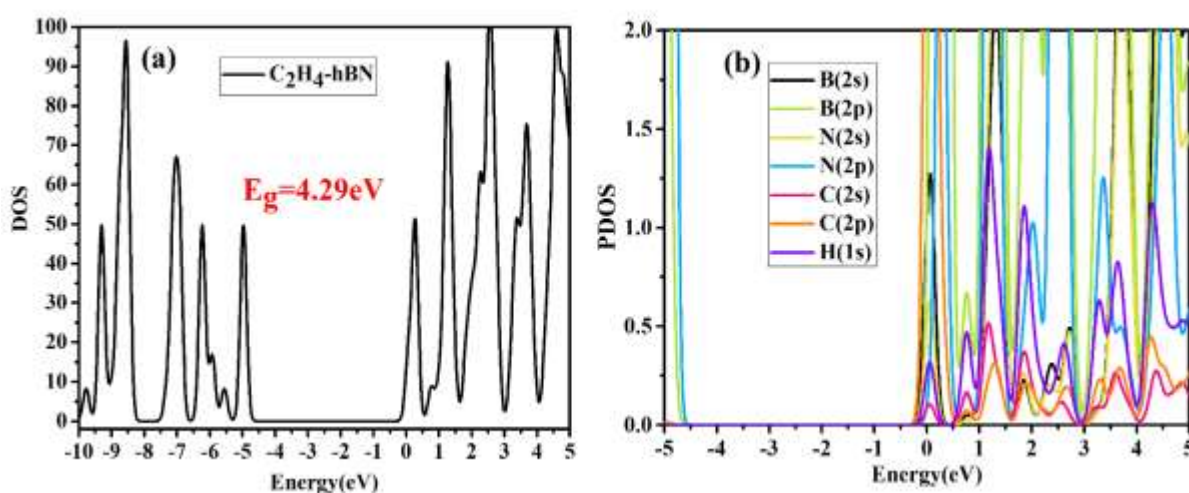
System	$E_{ads}(\text{eV})$	$D_{ads}(\text{\AA})$	C-H ($\text{\AA}$)	C-C ($\text{\AA}$)	C-O ($\text{\AA}$)	H-H ($\text{\AA}$)
F1	-1.429	2.948	1.09	1.331	-	-
F2	-2.028	2.260	1.09	1.360	-	-
F3	-1.341	2.841	-	-	1.145	-
F4	-1.986	1.964	-	-	1.149	-
F5	-1.625	2.590	-	-	1.173-1.179	-
F6	-1.528	4.092	-	-	1.177	-
F7	-1.386	2.141	-	-	-	0.760
F8	-1.330	2.214	-	-	-	0.767
F9	-1.440	2.865	1.10	-	-	-

5.2.3 Electronic properties analysis upon adsorption of thermal runaway gases onto pristine hBN and Cu-doped hBN

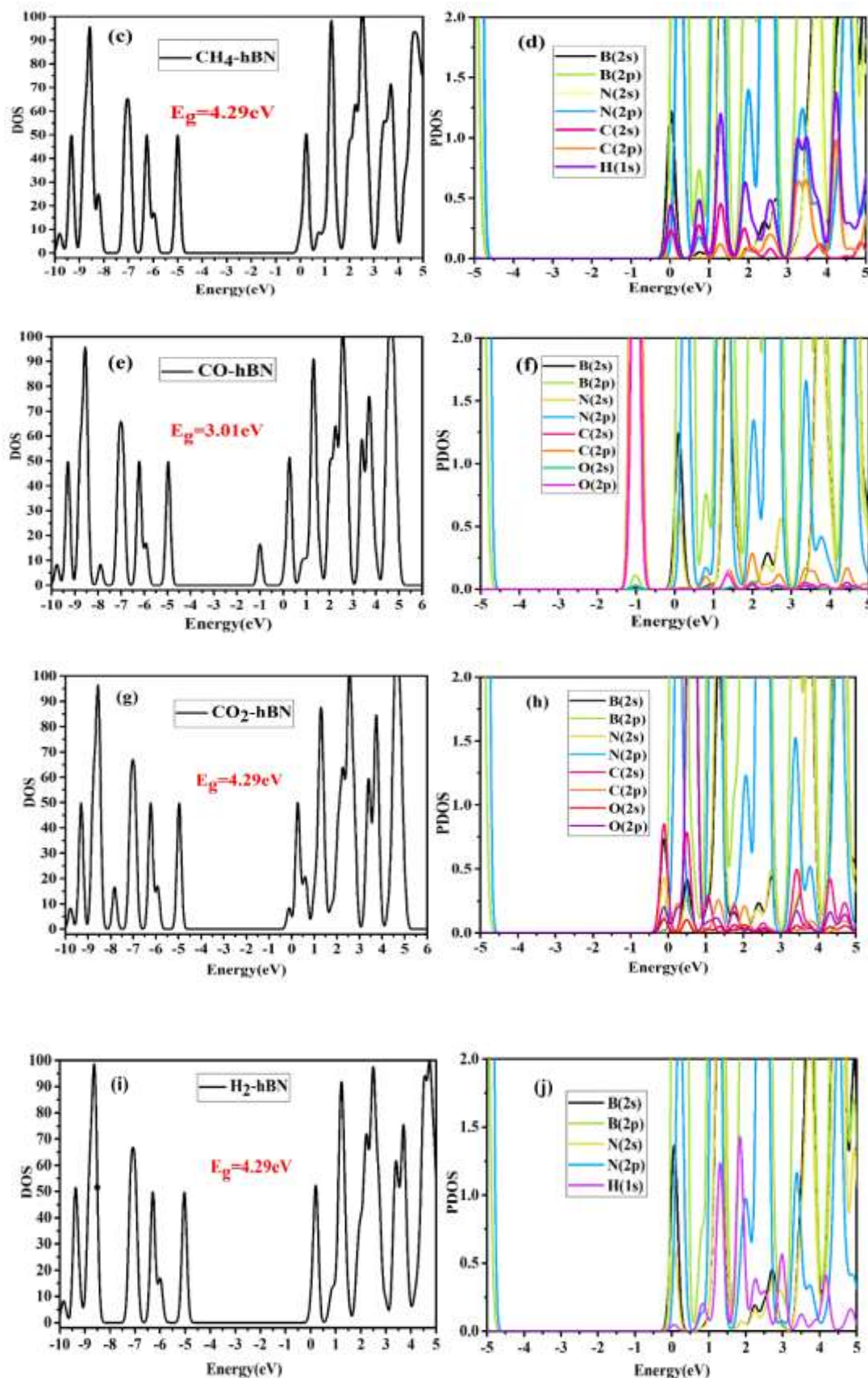
To analyze the electronic properties of the hBN and Cu-doped hBN system upon the adsorption of thermal runaway gases, we have calculated and plotted the DOS for C₂H₄-hBN, CH₄-hBN, CO₂-hBN, CO-hBN, H₂-hBN, C₂H₄-Cu-doped-hBN, CH₄-Cu-doped-hBN, CO₂-Cu-doped-hBN, CO-Cu-doped-hBN and H₂-Cu-doped-hBN adsorption configurations as shown in

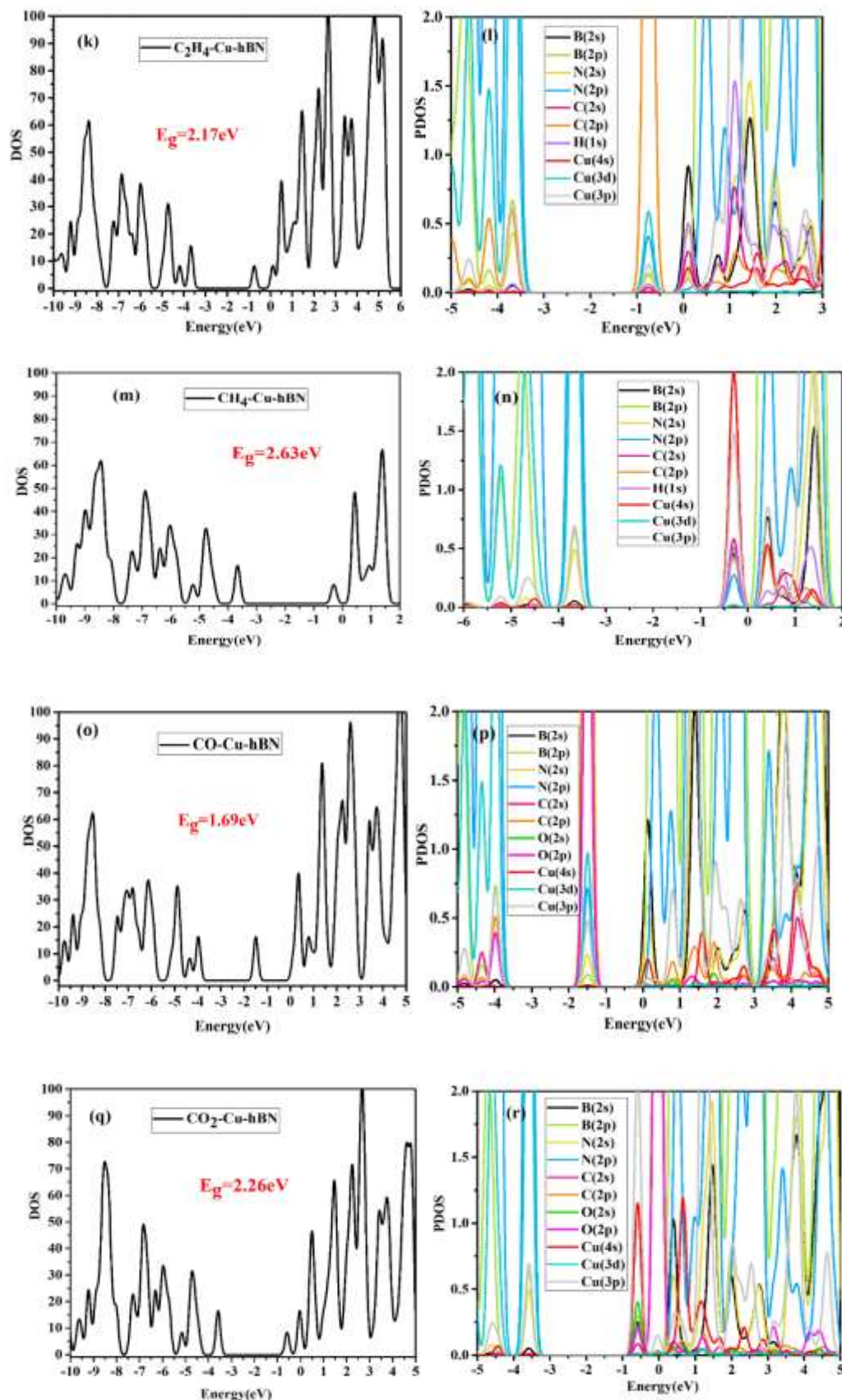
Figure 5. It was from Figure 5.3(a), Figure 5.3(c), Figure 5.3(g) and Figure 5.3(i), we observed that C_2H_4 , CH_4 , CO_2 , and H_2 gas molecules upon adsorption onto hBN do not introduce any impurity states within the band gap region as a consequence the band gap of the pristine hBN remained unchanged. These findings confirmed the existence of weak interaction between the C_2H_4 , CH_4 , CO_2 , H_2 gases and hBN, which might be due to weak charge transfer between them. In contrast, the adsorption of CO gas onto hBN introduces a new impurity state at -1 eV, causing the band gap to reduce from 4.29 eV to 3.01 eV as shown in Figure 5.3(e). However the adsorption of C_2H_4 and CO gas molecules onto Cu-doped-hBN creates impurity states at -1 eV and within the energy range from -2 to -1 eV causing the Fermi level to shift towards the CB thereby reducing the band gap from 3.10 eV to 2.17 eV and 1.69 eV as shown in Figure 5.3(k) and Figure 5.3(o) respectively whereas the adsorption of CH_4 , CO_2 and H_2 gas molecule onto Cu-doped hBN creates impurity states within the energy range from -1 to 0 eV also causes the Fermi level to shift towards the CB thereby reducing the band gap from 3.10 eV to 2.63 eV, 2.26 eV and 3.05 eV as shown in Figure 5.3(m), Figure 5.3(q), and Figure 5.3(s) respectively. It was based on the comparison we found that Cu-doped hBN exhibits better variation in the electronic properties than pristine hBN upon the adsorption of thermal runaway gases. This might be due to the strong charge transfer between the thermal runaway gases and Cu-doped hBN. To further analyse the contribution from the atomic orbitals of the thermal runaway gases, pristine hBN and Cu-doped hBN, we have calculated the PDOS for the above-mentioned adsorption configurations. From Figure 5.3 (b) and Figure 5.3 (d), we observed that in case of C_2H_4 -hBN and CH_4 -hBN systems, 2s, 2p atomic orbitals of C and 1s atomic orbitals of H atoms contribute weakly to the DOS within the energy range from 1 to 5 eV. Similarly, in the case of CO_2 -hBN and H_2 -hBN systems, we observed that the 2s, 2p atomic orbitals of C, O and 1s atomic orbitals of H atoms also contributed weakly within the energy range from 1 to 5 eV, as shown in Figure 5.3 (g) and Figure 5.3 (i), respectively. On the other side, for the CO-hBN systems, we observed from Figure 5.3 (f) that the impurity state at -1 eV existed due to the weak hybridization between the 2s, 2p, and 2p atomic orbitals of C and B atoms. The existence of

weak hybridization between the atomic orbitals confirmed weak bond formation between the thermal runaway gases and hBN. However, for the C_2H_4 -Cu-doped-hBN systems, we observed from Figure 5.3(l) that the impurity state at -1eV was due to the significant contribution from the 2p and 3d atomic orbitals of C and Cu atoms indicating sharing of electrons between these atomic orbitals to form covalent bonding between the C_2H_4 gas and Cu-doped hBN. For the CH_4 -Cu-doped-hBN systems we observed from Figure 5.3(n) that impurity state within the range was due to the contribution from the 4s and 2s atomic orbitals of Cu and C atoms indicating that electrons are shared between these atomic orbitals to form covalent bond between CH_4 gas and Cu-doped hBN whereas for the CO_2 -Cu-doped-hBN system we observed from Figure 5.3(r) that the 3p, 4s and 2s atomic orbitals of Cu and O atoms are involved in the sharing of the electrons and contribute towards the creation of impurity states within the energy range from -1 to 0 eV. For the CO-Cu-doped-hBN system, we observed from Figure 5.3(p) that the 2s, 2p and 3d atomic orbitals of C and Cu atoms contribute towards the creation of impurity states within the energy range from -2 to -1eV. It was on comparison we found that the Cu-doped hBN system exhibits better variation in the electronic properties compared to pristine hBN upon the adsorption of thermal runaway gases, clearly indicating that Cu-doped hBN can be utilized as a chemoresistive gas sensor. C_2H_4 -hBN and CH_4 -hBN systems, 2s, 2p atomic orbitals of C and 1s atomic orbitals of H atoms contribute weakly to the DOS within the energy range from 1 to 5eV. Similarly, in the case of CO_2 -hBN and H_2 -hBN systems, we observed that the 2s, 2p atomic orbitals of C, O and 1s atomic orbitals of H atoms also contributed weakly within the energy range from 1 to 5eV, as shown in Figure 5.3(g) and Figure 5.3(i), respectively



A deep insight into the adsorption





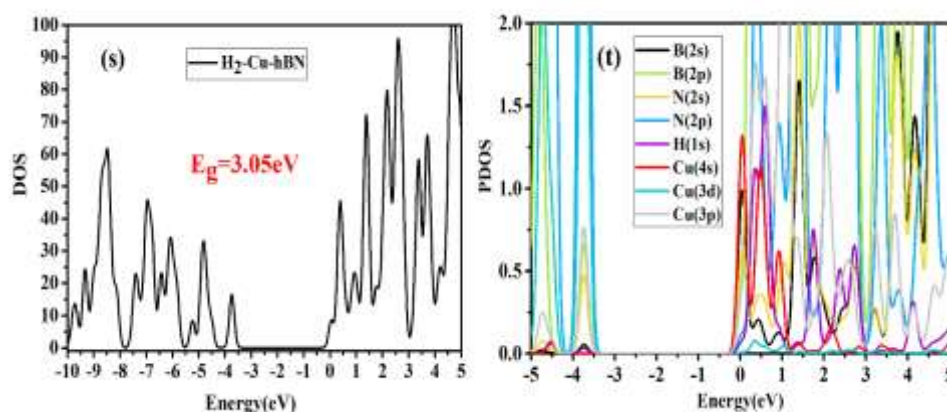


Figure 5.3 DOS and PDOS for the (a)-(b) C₂H₄-hBN, (c)-(d) CH₄-hBN, (e)-(f) CO-hBN, (g)-(h) CO₂-hBN, (i)-(j) H₂-hBN, (k)-(l) C₂H₄-Cu-doped hBN, (m)-(n) CH₄-Cu-doped hBN, (o)-(p) CO-Cu-doped hBN, (q)-(r) CO₂-Cu-doped hBN, (s)-(t) H₂-Cu-doped hBN systems respectively.

5.2.4. Charge density difference analysis

To understand the charge transfer mechanism between the thermal runaway gas and the sensing materials, we have calculated the charge density difference using equation (5.2) and plotted it in Figure (5.4).

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B \quad (5.2)$$

where ρ_{AB} , ρ_A , and ρ_B represent the charge densities onto the sensing material upon gas adsorption, charge densities onto the sensing material without gas molecules, and the charge densities of the isolated gas molecules, respectively. The yellow and cyan coloured regions in the charge density difference diagrams represent the electron accumulation and electron depletion regions, respectively. From Figure 5.4(a) and 5.4(b), we observed that the electron density around the C and H atoms increases and decreases upon the adsorption of C₂H₄ and CH₄ gases onto hBN, identified by the yellow and cyan coloured regions around the C and H atoms of the C₂H₄ and CH₄ gas molecules whereas upon the adsorption of CO₂ onto hBN, the C atom loses electrons to the nearby highly electronegative O atom, identified by the yellow and cyan coloured regions around the O and C atoms of the CO₂ gas as shown in Figure 5.4(c). We also observed that in case of C₂H₄-hBN, CH₄-hBN and CO₂-hBN systems electron gets uniformly accumulated and depleted within the layer. All these findings indicate that the atoms of the layer and gas molecule are primarily involved in the charge transfer among themselves. On the other side upon H₂ adsorption, we observed that the H atom loses electron

to the N atom the H atom, whereas upon CO adsorption, the C atoms gained electrons from the B atoms, identified by the yellow-coloured region, identified by the cyan colour around H atom whereas upon CO adsorption, the C atoms gained electrons from the B atoms identified by the yellow-coloured region as shown in Figure 5.4(c) and Figure 5.4(e) respectively. However, upon substitutional doping of the Cu atom, we found that the Cu atom loses electrons to the nearby electronegative N atom identified by the cyan and yellow coloured region around the Cu and N atoms as shown in Figure 5.4(f). These findings confirmed the nature of the Cu atom and hBN as electrons donor and acceptor respectively. Further upon the adsorption of C_2H_4 and CH_4 gas molecule onto Cu-doped hBN, we observed that the electron rich C atom loses electron to the electron deficient Cu atom identified by large cyan coloured region between them as shown in Figure 5.4(g) and Figure 5.4(h) respectively thereby confirming the nature of the Cu-doped hBN and C_2H_4 , CH_4 as electron acceptor and donor. For the CO-Cu-doped hBN systems, we observed from Figure 5.4(i) that high electron density exists around the O atoms identified by the yellow colour around it, but the lone pair on the C atom readily available for covalent bonding with the Cu atom makes the C site partially electron rich and highly reactive toward the electron-deficient Cu atom. As a consequence, the C atom loses electrons to the Cu atom, identified by the yellow-coloured region in the interacting region between Cu and CO_2 gas. For the CO_2 -Cu-doped hBN system, we observed from Figure 5.4(j) that upon CO_2 adsorption, that electrostatic interaction causes the electron rich O atom loses electron to the electron deficient Cu atom. For the H_2 -Cu-doped hBN systems, we found that the Cu atom being more electronegative than H atom withdraws electrons from it, identified by the large yellow colour between the Cu and H atoms, as shown in Figure 5.4(k). It was based on the comparison of the charge accumulation/depletion area in the interaction regime we found that large electron accumulation/depletion area exists in the interacting region for the Cu-doped hBN than pristine hBN upon the adsorption of thermal runaway gases. These findings indicates that significant charge transfer takes place between the doped Cu atom and thermal runaway gases which is the reason behind larger variation in the band gap of Cu-doped hBN than pristine hBN upon the adsorption of thermal runaway gases. Hence, our charge density difference analysis confirmed that substitutional doping of Cu atom is an cost-effective method to improves the charge transfer between the thermal runaway gases and the hBN layer.

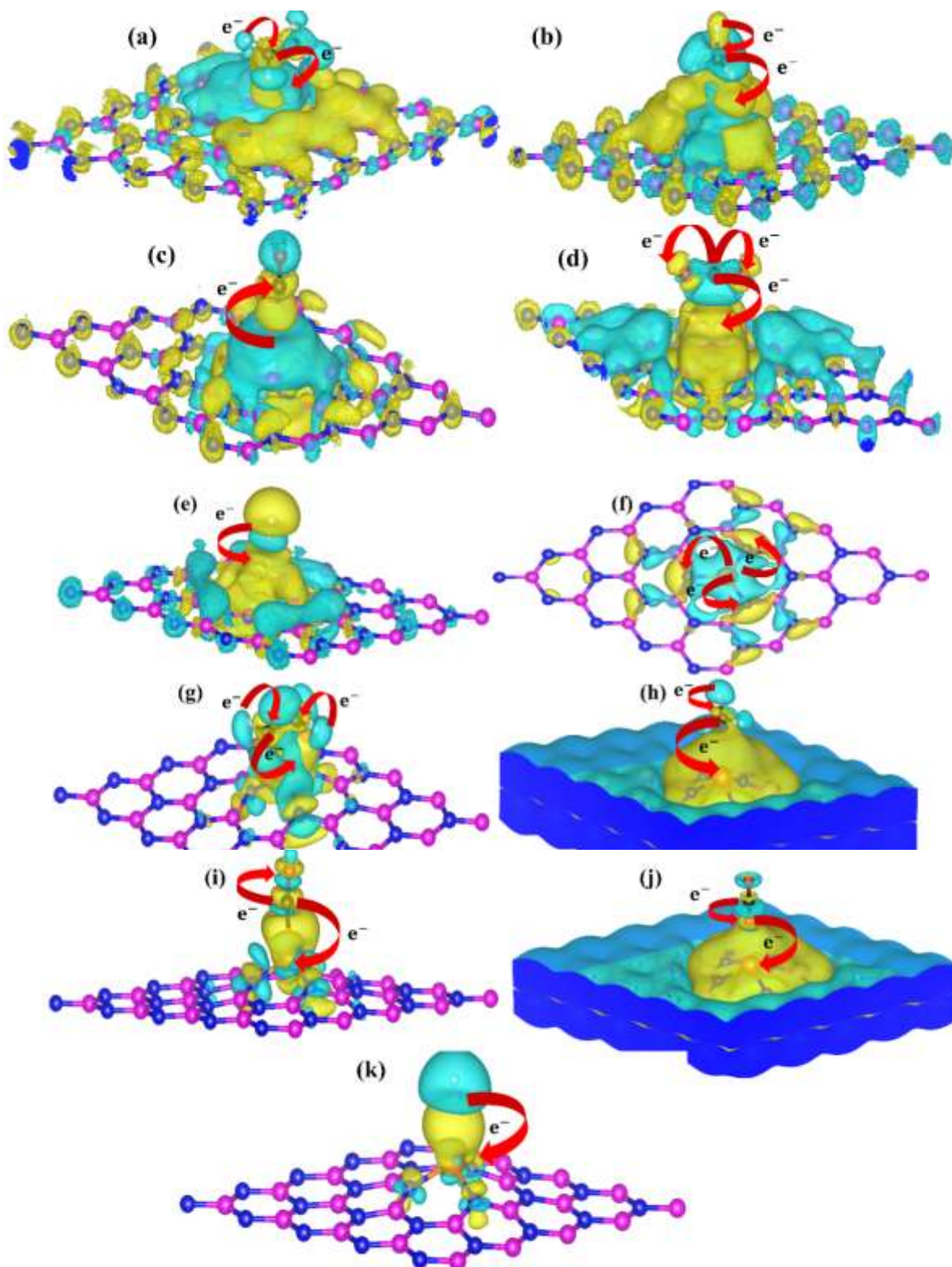


Figure 5.4 Charge density difference of (a) C₂H₄-hBN, (b) CH₄-hBN, (c) CO-hBN, (d) CO₂-hBN, (e) H₂-hBN, (f) Cu-doped hBN, (g) C₂H₄-Cu-doped hBN, (h) CH₄-Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO₂-Cu-doped hBN, (k) H₂-Cu-doped hBN respectively.

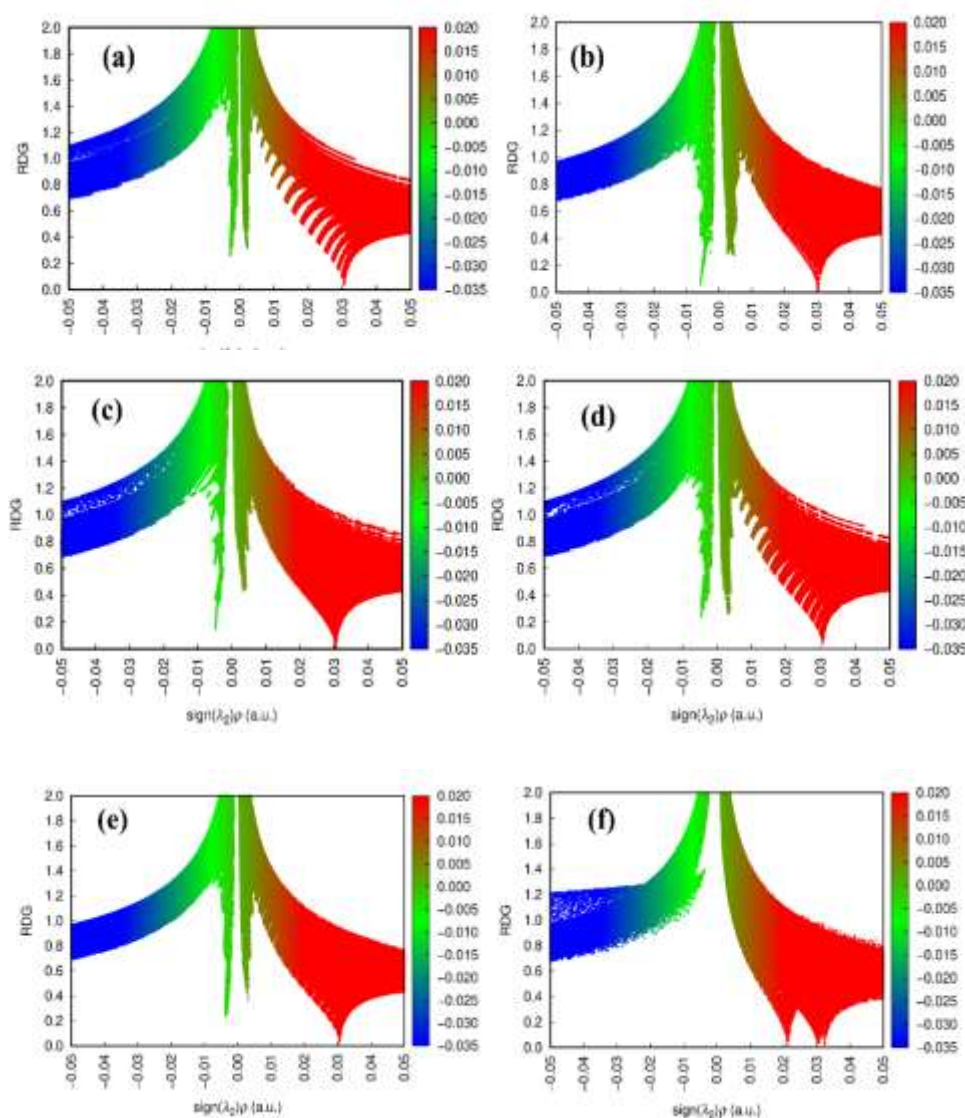
5.2.5 Non-covalent interaction analysis

Noncovalent interactions (NCIs) such as hydrogen bonding, van der Waals(vdW), and steric effects played a significant role in the adsorption of the gas molecule onto the sensing materials, thereby influencing the adsorption capabilities and recovery time of the sensing materials. Therefore, to understand the nature of the non-covalent interaction between the pristine hBN, Cu-doped hBN, and gas molecule, we have calculated the reduced density gradient (RDG) function using equation (5.3) and plotted it against $\text{sign}(\lambda_2) \rho(r)$ as shown in Figure 5.5.

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho|}{[\rho(r)]^{4/3}} \quad (5.3)$$

Here $\rho(r)$, $\nabla \rho(r)$, and λ_2 represent the electron density, gradient electron density, and second eigenvalues of the Hessian matrix, respectively. The quantity $\text{sign}(\lambda_2) \rho(r)$ is of great importance as it describes the fluctuation in the electron density near the critical points, which can be used to determine the nature of the non-covalent interactions. If $\text{sign}(\lambda_2) \rho(r) < 0$, $\text{sign}(\lambda_2) \rho(r) \approx 0$, and $\text{sign}(\lambda_2) \rho(r) > 0$, it indicates strong attractive, weak, and strong repulsive interactions. The RDG scatter plots showed a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) \approx 0$, for the C_2H_4 -hBN, CH_4 -hBN, CO -hBN, CO_2 -hBN, and H_2 -hBN adsorption configurations as shown in Figure 5.5(a)-5.5(e), respectively. These results indicate that weak vdW interaction exists upon the adsorption of thermal runaway gases onto pristine hBN, which can be verified from the corresponding RDG isosurface plot displaying green patches between the adsorbed gas molecules and pristine hBN as shown in Figure 5.6(a)-5.6(e). However, upon substitutional doping of the Cu atom, we observed that there is a decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$, as shown in Figure 5.5(f). The corresponding RDG isosurface plot in Figure 5.6(f) displays a strong attractive electrostatic interaction between the doped Cu atom and the nearby neighbouring N atom, identified by blue patches between them. Further, upon C_2H_4 adsorption onto Cu-doped hBN, we observed that the RDG value in the RDG scatter plot undergoes variation around $\text{sign}(\lambda_2) \rho(r) < 0$ as shown in Figure 5.5(g). The corresponding RDG isosurface plot revealed strong attractive electrostatics with steric effects between the Cu- C_2H_4 , identified by a blue-red patch between them as shown in Figure 5.6(g). The observed steric effect arose due to the repulsion between the nearby C-C atoms of the C_2H_4 gas molecule. For the CO-Cu-doped-hBN and H_2 -Cu-doped-hBN systems, we observed that the RDG value undergoes deviation around $\text{sign}(\lambda_2) \rho(r) < 0$, as shown in Figure 5.5(i) and Figure 5.5(k), whereas the corresponding RDG isosurface plot revealed that CO and H_2 gas interact

electrostatically with the Cu atom. On the other side, in the case of CH₄ and CO₂ adsorption onto Cu-doped hBN, we found from the RDG scatter plot that there was a relatively large deviation in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$ compared to $\text{sign}(\lambda_2) \rho(r) \approx 0$, as shown in Fig.5.5(h) and Fig.5.5(j), respectively. These results indicate that electrostatic interaction dominates vdW interaction, which can be verified from the corresponding RDG isosurface plot as shown in Fig.5.6(h) and Fig.5.6(j) respectively. In addition, we observed that within the hexagonal ring, there exists a repulsive steric effect between the nearby B-B or N-N atoms identified by the red patches. Hence, based on our RDG analysis, we found that the electrostatic interaction contributes to the adsorption energy in the case of Cu-doped hBN, whereas the vdW interaction contributes to the adsorption energy in the case of hBN upon the adsorption of thermal runaway gases.



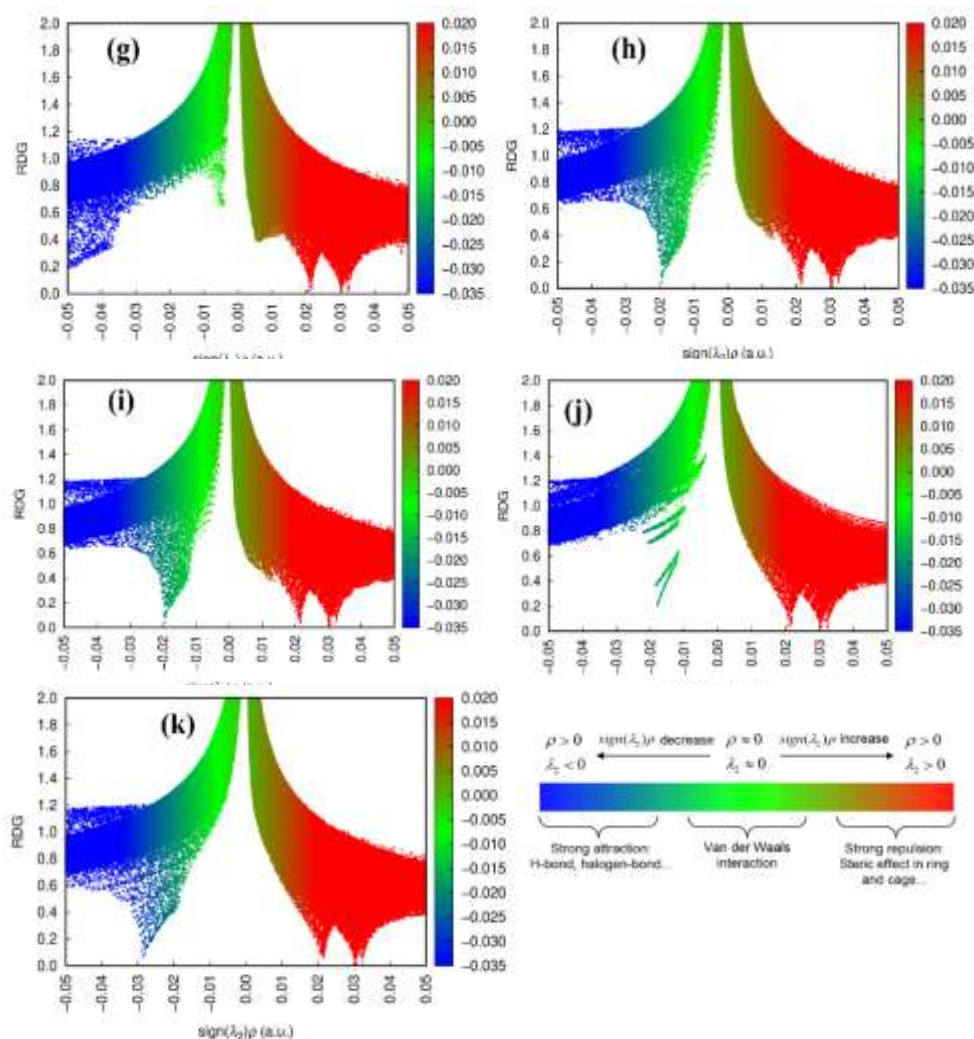


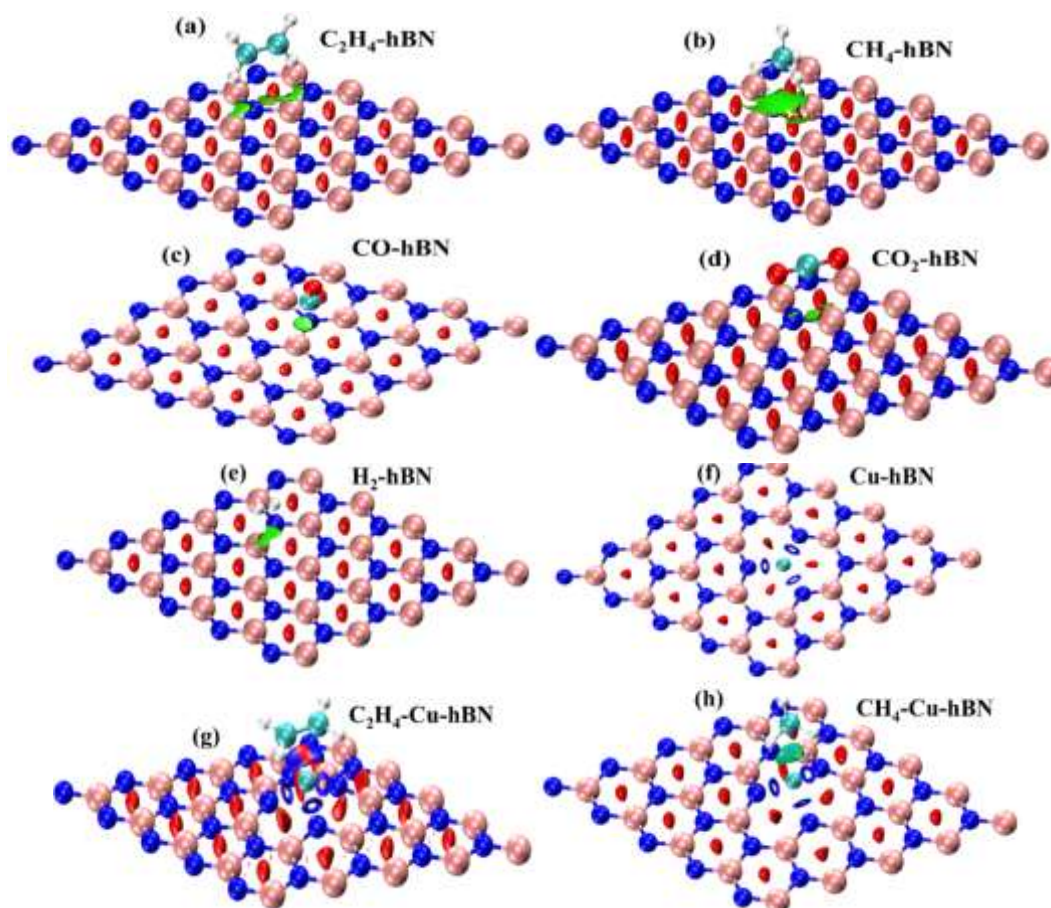
Figure 5.5: Reduced density gradient plot for (a) C₂H₄-hBN, (b) CH₄-hBN, (c) CO-hBN, (d) CO₂-hBN, (e) H₂-hBN, (f) Cu-doped hBN, (g) C₂H₄-Cu-doped hBN, (h) CH₄-Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO₂-Cu-doped hBN, (k) H₂-Cu-doped hBN, respectively

5.2.6 Global reactivity descriptors

To analyze the effect of the adsorption of thermal runaway gases onto the stability and chemical reactivity of the pristine hBN and Cu-doped hBN, we have calculated various type of global reactivity descriptors such as Ionization potential (IP), HOMO-LUMO gaps (E_g), electron affinity (EA), electrophilicity (ω), chemical softness (S), and hardness (η) reported in Table 5.3. Here, the ionizations potential and electron affinity represent the electron donating and accepting capability of the sensing material process, which is just the negative value of the HOMO and LUMO energies. The reported value in Table 5.3 suggested that hBN is a

chemically inert in nature due to its highest ionization potential (4.52 eV) and lowest electron affinity (0.22 eV), whereas the ionization potential and electron affinity of the pristine hBN remained unaltered upon the adsorption of C₂H₄, CH₄, CO₂, and H₂ gas molecules whereas the adsorption of CO gas molecules onto pristine hBN, causes the ionization potential and electron affinity to decrease and increase from 4.51 eV to 4.40 eV, and from 0.22 eV to 1.40 eV. These findings indicate that the C₂H₄-hBN, CH₄-hBN, CO₂-hBN, and H₂-hBN systems exhibit poor electron-donating and accepting capacity compared to CO-hBN, which is the reason behind the observed poor charge transfer between the C₂H₄, CH₄, CO₂, H₂ and hBN during the adsorption process. However, upon substitutional doping of Cu atoms, the ionization potential decreases from 4.51 eV to 3.60 eV, and the electron affinity increases from 0.22 eV to 0.50 eV. Further, upon the adsorption of C₂H₄, CH₄, CO, and CO₂ gases onto Cu-doped hBN the ionization potential decreases from 3.60 eV to 3.28 eV, 3.29 eV, 3.56 eV, 3.21 eV and the electron affinity increases from 0.50 eV to 1.11 eV, 0.66 eV, 1.87 eV, 0.95 eV whereas upon the adsorption of H₂ onto Cu-doped hBN the ionization potential and electron affinity both decrease from 3.60 eV and 0.50 eV to 3.36 eV and 0.31 eV respectively. It is based on the variation in the ionization potential and electron affinity we found that the band gap of the hBN underwent 0% and 30.06% variation upon the adsorption of C₂H₄, CH₄, CO₂, H₂ and CO gases. On the other side, the band gap of the Cu-doped-hBN underwent 30%, 15.16%, 45.48%, 27.09%, and 1.61% variation upon the adsorption of C₂H₄, CH₄, CO, CO₂, and H₂ gas. Since the variation in the band gap is directly related to the increment in the conductivity of the sensing materials. It was based on the comparison we found that Cu-doped hBN systems underwent large variation in the band gap upon the adsorption of thermal runaway gases, thereby validating that the Cu-doped hBN exhibits better variation in the conductivity than hBN making it a potential candidate to be utilized as chemoresistive sensors. The electrophilicity index is calculated to examine the chemical reactivity of the sensing surface. From Table 5.3, we found that there is no change in the electrophilicity index of pristine hBN upon the adsorption of C₂H₄, CH₄, CO₂, and H₂, except upon the adsorption of CO the electrophilicity index increases from 1.31 eV to 2.80 eV whereas, the electrophilicity index of pristine hBN increases from 1.31 eV to 1.36 eV upon substitutional doping of the Cu atom. However, upon the adsorption of C₂H₄, CH₄, CO, and CO₂, the electrophilicity index of Cu-doped hBN increases by 63.23%, 8.82%, 220.58%, and 40.44%, respectively, except for H₂-Cu-doped hBN, the electrophilicity factor decreases by 19.11%. These findings suggested that Cu-doped hBN would exhibit better

sensitivity and adsorption capability towards C_2H_4 , CH_4 , CO , and CO_2 due to its better chemical reactivity than pristine hBN. In addition, to determine the chemical stability of the sensing material, we have calculated the chemical hardness and softness factor because it describes the resistance and willingness of the material to undergo any change in its electronic properties. We found from the reported data in Table 5.3 that the chemical hardness factor for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN and H_2 -Cu-doped hBN systems were found to be 49.53%, 38.83%, 43.66%, 47.44% and 29.06%, relatively lower compared to the C_2H_4 -hBN, CH_4 -hBN, CO -hBN, CO_2 -hBN, and H_2 -hBN systems. On the other side, the chemical softness factor for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems was found to be 50%, 39.47%, 47.27%, 44.06%, and 3.03% relatively higher than the chemical softness factor for C_2H_4 -hBN, CH_4 -hBN, CO -hBN, CO_2 -hBN, and H_2 -hBN systems. The above calculated variation in the chemical hardness and softness factor validates that Cu-doped hBN are more likely to show significant variation in the electronic properties than pristine hBN which is consistent with our band gap calculation. Hence, the above-discussed global indices of reactivity descriptors suggested that Cu-doped hBN can be utilized as an efficient gas sensor to detect thermal runaway gases.



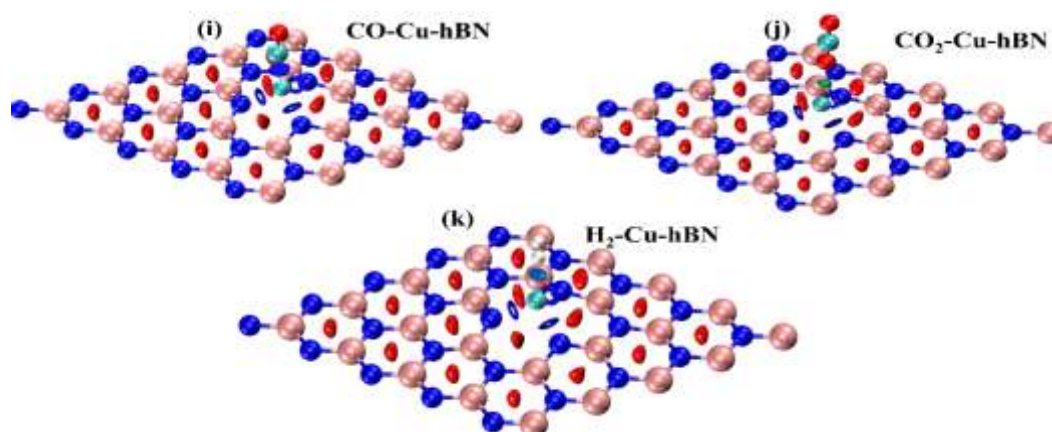


Figure 5.6: Reduced density gradient isosurface plot corresponding to (a) C₂H₄-hBN, (b) CH₄-hBN, (c) CO-hBN, (d) CO₂-hBN, (e) H₂-hBN, (f) Cu-doped hBN, (g) C₂H₄-Cu-doped hBN, (h) CH₄-Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO₂-Cu-doped hBN, (k) H₂-Cu-doped hBN, respectively. The blue, red, and green colour schemes shown in the RDG isosurface correspond to attractive strong hydrogen bonding, repulsive steric effect, and weak vdW interaction.

Table 5.3 Calculated HUMO-LUMO energies, HOMO-LUMO gaps (E_g), Ionization potential (IP), electron affinity (EA), electrophilicity (ω), chemical softness(S), and chemical hardness(η), respectively, for the pristine hBN, C₂H₄-hBN, CH₄-hBN, CO-hBN, CO₂-hBN, and H₂-hBN, Cu-doped hBN, C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems. All the reported values are in eV.

Adsorption Configurations	HOMO	LUMO	E_g	IP	EA	S	η	ω
Pristine hBN	-4.51	-0.22	4.29	4.51	0.22	0.23	2.15	1.31
C ₂ H ₄ -hBN	-4.51	-0.22	4.29	4.51	0.22	0.23	2.15	1.31
CH ₄ -hBN	-4.51	-0.22	4.29	4.51	0.22	0.23	2.15	1.31
CO ₂ -hBN	-4.51	-0.22	4.29	4.51	0.22	0.23	2.15	1.31
CO-hBN	-4.40	-1.40	3.00	4.40	1.40	0.33	1.50	2.80
H ₂ -hBN	-4.51	-0.22	4.29	4.51	0.22	0.23	2.15	1.31
Cu-doped hBN	-3.60	-0.50	3.10	3.60	0.50	0.32	1.55	1.36
C ₂ H ₄ -Cu-doped hBN	-3.28	-1.11	2.17	3.28	1.11	0.46	1.085	2.22
CH ₄ -Cu-doped hBN	-3.29	-0.66	2.63	3.29	0.66	0.38	1.315	1.48
CO-Cu-doped hBN	-3.56	-1.87	1.69	3.56	1.87	0.59	0.845	4.36
CO ₂ -Cu-doped hBN	-3.21	-0.95	2.26	3.21	0.95	0.44	1.13	1.91
H ₂ -Cu-doped hBN	-3.36	-0.31	3.05	3.36	0.31	0.33	1.525	1.10

5.2.7 Sensitivity and Selectivity Analysis of hBN and Cu-doped hBN

Table 5.4: Variation in the sensitivity of the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN at 300K, 500K, 700K, and 900K temperatures, respectively.

Temperature	C ₂ H ₄ -Cu-doped hBN	CH ₄ -Cu-doped hBN	CO-Cu-doped hBN	CO ₂ -Cu-doped hBN	H ₂ -Cu-doped hBN
300K	99.99%	99.98%	100%	99.99%	61.96%
500K	99.99%	99.57%	99.99%	99.99%	44.01%
700K	99.95%	97.96%	99.99%	99.90%	33.92%
900K	99.75%	95.16%	99.98%	99.55%	27.54%

Sensitivity is considered a crucial parameter in evaluating the gas sensing performance of semiconducting materials, as it describes how rapidly the sensing materials respond to changes in the concentration of gas molecules. For the semiconducting materials, sensitivity was determined by the electrical conductivity (σ), which undergoes variation upon gas adsorption. According to equation (5.4), the electrical conductivity of the semiconducting materials was found to be exponentially dependent on the band gap.

$$\sigma = AT^{3/2} e^{\left(\frac{-E_g}{2K_B T}\right)} \quad (5.4)$$

where σ is electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and K_B is the Boltzmann constant in eV/K. This indicates that large variations in the band gap led to an enhancement in the electrical conductivity, thereby affecting the sensitivity of the sensing materials. Therefore, we have performed DOS calculations to analyze the variation in the band gap upon adsorption of thermal runaway gases onto pristine hBN and Cu-doped hBN. From our DOS calculation, we found that the adsorption of C₂H₄, CH₄, H₂, and CO₂ gas molecules onto pristine hBN produces 0% variations in the band gap, whereas the adsorption of the CO gas molecule onto pristine hBN produces only 30.06% variations in the band gap with respect to pristine hBN. On the other side, Cu-doped hBN underwent 30%, 15.16%, 27.09%, 44.19%, and 1.61% variation in the band gap upon C₂H₄, CH₄, CO₂, CO, and H₂ adsorption, respectively. It was based on the comparison of the variation in the band gap; we found that Cu-doped hBN exhibits better sensitivity than pristine hBN upon the adsorption of these thermal runaway gases. Further, to determine the capability of the sensing material to distinguish between the specified target gas from other gases in the environment. We have calculated the sensing response(S) at 300K, 500K, 700K, and 900K using equation (5.5) and reported it in Table 5.4 for the Cu-doped hBN upon adsorption of thermal runaway gases.

$$S = \left| \frac{\sigma_{gas}^{-1} - \sigma_{pure}^{-1}}{\sigma_{pure}^{-1}} \right| \times 100 = e^{\left(\frac{-\Delta E_g}{2K_B T} \right)} - 1 \quad (5.5)$$

where σ_{gas}^{-1} and σ_{pure}^{-1} represents the electrical conductivity of the Cu-doped hBN with and without gas molecules, respectively. The reported sensing response at 300K for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN configurations was found to be 99.99%, 99.98%, 100%, 99.99% and 61.96% respectively. Moreover, as the temperature increases from 300K to 900K, the sensing response of the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN configurations decreases by 0.25%, 4.82%, 2%, 0.44% and 55.55% respectively. It was on comparison that we found that CO-Cu-doped hBN systems exhibit the highest sensing response, and H₂-Cu-hBN systems exhibit the lowest sensing response. The high and low sensing response of Cu-doped hBN towards CO and H₂ gas molecules can be attributed to the 44.19% and 1.61% variation in the band gap, as suggested by our DOS calculation. Since there exists a significant difference in the sensing response of Cu-doped hBN upon the adsorption of H₂ gas. These findings indicate that Cu-doped hBN-based gas sensors can easily differentiate C₂H₄, CH₄, CO, and CO₂ from H₂, whereas it is difficult for the Cu-doped hBN to differentiate between C₂H₄, CH₄, CO, and CO₂. Hence, the sensitivity and selectivity analysis suggests that the Cu-doped hBN holds the potential to be used as a gas sensor in thermal runaway conditions.

5.2.8 Recovery time analysis of Cu-doped hBN

Recovery time is considered a crucial parameter for a gas sensor, as it indicates the sensor's ability to return to its original resistance state after the desorption of gas molecules from the sensing surface. Through a literature survey, we found that thermal runaway condition arises above 300°C ≈ 573K in lithium-ion batteries.[24, 62] Therefore, we have calculated the recovery time (τ) for the Cu-doped hBN system upon the adsorption of thermal runaway gases at temperatures above 500K using transition state theory and the van't Hoff-Arrhenius equation as mentioned in equation (5.6) below:

$$\tau = v^{-1} e^{\left(\frac{E_{bp}}{K_B T} \right)} \quad (5.6)$$

where T is the testing temperature measured in Kelvin (K), v is the attempted frequency factor, and K_B is the Boltzmann constant, whose values are 10¹² Hz for the visible radiation and 8.62 × 10⁻⁵ eV/K respectively. E_{bp} is the potential barrier for the desorption of gas molecules, which is equivalent to adsorption energy (E_{ads}) because adsorption and desorption are reverse processes to each other. The recovery time for the C₂H₄-Cu-doped hBN, CO-Cu-doped hBN,

CO₂-Cu-doped hBN, H₂-Cu-doped hBN, and CH₄-Cu-doped hBN configurations at 500K under visible light was found to be 2.722×10^8 , 1.027×10^8 , 2.367×10^4 , 3.807×10^{-2} , and 3.236×10^2 sec, respectively. The above-reported recovery time suggested that the desorption time at 500K for C₂H₄-Cu-doped hBN, CO-Cu-doped hBN, and CO₂-Cu-doped hBN is too long, making the desorption of the thermal runaway gases difficult, indicating poor reusability or potential use of Cu-doped hBN as a gas adsorbent. According to equation (5.6), the recovery time was found to be exponentially dependent on adsorption energy and temperature, meaning that if adsorption energy is kept constant, then by increasing the temperature or the attempt frequency, we can improve the recovery time of Cu-doped hBN. Further, we have calculated the recovery time under UV radiation at elevated temperature for the C₂H₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, H₂-Cu-doped hBN, and CH₄-Cu-doped hBN configurations. The reported data in Table 5.6 suggested that the recovery time for the C₂H₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, H₂-Cu-doped hBN, and CH₄-Cu-doped hBN configurations reduces from 2.722×10^8 to 2.253×10^{-4} sec, 1.027×10^5 to 1.311×10^{-1} sec, 2.367×10^1 to 3.202×10^{-6} sec, 3.807×10^{-1} to 5.739×10^{-8} sec, and 3.236×10^{-1} sec to 1.151×10^{-7} sec, respectively, as the temperature increases from 500K to 900K under UV radiation. The observed reduction in the recovery time can be attributed to the fact that both high temperatures and UV radiation provide additional input energies required for the desorption of the thermal runaway gas from the surface of Cu-doped hBN. All these findings indicate that annealing at high temperature under UV radiation effectively improved the recovery time of the Cu-doped hBN systems. Hence, our recovery time analysis confirmed that above 500K Cu-doped hBN systems can be used as a sensing material at elevated temperatures to detect thermal runaway gases.

Table 5.5: Calculated the recovery time for the adsorption of C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems at different temperatures under visible light radiation.

Adsorption Systems	τ under visible light at 500K	τ under visible light at 700K	τ under visible light at 800K	τ under visible light at 900K
C ₂ H ₄ -Cu-doped hBN	2.722 x10 ⁸ s	3.948x10 ² s	5.914 s	2.253x10 ⁻¹ s
CO-Cu-doped hBN	1.027 x10 ⁸ s	1.968x10 ² s	3.216s	1.311x10 ⁻¹ s
CO ₂ -Cu-doped hBN	2.367x10 ⁴ s	4.964x10 ⁻¹ s	1.713x10 ⁻² s	3.202x10 ⁻³ s
H ₂ -Cu-doped hBN	3.807 x10 ² s	2.598 x10 ⁻³ s	5.354x10 ⁻⁴ s	5.739x10 ⁻⁵ s
CH ₄ -Cu-doped hBN	3.236x10 ² s	2.313x10 ⁻² s	1.171x10 ⁻³ s	1.151x10 ⁻⁴ s

Table 5.6: Calculated the recovery time for the adsorption of C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems at different temperatures under visible light and UV radiation.

Adsorption Systems	τ under UV at 500K	τ under UV at 700K	τ under UV at 800K	τ under UV at 900K
C ₂ H ₄ -Cu-doped hBN	2.722 x10 ⁵ s	3.948x10 ⁻¹ s	5.914x10 ⁻³ s	2.253x10 ⁻⁴ s
CO-Cu-doped hBN	1.027 x10 ⁵ s	1.968x10 ⁻¹ s	3.216x10 ⁻³ s	1.311x10 ⁻¹ s
CO ₂ -Cu-doped hBN	2.367x10 ¹ s	4.964x10 ⁻⁴ s	1.713x10 ⁻⁵ s	3.202x10 ⁻⁶ s
H ₂ -Cu-doped hBN	3.807 x10 ⁻¹ s	2.598 x10 ⁻⁶ s	5.354x10 ⁻⁷ s	5.739x10 ⁻⁸ s
CH ₄ -Cu-doped hBN	3.236x10 ⁻¹ s	2.313x10 ⁻⁵ s	1.171x10 ⁻⁶ s	1.151x10 ⁻⁷ s

5.2.9 Comparison of the adsorption energies, band gap, and sensitivity

In this section, we have compared the adsorption energies, change in the band gap, and sensitivity at 300K for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems with respect to various previously reported theoretical work. From the reported adsorption energy in Table 5.7, we found that Cu-doped hBN exhibits better adsorption capabilities than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ systems towards thermal runaway gases. In addition, we also observed that Cu-doped hBN exhibited better variation in the band gap than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ upon the adsorption of CO, CO₂ gas molecules, whereas Rh@PdS₂ exhibited the highest variation in the band gap upon the adsorption of C₂H₄

and CH₄. On the other side, C₂H₄/Rh@PdS₂, C₂H₄/Rh-PdS₂, and H₂/Rh@PdS₂, H₂/Rh-PdS₂, exhibited 100% variation in the band gap because upon the adsorption of C₂H₄ and H₂ gas molecules, Rh@PdS₂ and Rh-PdS₂ undergo a transition from semiconductor to metal. Further, Rh@PdS₂ exhibited the highest sensitivity towards the adsorption of H₂ gas molecules. In contrast, the sensitivity of the Cu-doped hBN was found to be better than Cu@HfS₂, Cu@HfS₂, Rh@PdS₂, and Rh-PdS₂ upon the adsorption of CH₄, CO, and CO₂ gas molecules. Hence, the comparison analysis suggested that Cu-doped hBN served as a more efficient sensing material than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ towards the detection of CO and CO₂ gas molecules.

Table 5.7: Comparison of the adsorption energies, change in the band gap, and sensitivity at 300K for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems with respect to various previously reported theoretical work.

Systems	Adsorption Energy(eV)	ΔE_g (eV)	Sensitivity	Reference
Pt-SnSe/C ₂ H ₄	-0.920	16.3%	97.10%	[64]
Pt-SnSe/CO	-1.170	24.7%	99.50%	
Pt-SnSe/CO ₂	-0.130	0.4%	10%	
C ₂ H ₄ /Cu@HfS ₂	-0.947	6.36%	-	[54]
CH ₄ /Cu@HfS ₂	-0.234	1.10%	-	
CO/Cu@HfS ₂	-0.984	9.66%	-	
CO ₂ /Cu@HfS ₂	-0.250	1.44%	-	
H ₂ /Cu@HfS ₂	-0.229	4.49%	-	
C ₂ H ₄ /Cu-HfS ₂	-0.858	22.88%	99.70%	
CH ₄ /Cu-HfS ₂	-0.304	5.49%	-	
CO/Cu-HfS ₂	-0.750	22.06%	99.60%	
CO ₂ /Cu-HfS ₂	-0.311	19.65%	99.20%	
H ₂ /Cu-HfS ₂	-0.159	6.04%	-	
C ₂ H ₄ /Rh@PdS ₂	-1.340	100%	-99.99%	[59]
CH ₄ /Rh@PdS ₂	-0.160	18.95%	81.58%	
CO/Rh@PdS ₂	-1.510	29.19%	92.61%	
CO ₂ /Rh@PdS ₂	-0.150	24.18%	88.45%	
H ₂ /Rh@PdS ₂	-0.450	100%	-99.99%	
C ₂ H ₄ /Rh-PdS ₂	-0.610	100%	-1	
CH ₄ /Rh-PdS ₂	-0.300	4.05%	50.34%	
CO/Rh-PdS ₂	-1.940	26.35%	97.26%	
CO ₂ /Rh-PdS ₂	-0.230	4.62%	54.94%	

H ₂ /Rh-PdS ₂	-0.610	100%	-1	Present Work
C ₂ H ₄ -Cu-doped hBN	-2.173	30%	99.99%	
CO-Cu-doped hBN	-2.097	44.19%	100%	
CO ₂ -Cu-doped hBN	-1.594	27.09%	99.99%	
H ₂ -Cu-doped hBN	-1.447	1.61%	61.96%	
CH ₄ -Cu-doped hBN	-1.545	15.16%	99.98%	

5.3 Conclusions

In this work, we have systematically investigated the adsorption mechanisms of thermal runaway gases onto the pristine hBN and Cu-doped hBN using ab initio calculations. From our adsorption energy calculations, we found that the adsorption of C₂H₄, CH₄, CO, CO₂ and H₂ gas molecules onto pristine hBN was physisorption due to poor charge transfer and low adsorption energy. This leads to poor variation in the electrical conductivity, sensitivity, selectivity and very low recovery time, confirming that pristine hBN cannot be used as a gas sensor to detect thermal runaway gases. Therefore, to enhance the gas sensing performance of hBN, we have substituted the Cu atom at N and B vacancies. It was based on the formation and binding energy; Cu atom doped at B vacancy was found to be the most stable configuration. After doping Cu atom, the adsorption energy for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN and H₂-Cu-doped hBN systems was found to be high, resulting in chemisorption. DOS plots confirmed that the band gap reduces to 2.17eV, 2.63eV, 1.69eV, 2.26eV and 3.05eV respectively upon the adsorption of C₂H₄, CH₄, CO, CO₂ and H₂ gas molecules onto Cu-doped hBN whereas the PDOS plots confirmed that the hybridization of the 3d atomic orbitals of Cu atom with the atomic orbitals of C₂H₄ and CO gas molecules is responsible for the stronger interaction in case of C₂H₄ and CO gas molecules with Cu-doped hBN. The RDG results revealed that weak vdW-type non-covalent interaction exists between the thermal runaway gases and pristine hBN, whereas electrostatic interaction exists due to the charge transfer between the C₂H₄, CO, CO₂, H₂ gas, and Cu-doped hBN, verified from the charge density difference calculations. Such a large variation in the band gap indicates that Cu-doped hBN is highly sensitive towards the adsorption of all these gases. However, the sensing response for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems indicates that Cu-doped hBN is unable to differentiate between C₂H₄, CH₄, CO, and CO₂ but able to differentiate H₂ from the rest of the gas. Furthermore, the recovery time calculated for the C₂H₄-Cu-doped hBN, CH₄-Cu-doped hBN, CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems at 300K was found to be too high. But we also found that annealing within the temperature

range from 500 K to 900 K under UV exposure improves the recovery time of all the system configurations. Hence, we conclude from our DFT results that substitutional doping of the Cu atom is a cost-effective method to improve the recovery time, sensitivity, selectivity, and adsorption capability of hBN upon the adsorption of thermal runaway gases, making it a promising sensing material at elevated temperatures towards the early detection of thermal runaway gases.

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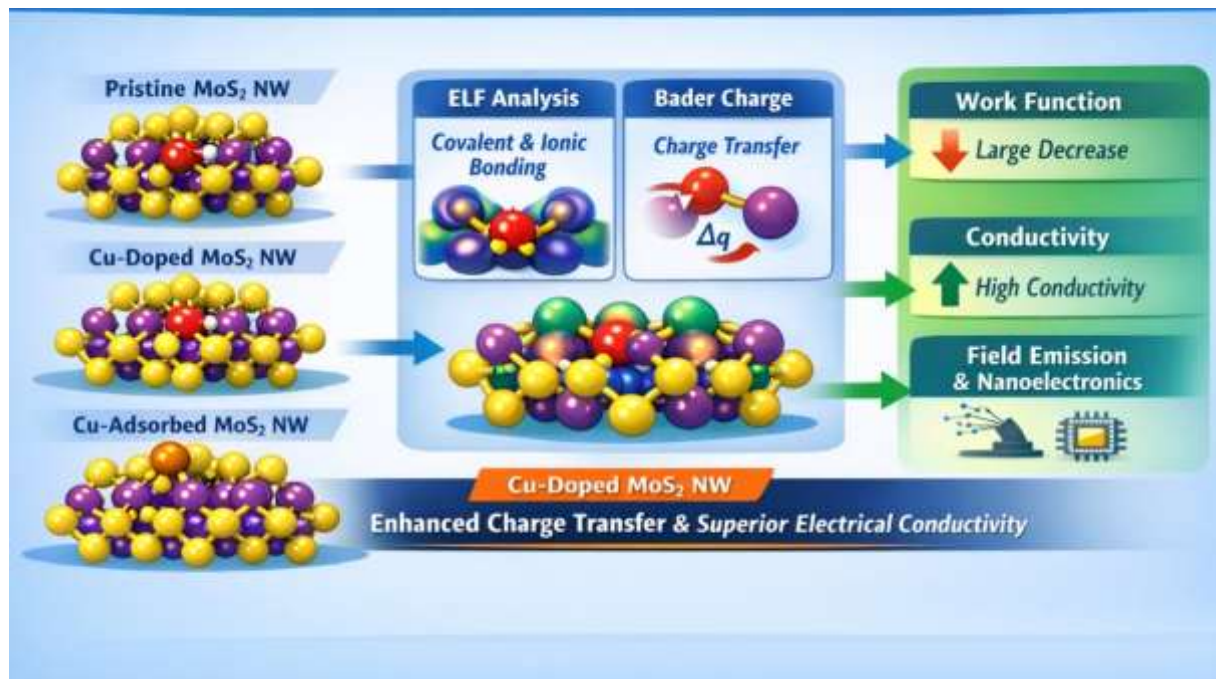
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Chapter 6

Effect of Substitutional Doping and Cu Adsorption on MoS₂ Nanowire: A Comparative DFT Study



In this study, we investigated the effect of substitutional doping (Cu-doped MoS₂NW) and surface-adsorbed Cu atoms (Cu-MoS₂NW) on the electronic properties of MoS₂ nanowires (NWs) using Density Functional Theory (DFT). Our adsorption study revealed that the adsorption of the Cu atom was a chemisorption. Electron Localization Function (ELF) analysis indicates that the Cu atom formed a covalent and ionic bond with MoS₂NW upon adsorption and substitutional doping, respectively. These findings suggest that a charge transfer occurred between the Cu atom and MoS₂NW during the interaction, confirmed by the Bader charge method. Further, the work function calculation indicates that Cu-doped MoS₂NW exhibits a large negative variation in the work function, indicating enhanced electron emission capability of the Cu-doped MoS₂NW systems. All of our systems are thermodynamically stable, as determined by our cohesive energy calculations. Overall, the DFT results suggest that Cu-doped MoS₂NW systems exhibit superior electrical conductivity, enhanced charge transfer, and larger variation in the work function compared to pristine MoS₂NW and Cu-MoS₂NW. These findings confirm that substitutional doping is an effective way to modify the electronic properties of MoS₂ nanowires (NWs). Therefore, Cu-doped MoS₂NW systems hold promise for applications in field-emission and nanoelectronics devices.

6.1 Introduction

Two-dimensional (2D) materials such as graphene[1], hexagonal boron nitride(hBN)[2, 3], Transition metal dichalcogenides (TMDs)[4], and black phosphorene[5] have attracted considerable attention for both the theoretician and experimentalists due to their wide range of application in the various nanoelectronics and optoelectronics devices. Therefore, among the various 2D materials, MoS₂ which is a layered transition metal dichalcogenide formed by the vertical stacking of weakly coupled S-Mo-S layers has attracted considerable interest of the researchers due to their unique physical, catalytic, optical, and electronic properties they are finding their applications in the field of hydrogen evolution reaction (HER)[6], storage[7], gas sensors[8], catalysis, energy conversion[9], photodetectors[10], photocatalysis, photoelectrochemical and stretchable electronics. Contrary to graphene zero band gap limitations, MoS₂, in its bulk form, is an indirect band semiconductor with a band gap value of 1.2eV, whereas an atomically thin layer of MoS₂ is a direct band semiconductor with a band gap value of 1.8eV[11]. As a consequence, MoS₂ exhibits basic properties like gate control, wide band gap, high current capability, and good electrical transport. All these findings suggest that MoS₂ can serve as an alternative to graphene for the application of nanoelectronics and optoelectronics. Currently, the trend in the research is primarily focused on utilizing 2D materials to their maximum potential in various applications. However despite such advances MoS₂ also exhibit low electron mobility compared to graphene[12] which hinder their practical implementation in various nanoelectronics devices like transparent electrode etc. Therefore, there is a need to modulate the intrinsic properties of MoS₂ to make them fit for practical use. In this regard, researchers have adopted various effective methods to modulate the intrinsic properties of materials, such as defect engineering[13], substitutional doping[14], adatom adsorption[15], and substrate engineering[16]. Among the various methods, it has been well proven that the adsorption of transition metal (TM) atoms onto 2D material effectively modulates the intrinsic properties of 2D materials. For example- Xu et al. studied the adsorption of various alkali metals (Li, Na), alkaline earth metals (Be, Mg), 3d TM atoms (Ti, V, Cr, Mn, Fe, Co), and precious metals (Ag, Au, Pt) onto dumbbell C₄N[17]. Their study revealed that the adsorption of the above-mentioned metals opens the zero-band gap of dumbbell C₄N, making it a promising candidate for electronic devices. Similarly, Zhang et al. studied the structural, electronic, magnetic, and optical properties of 4d TM atoms adsorbed onto blue phosphorene[18]. Their study revealed that adsorbing 4dTM onto blue phosphorene effectively modifies blue phosphorene's structural, electronic, magnetic, and optical properties. On the

other side, there have been various reports regarding the adsorption of various TM atoms onto the MoS₂ monolayer for various applications. Kadioglu et al. investigated the adsorption of Au, Cu, and Au_xCu_y nanoclusters on MoS₂ monolayer for sensing CO and H₂O.[19] Their results revealed that the adsorption of Au, Cu, and Au_xCu_y nanoclusters onto the MoS₂ monolayer enhanced the chemical activity and sensitivity towards CO and H₂O molecules. Sharma et al. investigated the catalytic activity of Cu-embedded MoS₂ monolayer for CO[20]. They found that the basal plane of the MoS₂ sheet gets activated upon substitutional doping of the Cu atom at S vacancy, which catalyzes the oxidation of CO effectively without poisoning. Rawal et al. studied the effects of defect on the catalytic activity of the 29 adatoms of Cu, Ag, and Au nanoparticles (NP) onto MoS₂ monolayer towards CO[21]. Wang et al. investigated the structural, electronic, and magnetic properties of adsorbed transition metal from Sc to Zn onto MoS₂ monolayer using DFT. They conclude that all the TM atoms got adsorbed chemically except Zn, whereas the electronic and magnetic properties of the MoS₂ monolayer can be effectively modified by adsorbing different TM atoms. Thus, TM adsorbed MoS₂ monolayer can be utilized for spintronics[22]. In another study, Li et al. emphasized that the adsorption of alkali metal, alkaline earth metals, 3d TM, noble metal, and non-metal atoms induce magnetic moments and transforms the band gap from semiconductor to metallic, semi-metallic, making them promising candidates for spintronics and electronic devices[23]. Moreover, Joseph et al. synthesized Cu-doped MoS₂ hydrothermally to analyze the effect of Cu doping on the thermoelectric properties of MoS₂[24]. Recently, Zhou et al.[25]reported a method for selectively exposing and activating the inert basal planes of 2H-MoS₂ for CO₂ hydrogenation to methanol, achieved through the physically constrained sulfidation of ultrafine MoO₃ nanocores into hollow, few-layer MoS₂ spheres within a mesoporous silica framework. The spherical curvature of MoS₂ induces strain and sulfur vacancies (S_v) on the typically inactive basal planes. This increases the exposure of in-plane sulfur vacancies while minimizing the exposure of edge vacancies, significantly enhancing its catalytic performance in synthesizing CH₃OH from the hydrogenation of CO₂. In contrast, the adsorption of the Cu atom onto MoS₂ facilitated the activation of H₂, delivering a remarkable CH₃OH production rate of 6.11 mol·molMo⁻¹·h⁻¹ and a high CH₃OH selectivity of 72.5% under reaction conditions of 260°C, 5 MPa, and 24,000 mL·gcat⁻¹·h⁻¹. They conclude that the Cu/MoS₂/SiO₂ catalyst demonstrates excellent stability, maintaining its silica-encapsulated hollow core-shell structure throughout the reaction process. Wang et al. studied the electrocatalytic activity of the Cu-decorated MoS₂ monolayer paving the way for application in electronics and energy storage[26]. The above literature survey suggests that there exists a plethora of literature regarding the Cu decoration

onto various MoS₂ nanostructures. However, to the best of the author's knowledge, there have been no reports regarding the effect of substitutional doping (Cu-doped MoS₂NW) and surface-adsorbed Cu atom (Cu-MoS₂NW) on the electronic properties of MoS₂ NW. This reported gap in the research motivated us to investigate the electronic properties of MoS₂ NW upon substitutional doping and surface-adsorption of Cu atom. Therefore, in this work, we have extensively investigated the effect of substitutional doping and surface-adsorption of Cu atoms onto electronic properties of MoS₂ NW using DFT. We have selected the Cu atom as a dopant for this study because it has been well proved experimentally that it has good chemistry with MoS₂. The adsorption of the Cu atom was analyzed by calculating the adsorption energy and distances. In addition, the electronic properties and conductivity of the Cu-decorated MoS₂ NW were calculated through DOS, PDOS, and work function. Further, the structure stability of the optimized Cu-decorated MoS₂ NW structures nature of the bond formation, and the charge transfer mechanism during the Cu interaction with MoS₂ NW were analyzed utilizing cohesive energy, ELF, and the Bader charge method. Finally, we have compared our calculated DFT results for both the systems

6.2 Computational Details

We have used the Linear Combination of Atomic Orbital (LCAO) calculator in the Quantum ATK[27] package to ensure accuracy while calculating the electronic properties of the various optimized structures. To approximate the nucleus and valence electrons interaction, the Fritz-Haber-Institute (FHI)[28] pseudopotential was implemented. For transition metals (TM) atoms such as Cu and Mo, the Double Zeta Polarized (DZP)[29] basis set was considered to ensure accuracy during the calculation. To consider the electron-electron interaction effectively, we have considered Generalized Gradient approximation (GGA)[30] with the predefined function Perdew Burke Ernzhoeof (PBE)[31] as an exchange-correlation function (XC). Further, we have selected 200 Ha (400 eV) and 10⁻⁶ eV as the cutoff energy and energy convergence criteria for the ground state energy calculation. According to the Monkhorst-Pack grid scheme, we have implemented 1 × 1 × 51 K points for calculating the density of states (DOS). For the adsorption study, MoS₂ NW was grown along the Z axis by continuously repeating the 1x1 unit cell of MoS₂ monolayer four times along the X and Y directions, resulting in 4 x 4 supercells. The 4x4 supercells contain 16 Mo and 32 S atoms with a vacuum layer of 10 Å was applied along the X and Y directions to prevent interactions between the adjacent periodic replicas. Eqs. 6.1 and Eqs. 6.2 were used to determine the strength of the interaction during the adsorption of the Cu atom onto the surface of MoS₂ NW and the thermodynamic stability of the various adsorption configurations, respectively.

$$E_{\text{ads}} = E_{\text{Total}} - E_{(\text{MoS}_2)} - E_{(\text{Cu})} \quad (6.1)$$

$$E_{\text{coh}} = \frac{E_{(\text{MoS}_2)} - [n_{(\text{Mo})}E_{(\text{Mo})} + n_{(\text{S})}E_{(\text{S})}]}{N} \quad (6.2)$$

where E_{Total} represents the total energy of the Cu adsorbed MoS_2 NW, $E_{(\text{MoS}_2)}$ represents the energy of the MoS_2 NW, $E_{(\text{Cu})}$ represents the energy of the isolated copper atom, $E_{(\text{S})}$ represents the energy of the isolated sulfur atom, $E_{(\text{Mo})}$ represent the energy of the isolated Mo atom, $n_{(\text{Mo})}$, $n_{(\text{S})}$, represents the number of Mo and S atoms, and N represents the total atoms within the system, respectively.

6.3 Results and Discussion

6.3.1 Structure and Electronic Properties Analysis of MoS_2 monolayer and MoS_2 NW

To investigate the differences in the geometrical and electronic properties of the MoS_2 monolayer and MoS_2 NW. For this purpose, initially, we optimized the geometry. After optimization, the resulting optimized lattice parameters for the optimized MoS_2 monolayer were $a = 3.244 \text{ \AA}$ and $c = 12.880 \text{ \AA}$ with a c/a ratio of 3.97, consistent with the previous theoretical calculation.[32] Further, the band structure was plotted for the optimized MoS_2 monolayer. The resulting band structure in Figure 6.2(a) illustrates that the MoS_2 monolayer exhibits a direct band gap of about 1.56 eV, verified from the DOS plot in Figure 6.2(b) and agreed with the previously reported theoretical studies[33]. In the optimized MoS_2 NW shown in Figure 6.1(b), each S atom is coordinated with multiple Mo atoms, resulting in a distorted octahedral arrangement of atoms within the layer, confirming the existence of the 1T phase in MoS_2 NW. This type of structural arrangement of atoms within the layer facilitates high tensile strength and significant overlapping between the d orbitals of Mo atoms, facilitating a pathway for efficient electron movement, which is advantageous for the application of a field effect transistor[34], energy storage[34], and as a catalyst in electrochemical reactions[35]. The diameter, height, and Mo-S bond length for the optimised MoS_2 NW were 7.44 Å, 20 Å, and 2.35 Å, respectively. Moreover, the resulting DOS plot in Figure 6.3 illustrates the existence of continuous impurity states near the Fermi level (E_F), reducing the band gap from 1.56 eV to zero, confirming the metallic behaviour of the 1T phase of MoS_2 NW, consistent with the study performed by Seivane et al[36]. The observed transition from the semiconductor to a metal was due to the quantum confinement effect. Hence, the complete agreement of the calculated band gap value proved the validity and reliability of our computational procedure.

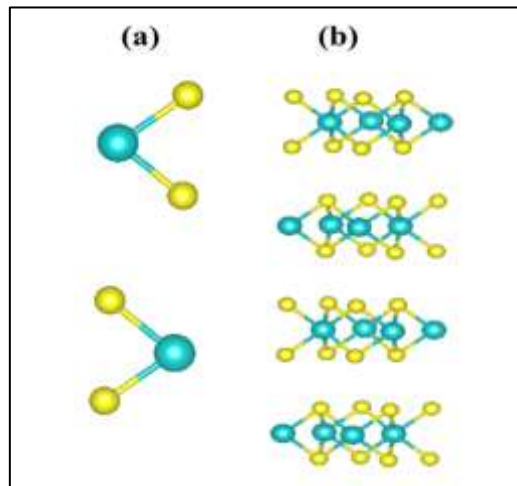


Figure 6.1. Optimized (a) MoS₂ monolayer and (b) MoS₂ NW structure. The atoms in yellow and cyan colours represent the S and Mo atoms, respectively.

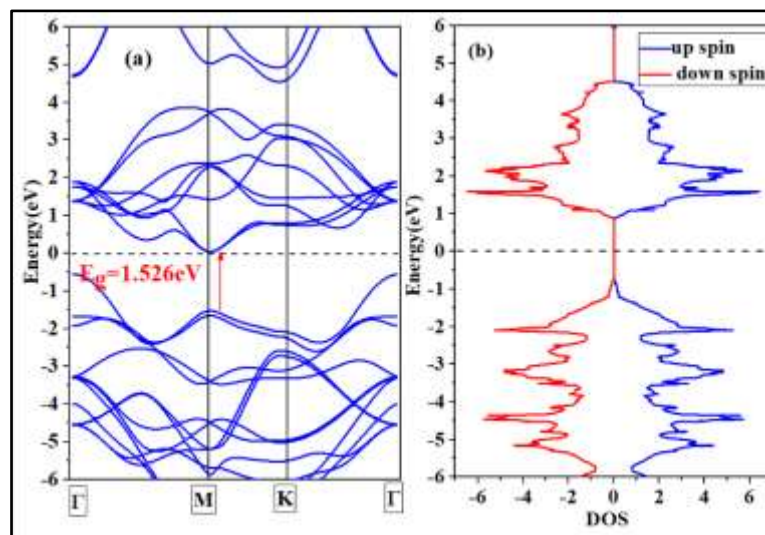


Figure 6.2. Plotted (a) Band structure and (b) DOS for the MoS₂ monolayer, respectively.

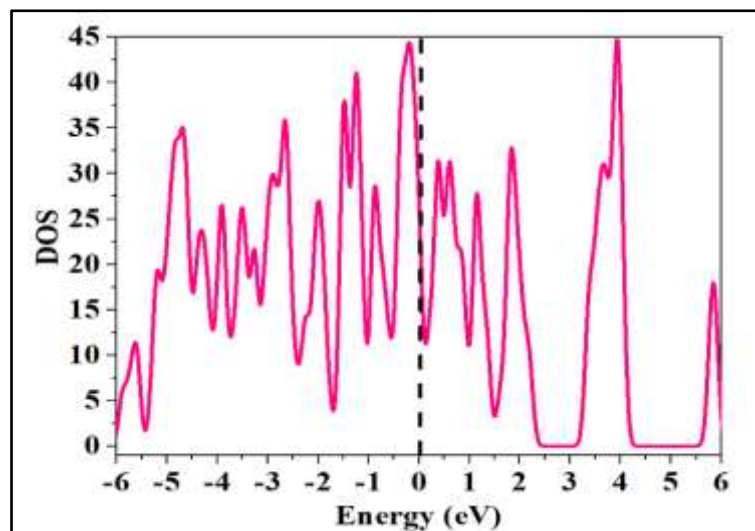


Figure 6.3. DOS plot for the MoS₂ NW. The black dotted line represents the fermi level set to zero for reference.

6.3.2 Adsorption of Cu atom onto MoS₂ NW

Table 6.1. The calculated adsorption energies and heights for the Cu atom adsorbed onto MoS₂ NW at Mo and S sites

Adsorption height (Å)	Adsorption energy(eV)	Adsorption height (Å)	Adsorption energy(eV)
1.80	-0.03805	2.0	0.04943
1.85	-0.40184	2.25	-1.49111
2.0	-0.96301	2.50	-1.70622
2.05	-1.02261	2.55	-1.67339
2.10	-1.04492	2.60	-1.62624
2.20	-0.99535	2.65	-1.56628
2.25	-0.9423	2.70	-1.4974
2.28	-0.89945	2.75	-1.42075
2.50	-0.51971	3.0	-0.97992
2.75	-0.06315		
3.0	0.31902		

To analyze the interaction of the Cu atom with MoS₂ NW, we have considered the S site (on top of the S atom) and the Mo site (on top of the Mo atom) as the preferential adsorption sites for the Cu atom. This is because both Mo and S atoms contain vacant d and p orbitals that can readily accept electrons from the Cu atom through charge transfer during the interaction. Therefore, we have considered different orientations of the Cu atom at the Mo and S sites, as shown in Figure. 6.4(a) to 6.4(s) as the input geometries for the adsorption study. Further, adsorption energies were calculated using Eqs.6.1 and reported in Table 6.1 for all these different adsorption configurations. From the reported values in Table 6.1, we found that the adsorption energies gradually decrease, reach minima, and then increase with increasing adsorption heights. On plotting the adsorption energy as a function of adsorption height, the resulting curve was found to be a U-shaped curve as shown in figure 6.5. The minima of the adsorption energy curve correspond the minimum adsorption energies and optimized adsorption height. From Figure 6.5, we found that the Cu atom preferred to be adsorbed at a height of 2.10Å and 2.50 Å with the adsorption energies -1.04eV and -1.70 eV at the S and Mo sites, respectively. It was based on energy minimization; we found that the Cu atom preferred to be adsorbed at the Mo site. Therefore, the Cu atom adsorbed at the Mo site was referred to as “Cu-MoS₂NW” and selected for the rest of the calculation. The reported negative value of the adsorption energies in Table 6.1 indicates that the adsorption process was exothermic, spontaneous, and energetically favourable. Additionally, the calculated sum of the corresponding atomic radii for the Cu-Mo atoms (2.73Å) was larger than the reported adsorption height (2.50Å) on the comparison. This indicates that covalent interaction exists between the Cu atom and MoS₂ NW during the adsorption. Hence, the calculated high

adsorption energy and the existence of covalent interaction between the Cu atom and MoS₂NW suggest that the adsorption of the Cu atom onto MoS₂ NW was a chemisorption.

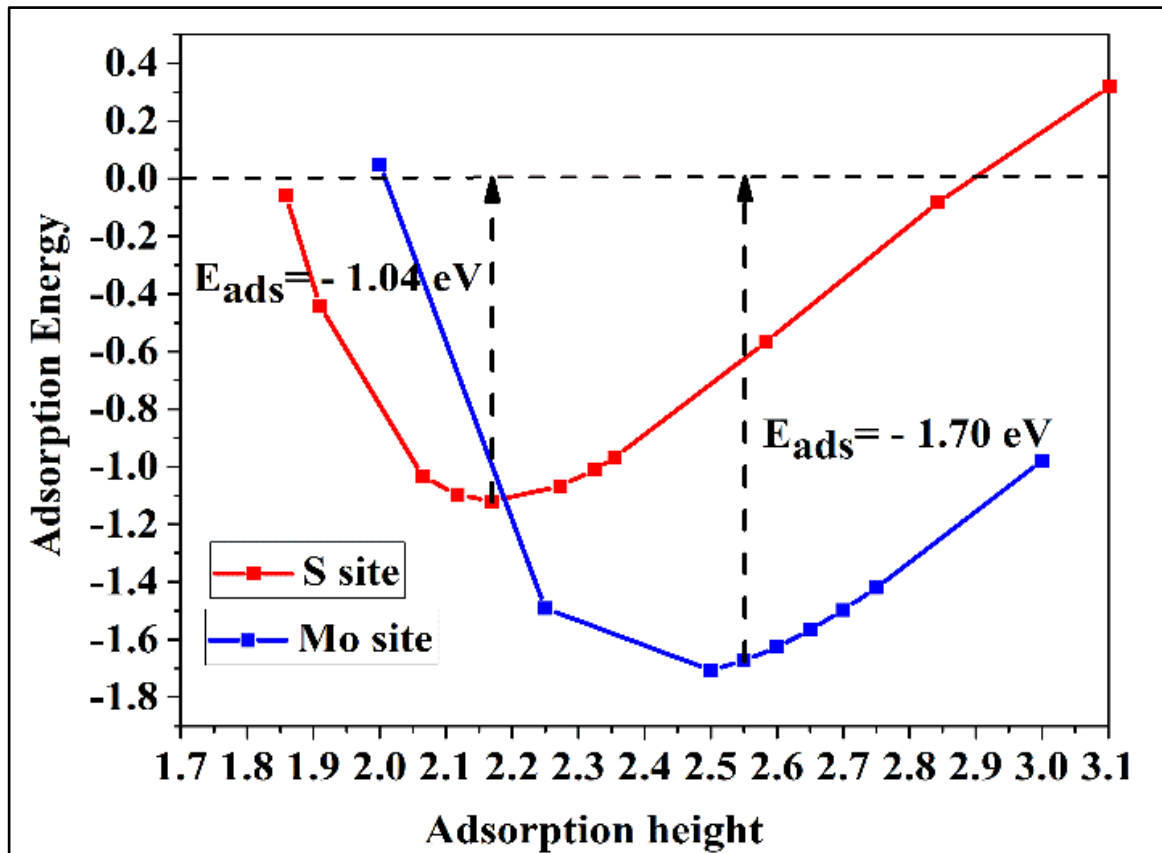
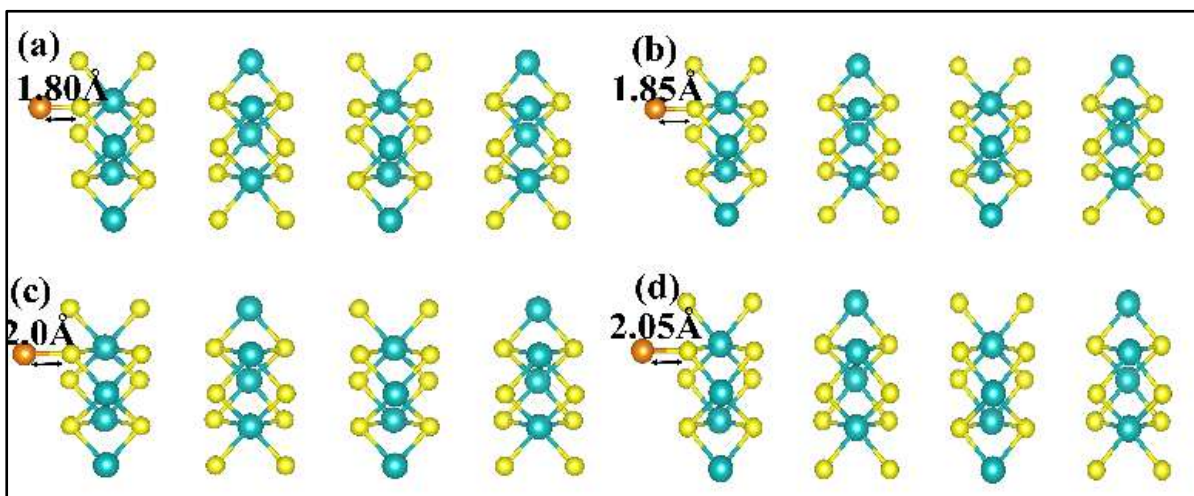
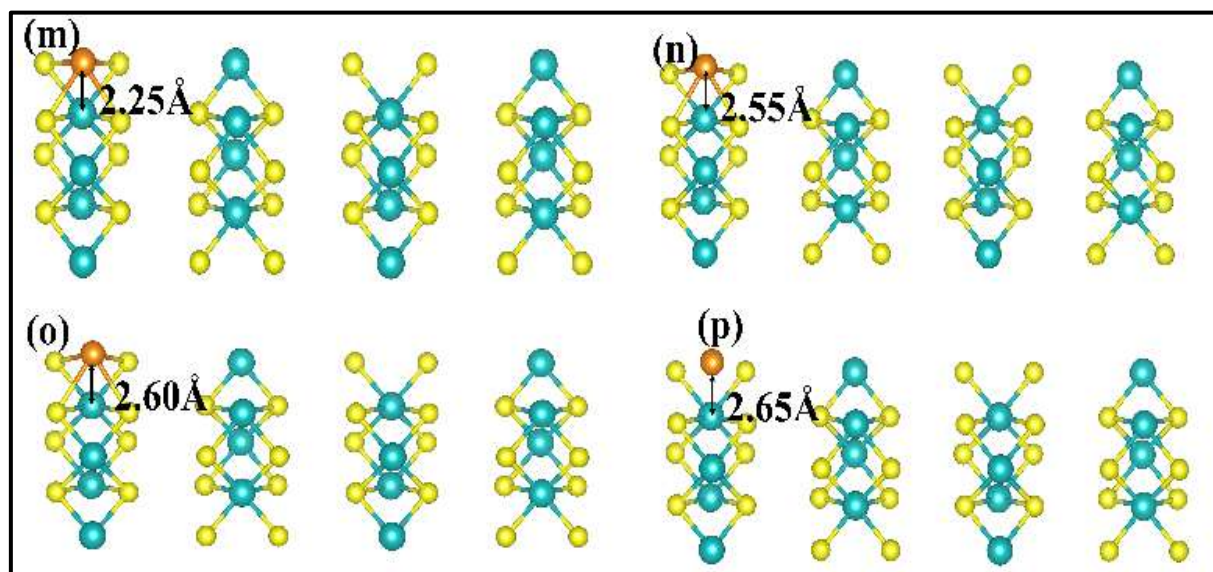
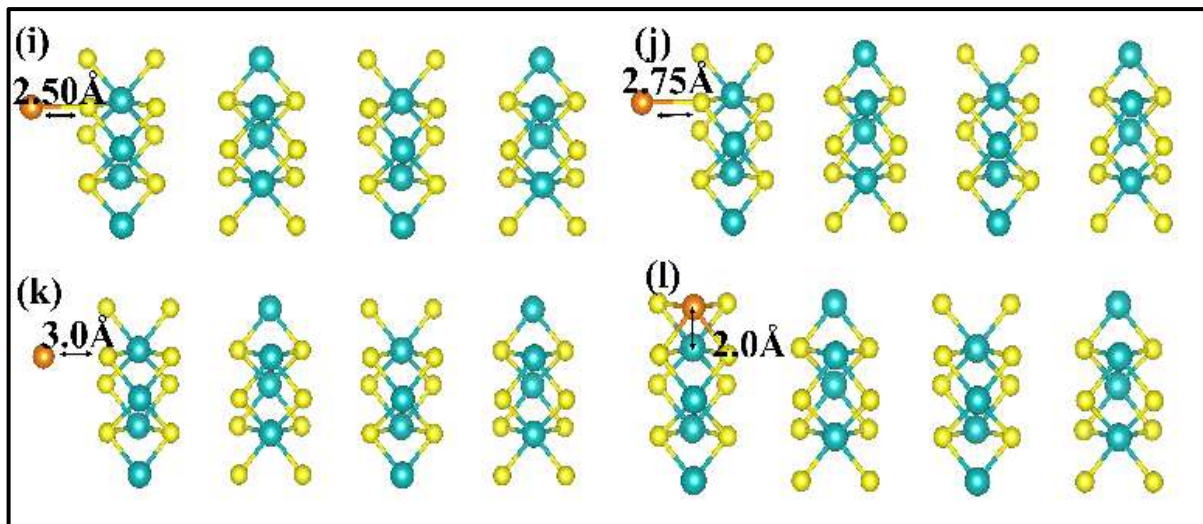
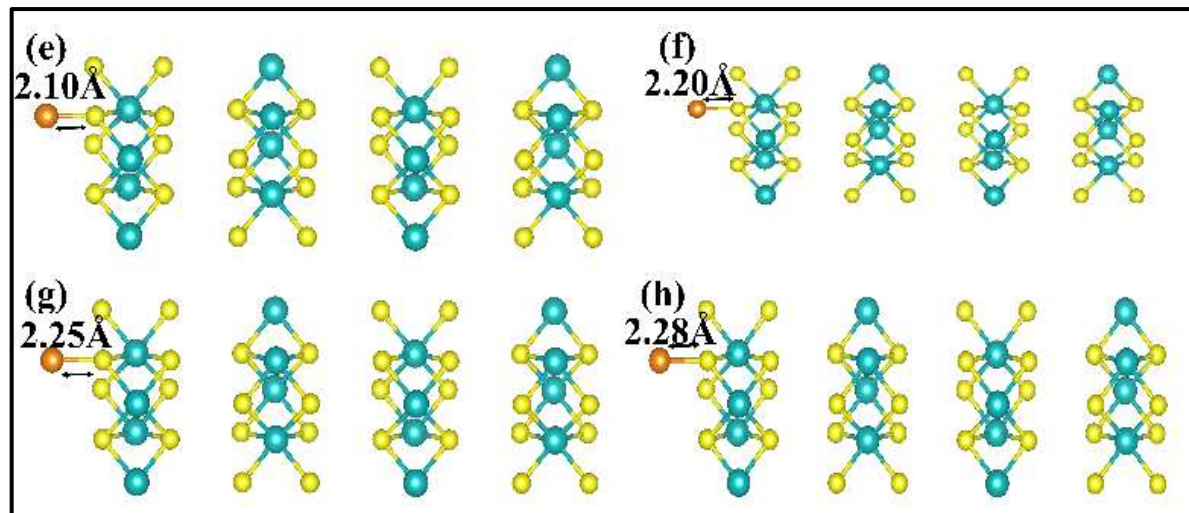


Figure 6.4. The plotted red and blue curves represent the variation of the adsorption energy with adsorption heights for Cu adsorbed onto MoS₂ NW at S and Mo sites, respectively.



Effect of Substitutional Doping



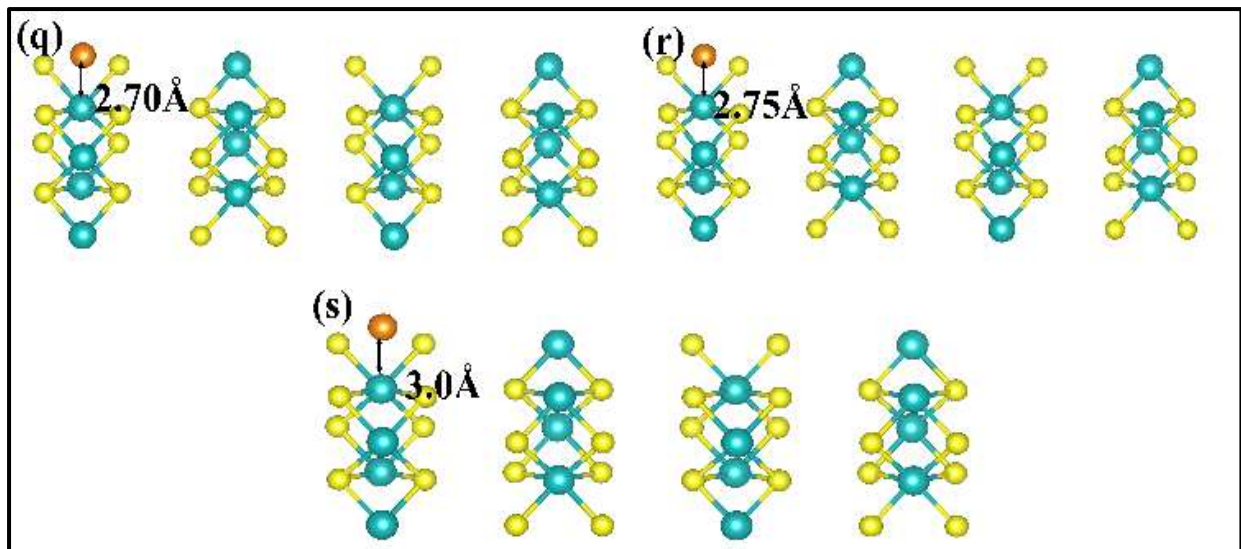


Figure 6.5. Top view of the different optimized adsorption configurations (a)-(k) at the S site and (l)-(s) at the Mo site, respectively

6.3.3 Comparison of the calculated adsorption energies for the Cu-MoS₂ NW

In this section, we have compared our calculated adsorption energy for the Cu-MoS₂NW with the previously reported adsorption energies for TM adsorbed onto various 2D materials by different authors. From the reported adsorption energies in Table 2, we found that the Cu atom got adsorbed onto the SnO monolayer, GaN monolayer, MoS₂ monolayer, and graphene monolayer, with adsorption energies 1.342eV, 1.07eV, 0.407eV, 1.307eV, and 1.13eV respectively. The comparison showed that the adsorption energy for the Cu-MoS₂NW was higher than the Cu atom adsorbed onto the SnO monolayer, GaN monolayer, MoS₂ monolayer, and graphene monolayer. This indicates that MoS₂NW has a better adsorption affinity for Cu atoms than SnO monolayer, GaN monolayer, MoS₂ monolayer, and graphene monolayer.

Table 6.2. Comparison of the calculated adsorption energies for the Cu-MoS₂NW with previously reported adsorption energies for TM adsorbed onto various 2D materials.

Systems	Adsorption energy (eV)	Reference
Cu-SnO monolayer	1.342eV	[37]
Cu-GaN monolayer	1.07eV	[38]
Cu-hBN monolayer	0.407eV	[39]
Cu-MoS ₂ monolayer	1.307eV	[21]
Cu-graphene monolayer	0.228eV	[40]
Cu-MoS ₂ NW	1.70eV	Present work

6.3.4 Structure analysis of the Cu-doped MoS₂ NW

In this section, we have analyzed the structural properties of the substitutional doped structure. For this purpose, we replaced one of the atoms of MoS₂ NW from the lattice with the Cu atom and optimized the doped structure. After optimization, we found that the doped Cu atom was displaced and the doped Cu atom was displaced and occupied the interstitial sites where it

bonded with the neighbouring three S atoms, as shown in Figure 6.6. From Figure 6.6(b), we found that the three Cu-S bond lengths in the optimized structure were found to be 2.30Å, 2.26Å and 2.28Å which is shorter than the Mo-S (2.35Å) bond length of the pristine MoS₂ NW. This indicates that the dopant atom causes the overall structure to be somewhat corrugated due to the protrusion of the Cu atom away from the surface of MoS₂ NW. Moreover, the Mo-S bond lengths in the resulting optimized structure no longer remained a fixed value and underwent variations from 2.36Å-2.63Å. On comparison, we found that the variations in the Mo-S bond lengths upon substitutional doping were more significant than the Mo-S (2.35Å) bond length of the pristine MoS₂ NW. This indicates that the surface of the MoS₂ NW undergoes expansion to accumulate the large atomic radius Cu atom (1.28Å) within the lattice. These findings suggest that substitutional doping of the Cu atom causes structural distortion within the lattice. For the rest of the study, we have abbreviated the optimized substitutional doped structure as “Cu-doped MoS₂ NW”. To determine the bonding strength of the Cu atom with the MoS₂ NW and the stability of the Cu-doped MoS₂ NW structures, we have calculated the binding energy (E_b) and formation energy (E_f) using Eqs. (6.3) and Eqs. (6.4) respectively.

$$E_b = E_{\text{Cu-MoS}_2 + \text{gas}} - (E_V + E_{\text{Cu}}) \quad (6.3)$$

$$E_f = E_{\text{Cu+MoS}_2} - E_{\text{MoS}_2} - \mu_{\text{Cu}} + \mu_X \quad (6.4)$$

where $E_{\text{Cu-MoS}_2}$, E_V , E_{Cu} , μ_{Cu} and μ_X Represents the total energies of the substitutional doped Cu atom into MoS₂ NW, total energies of the defected MoS₂ NW, total energies of the isolated Cu atom, and chemical potentials of the isolated Cu and ejected atoms from the MoS₂ NW, respectively. According to equations (6.3) and (6.4), the binding and formation energies for the Cu-doped MoS₂ NW were -11.326eV and -5.662eV, respectively. The calculated high formation and binding energy suggests that the Cu atom binds strongly with the MoS₂ NW, and the Cu-doped MoS₂ NW structures are stable.

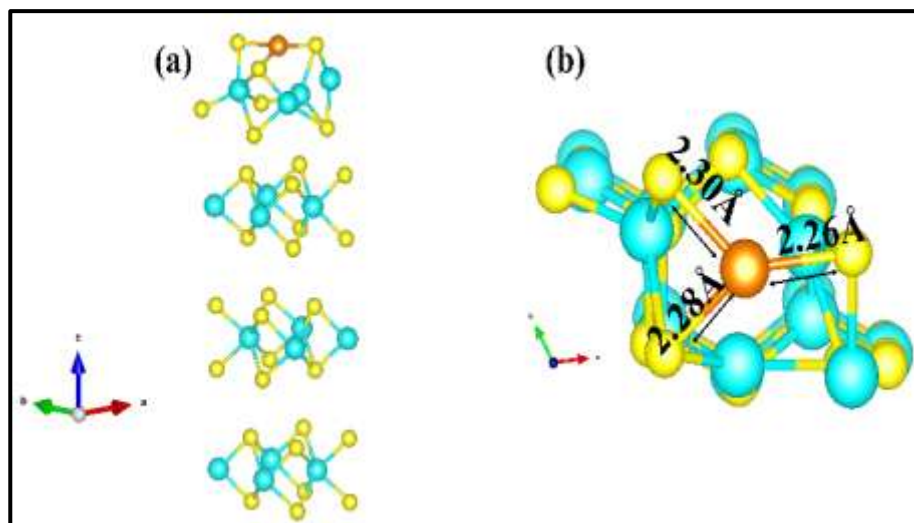


Figure 6.6. (a)Side view and (b) Top view of the optimized Cu-doped MoS₂ NW structures.

6.3.5 Thermodynamic stability of the Cu-MoS₂NW and Cu-doped MoS₂NW systems

To analyze the thermodynamic stability of the substitutionally doped and Cu-adsorbed optimized structures, we have calculated the cohesive energy/atom ($E_{coh}/atom$) using Eqs. 2[55] And reported in Table 6.4. According to Eqs. 6.2, we found that the cohesive energy for the MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂NW systems was found to be -5.22eV/atom, -5.15eV/atom, and -eV/atom respectively. The calculated negative value of the cohesive energy suggests that all our systems are thermodynamically stable. On comparison, we found that the increasing order of thermodynamic stability is Cu-doped MoS₂NW> Cu-MoS₂NW>MoS₂NW. The observed low cohesive energy of Cu-doped MoS₂NW and Cu-MoS₂NW systems with respect to MoS₂ NW can be attributed to the strong interaction of the Cu atom with the surface atoms, thereby reducing the interaction of the surface atoms with the bulk atom. As a consequence, it reduces the overall cohesive energy of the systems. From Table 6.3 and Table 6.4, we found that various computational studies suggest that generally, on doping the cohesive energy decreases as observed in the different 2D and 1D nanostructures like Aluminene (Planar), Aluminene(P6mmm), Aluminene (4-layers slab, 8-Pmmn), Aluminene (Triangular, Pmmn), Indiene, Cu-graphene, SnGe, SnSi, Stanene, Mo₆Se₆ NW, Mo₆S₂Se₃ NW, Mo₆S₄I₂ NW, Mo₆S₂Se₃ NW, Mo₆S₂Se₃ NW Mo₁₂S₁₈ NW and Mo₁₂Se₁₈NW respectively. A similar trend was observed for the MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂ NW systems. Also, the calculated high cohesive energy suggests that MoS₂NW, Cu-doped MoS₂NW, and Cu-MoS₂ NW systems can be synthesized experimentally via high-energy methods such as Chemical Vapour Deposition (CVD) and molecular beam epitaxy (MBE). This finding was consistent with the Ding et al. results that SiX and XSi₃ (where X = B, C, N, Al, and P atoms) could be synthesized via CVD and MBE methods based on cohesive energy calculations[56].

Table 6.3. Reported cohesive energies for the various 2D materials and 1D materials along with MoS₂NW, Cu-doped MoS₂NW, and Cu-MoS₂NW

System	Cohesive energy (eV)	Reference
Aluminene(Planar)	-1.96eV/atom	[41]
Aluminene(P6mmm)	-2.32eV/atom	
Aluminene(Buckled)	-3.47eV/atom	
Aluminene(P3m1)	-3.27eV/atom	
Aluminene(Triangular,Pmmn)	-2.76eV/atom	

Aluminene(Triangular,Pmmn)	-3.27eV/atom	
Aluminene(4-layerslab, 8-Pmmn)	-3.16eV/atom	
Gallenene (Puckered)	-2.32eV/atom	
Indiene (Planar)	-1.81eV/atom	
Indiene (Buckled)	-1.83eV/atom	
Indiene (Pucker,sw)	-1.88eV/atom	
Silicene (Buckled)	-4.57 eV/atom	[41]
Silicene (P3m1)	-3.91 eV/atom	[42]
Germanene (Buckled)	-3.24 eV/atom	[42]
Germanene (P3m1)	-2.93 eV/atom	[43]
Stanene (Buckled)	-3.31 eV/atom	[44]
Stanene (P3m1)	-2.73 eV/atom	[42]
Plumbene (Buckled)	-2.28 eV/atom	[45]
SiGe (Buckled)	-4.81 eV/atom	[46]
SiGe (P3m1)	-2.56 eV/atom	[47]
SnSi (Buckled)	-3.61 eV/atom	[48]
SnSi (P3m1)	-.2.28 eV/atom	[49]
SnGe (Buckled)	-3.79 eV/atom	[48]
SnGe(P3m1)	-2.25 eV/atom	[49]
Cu-graphene	2.490eV	[50]
α -CuC	4.99eV	[51]
β -CuC	4.97eV	
α -LiC	4.66eV	
β -LiC	4.66eV	
Cu ₂ Si ₃	3.45eV	
Bulk MoS ₂	4.95eV/atom	[52]
MoS ₂ monolayer	4.96eV/atom	
Table 4. Reported cohesive energies for the various 1D materials along with MoS ₂ NW, Cu-doped MoS ₂ NW, and Cu-MoS ₂ NW		
System	Cohesive energy (eV)	Reference
Mo ₆ Se ₆ NW	-4.97eV/atom	[53]
Mo ₆ S ₃ Se ₃ NW	-5.15eV/atom	
Mo ₆ S ₄ I ₂ NW	-4.93eV/atom	
Mo ₆ Se ₄ I ₂ NW	-4.69eV/atom	
Mo ₆ S ₂ Se ₂ I ₂ NW	-4.81eV/atom	
Mo ₁₂ S ₁₈ NW	-4.88eV/atom	
Mo ₁₂ Se ₁₈ NW	-4.57eV/atom	
Mo ₁₂ S ₆ I ₁₂ NW	-3.86eV/atom	
Mo ₁₂ Se ₆ I ₁₂ NW	-3.73eV/atom	
Mo ₁₂ Se ₉ I ₉ NW	-3.67eV/atom	
MoS ₂ NW	-5.22eV/atm	
Cu-doped MoS ₂ NW	-3.20eV/atom	Present work
Cu-MoS ₂ NW	-5.15eV/atom	Present work

6.3.6 Electron Localization Function Analysis

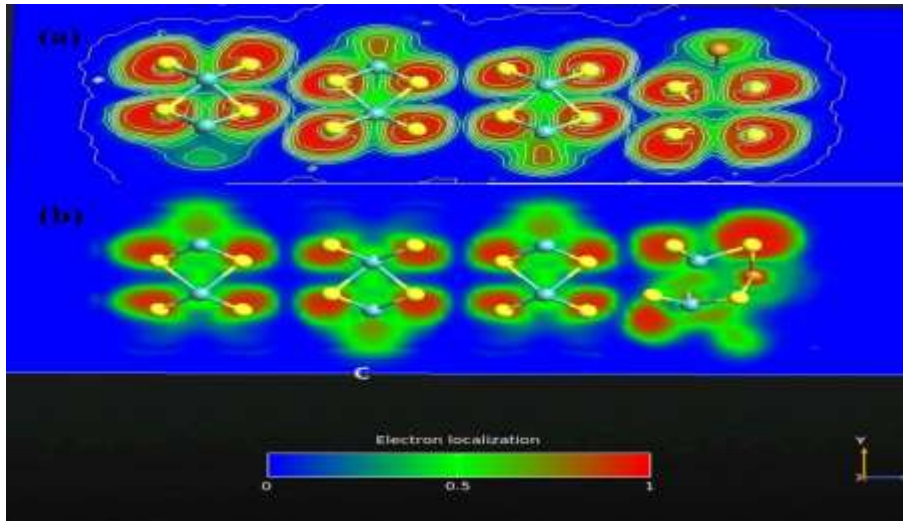


Figure 6.7 ELF plot for (a) Cu-MoS₂ NW system and (b) Cu-doped MoS₂ NW system, respectively. The ELF magnitude is given in a color scheme in which red, blue, and green correspond to high electron density, low electron density, and free electrons, respectively.

We have utilized ELF as an effective tool to visualize electron density distribution, lone pairs, and bonding pairs of electrons around the interacting atom. Therefore, we have performed an ELF calculation for the Cu-MoS₂ NW and Cu-doped MoS₂ NW systems. The ELF plot shown in Figure 6.7 illustrates that the ELF value varies between 0 and 1, with red, blue, and green colours corresponding to the ELF value 1, 0, and 0.5, respectively. The ELF value close to 1 corresponds to a region where electrons are fully localized or have a high electron density. In contrast, the ELF values close to 0 and 0.5 correspond to areas with low electron density and partially delocalized electrons. From Figure 6.7(a), we found a large region of high electron density around the S atoms identified by sizeable red color spherically symmetric rings with a small area of partially delocalized electrons between the Mo-S atoms identified by green spherically unsymmetrical rings. These findings suggest that covalent interaction with a partially ionic nature exists between the Mo and S atoms in the case of the Cu-MoS₂NW system. Additionally, a region of partially delocalized electrons exists between the Cu and Mo atoms, indicating that the Cu and Mo atoms mutually share transferred electrons during the interaction. This confirms that strong covalent bonding exists between the Cu and Mo atoms during the Cu adsorption, which is consistent with our adsorption study. Similarly, for the Cu-doped MoS₂ NW, we found a large spherically red color region around the S atoms rather than Cu atoms, as shown in Figure 6.7(b). These findings suggest that electrons are strongly localized around the S atom compared to the Cu atom, indicating that the Cu atom loses electrons to the nearby S atom, thereby increasing the electron density around the S atom. All these findings confirmed that the interaction of the Cu atom with the nearby S atoms is purely electrostatic. Moreover, a green-colored region exists between the Mo-S atoms, indicating that

electrons are mutually shared between the Mo-S atoms, again confirming that covalent bonding exists between Mo-S atoms. Hence, our ELF result suggests that covalent and electrostatic interaction exists between the Cu atom and MoS₂ NW in the case of Cu-MoS₂ NW and Cu-doped MoS₂ NW systems.

6.3.7 Effect of Cu adsorption on the electronic properties of MoS₂ NW

To analyze the effect of introducing the Cu atom as a foreign atom onto MoS₂ NW, we have calculated DOS and PDOS for the Cu- MoS₂ NW and Cu-doped MoS₂NW systems. From Figures 8(a) and 9(a), we found that continuous impurity states exist around the Fermi level (E_F) for both systems. This indicates that the metallic nature of the MoS₂ NW remained preserved even upon substitutional doping and Cu adsorption onto MoS₂ NW. We also found an increase in the peak intensity for both systems. This indicates that charge transfer occurs during the interaction of the Cu atom with the MoS₂ NW. On comparison, we found that the peak intensity of Cu-doped MoS₂ NW was higher than that of Cu-MoS₂ NW, indicating that significant charge transfer occurs in the case of Cu-doped MoS₂ NW. Significant charge transfer indicates better electrical conductivity of the Cu-doped MoS₂ NW than Cu-MoS₂ NW and pristine MoS₂ NW, making the Cu-doped MoS₂ NW a promising candidate for nanoelectronics. We also observed a shift in the Fermi level towards the conduction band, indicating that the Cu atom has an n-type doping effect. Further, PDOS was calculated to determine the contribution of the atomic orbital to the DOS. The PDOS plot in Figures 6.8(c) and 6.8(d) illustrates there exists multiple overlapping between the 4d(d_{xy}) and 3p(p_z)-S atomic orbitals in the energy range from -1eV to 2eV leading to the strong hybridization between the atomic orbitals to form molecular orbitals responsible for the formation of a covalent bond. Similarly, from Figures 6.8(b) and 6.8(c), we found that the 4s-Cu and 4d(d_{xy})-Mo atomic orbitals overlap in the energy range 0eV to 1eV, indicating strong hybridization and charge was transferred from the 4s orbital of Cu atom to 4d(d_{xy}) orbital of Mo atom during the interaction. In contrast, for the Cu-doped MoS₂ systems, the PDOS plot in Figures 6.9(c) and 6.9(d) illustrated that multiple overlapping exists between the 5s-Mo and 3p(p_z)-S atomic orbitals in the energy range from 0eV to 1eV, indicating strong hybridization between the atomic orbitals to form molecular orbitals involved in the formation of the strong covalent bond between them. From Figures 6.9(b) and 6.9(c), we found that electron transferred from the 4s-Cu atomic orbital to the 3p(p_z)-S atomic orbitals was responsible for the formation of the ionic bond between the Cu and nearby S atoms during the interaction. This type of hybridization indicates that the electronic states are not isolated but are aligned with the existing electronic

states of MoS₂ NW. Consequently, these electronic states act as effective charge carriers, facilitating easy charge transfer from the Cu atom to the MoS₂ NW. These findings indicate that the Cu atom-induced electronic states are less likely to trap charge carriers for long periods, reducing the probability of acting as recombination centers. Moreover, we also noted that the contribution from the Cu atom to the DOS was considerably more significant in the Cu-doped MoS₂ NW compared to the Cu-MoS₂ NW system. This is consistent with our observation that a substantial charge was transferred from the Cu atom to MoS₂ NW in the case of Cu-doped MoS₂ NW, which is consistent with our DOS calculation. Hence, our DOS and PDOS results were in good agreement with each other.

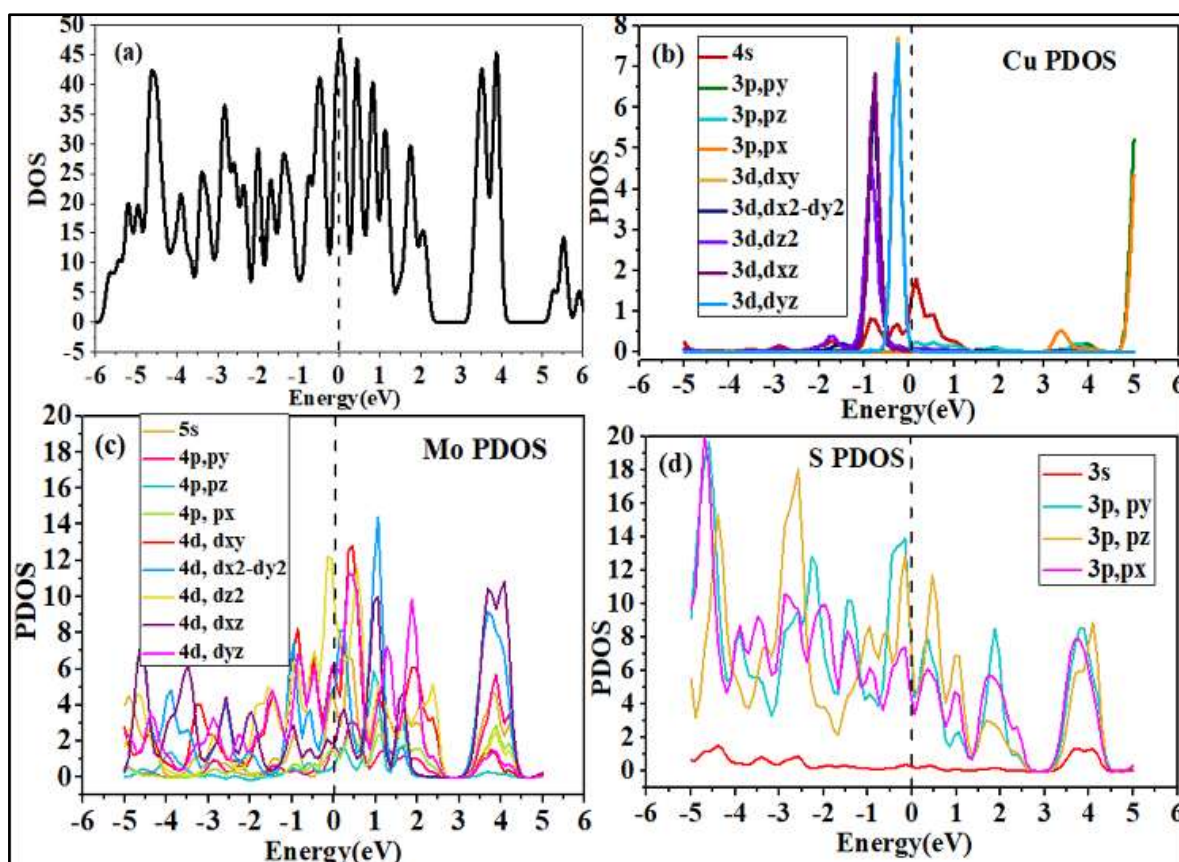


Figure 6.8 Calculated (a) DOS for the Cu adsorbed MoS₂ NW. PDOS for (b) Cu, (c) Mo, and (d) S atoms, respectively. The black dotted line represents the Fermi level.

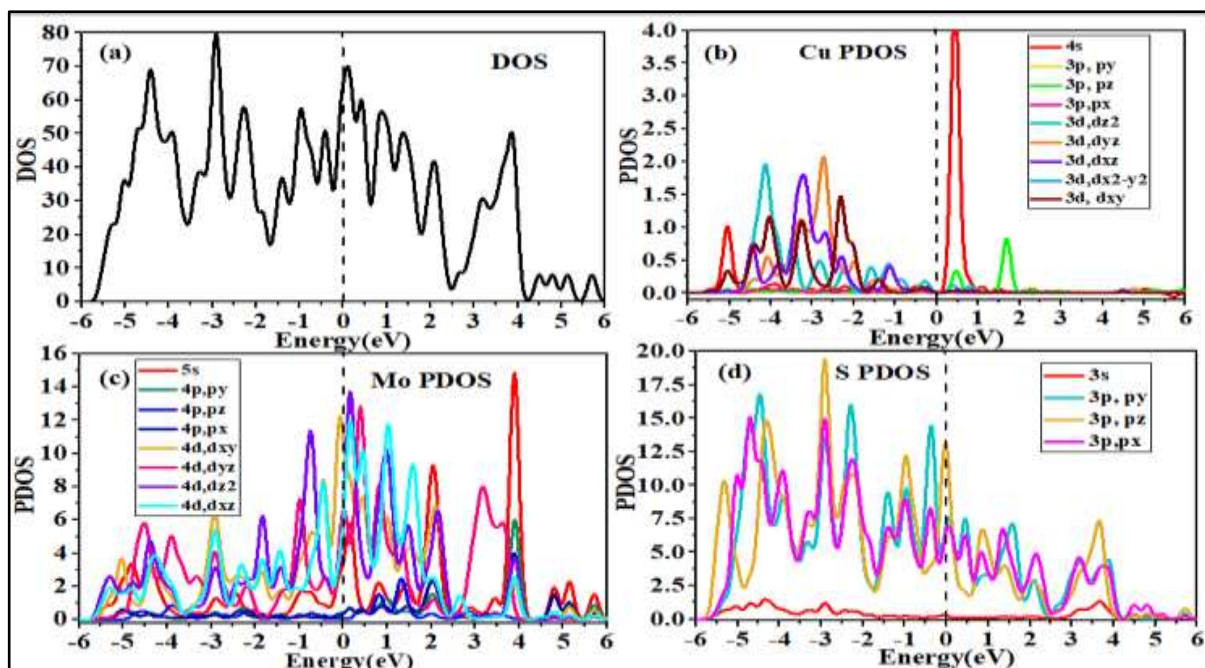


Figure 6.9 Calculated (a) DOS for the Cu-doped-MoS₂ NW. PDOS for (b) Cu, (c) S, and (d) Mo atoms, respectively

6.3.8 Bader Charge and Electron Density Difference Analysis

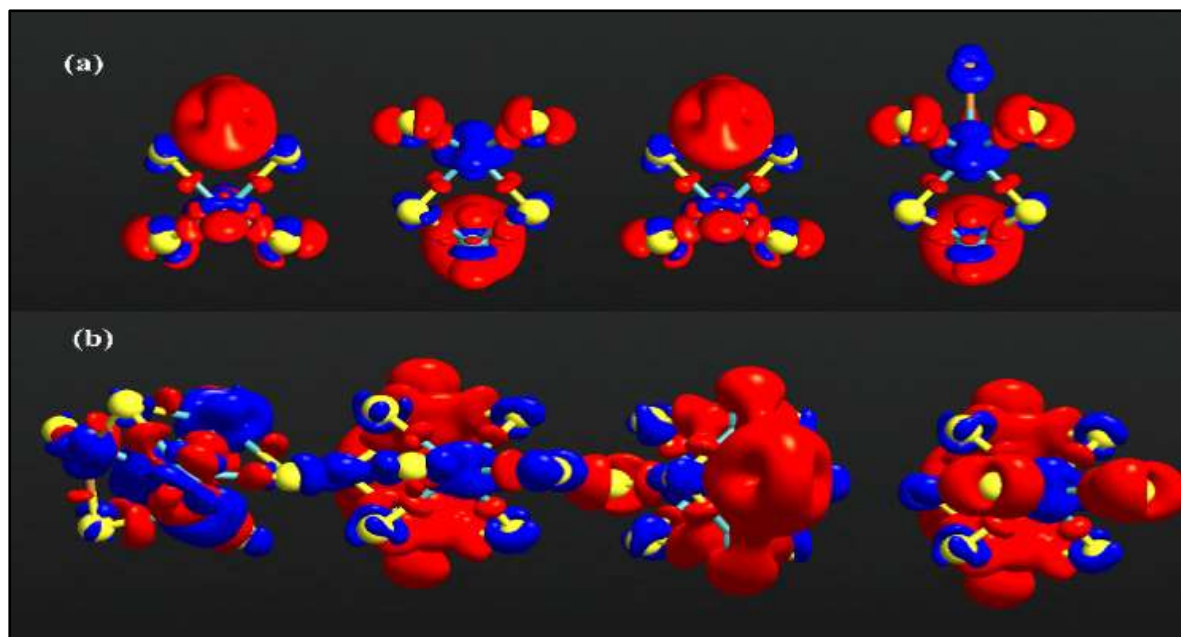


Figure 6.10. Electron density difference diagram for (a) Cu-MoS₂ NW and (b) Cu-doped MoS₂ NW systems. The red and blue regions indicate charge gain and charge loss regions, respectively.

We have performed the Bader charge method and Electron density difference for the Cu-MoS₂ NW and Cu-doped MoS₂ NW systems to analyze the charge transfer mechanism during the interaction. The positive and negative values of the Bader charge indicate charge loss and gain during the interaction. According to the Bader charge method, we found that the Cu atom loses 0.047e to the MoS₂NW in the case of Cu-MoS₂NW, whereas the surface Mo atoms lose

0.692e, 1.344e, 1.414e, and 1.880e to the adjacent S atoms, as shown in Figure 6.11(a). In contrast, for the Cu-doped MoS₂ NW system, we found that the Cu atom loses 0.371e, whereas the nearby neighbouring S atoms gain -0.586e, -0.848e, and -0.745e, as shown in Figure 6.11(b). In comparison, we found that significant charge transfer was observed from the Cu atom in the case of Cu-doped MoS₂NW. These findings validate that the Cu-doped MoS₂NW system exhibits better electrical conductivity than the Cu-MoS₂ NW system. Further, to validate our findings, we have described the charge transfer qualitatively using the electron density difference diagram for the Cu-doped MoS₂NW and Cu-MoS₂NW. The red and blue regions indicate the charge gained and loss region in Figure 6.10. The electron density difference diagram in Figure 6.10(a) illustrates the blue-coloured region around the Cu and Mo atoms, whereas the red-coloured region around the S atom. The red and blue region indicates that the S atom gains electrons, whereas the Mo and Cu atoms lose electrons in the case of Cu-MoS₂NW. In contrast to the Cu-doped MoS₂NW, Figure 6.10(b) illustrates a large red region around the S atom and a large blue region around the Mo and Cu atoms. Large blue and red areas indicate that a substantial charge was gained by the S atom and lost by the Mo and Cu atoms during the interaction. This again suggests that substantial charge transfer occurs from the doped Cu atom to the MoS₂ NW during the interaction. The observed charge lost and gained can be attributed to the difference in the electronegativity between the interacting atoms. According to the Pauling scale, the electronegativity of Mo(χ_{Mo}), S(χ_{S}), and Cu(χ_{Cu}) differ by 13.68% and 35.78% with respect to χ_{Cu} . Slight differences in the electronegativity make Cu and Mo atoms partially positive and negative. This creates a local weak electric field between the Cu and surface atoms, resulting in a weak charge transfer from the Cu atom to the MoS₂NW in the case of Cu-MoS₂NW. Consequently, valence electrons are mutually shared, confirming that the Cu atom interacts with MoS₂ NW via covalent interaction, which agrees with our ELF study. Conversely, considerable differences in the electronegativity between the S-Cu atoms make Cu and nearby S atoms electrons deficient and electrons-rich species. This creates a strong electric field between the interacting S-Cu atoms, causing substantial charge transfer from the Cu atom to the nearby S atom. This is why, upon geometry optimization, the Cu atom got occupied at the interstitial sites where the Cu atom got bonded with the three S atoms to maximize the electrostatic interaction. Hence, our Bader charge analysis agrees with electron density difference results.

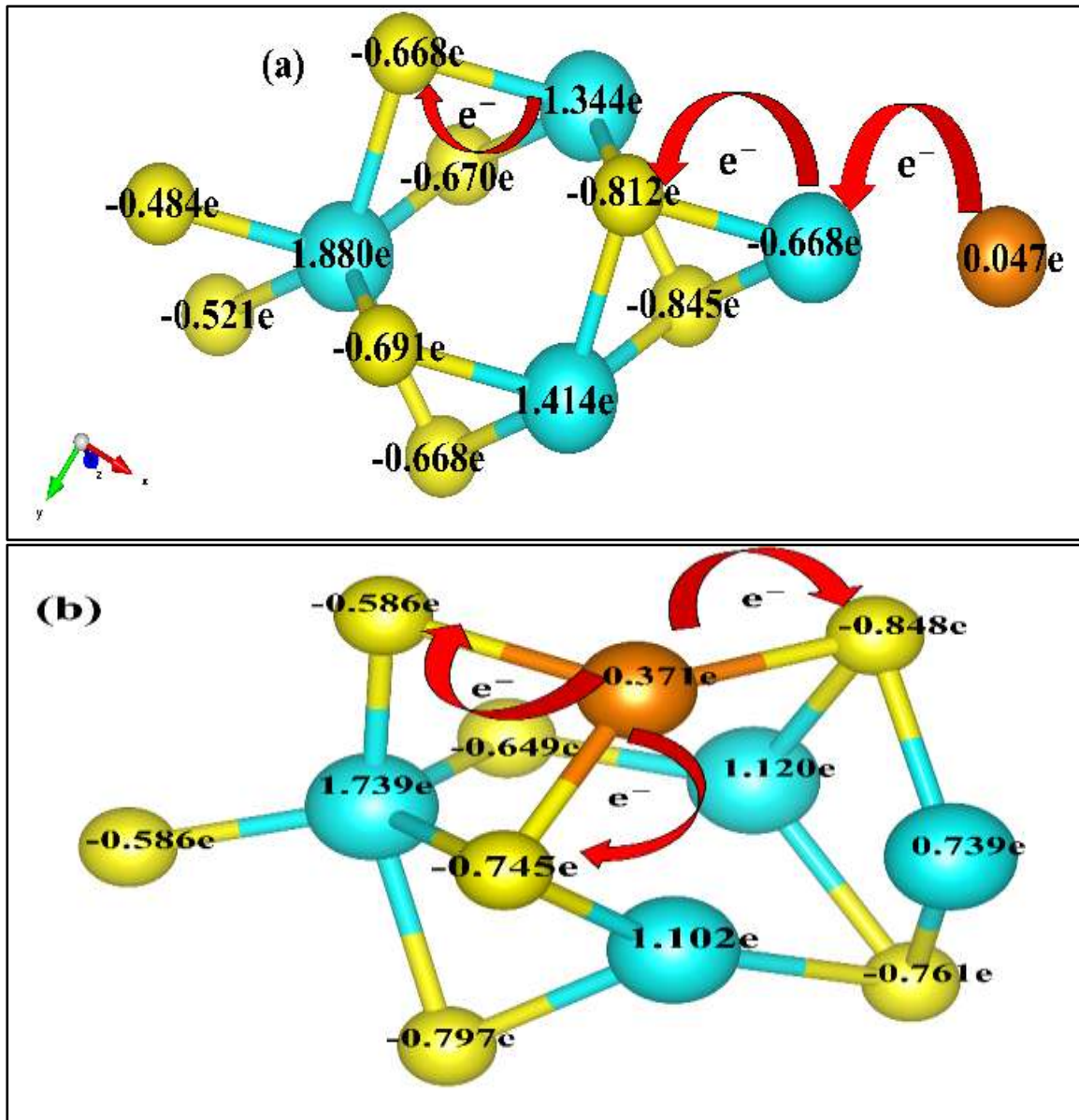


Figure 6.11: Calculated Bader charge distribution for the surface atoms of (a) Cu-MoS₂ NW and (b) Cu-doped MoS₂ NW, respectively. The red arrows represent the directions of electron transfer from the Cu atom to the MoS₂ NW.

6.3.9 Effect of Cu adsorption on the work function of MoS₂ NW

The work function is considered an essential parameter for nanoelectronic devices because any variation in the work function influences the charge injection capability of the material, thereby significantly impacting the performance of nanoelectronic devices. It is observed that the adsorption of transition metal atoms strongly influences the work function. For example- Chi et al. studied the variation in the work function of GaN NW and GaN monolayer upon the alkali metal adsorption using the first principle calculation. They reported that the work function of the GaN monolayer changes from 4.21eV to 2.47eV, 1.88eV, 1.49eV, 1.29eV, and 0.84eV upon the adsorption of Li, Na, K, Rb, and Cs metal atoms onto GaN monolayer[57]. In contrast, they

also observed that the work of the pristine GaN NW changes from 4.11eV to 2.45eV, 2.32eV, 2.06eV, 1.81eV, and 2.38eV upon the adsorption of Li, Na, K, Rb, and Cs metal atoms onto GaN. In another study, Sahin et al.[54] reported that the work function of the silicene changes from 4.77eV to 4.39eV, 4.25eV, 4.09eV, 4.68eV, 4.81eV, 4.47eV, 4.77eV, 4.84eV, 4.65eV, 4.73eV, 4.81eV, 5.0eV, 4.97eV and 4.90eV upon the adsorption of Li, Na, K, Be, Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Mo and W onto silicene. Therefore, based on the above findings, we have also evaluated the variation in the work function of the MoS₂ NW upon substitutional doping and adsorption of the Cu atom. For this purpose, the work function of the pristine MoS₂NW and Cu-doped MoS₂ NW and Cu-MoS₂ NW was calculated using Eqs (6.5).

$$\phi = E_{\text{inf}} - E_F \quad (6.5)$$

Where E_{inf} and E_F represent the electrostatic potential at infinity and Fermi level energy, the electrostatic potential at infinity is assumed to be zero in the present work. Further, the variation in the work function ($\Delta\phi$) for the Cu-doped MoS₂ NW and Cu-MoS₂ NW was calculated by subtracting the work function of the Cu-doped MoS₂ NW and Cu-MoS₂ NW from that of the pristine MoS₂ NW. The computed work function values for the pristine MoS₂ NW, Cu-doped MoS₂ NW, and Cu-MoS₂ NW were found to be 4.99 eV, 3.792 eV, and 3.845 eV, respectively. These findings indicate that the value of the work function decreases and undergoes negative variation to 24% and 22.9% upon substitutional doping and adsorption of Cu atom onto MoS₂NW. A similar trend in the work function was observed by Ouma et al.[55] While studying the effect of substitutional doped and adatoms 3d TM onto the TcS₂ monolayer. The observed variation in the work function of Cu-doped MoS₂ NW and Cu-MoS₂ NW was due to the existence of a strong electric field between the substitutional doped Cu atom and MoS₂NW that facilitates redistribution of electron density around the dopant site and substantial charge transfer from the Cu atom to MoS₂NW. According to Eqs. 6.6, an exponential relationship exists between the emitted electron current densities and variation in the work function.

$$j = AT^2 e^{\left(\frac{-\Delta\phi}{k_B T}\right)} \quad (6.6)$$

Where j is the emitted electron current densities (A/m²), A is a Richard constant (A/m² K²), ϕ is the work function of the material in eV, T is the temperature in K, and k_B is the Boltzmann constant in eV/K respectively. Therefore, a significant variation in the work function of Cu-doped MoS₂NW than Cu-MoS₂NW indicates better electron emission capability of Cu-doped MoS₂NW. Hence, the work function analysis suggests that the Cu-doped MoS₂NW system can be utilized in field emission devices.

4.0 Conclusion

In this study, we have systematically investigated the structural and electronic properties of substitutional doping and adsorption of Cu atom onto MoS₂ NW using first-principles calculation. According to the adsorption study, the Cu atom prefers to be adsorbed at the Mo site with an adsorption energy of about -1.70eV. This results in the chemical bond formation between the Cu atom and MoS₂NW during the interaction. In contrast, substitutional doping of the Cu atom distorts the structure to accommodate the Cu atom and exhibits strong covalent bonding with the Cu atom. According to the Bader charge method, the Cu atom loses 0.047e and 0.371e to the MoS₂ NW in the case of Cu-MoS₂NW and Cu-doped MoS₂NW, respectively. Significant charge transfer leads to enhancement in the conductivity and variation in the work function. The DOS results suggest that the Cu atom induces an electronic state near the Fermi level, facilitating easy charge transfer from the Cu atom to MoS₂NW. There was also a shift in the Fermi level towards CB, indicating that the Cu atom has an n-type effect on substitutional doping and adsorption. From the work function calculation, we found that the work function of the Cu-doped MoS₂ NW and Cu-MoS₂NW systems undergo 24% and 22.9% with respect to that of pristine MoS₂NW. Further from the PDOS study, we found that in case of Cu-MoS₂NW strong hybridization exists between the 4d(d_{xy})-Mo and 3p(p_z)-S atomic orbitals responsible for the formation of covalent bond whereas for the Cu-doped-MoS₂ systems, hybridization between the 4s-Cu atomic orbital to the 3p(p_z)-S atomic orbitals was responsible for the formation of the ionic bond between the Cu and nearby S atoms during the interaction. Moreover, our calculated cohesive energy suggests that the pristine MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂NW systems are thermodynamically stable. Finally, our DFT result suggests that substitutional doping is an effective way to modulate the electronic properties of MoS₂NW as Cu-doped MoS₂ NW systems exhibit better electrical conductivity than pristine MoS₂NW and Cu-MoS₂NW due to better charge transfer and variation in the work function. Thus, the Cu-doped MoS₂NW system is a promising candidate for nanoelectronics and field emission device applications.

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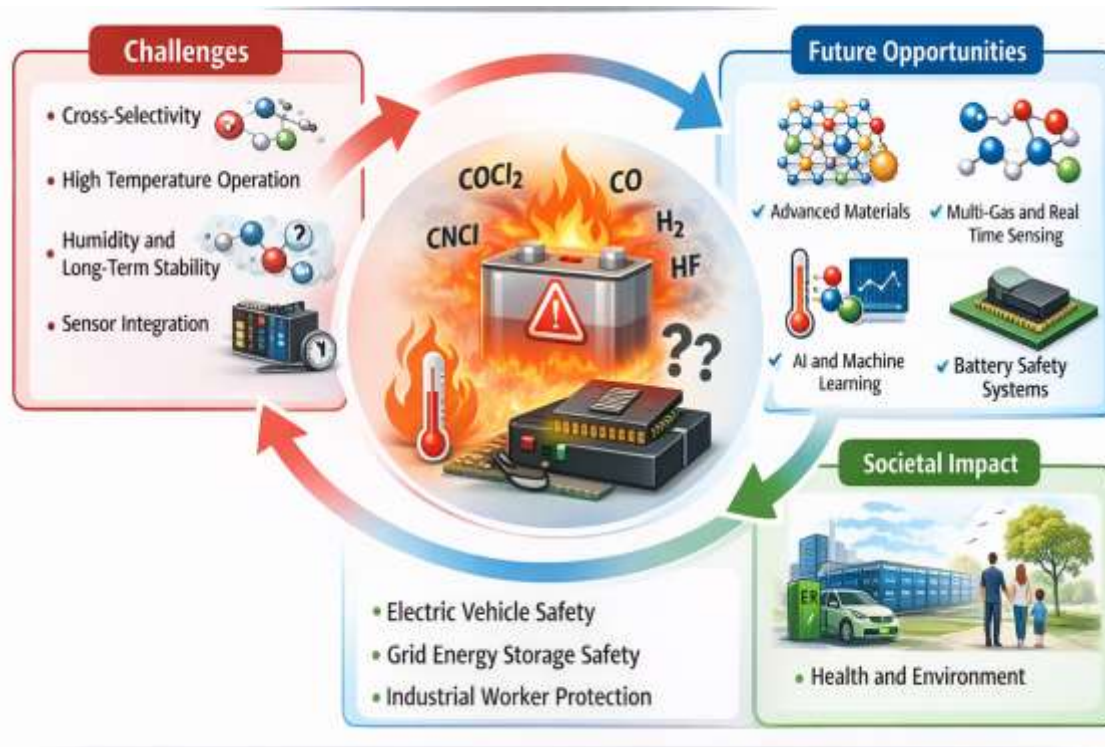
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Chapter 7

Conclusions, Future Scope and Social Impact



The main goal of this chapter is to highlight the key findings, significant observations, results and discussions arising from our current research work. In addition, this chapter presents the salient outcomes of the thesis, along with how the limitations of our current research study have opened pathways for future research. The potential directions include advancing computational methodologies, developing effective strategies to enhance the selectivity and sensitivity of the proposed sensing materials, and exploring various 2D materials for sensing applications to detect industrial toxic gases such as COCl_2 , CNCl , as well as thermal runaway gases generated by lithium-ion batteries. Finally, the chapter discusses how the present research work contributes towards the betterment of our society.

7.1 SUMMARY OF RESEARCH WORK

Gas sensing is an interesting area of research due to its applications in industrial safety, healthcare, and environmental monitoring. A proper understanding of the interaction between the target gas and the sensing surface at the atomic level is essential for fabricating high-performance sensors. Therefore, the current thesis presents a detailed theoretical investigation of the adsorption of industrial toxic gases, such as COCl_2 and CNCl , and thermal runaway gases generated from lithium-ion batteries onto Cu-decorated hBN nanosheets using DFT. The current DFT study involves the structural optimisation of various adsorption configurations and the analysis of the electronic and sensing properties of Cu-decorated hBN to evaluate its practical implementation as a sensing material for the detection of toxic industrial gases, such as COCl_2 , CNCl , and thermal runaway gases. The key contributions discussed in the various chapters of the present thesis are summarised as follows:

CHAPTER 1- Air pollution due to the release of hazardous toxic gases such as C_2H_4 , CH_4 , CO_2 , CO , H_2 during the thermal runaway condition in Li-ion batteries, COCl_2 and CNCl from the industrial activities has posed a serious threat to human health and the environment. Effective mitigation of this problem requires the development of highly sensitive, selective, and reliable gas-sensing technologies capable of real-time monitoring. This chapter provides a comprehensive overview of chemoresistive gas sensors, emphasising their working principles based on gas adsorption, charge transfer, and conductivity modulation in n-type and p-type semiconductors. Special attention is given to two-dimensional (2D) materials, due to their large surface-to-volume ratio, tunable electronic properties, and abundant active sites, which make them promising candidates for next-generation gas sensors. The sensing mechanisms, advantages, and limitations of various 2D materials—including graphene, reduced graphene oxide, transition metal dichalcogenides, black phosphorene, $\text{g-C}_3\text{N}_4$, MXene, metal–organic frameworks, and hexagonal boron nitride—are systematically discussed. Strategies such as elemental doping, surface functionalization, and substrate engineering are highlighted as effective routes to enhance sensor sensitivity, selectivity, and response dynamics. Finally, the chapter outlines research objectives that integrate with DFT calculations to elucidate gas adsorption mechanisms, optimize sensing performance, and guide the design of high-performance, stable, and practical gas sensors for the detection of toxic gases. .

CHAPTER 2- In this chapter, the theoretical foundations and practical realisation of Density Functional Theory (DFT) are taught as a powerful framework for studying many-electron

systems. It explains how the Hohenberg–Kohn theorems establish the electron density as the central quantity that uniquely determines the ground-state wave function, the total energy, the external potential, and all observables, thereby reducing the complexity of the many-body Schrödinger equation. The chapter shows how the variational principle leads to an energy functional whose minimum corresponds to the actual ground state, while also highlighting why early approaches like the Thomas–Fermi model are inadequate due to their neglect of exchange and correlation effects and their inability to describe molecular stability. A key learning outcome is the introduction of exchange–correlation energy, which accounts for both Pauli exclusion (exchange) and electron–electron interactions (correlation), and the recognition that its exact form is unknown and must be approximated. The Kohn–Sham formulation is considered the most practical implementation of DFT, replacing the interacting many-body problem with an auxiliary non-interacting system that reproduces the correct electron density through a self-consistent cycle, which forms the basis of modern first-principles calculations. The chapter also clarifies the interpretation and limitations of Kohn–Sham eigenvalues, the origin of the band-gap problem due to derivative discontinuities in the exchange–correlation functional, and why local and semi-local approximations such as LDA and GGA often underestimate band gaps. Finally, by comparing the Kohn–Sham, Hartree, Hartree–Fock, and Dyson equations, the chapter provides insight into how DFT connects to many-body theory, emphasising both its computational efficiency and the ongoing need for improved functionals to describe strongly correlated systems accurately.

CHAPTER 3- The adsorption behaviour of a pristine hBN monolayer and Cu-decorated hBN monolayer for the detection of toxic gases, such as COCl_2 , was investigated using first-principles calculations based on DFT. The results indicated that the interaction between COCl_2 and pristine hBN was weak, as evidenced by low adsorption energies across various configurations, leading to a poor recovery time. To improve the adsorption affinity of hBN, we introduced copper (Cu) atoms through substitutional doping (Cu-doped hBN) and surface adsorption (Cu-hBN). The adsorption study revealed strong chemical interactions, with COCl_2 adsorption onto Cu-hBN and Cu-doped hBN. Further analyses, including Density of States (DOS), Hirshfeld atomic charges, charge density differences, ELF, and Reduced Density Gradient (RDG) calculations, were performed for the Cu-doped hBN and Cu-hBN configurations. The resulting DOS plots demonstrated that COCl_2 adsorption enhanced electrical conductivity by 72.25% and 54.13%, respectively, due to a reduction in the band gap. Hirshfeld and ELF analyses indicated significant charge transfer in the COCl_2 -Cu-doped hBN

and COCl_2 -Cu-hBN systems compared to the COCl_2 -hBN configuration. ELF analysis further showed that the Cu atoms transferred electrons to COCl_2 , confirming that the adsorbates acted as electron donors and that COCl_2 served as an electron acceptor. Additionally, RDG analysis revealed that van der Waals interactions predominated in the COCl_2 -hBN system, while strong, attractive interactions were observed in the COCl_2 -Cu-doped-hBN and COCl_2 -Cu-hBN systems. Finally, the recovery time for both the COCl_2 -Cu-doped-hBN and COCl_2 -Cu-hBN systems was measured at elevated temperatures under visible light.

CHAPTER 4- In this chapter, we have investigated the adsorption of toxic gas such as Cyanogen Chloride (CNCl) onto the pristine and Cu-decorated hexagonal boron nitride (hBN) using DFT. The adsorption of CNCl gas molecules onto pristine hBN was a physisorption, resulting in a poor recovery time. However, Cu decoration on hBN enhanced the adsorption energy and modified its electronic properties. The calculated adsorption energies suggest that CNCl adsorption onto Cu-hBN is physisorption, with an enhanced adsorption energy. Furthermore, various parameters, including DOS, charge density differences, and ELF, were calculated for the most stable adsorption configuration. The DOS result revealed that CNCl adsorption enhances the conductivity by reducing the band gap. It was due to charge transfer from CNCl gas to Cu-hBN, as verified by the charge density difference. The reduction in the band gap resulted in a 31.54% variation in the work function, indicating highly sensitive behaviour of the Cu-hBN system. Additionally, RDG analysis suggests that the non-covalent interaction between CNCl and Cu-hBN was responsible for the physisorption. Finally, the recovery time for CNCl adsorbed onto Cu-hBN was found to be 1.596×10^{-5} , 2.525×10^{-7} sec, and 2.098×10^{-8} sec at 300K, 400K, and 500K, respectively.

CHAPTER 5- In this chapter, Lithium-ion batteries, due to their environmental friendliness and high energy capacity, are extensively used in the field of transportation and energy storage. However, thermal runaway in lithium-ion batteries poses a serious threat to human life. Therefore, to address these issues, we have investigated the adsorption mechanisms of thermal runaway gases (C_2H_4 , CO, CO_2 , H_2 , and CH_4) on pristine hBN and Cu-doped hBN using DFT. The adsorption of C_2H_4 , CO, CO_2 , H_2 , and CH_4 gas molecules onto pristine hBN was physisorption, resulting in poor recovery time, charge transfer, selectivity and sensitivity. However, substitutional doping of the Cu atom at the B vacancy leads to chemical adsorption of thermal runaway gases. DOS calculations showed that the adsorption of C_2H_4 , CO, CO_2 , H_2 , and CH_4 gas molecules reduces the band gap of Cu-doped hBN, indicating chemoresistive behaviour. Further, various other calculations, including charge density differences, showed

that C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas act as electron donors, and Cu-doped hBN as an electron acceptor. In contrast, RDG calculation confirmed that weak vdW and strong attractive types of non-covalent interaction exist in the case of pristine hBN and Cu-doped hBN, respectively. Finally, our DFT results confirmed that Cu-doped hBN exhibits enhanced sensitivity and recovery time to thermal runaway gases, making it a potential sensing material for gas sensors.

CHAPTER 6- In this study, we have investigated the effect of substitutional doped (Cu-doped MoS_2NW) and surface-adsorbed Cu atom (Cu- MoS_2NW) on the electronic properties of MoS_2 nanowire (NW) using DFT. Our adsorption study revealed that the adsorption of the Cu atom was a chemisorption. ELF analysis indicates that the Cu atom forms covalent bonds with MoS_2NW upon adsorption and ionic bonds upon substitutional doping. These findings suggest that a charge transfer occurred between the Cu atom and MoS_2NW during the interaction, confirmed by the Bader charge method. Further, the work function calculation indicates that Cu-doped MoS_2NW exhibits a significant negative variation in the work function, indicating enhanced electron emission capability of the Cu-doped MoS_2NW systems. All of our systems are thermodynamically stable based on our cohesive energy calculations. Overall, the DFT results suggest that Cu-doped MoS_2NW systems exhibit superior electrical conductivity, enhanced charge transfer, and larger variation in the work function compared to pristine MoS_2NW and Cu- MoS_2NW . These findings confirmed that substitutional doping is an effective means of modifying the electronic properties of MoS_2NW . Therefore, Cu-doped MoS_2NW systems hold potential for applications in field emission and nanoelectronics devices.

7.2 SAILENT FEATURES OF THE THESIS

The present thesis highlights the following salient features and key contributions: -

- 1. Adsorption behaviour and strong affinity of Cu-decorated hBN-** The adsorption energies calculated for $COCl_2$ and thermal runaway gases like C_2H_4 , CO , CO_2 , CH_4 and H_2 adsorbed onto Cu-decorated hBN were found to be relatively higher than in the case of $CNCl$ gas adsorbed onto Cu-decorated hBN. This is because elemental Cu doping of hBN plays a pivotal role in enhancing its gas-sensing performance. The Cu dopant introduces localized electronic states near the Fermi level. These Cu-induced active sites interact strongly with oxygen-containing analytes through orbital hybridization between Cu (3d) states and O (2p) states, accompanied by significant charge transfer. As a consequence, Cu decoration substantially improves the sensitivity, selectivity, and overall sensing performance of hBN, particularly toward oxygen-containing analytes such as $COCl_2$, CO and CO_2 .

2. Effect of Annealing under UV illumination on the recovery time- The calculated recovery time at room temperature was found to be considerably high. This indicates that the desorption kinetics of adsorbed gas molecules from the surface of the Cu-decorated hBN were very slow, hindering the reusability and continuous operation of Cu-decorated hBN-based gas sensors under ambient conditions. But annealing at elevated temperature in the presence of ultraviolet radiation facilitates faster desorption of the adsorbed species. As a consequence, the recovery time of the Cu-decorated hBN for all the gases improves significantly, thereby validating that annealing under ultraviolet radiation is an effective strategy to enhance the reusability of the Cu-decorated hBN-based gas sensor.

3. Enhanced selectivity of Cu-decorated hBN towards toxic gases and thermal runaway gases – The Cu-decorated hBN-based gas sensor exhibits high selectivity between the toxic industrial gases, such as CNCl, COCl₂ and thermal runaway gases. The observed variation in selectivity arises from differences in charge transfer, leading to significant modulation of electronic properties upon gas adsorption. However, the proposed Cu-decorated hBN-based gas sensor also showed poor selectivity in distinguishing between C₂H₄, CO, CO₂, and CH₄, owing to their comparable molecular sizes, electronic configurations, and similar interactions with the Cu active site. While this limits fine-level differentiation among these gases, the sensor remains highly effective for broader classification between toxic gases and thermal runaway indicators.

7.3 FUTURE PERSPECTIVE

The research presented in this thesis provides a detailed theoretical framework for the application of 2D materials as sensing materials for the detection of toxic industrial gases such as COCl₂ and CNCl, and of Thermal runaway gases such as C₂H₄, CO, CO₂, H₂, and CH₄ released from lithium-ion batteries, using DFT. It is through DFT that we have gained detailed insights into the adsorption of these toxic gases, the charge-transfer process, the modulation of electronic properties upon adsorption, and the role of non-covalent interactions in gas sensing. Although the current DFT study provides valuable insight into gas-surface interactions for researchers advancing gas sensors, several essential aspects remain open and require further investigation.

1. Enhancement in the computational methodology beyond standard DFT for gas sensing studies- In future, the DFT studies may involve the usage of hybrid exchange correlation functions such as HSE06 to accurately predict the modulation in the band gap of 2D materials upon the adsorption of gas. In addition, spin polarisation calculations can be performed to

identify the whether the adsorption of the toxic gases such as COCl_2 and CNCl , and Thermal runaway gases such as C_2H_4 , CO , CO_2 , H_2 , and CH_4 released from lithium-ion batteries induces magnetic moment and the correlation between magnetism and sensing response, thereby determining whether the proposed sensing material can be used as a spintronic sensor to detect these toxic gases.

2. Exploration of various novel 2D materials as gas-sensing materials- Besides hBN, there exist multiple families of two-dimensional materials such as 2D Transition metal dichalcogenides (MoS_2 , WS_2 , MoSe_2 , WSe_2), MXene ($\text{Ti}_3\text{C}_2\text{T}_x$, V_2CT_x , Nb_2CT_x , Hf_2MnC_2 , Hf_2VC_2 , Cr_2TiC_2), 2D layered Transition metal oxide semiconductors (TiO_2 , MnO , FeO , SrTiO_3 , LaMnO_3 , LaCoO_3 , CaMnO_3 , V_2O_3 , VO_2), 2D layered halide perovskites (Caesium Tin Chloride (Cs_2SnCl_6), Caesium Tin Bromide (CsSnBr_6), Caesium Tin Iodide (Cs_2SnI_6), Butyl Ammonium lead Bromide(BA_2PbBr_4)), 2D layered double hydroxide (Ni-Al-LDH , Co-Al-LDH , Zn-Al-LDH , Mg-Al-LDH , Co-Fe-LDH), 2D layered metal oxides (ZnO , SnO_2 , In_2O_3), Graphene and their derivatives whose gas sensing properties towards these toxic and hazardous gases can be explored using DFT.

3. Application as a VOC-based biosensor for early lung cancer detection- The early detection of volatile organic compounds such as ethane, n-pentane, aldehydes like hexanal, nonanal, ketones like acetone, 2-butanone and certain aromatic hydrocarbons, including Benzene and Toluene. In the future, the sensing properties of various 2D transition-metal dichalcogenides will be studied. 2D layered Transition metal oxide semiconductors, 2D layered halide perovskites, 2D layered double hydroxide, 2D layered metal oxides, Graphene and their derivatives can be investigated using DFT towards the detection of these VOCs, which would lead towards the development of highly sensitive and selective breath analysers, thereby transforming lung cancer screening and monitoring.

4. Effective strategies for enhancing the gas-sensing performance of the hBN- In the future, the gas-sensing performance of the hBN monolayer can be further explored and enhanced using several effective strategies. These include surface functionalization, wherein the surface properties of hBN can be tuned through substitutional doping with transition metals atoms such as Fe, Co, Ni, Ag, Au, Pt, and Pd, as well as by coating the hBN surface with conducting polymers including polyaniline (PANI), polythiophene (PTH), poly(3,4-ethylenedioxythiophene) (PEDOT), Polypyrrole, and polyacetylene. Additionally, defect engineering approaches can be employed by creating vacancies at the interstitial sites of the

hBN monolayer. Furthermore, synergistic effects arising from heterostructure formation with suitable materials, such as MoS₂, graphene, MXene, ZnO, SnO₂, TiO₂, and metal–organic frameworks (MOFs), can be investigated to improve sensing performance in future.

7.4 SOCIETAL IMPACT AND CONCLUSIONS

The rapid expansion of industrialisation, urbanisation, and automobilization has increased air pollution and airborne diseases, posing a serious threat to human health and environmental safety. A gas sensor capable of exhibiting high sensitivity, selectivity, sensing response and stability is of utmost importance in this situation. Therefore, when hBN is substitutionally doped with a Cu atom and analysed using DFT, it has emerged as a cost-effective method to improve the sensitivity and selectivity of the hBN-based gas sensor. Such advancements in hBN-based gas sensors can enable early detection of hazardous gases in automobiles, industries, and urban areas, thereby minimising health risks and both industrial and automotive accidents. In the long term, the implementation of efficient, low-power, and cost-effective Cu-decorated hBN-based gas sensors can support cleaner air, safer workplaces, and sustainable technological development, contributing positively to societal well-being.



Adsorption mechanism of Phosgene gas onto the pristine hBN and Cu-decorated hBN: A DFT study

Anurag Bhandari^a, Piyush Dua^b, Mukhtiyar Singh^a, Kamal Upreti^c, Shubham Mahajan^d, S.S. Askar^e, Mohamed Abouhawwash^{f,g}, Nitin K. Puri^{a,h,*}

^a Department of Applied Physics, Delhi Technological University, Delhi, 110042, India

^b Department of Applied Sciences, DSS Global University, Solasqui, Central Hape Town, Delatras, Uttarakhnad, 248011, India

^c Department of Computer Science, CTRIST, Delhi, NCR Campus, Ghaziabad, India

^d Ansys School of Engineering & Technology, Ansys University Maryana, India

^e Department of Statistics and Operations Research, College of Science, King Saud University, Riyadh, 11451, Saudi Arabia

^f Department of Animal Science, Michigan State University, East Lansing, MI, 48824, USA

^g Department of Mathematics, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

^h National Institute of Electronics & Information Technology (NIELIT), Patna, India, 801106

ABSTRACT

The adsorption behavior of pristine hBN monolayer and Cu-decorated hBN monolayer towards the detection of toxic gas such as COCl_2 were explored using the first principle calculations based on Density Functional Theory (DFT). The calculated low adsorption energy for the A4 configurations indicates that the interaction of the COCl_2 gas with pristine hBN was weak, resulting in poor recovery time. Therefore, to enhance the adsorption affinity of hBN, the Cu atom was adsorbed onto the surface of hBN (Cu-hBN) and substitutionally doped (Cu-doped hBN). It was based on energy minimization, and B2 and C2 configurations were the most stable configurations among the different adsorption configurations. The adsorption study revealed that strong chemical interaction exists, and the adsorption of COCl_2 gas onto Cu-hBN and Cu-doped hBN was a chemisorption. Further, various calculations such as DOS, Hirshfeld atomic charge, charge density differences, ELF, and RDG were calculated for the most stable configurations. The resulting DOS plot revealed that the COCl_2 adsorption enhances the electrical conductivity due to the 72.25 % and 54.13 % reduction in the band gap. Hirshfeld and ELF analysis showed that substantial charge transfer occurs in the case of B2 and C2 compared to A4 configurations. ELF analysis revealed that the Cu atom loses electrons to the COCl_2 , confirming the behavior of adsorbates as electron donors and COCl_2 as electron acceptors. Furthermore, RDG analysis revealed vdW interaction in the case of A4, whereas strong, attractive interaction exists in the case of B2 and C2 adsorption configurations. Finally, the calculated recovery time for B2 and C2 adsorption configurations at elevated temperatures under visible light suggests that Cu-doped hBN and Cu-hBN systems can be utilized as a sensing material in gas sensors to detect COCl_2 gas at high temperatures.

1. Introduction

Toxic carbonyl compounds such as phosgene [1] (COCl_2), a colorless gas, are primarily used in industries to produce polymeric isocyanates, carbamates, pharmaceuticals, and pesticides. It has also been used as a chemical warfare agent during World War I [2]. Exposure to its vapor resulted in throat swelling, change in voice, pulmonary irritation, or pulmonary edema. [3,4]. Recently, accidental exposure to the COCl_2 gas due to the derailment of a freight train carrying vinyl chloride resulted in an environmental hazard near East Palestine, Ohio. [5]. Therefore, considering the industrial utility and the adverse effects of COCl_2 gas on the environment and human health, there is an inevitable need to detect and monitor COCl_2 gas under the permissible limit of 0.1 ppm in the air for the safety of human civilization and a cleaner environment. In this

regard, robust gas sensors capable of exhibiting better selectivity, sensitivity, and fast recovery time in harsh environments are required.

A wide range of research is ongoing in the search for optimal gas-sensing materials capable of detecting hazardous and toxic gas molecules. At present researchers have extensively explored as a gas sensing material diverse range of layered two-dimensional materials (2D) such as graphene [6], black phosphorene [7], germanene [8], silicene [9], transition metal chalcogenides (TMCs) [10], transition metal dichalcogenides (TMDs) [11,12], Aluminium Nitride (AlN) [13], indium Nitride (InN) [14] and MXene [15] due to their high surface area to volume ratio, a large number of active sites, tunable band gap, and optical properties, good compatibility with the device integration [16]. Despite such unique properties, these materials exhibit poor selectivity and sensitivity at high temperatures, which hinder the practical

* Corresponding author.

E-mail addresses: dr-patna@nietlit.gov.in, nitinkumarper@dtu.ac.in (N.K. Puri).

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implementation of these materials as gas-sensing materials to detect toxic and hazardous gas molecules in harsh environments [17]. Therefore, sensing materials capable of exhibiting good sensitivity and selectivity in harsh environments are required. In this regard, atomically thin hexagonal boron nitride (hBN), known as “white graphene,” can be considered a promising sensing material in harsh environments due to its exceptional properties, such as wide band gap, high thermal conductivity, better temperature stability, resistance to oxidation, and excellent chemical inertness [18,19]. However, numerous studies exist reporting the usage of hBN monolayer as a gas sensor and biosensor [20, 21]. On the other hand, these studies have also reported the sluggish response, poor selectivity, and instantaneous recovery time of the hBN-based gas sensor due to the weak interaction between the gas and hBN [22–24]. Therefore, to counter the problem of weak gas adsorption capability of the sensing material, researchers have adopted the technique of surface functionalization through elemental doping [25–27], substrate engineering [28,29], and defect engineering [30–32]. It has been well proven that doping Transition metal (TM) onto 2D materials significantly enhances the adsorption capability of 2D materials. For example, Liu et al. investigated the gas sensing capability of TM (Fe, Pd, Co) doped MoTeSe monolayer in detecting thermal runaway gases of lithium-ion batteries. He concluded that adding TM dopants enhances the conductivity and adsorption capability of the MoTeSe monolayer [33]. N Yuskel et al. examined the gas-sensing capability of both Pt and Pd-doped graphene sheets in detecting propylene oxide (PO). His findings indicate that Pt and Pd-doped graphene sheets can effectively adsorb PO. In another study, Wang et al. discovered that the adsorption of four greenhouse gases such as CH_4 , N_2O , CO_2 , and SF_6 , onto pristine GeSe monolayer was physisorption. However, after modifying it with a Pd atom, he observed better adsorption affinity and sensitivity in the Pd-GeSe monolayer for N_2O and SF_6 gas molecules [34]. Despite such advances, numerous kinds of literature exist reporting the utilization of various morphologies of hBN as a gas sensor to detect COCl_2 gas. For example, Mohammadi et al. reported that the adsorption of H_2S , Cl_2 , NH_3 , and COCl_2 gas onto $\text{B}_{12}\text{C}_6\text{N}_6$ was physisorption. However, Li-decorated $\text{B}_{12}\text{C}_6\text{N}_6$ exhibits excellent sensitivity towards Cl_2 and COCl_2 gas molecules [35]. Hussain et al. studied the adsorption of COCl_2 onto Cu-decorated $\text{B}_{12}\text{N}_{12}$ nanocage. His finding indicates that Cu atom decoration onto $\text{B}_{12}\text{N}_{12}$ nanocage enhances the adsorption strength, stability, and chemical reactivity of $\text{B}_{12}\text{N}_{12}$, and Cu-decorated $\text{B}_{12}\text{N}_{12}$ nanocage can be used as an efficient gas sensor for the detection of COCl_2 gas molecule [36]. Beheshtain et al. emphasized that Sc-doped boron nitride nanotube (BNNT) can be utilized as an electronic sensor to detect COCl_2 gas molecules. This can be attributed to the significant enhancement in the adsorption strength and electrical conductivity of Sc-BNNT [37]. However, from the above literature survey, we found that there have been no reports regarding the adsorption behavior of Cu-decorated hBN towards COCl_2 . This lack of prior research led us to investigate the adsorption behavior of Cu-decorated hBN towards COCl_2 gas. For this purpose, we have decorated Cu atoms onto hBN via (a) substitutional doping [38,39] and (b) surface charge transfer doping [40,41]. Therefore, in the present study, we have investigated the adsorption of COCl_2 onto substitutionally doped Cu atoms and adsorbed Cu atoms using DFT. Here, the adsorption energy and distances were calculated to determine the interaction strength upon COCl_2 adsorption onto the hBN, substitutionally doped Cu atom, and surface-adsorbed Cu atom. Further, to analyze the effect of COCl_2 gas adsorption, we have calculated DOS and PDOS for various adsorption configurations, respectively. For the quantitative and qualitative analysis of the charge transfer during the interaction of COCl_2 with the adsorbents, we calculated the charge density difference and Hirshfeld atomic charge. Further, RDG and ELF analyses were performed to examine any non-covalent interaction and electron density distribution around the interacting atoms. Finally, the recovery time and sensitivity were calculated to examine the performance of the Cu-doped hBN, Cu-hBN, and pristine hBN systems upon COCl_2 adsorption.

2. Computational details

All the computational calculations were carried out within the framework of DFT using the QUANTUM ESPRESSO software package. [42]. To describe the correlation between the electrons, we have used Generalized Gradient Approximation (GGA) [43] with Perdew Burke-Ernzerhof (PBE) [44] as an exchange-correlation (XC) function. A Plane wave basis within the framework of the projector augmented wave (PAW) [45] was implemented with ultrasoft pseudopotential to represent the electron-ion interaction. For the proper convergence of the self-consistent field (SCF) calculation, we have performed a convergence test to determine the optimized cut-off energy and K points. The convergence test results shown in Fig. 1(a) and (b) illustrate that 55Ry and $7 \times 7 \times 1$ are the optimized cut-off energy and K points. To simulate, the hBN monolayer 5X5 supercell was created by repeating the unit cell 5 times along the X and Y axes. Further, a vacuum layer of 20 Å was applied along the z-axis to obstruct the interaction between the periodic replicas. We have implemented the “Grimme DFT-D2” [46] method to consider the weak vanderwaal (vdW) interaction accurately in the layered structure. All the geometries were completely optimized until the energy, pressure, and force convergence were less than 10^{-6} Ry, 0.5 kbar, and 10^{-3} Ry/Bohr, respectively, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme. VESTA software was utilized to calculate the adsorption distance and bond angle and visualize the charge density difference diagram for various optimized adsorption configurations. In addition, Multiwin and VMD software were also utilized to visualize the RDG scatter and RDG isosurface plots.

3. Result and discussions

3.1. Electronic and structural properties analysis of the pristine hBN

In the present section, the electronic and structural properties of the pristine hBN were investigated to differentiate the electronic and structural properties modification pristine hBN undergoes upon Cu decoration and COCl_2 adsorption. Therefore, we have optimized the geometry and found that the resulting optimized structure exhibits an alternate periodic arrangement of N and B atoms bonded to nearby three B and N atoms, giving rise to sp^2 hybridized honeycomb-like planar structure shown in Fig. 2(a). Moreover, the optimized B–N bond length, the bond angle between B–N–B, and the nearest distance between the B–B or N–N atoms were found to be 1.45 Å, 120° , and 2.51 Å, respectively. [47–49]. These findings were consistent with the experimental results reported by various authors. Further, we have performed a DOS calculation to investigate the electronic properties of the optimized structure. The DOS plot shown in Fig. 2(b) revealed that the optimized structure behaved as an insulator with an energy band gap of about 4.29eV, consistent with the band gap (4.30eV) calculated by Kim et al. [50]. Therefore, the agreement of our calculated band gap with the previously theoretical result validates the reliability of our DFT calculation. We have performed PDOS calculations to study the contribution from the individual atomic orbitals to the TDOS. The resulting PDOS plot in Fig. 2(c) revealed that the contributions to the valence band (VB) and conduction band (CB) were primarily from the 2p orbitals of the N and B atoms, respectively. We have utilized the Electron Localization Function (ELF) to visualize the electron density around the atoms. The ELF plot in Fig. 2(d) illustrated a region of high and low electron densities around the N and B atoms identified by the red and blue-colored regions, respectively. The observed variation in the electron densities can be attributed to the difference in the electronegativity. Being highly electronegative, the N atom withdraws electrons from the B atom, making the N and B sites electron-rich and electron-deficient sites, respectively. This confirmed the behavior of N and B atoms as an electron donor and acceptors, respectively. Hence, the structural and electronic properties analysis suggest that the resulting optimized structure behaved as an hBN monolayer.

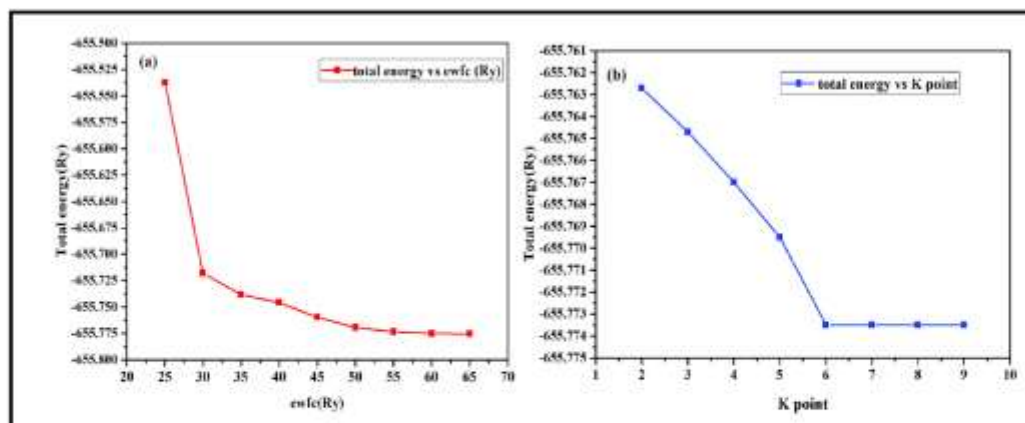


Fig. 1. Convergence test for the (a) cut-off energy and (b) K points.

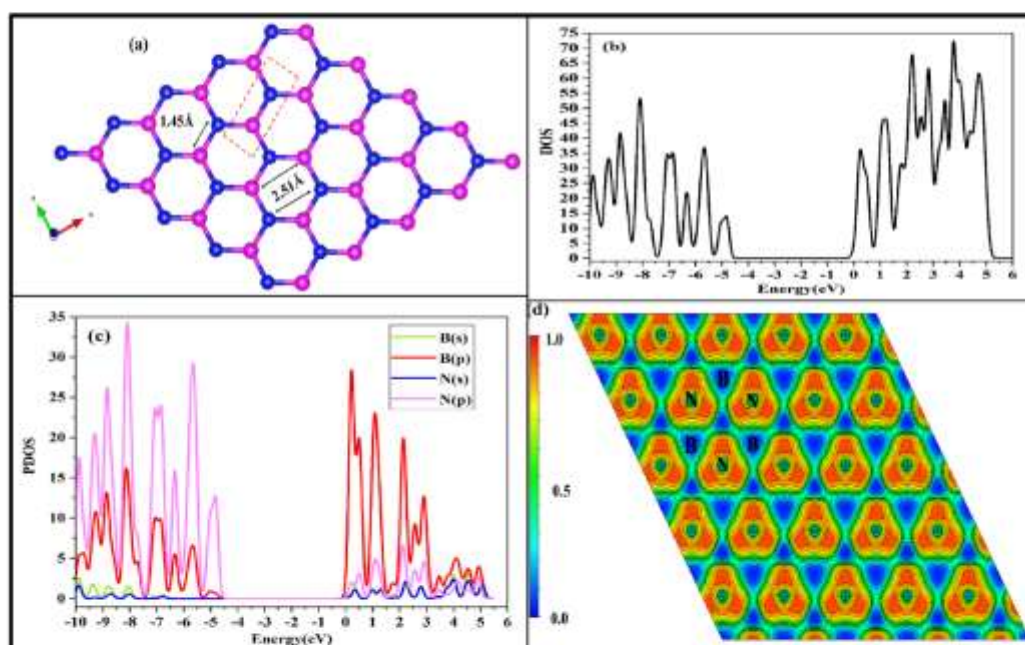


Fig. 2. (a) Optimized structure of hBN monolayer with the red colored box representing the unit cell. The atoms in blue and pink correspond to the N and B atoms, (b) DOS, (c) PDOS, and (d) ELF plot. The red, blue, and green colored areas correspond to high, low, and partially delocalized regions, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.2. Adsorption of COCl_2 gas onto the pristine hBN monolayer

To explore the interaction of the COCl_2 gas with the pristine hBN monolayer, we have considered the B site (top of the B atom) and N site (top of the N atom) as the most preferential adsorption sites because B and N sites are electron-deficient and rich sites, suggested by our ELF calculation in the previous section. Hence, they served as active sites for

the COCl_2 gas adsorption onto the hBN. Therefore, we have considered various possible orientations of the gas at the B and N sites as the input geometries for optimization. Upon optimization, we obtained four different optimized structures abbreviated as A1, A2, A3, and A4. The resulting optimized structures shown in Fig. 3 revealed that the N-B, C=O, and C-Cl bond lengths did not vary too much from that of the N-B bond length in pristine hBN and C=O, C-Cl bond lengths in isolated

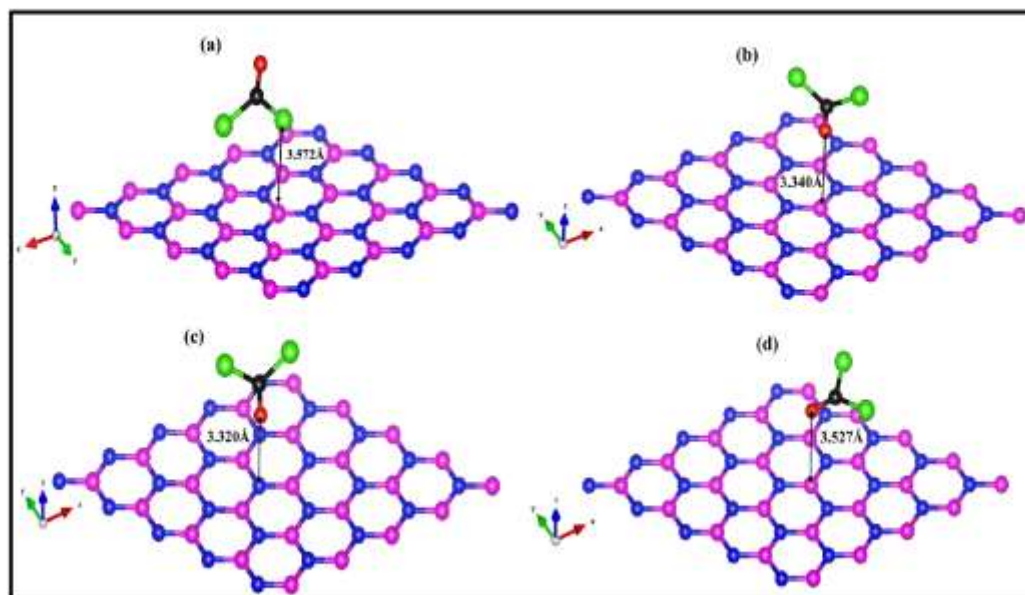


Fig. 3. Top observation of the optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The arrows in black represent the distance from the hBN surface to the COCl₂ gas. The red, black, and green atoms represent the O, C, and Cl elements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

COCl₂ molecules. This can be attributed to the weak interaction between the COCl₂ and pristine hBN. From Fig. 3(a) and (d), we observed that in the case of A1 and A4 adsorption configurations, the COCl₂ gas orients itself parallel and perpendicular to the z-axis and got adsorbed at a distance of 3.572 Å and 3.527 Å with the Cl and O atoms facing toward the B site. In contrast, for the A2 and A3 adsorption configurations, we observed that the COCl₂ gas orients itself along the z-direction and got adsorbed at a distance of 3.340 Å and 3.320 Å with the O atoms facing toward the B and N sites, as shown in Fig. 3(b) and (c), respectively. From Table 1, we found that the adsorption distances for all the optimized structures lie within the range of 3.320 Å–3.572 Å, which is greater than the sum of the atomic radius of O, C, Cl, B, and N atoms, indicating that the adsorption of COCl₂ gas onto hBN was physisorption. Further, to determine the interaction strength and most stable adsorption configuration among the different optimized structures, we have calculated the adsorption energies for all the optimized structures using equation (1) (see Table 1).

$$E_{\text{ads}} = E_{\text{hBN-gas}} - (E_{\text{hBN}} + E_{\text{gas}}) \quad (1)$$

where $E_{\text{hBN+gas}}$, E_{hBN} , and E_{gas} represents the total energies of the pristine hBN upon gas adsorption, pristine hBN, and isolated COCl₂ gas molecule, respectively. According to equation (1), the calculated

adsorption energies for the A1, A2, A3, and A4 adsorption configurations were found to be −0.501 eV, −0.439 eV, −0.435 eV, and −0.533 eV, respectively. The reported negative value of the adsorption energies in Table 1 validates that the adsorption of COCl₂ onto pristine hBN was physisorption, spontaneous, and exothermic. It was based on the comparison of the reported adsorption energies in Table 1, we found the A4 adsorption configuration to be the most stable adsorption configuration among the different adsorption configurations due to its lowest adsorption energy. Therefore, we have considered A4 as the final structure for the rest of the study. Hence, based on the results from the adsorption study, we found that the pristine hBN exhibits weak adsorption affinity towards the COCl₂ gas.

3.3. Structural and electronic properties analysis of the Cu-doped hBN monolayer

In the previous section, we observed that hBN exhibits poor gas adsorption affinity towards COCl₂ gas molecules. It is well known that doping 2D materials with Transition metal (TM) atoms effectively enhances the gas adsorption ability of 2D materials [51]. Among the various Transition Metal (TM) atoms, we have selected the Cu atom as the dopant because it is cost-effective, readily available, surplus in nature, and does not get poisoned by the analyte. Therefore, in this section, we have investigated the effect of substitutional doping the Cu atom on the structural and electronic properties of hBN. For this purpose, we have created the B and N vacancies by ejecting a single B and N atom from the hexagonal lattice. After creating the vacancy, the Cu atom embedded at the B and N vacancies was allowed to relax. Upon relaxation, we obtained two doped structures abbreviated as 'Cu-V_B-hBN' (Cu-doped at B vacancy) and 'Cu-V_N-hBN' (Cu-doped at N vacancy), respectively. The resulting relaxed doped structure revealed that the hexagonal B–N ring no longer remained intact and underwent distortion. It was due to the large atomic radius of the Cu (1.28 Å) atom

Table 1
Calculated B–N bond lengths in Å, adsorption distance, and energies in Å and eV for the different optimized structures.

Optimized structures	Adsorption distance (Å)	Adsorption Energy (eV)	B–N bond length (Å)
A1	3.572	−0.501	1.451
A2	3.320	−0.439	1.449
A3	3.340	−0.435	1.449
A4	3.527	−0.533	1.450

compared to the B (0.85 Å) and N (0.65 Å) atoms that the hexagonal B-N ring underwent an expansion to accommodate the substitutional doped Cu atom within the hexagonal lattice. From Fig. 4(a) and (b), we observed that in the case of 'Cu-V_B-hBN' and Cu-V_N-hBN doped structures, the Cu atom got bonded with the adjacent three N and B atoms respectively. The atomic distance between the Cu atom with the adjacent three N and B atoms were 1.739 Å and 1.763 Å, which is comparable with the Cu-B (1.87 Å) and Cu-N (2.10 Å) bond lengths reported by Balkani et al. in their studies [52]. The differences in the calculated bond lengths were due to the usage of different basis sets in the SCF. We found on the comparison that the calculated Cu-B and Cu-N bond lengths were longer than the B-N bond lengths of the pristine hBN. This indicates that the doped Cu atom slightly bulges outward from the surface, making it a highly preferential adsorption site for the gas molecule. Also, the averaged B-N bond lengths in the case of Cu-V_B-hBN and Cu-V_N-hBN doped structures were 1.439 Å and 1.445 Å, smaller than the B-N bond lengths of the pristine hBN. This indicates that the doped Cu atom causes the overall structure to be somewhat corrugated. Further, to determine the bonding strength of the Cu atom with the hBN monolayer and the stability of the doped structures, we have calculated the binding energy (E_b) and formation energy (E_f) using equations (2) and (3) for the Cu-V_B-hBN and Cu-V_N-hBN configurations respectively.

$$E_b = E_{\text{Cu-hBN-gas}} - (E_v + E_{\text{Cu}}) \quad (2)$$

$$E_f = E_{\text{Cu-hBN}} - E_{\text{hBN}} - \mu_{\text{Cu}} + \mu_{\text{N}} \quad (3)$$

where $E_{\text{Cu-hBN}}$, E_v , E_{Cu} , μ_{Cu} and μ_{N} represents the total energies of the substitutional doped Cu atom into hBN, total energies of the defected hBN, total energies of the isolated Cu atom, and chemical potentials of the isolated Cu and ejected atoms from the hexagonal lattice, respectively. According to equations (2) and (3), the binding and formation energies for the Cu-V_B-hBN were -5.048 eV and 5.379 eV, whereas for the Cu-V_N-hBN were 1.31 eV and 9.42 eV, respectively. The calculated formation energy suggests that the Cu atom can be doped easily at the B vacancy compared to the N vacancy due to the low formation energy of the Cu-V_B-hBN. This result is consistent with the theoretical studies in which it was proved that doping TM metal atoms at B vacancy is energetically more favourable than N vacancy [53,54]. Further, Cu-V_B-hBN has the lowest binding and formation energies compared to Cu-V_N-hBN. These findings suggest that Cu-V_B-hBN was the most stable configuration among the Cu-V_B-hBN and Cu-V_N-hBN doped structures. Therefore, in the subsequent section, we have selected the Cu-V_B-hBN as the final doped structure to study the interaction with the COCl₂ gas and referred to Cu-V_B-hBN as 'Cu-doped hBN' for the rest of the study. In addition, the DOS plot in Fig. 5(a) revealed that substitutional doping of the Cu atom introduces a new impurity state at -4 eV, reducing the energy band gap from 4.29 eV to 3.10 eV. Consequently, there was an enhancement in the

peak intensity of the conduction band, indicating an increment in the conductivity of the hBN. In addition, the PDOS plot in Fig. 5(b) illustrated there exists multiple overlapping between the 3d-Cu and 2p-N atomic orbitals within the energy range from -4 eV to -10 eV, indicating strong hybridization between the atomic orbitals to form molecular orbitals involved in the bond formation. These findings indicate that strong chemical (ionic/covalent) interaction exists between the substitutionally doped Cu atom and the nearby neighbouring N atom. Hence, the structural and electronic properties analysis suggests that the substitutional doped Cu atom induces distortion in the structure and modifies the electronic properties of the hBN.

3.4. Adsorption of COCl₂ gas onto the Cu-doped hBN monolayer

To analyze the interaction of COCl₂ gas with the Cu-doped hBN systems, we have considered the dopant site as the most preferential adsorption site because of the protrusion the COCl₂ gas can easily interact with the Cu atom. Therefore, different orientations of the COCl₂ gas above the doped Cu atom were considered the input geometries for optimization. After optimization, we obtained two adsorption configurations abbreviated as B1 and B2. For the B1 and B2 adsorption configurations, we observed that the COCl₂ gas orients itself in a direction perpendicular and parallel to the z-axis and got adsorbed at a distance of 2.236 Å and 2.198 Å with the O atom facing towards the Cu atom, as shown in Fig. 6(a) and (b), respectively. We also observed from Table 2 that upon COCl₂ adsorption, the C=O and C-Cl bond lengths become longer than the C=O (1.180 Å) and C-Cl (1.720 Å) bond lengths of the isolated COCl₂ gas molecules. In addition, for the B1 adsorption configuration, we observed that the three Cu-N bond lengths got elongated from 1.730 Å to 1.852 Å, 1.856 Å and 1.859 Å upon COCl₂ gas adsorption. In contrast, for the B2 adsorption configuration, we observed that the three Cu-N bond lengths got elongated from 1.730 Å to 1.856 Å, 1.861 Å, and 1.862 Å upon COCl₂ gas adsorption. The observed elongation in the C=O, C-Cl, and Cu-N bond lengths might be due to the attractive electrostatic interaction between the COCl₂ gas and Cu-doped hBN. Further, to determine the strength of the interaction between the COCl₂ gas and Cu-doped hBN, we have calculated the adsorption energies for the B1 and B2 adsorption configurations using equation (4).

$$E_{\text{ads}} = E_{\text{Cu-doped-hBN-gas}} - (E_{\text{Cu-doped-hBN}} + E_{\text{gas}}) \quad (4)$$

where $E_{\text{Cu-doped-hBN-gas}}$, $E_{\text{Cu-doped-hBN}}$ and E_{gas} represent the total energy of the Cu-doped hBN system upon COCl₂ adsorption, the total energy of the Cu-doped hBN without COCl₂, and the total energy of the isolated COCl₂ gas. According to equation (4), the adsorption energies for the B1 and B2 adsorption configurations were found to be -1.851 eV and -1.939 eV, respectively. The reported high adsorption energy and

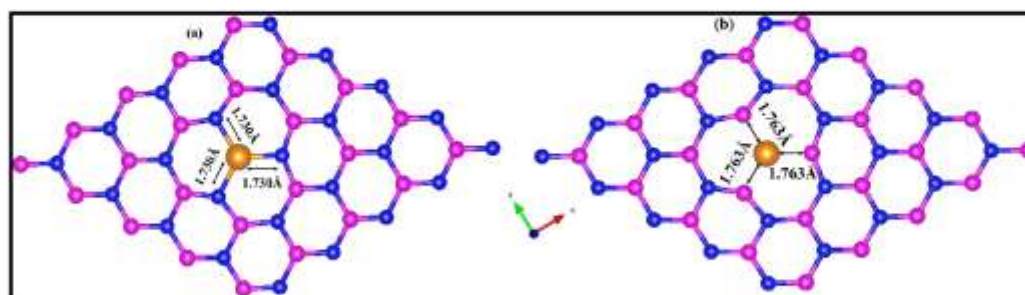


Fig. 4. Top observation of the optimized (a) Cu-V_B-hBN and (b) Cu-V_N-hBN doped systems. The atom in orange represents the Cu element. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

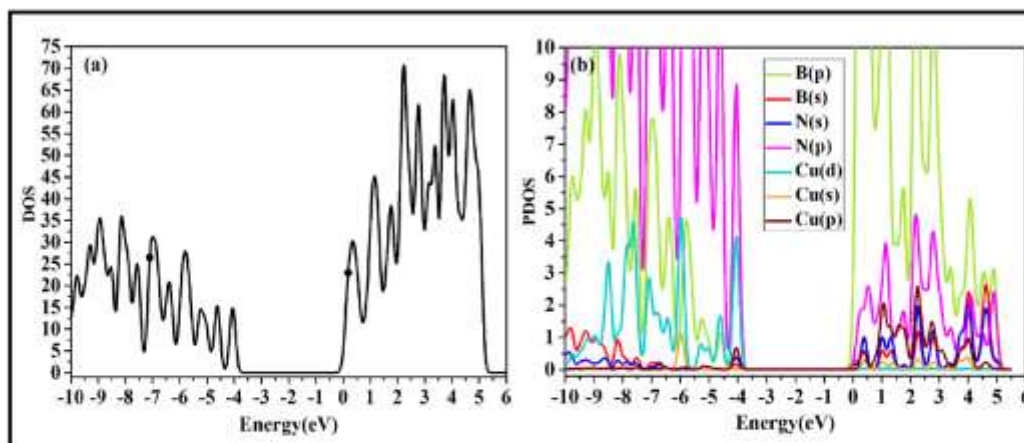


Fig. 5. (a) DOS and (b) PDOS plot upon substitutional doping of the Cu atom within the hBN.

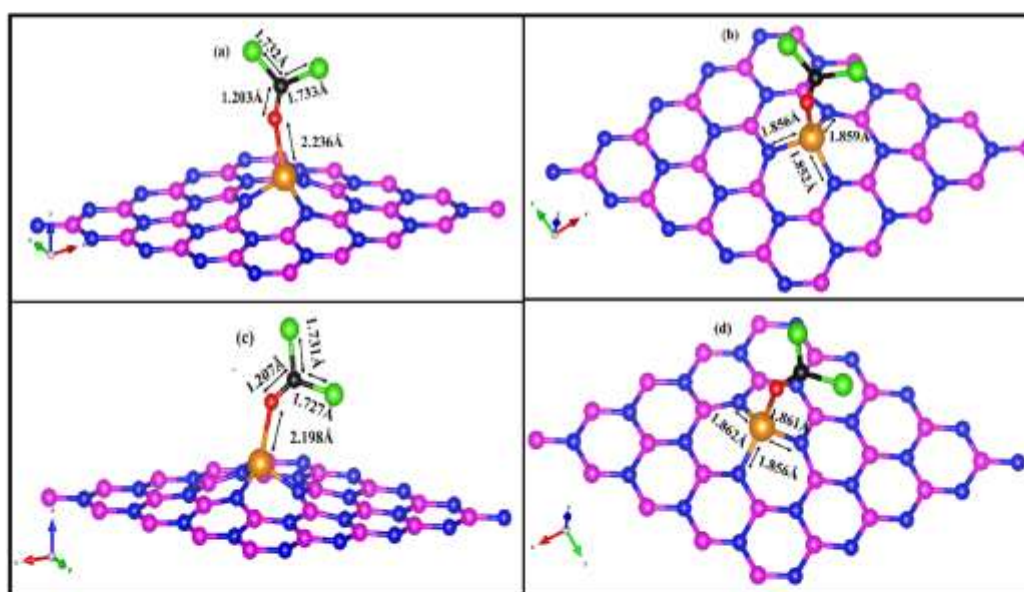


Fig. 6. (a) Lateral observation and (b) Top observation of the optimized B1 adsorption configuration and (c) Lateral observation and (d) Top observation of the optimized B2 adsorption configuration, respectively.

Table 2
Calculated adsorption distance, energy, C=O, C-Cl, and Cl-C bond lengths of the COCl₂ gas for the different optimized adsorption configurations.

Optimized structures	Adsorption distance (Å)	Adsorption energy (eV)	C=O bond length (Å)	C-Cl bond lengths (Å)
B1	2.236 Å	-1.851 eV	1.203 Å	1.732-1.733 Å
B2	2.198 Å	-1.939 eV	1.207 Å	1.727-1.731 Å

short adsorption distances in Table 2 for the B1 and B2 adsorption configurations suggest that the adsorption process was chemisorption. This finding indicates that COCl₂ binds strongly with the Cu-doped hBN. Based on the comparison of the adsorption energies, we found that the B2 adsorption configuration was the most stable adsorption configuration among the B1 and B2 adsorption configurations due to its lowest adsorption energy. Therefore, we have selected the B2 adsorption configurations for the recovery time and sensitivity analysis in the subsequent section of the present study. Hence, our adsorption study validates

A. Bhandari et al.

Journal of Physics and Chemistry of Solids 204 (2025) 112716

that substitutional doping of the Cu atom effectively enhances the adsorption ability of hBN for COCl_2 .

3.5. Structure and electronic properties analysis of the Cu-hBN

To analyze the effect Cu adsorption had on the structure and electronic properties of hBN. For this purpose, we have considered the N site the most preferential adsorption site for the Cu atom based on the previous theoretical studies [55]. Therefore, in this study, we have optimized the Cu atom adsorbed above the N sites and abbreviated the resulting optimized structure as 'Cu-hBN'. The resulting optimized structure shown in Fig. 7(a) and (b) revealed that the Cu atom adsorbed at 2.207 Å from the surface, and the B-N bond length elongated from 1.450 Å to 1.468 Å. The observed elongation in the B-N bond lengths indicates that the monolayer undergoes expansion to increase the available space for the adsorption of the Cu atom onto the surface. Further, to determine the thermodynamic stability of the structure and strength of the interaction between the adsorbed Cu atom and hBN, we have calculated the cohesive energy/atom (E_{coh} /atom) and adsorption energy (E_{ads}) for the Cu-hBN using equations (5) and (6) respectively.

$$E_{\text{coh}} = \frac{E_{\text{hBN-Cu}} - [x^*E_{\text{B}} + y^*E_{\text{N}} + E_{\text{Cu}}]}{N} \quad (5)$$

$$E_{\text{ads}} = E_{\text{hBN-Cu}} - [E_{\text{hBN}} + E_{\text{Cu}}] \quad (6)$$

where $E_{\text{hBN-Cu}}$, E_{hBN} , E_{B} , E_{N} , and E_{Cu} represents the total energies of the adsorbed Cu atom onto hBN, pristine hBN, isolated B, N, and Cu atoms, whereas x , y , and N represent the number of B, N, and total atoms within the unit cell, respectively. According to equations (6) the adsorption energy for the Cu-hBN was -0.33eV . In contrast, the cohesive energy/atom for the Cu-hBN using equation (5) was found to be -1.40eV/atom . The calculated low value of the adsorption energy suggests that the adsorbed Cu atom binds weakly with the hBN, and the adsorption of the Cu atom onto the hBN was physisorption. The

calculated negative value of the cohesive energy suggests that the Cu-hBN configurations remained thermodynamically stable. From Fig. 7 (c), we observed an impurity state in the energy range from -4eV to -3eV , reducing the energy gap from 4.29eV to 2.42eV . It was revealed by the PDOS plot in Fig. 7(d) that the impurity state was due to the contribution from the $4s$ -Cu and $2p$ -N atomic orbitals, and there exists weak interaction between the atoms due to weak hybridization between the atomic orbitals. This result was consistent with our findings that the Cu atom binds weakly with the hBN. Hence, our DOS, PDOS and adsorption results are in agreement with each other.

3.6. Adsorption of COCl_2 gas onto the Cu-hBN

To analyze the interaction of COCl_2 gas with the Cu-hBN, we have considered different orientations of the COCl_2 gas above the adsorbed Cu atom as the input geometries for the optimization. After optimization, we obtained two adsorption configurations abbreviated as C1 and C2. For the C1 and C2 adsorption configurations, we observed that the COCl_2 gas orients itself perpendicular and parallel to the z -axis and got adsorbed at a distance of 1.840 Å and 1.841 Å with the O atom of COCl_2 gas facing toward the Cu atom, as shown in Fig. 8(a) and (c). From the reported data in Table 3, we found that upon COCl_2 adsorption, there was a variation in the B-N, C=O, and C-Cl bond lengths. As the C=O and C-Cl bond lengths for the C1 adsorption configuration increase from 1.180 Å to 1.268 Å and from 1.720 Å to 1.782 Å . In contrast, for the C2 adsorption configuration, the C=O and C-Cl bond lengths increase from 1.180 Å to 1.271 Å and from 1.720 Å to 1.791 Å . In addition, the B-N bond lengths vary from 1.481 Å – 1.482 Å and 1.481 Å – 1.485 Å in the case of C1 and C2 adsorption configurations, as shown in Fig. 8(b) and (d), respectively. The observed elongation in the B-N, C=O, and C-Cl bond lengths might be due to the strong attractive electrostatic interaction between the COCl_2 gas and Cu-hBN. Therefore, to determine the strength of the interaction, we have calculated adsorption energies using equation (7) for the C1 and C2 adsorption configurations.

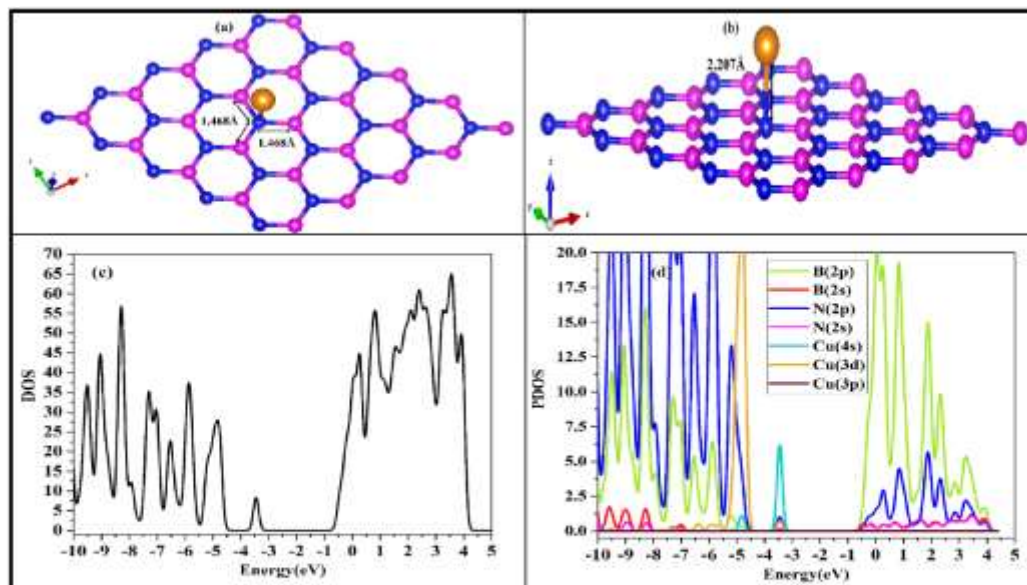


Fig. 7. (a) Lateral observation and (b) Top observation of the optimized structure upon Cu adsorption. (c)TDOS and (d) PDOS plot upon Cu adsorption onto hBN, respectively.

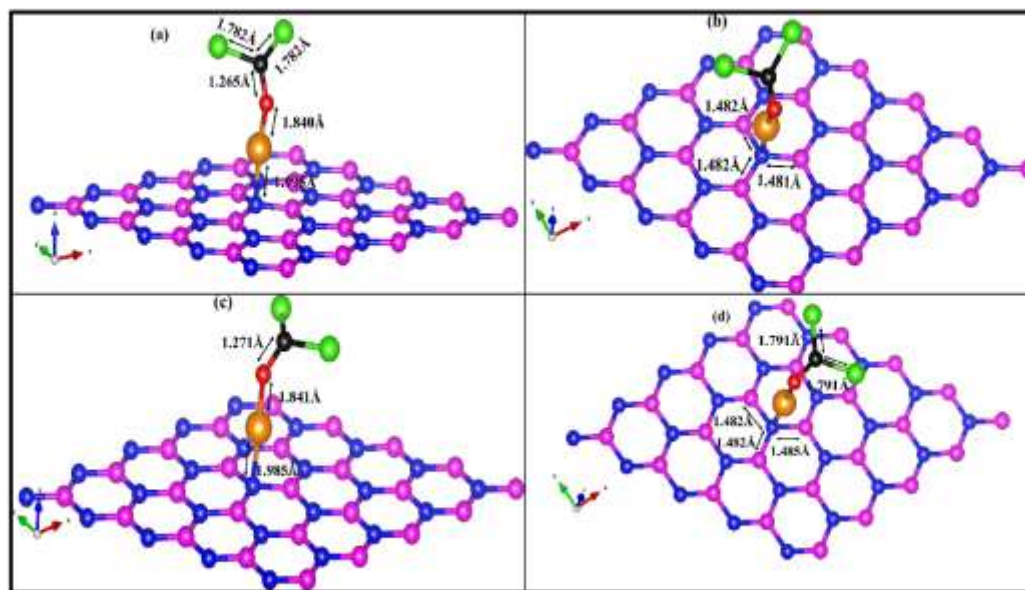


Fig. 8. (a) Lateral observation and (b) Top observation of the optimized C1 adsorption configuration and (c) Lateral observation and (d) Top observation of the optimized C2 adsorption configuration, respectively.

Table 3

Calculated adsorption distance, energy, C–O, C–Cl, and Cl–C bond lengths of the COCl_2 gas for the different optimized adsorption configurations.

Optimized structures	Adsorption distance (Å)	Adsorption energy (eV)	C–O bond length (Å)	C–Cl bond lengths (Å)
C1	1.840 Å	−1.101 eV	1.265 Å	1.782 Å
C2	1.841 Å	−1.155 eV	1.271 Å	1.791 Å

$$E_{\text{ads}} = E_{\text{hBN-Cu-COCl}_2} - (E_{\text{hBN-Cu}} + E_{\text{COCl}_2}) \quad (7)$$

where $E_{\text{hBN-Cu-COCl}_2}$, $E_{\text{hBN-Cu}}$ and E_{COCl_2} represents the total energies of the Cu-hBN upon COCl_2 adsorption, Cu-hBN without gas molecule, and isolated COCl_2 gas, respectively. Using equation (7), the calculated adsorption energies for the C1 and C2 adsorption configurations were −1.101 eV and −1.155 eV, respectively. The calculated high value of the adsorption energies for the C1 and C2 adsorption configurations suggests that the adsorption of COCl_2 gas onto Cu-hBN was chemisorption, confirming the existence of ionic/covalent interaction between the COCl_2 gas and Cu-hBN. Hence, these findings suggest that COCl_2 gas binds strongly with the Cu-hBN systems. Further, a comparison of the reported adsorption energies for the different adsorption configurations in Table 3 suggests that C2 was the most stable adsorption configuration among the different adsorption configurations due to its lowest adsorption energy. Therefore, we have also selected the C2 adsorption configuration for the recovery time and sensitivity analysis in the subsequent section of the present study.

3.7. Comparison of the adsorption energies with other various systems

In this section, we have compared the adsorption energies of the B2 and C2 adsorption configurations with the various systems from the literature, specifically regarding the sensing of COCl_2 gas molecules. However based on the literature survey in terms of sensing COCl_2 , a

wide range of various systems such as $\text{B}_{12}\text{N}_{12}$ nanocage, $\text{B}_{12}\text{P}_{12}$, Cu- $\text{B}_{12}\text{N}_{12}$ nanocage, Cu- $\text{B}_{12}\text{P}_{12}$, BN nanotubes, Sc-doped BN nanotubes, Li- $\text{B}_{12}\text{C}_6\text{N}_6$, Cr-graphene, BN nanoflake, BN nanorings, $\text{B}_{24}\text{N}_{24}$ nanocage and Al- $\text{B}_{24}\text{N}_{24}$ nanocage exhibited adsorption energy values of −0.097 eV, −0.175 eV, −1.233 eV, −0.043 eV, −0.182 eV, −0.79 eV, −0.719 eV, −0.141 eV, −0.254 eV, −0.043 eV and −0.920 eV, respectively. The B2 adsorption configuration demonstrates better adsorption energy, whereas the C2 adsorption configuration also demonstrates better adsorption energy than all reported systems except Cu- $\text{B}_{12}\text{P}_{12}$. Hence, the comparison results confirmed that both B2 and C2 adsorption configurations have efficient adsorption ability towards COCl_2 adsorption.

3.8. Charge density difference and hirshfeld charge analysis

To gain an understanding of the charge transfer process upon COCl_2 adsorption onto pristine hBN, Cu-doped hBN, and Cu-hBN, we have analyzed the charge transfers quantitatively and qualitatively using the Hirshfeld and charge density difference (CDD) methods for the A4, B2, and C2 adsorption configurations, respectively. The charge density difference ($\Delta\rho$) for all these adsorption configurations was calculated using the following equation (8).

$$\Delta\rho = \rho_{\text{AB}} - \rho_{\text{A}} - \rho_{\text{B}} \quad (8)$$

where ρ_{AB} , ρ_{A} , and ρ_{B} represent the charge densities of the complexes with gas molecules, the charge densities of the complexes without gas molecules, and the charge densities of the isolated gas molecules, respectively. The yellow and cyan-colored in the charge density difference diagrams represent the electron accumulation and depletion regions. From Fig. 9(a), we observed that upon COCl_2 adsorption onto hBN, a small yellow-colored region exists around the O atom, and large blue and yellow-colored regions exist between the B and N atoms. These findings indicate that B and N atoms primarily interact with each other,

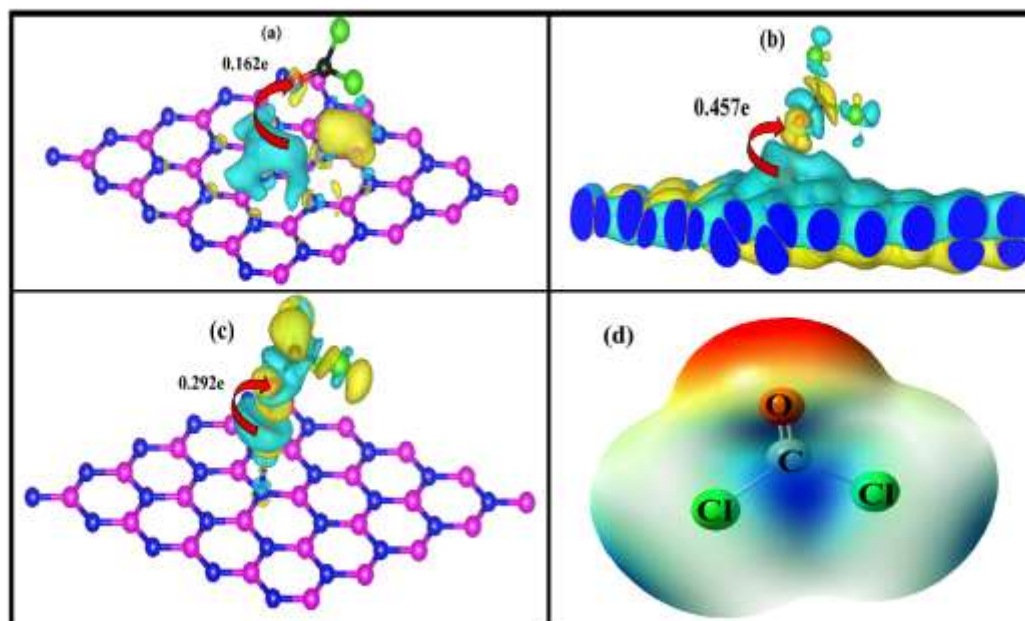


Fig. 9. Charge density difference diagram for (a) A4, (b) B2, and (c) C2 configurations. The yellow and cyan color in the CDD diagrams represents the electron accumulation and depletion regions, respectively (d) ESP map for the optimized COCl_2 gas molecule. The blue and red colors represent the positive and negative charge sites. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

resulting in weak charge transfer between hBN and COCl_2 . As a consequence, there exists a weak interaction between the hBN and COCl_2 . In addition, we also observed a large cyan and a yellow-colored region around the Cu and O atoms, indicating a strong charge transferred from the Cu atom to the COCl_2 . These findings confirmed the nature of the Cu atom and COCl_2 as an electron donor and acceptors, respectively. Further, we calculated the electrostatic potential (ESP) for the COCl_2 to gain additional insights into the charge transfer mechanism, as shown in Fig. 9(d). The red and blue color in the ESP map corresponds to positive and negative charge distribution. From Fig. 9(d), we found that a negative charge distribution exists around the O atom, identified by the red color, whereas a positive charge distribution exists around the C and Cl atoms, identified by the blue color, respectively. The observed charge distribution can be attributed to the difference in the electronegativity between the atoms. O atom, being highly electronegative compared to the C atom, withdraws electrons from it. As a consequence, the electron density around the O atom increases, making it an electron-rich and C atom electron-deficient species. These findings indicate that the strong electrostatic attraction between the Cu atom and COCl_2 was responsible for the orientation of the COCl_2 with the O atom facing toward the Cu atom upon optimization and strong charge transfer in the case of B2 and C2 adsorption configurations. The Hirshfeld charge analysis validate that a weak charge transfer of $-0.162e$ takes place in the case of A4 adsorption configuration compared to strong electron transfer of $-0.457e$ and $-0.292e$ in the case of B2 and C2 configurations. This finding is in support of the results from the charge density difference calculations. Hence the results of our Hirshfeld and charge density difference calculations are in good agreement with each other.

3.9. Non-covalent interaction analysis

Noncovalent interactions (NCIs) are of great importance in gas sensing since they play a vital role in the adsorption of the gas, thereby influencing the adsorption energy and the recovery time of the sensing materials. Therefore, to analyze the existence of any non-covalent interaction between pristine hBN, Cu-doped hBN, Cu-hBN, and COCl_2 , we have calculated the variation in the value of the reduced density gradient (RDG) function [36] with $\text{sign}(\lambda_2) \rho(r)$ for the A4, B2, and C2 adsorption configurations. Further, we have utilized the RDG scatter plot and RDG isosurfaces for all these adsorption configurations to visualize the variation in the RDG function. Here, the RDG function ($s(r)$) defined in equation (9) represents a relation between the electron density ($\rho(r)$) and its gradient ($|\nabla\rho(r)|$). The quantity $\text{sign}(\lambda_2) \rho(r)$ is of great significance as it describes the fluctuation in the electron density near the critical points, which is helpful in determining the nature of the non-covalent interactions. If $\text{sign}(\lambda_2) \rho(r) < 0$, $\text{sign}(\lambda_2) \rho(r) = 0$, and $\text{sign}(\lambda_2) \rho(r) > 0$, it indicates attractive strong hydrogen bonding, van der Waals interaction (vdW), and repulsive strong steric effects.

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{[\rho(r)]^{4/3}} \quad (9)$$

The blue, red, and green color schemes shown in the RDG isosurface correspond to attractive strong hydrogen bonding, repulsive steric effect, and weak vdW interactions. We observed that the RDG scatter plots underwent a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) > 0$ for all the adsorption configurations, as shown in Fig. 10. This confirmed the existence of a strong repulsive steric effect. Further, the corresponding RDG isosurfaces revealed that strong steric effects exist between the B and N atoms of the hBN layer. The observed steric effect arose due to the strong electrostatic repulsion between the positively

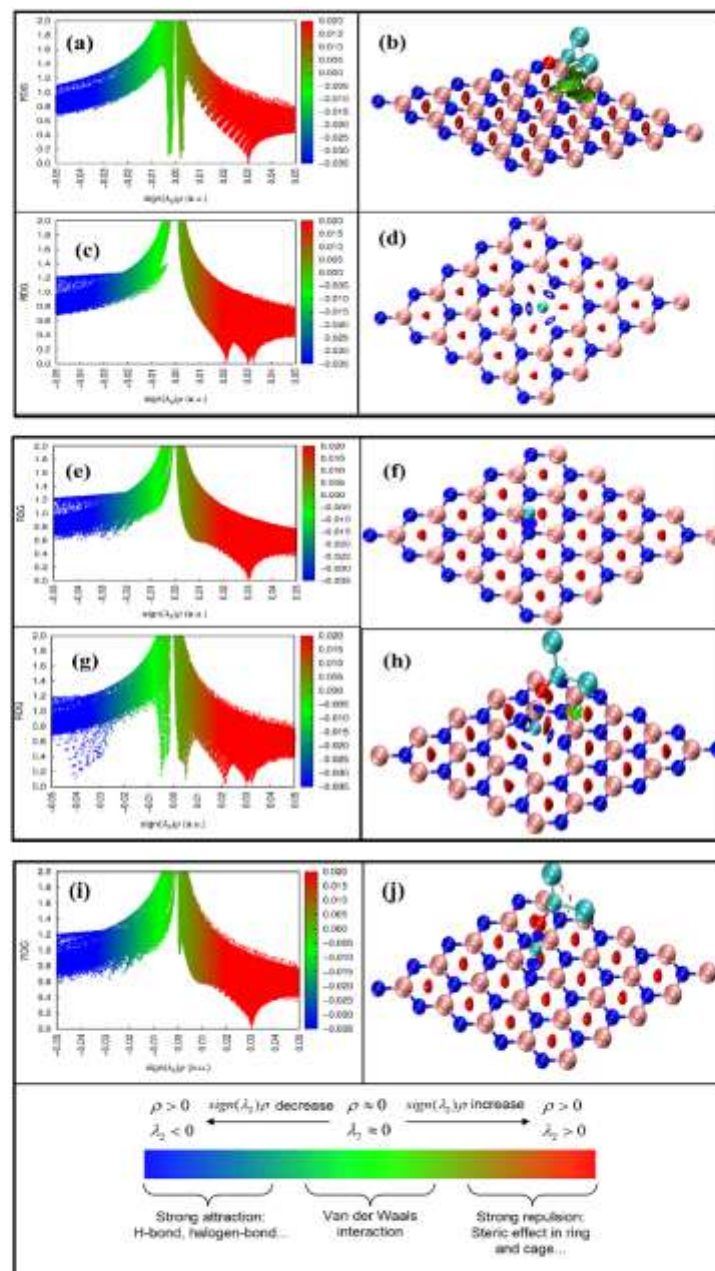


Fig. 10. RDG scatter plot for the (a) A4, (c) Cu doped-hBN, (e) Cu-hBN, (g) B2, and (i) C2 adsorption configurations, respectively. Isosurface plot for the (b) A4, (d) Cu doped-hBN, (f) Cu-hBN, (h) B2, and (j) C2 adsorption configurations, respectively.

charged Cl and B atoms as the COCl_2 gas approached. From Fig. 10(a), we observed a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) \approx 0$ in the case of A4 adsorption configuration. The corresponding RDG isosurface shown in Fig. 10(b) verified that weak vdW interaction exists between the COCl_2 gas and hBN identified by the green patches. This confirmed that weak vdW interaction was responsible for the physisorption of the COCl_2 gas onto hBN. However, upon substitutional doping of the Cu atom and Cu adsorption, we observed from the RDG scatter plot in Fig. 10(c) and (e) a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$. The RDG isosurface plot revealed that strong attractive H bonding exists between the Cu atom and the nearby neighbouring N atom identified by blue patches as shown in Fig. 10(d) and (f), respectively. This can be attributed to the electrons transfer from the positively charged Cu atom to the nearby negatively charged N atom, creating a strong, attractive interaction between the oppositely charged species. These findings confirmed that the doped Cu atom in the case of Cu-doped hBN and Cu-hBN systems interacts electrostatically with the hBN. In contrast, upon COCl_2 adsorption, we found from the RDG scatter plot that there is a sharp decline in the RDG value around $\text{sign}(\lambda_2) \rho(r) < 0$ for the B2 and C2 adsorption configurations, as shown in Fig. 10(g) and (i), respectively. These results indicate a strong, attractive electrostatic interaction between the Cu atom and COCl_2 identified by the blue patches, as shown in Fig. 10(h) and (j). These findings validated that it was due to the strong electrostatic interaction that COCl_2 binds strongly to the Cu-doped hBN and Cu-hBN systems, resulting in high adsorption energy. Hence, our RDG results are in good agreement with those of our adsorption study.

3.10. Electron Localization Function analysis (ELF)

To analyze how the electrons are distributed around the interacting atoms upon COCl_2 adsorption onto hBN, Cu-doped hBN, and Cu-hBN, we have utilized the ELF to visualize the distributions of electrons in the A4, B2, and C2 adsorption configurations. The corresponding ELF plot for all these configurations is shown in Fig. 11. From Fig. 11(d), we observed that upon COCl_2 adsorption onto pristine hBN, there exists an intense red-colored region around the O and Cl atoms, indicating that electrons are strongly localized to the COCl_2 gas. There also exists a large region of low electron density exists in between the COCl_2 gas and the hBN monolayer, which is identified by the blue-colored region. These

findings suggest a weak interaction exists between the COCl_2 gas and the hBN monolayer. Further, to validate our findings, we have plotted the bottom view of the ELF plot for the A4 configuration, as shown in Fig. 11(a). Due to the weak interaction, we found that electron density distribution around the monolayer upon COCl_2 adsorption was identical to that without COCl_2 gas. But, for the B2 and C2 adsorption configurations, we found there was a decrement in the intensity of the red color around the Cu atom and an increment in the intensity of the red color around the O atom, as shown in Fig. 11(e) and (f) respectively. These results indicate that electrons are transferred from the Cu atom to the COCl_2 gas during COCl_2 gas adsorption. However, the Cu atom intensity in the C2 configuration was higher than in the case of the B2 configuration, indicating a stronger charge transfer took place from Cu-doped hBN than Cu-hBN to COCl_2 , which is consistent with our Hirshfeld analysis. The bottom view of the ELF plot for the C2 configuration shown in Fig. 11(c) revealed that the electron density distribution around the atoms remained unaltered upon COCl_2 adsorption onto Cu-hBN. Similarly, the bottom view of the ELF plot for the B2 configuration shown in Fig. 11(b) revealed that the electron density distribution around the atoms remained unaltered upon COCl_2 adsorption onto Cu-doped hBN and a low electron density at the doping site. Hence, these findings suggest that the Cu atom was the primary active site for the adsorption of the COCl_2 gas onto Cu-doped hBN and Cu-hBN systems, respectively. This is because of the strong electrostatic interaction COCl_2 primarily interacts with the Cu atom. As a consequence, the interaction of the COCl_2 with the hBN becomes weak during the COCl_2 adsorption.

3.11. Frontier molecular orbital analysis

The Frontier Molecular Orbitals (FMO) include the Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO), which provide useful information regarding the alteration in the electronic properties upon the adsorption of the specified gas molecule on the adsorbent. Therefore, we have calculated the HOMO-LUMO energies for the various adsorption configurations. The data presented in Table 5 indicate that hBN exhibits insulating behavior with a HOMO-LUMO energy gap of 4.29 eV. In the pristine hBN, the HOMO and LUMO energy levels lie at -4.51 eV and -0.22 eV, respectively. However, upon substitutional doping, it was observed that the HOMO energy level shifts from -4.51 eV to -3.60 eV, and the LUMO energy

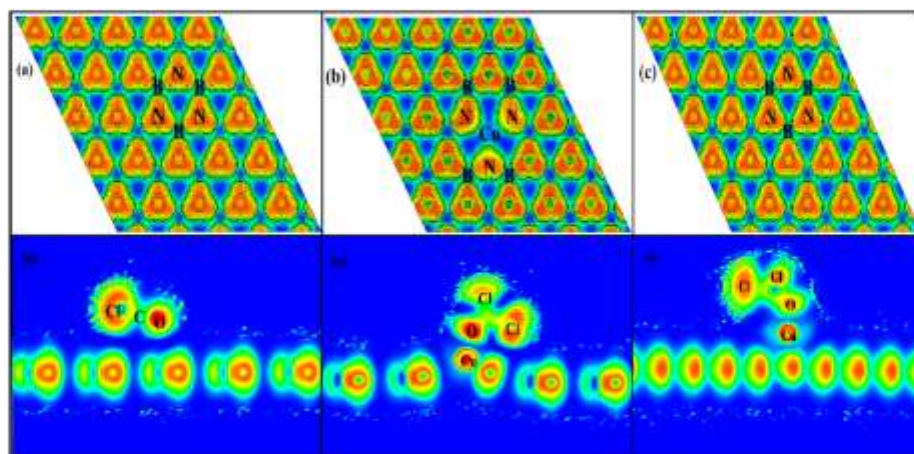


Fig. 11. Bottom view of the ELF map for (a) A4, (b) B2 and (c) C2 adsorption configurations. Lateral view of the ELF map for (d) A4, (e) B2, and (f) C2 adsorption configurations, respectively.

level shift from -0.22eV to -0.50eV . Similarly, upon adsorption of the Cu atom, it was observed that the HOMO energy level shift from -4.51eV to -3.17eV , and the LUMO energy level shift from -0.22eV to -0.75eV , respectively. These changes in the position of HOMO and LUMO reduce the energy band gap by 27.74 % and 43.58 % for the Cu-doped hBN and Cu-hBN systems, respectively. Furthermore, the adsorption of COCl_2 onto hBN shifts the HOMO from -4.51eV to -4.35eV and the LUMO from -0.22eV to -1.73eV , thereby reducing the band gap to 2.62eV . For the B2 and C2 adsorption configurations, the HOMO shifts to -3.14eV and -2.09eV , whereas the LUMO shifts to

-2.28eV and -0.98eV . Here the shifts in the position of HOMO and LUMO narrows the band gap from 3.10eV to 0.86eV and from 2.42eV to 1.11eV for the B2 and C2 adsorption configurations respectively. The reduction in the band gap indicates that doping of Cu atom favours the adsorption of the COCl_2 . We also found on comparison that the B2 and C2 configuration exhibits excellent conductivity than A4 configurations. The observed reduction in the energy gap, as well as changes in the position of the HOMO and LUMO, can be attributed to the destabilization and stabilization of the HOMO and LUMO, respectively. Further, we have analyzed the distribution of HOMO-LUMO orbitals for all these

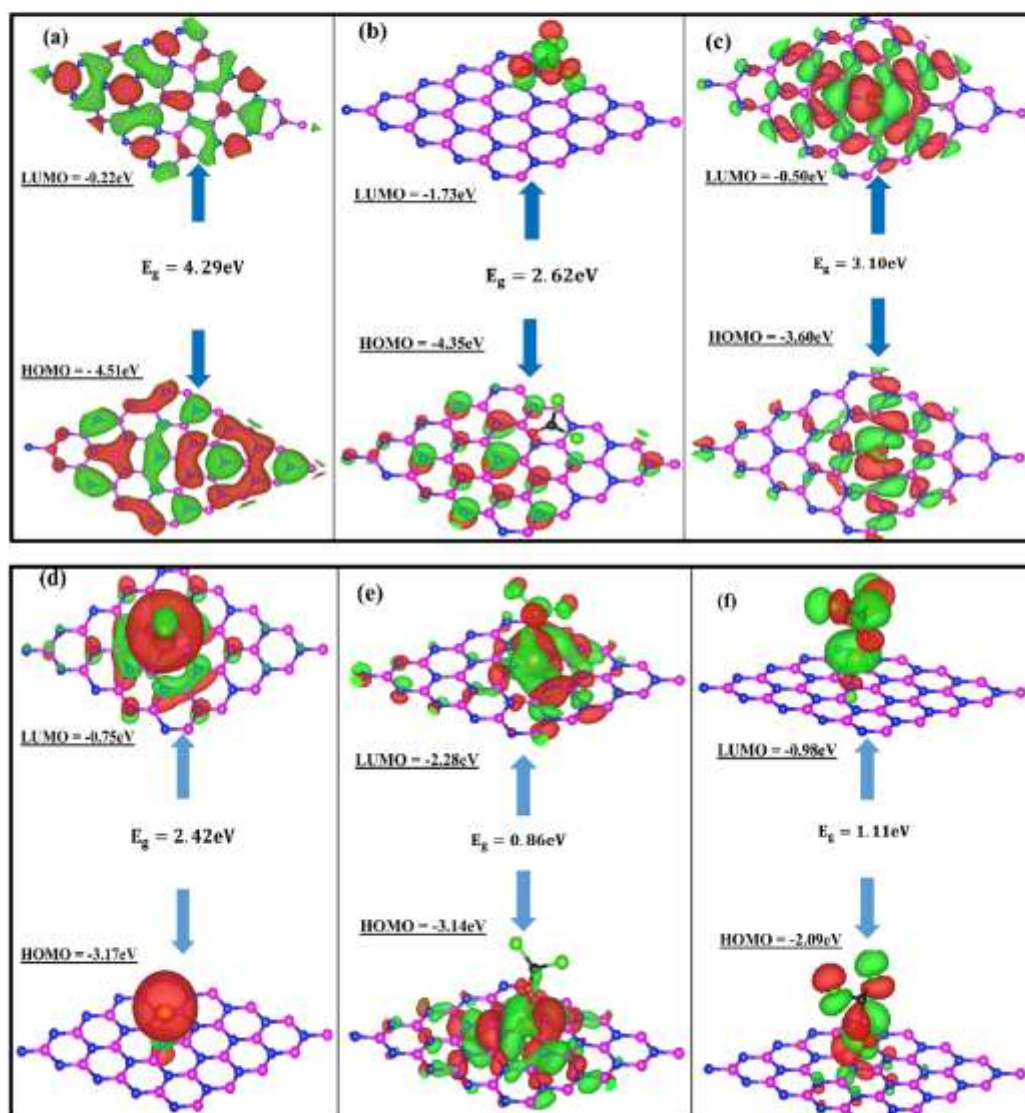


Fig. 12. HOMO and LUMO for (a) pristine hBN, (b) A4, (c) Cu-doped hBN, (d) Cu-hBN, (e) B2 and (f) C2 adsorption configurations, respectively.

configurations to justify the observed variation in the HOMO-LUMO energies. From Fig. 12(a), we observed that the HOMO-LUMO orbitals are concentrated around the N and B atoms indicating that in case of hBN both N and B atoms are involved in charge transfer process. But upon substitutional doping and Cu adsorption, we observed that the HOMO orbitals got concentrated around the Cu atom, and LUMO orbitals got concentrated around the nearby neighbouring N atoms, as shown in Fig. 12(c) and (d), respectively. This happens because the Cu atom causes a redistribution of electrons in the hBN by losing excessive electrons to the nearby highly electronegative N atom. On the other side, for the B2 and C2 adsorption configurations, we observed that upon COCl₂ adsorption, the HOMO remained distributed around the Cu atom, whereas the LUMO orbitals got distributed around the COCl₂ as shown in Fig. 12(e) and (f). It was due to the charge transfer from the Cu atom to COCl₂ we observed a shift in the LUMO around the COCl₂. Hence the HOMO-LUMO analysis suggest that COCl₂ adsorption modifies the electronic properties of Cu-doped hBN and Cu-hBN by reducing the band gap making them a promising candidate to be utilized as an electronic sensor.

3.12. Global indices of reactivity

To determine the chemical reactivity, sensing ability and performance of the surface sensing materials, we have calculated various quantum descriptors such as ionization potential (IP), HOMO-LUMO gaps (E_g), electron affinity (EA), chemical potential(μ), electrophilicity (ω), chemical softness(S), and hardness(η). These quantum descriptors were reported in Table 4 and calculated using the below equations (10)–(14).

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (10)$$

$$\mu = \frac{-E_{\text{HOMO}} - E_{\text{LUMO}}}{2} \quad (11)$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (12)$$

$$S = \frac{1}{2\eta} \quad (13)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (14)$$

The negative value of the HOMO and LUMO energies represent the ionization potential and electron affinity in Table 5. The reported value in Table 5 indicates that hBN has the highest ionization potential (4.52eV) and lowest electron affinity (0.22eV) among the various adsorption configurations. It was due to the chemically inert nature of the hBN layer. In contrast, upon substitutional doping of the Cu atom we found that the ionization potential decreases to 3.60eV and the electron

affinity increases to 0.50eV. Similarly, upon Cu adsorption onto hBN, we found that the ionization potential decreases to 3.17eV, and the electron affinity increases to 0.75eV. Further, we found that COCl₂ adsorption onto hBN decreases the ionization potential to 4.35eV and increases the electron affinity to 1.73eV. For the B2 adsorption configuration, the adsorption of the COCl₂ decreases the ionization potential to 3.14eV and increases the electron affinity to 2.28eV, whereas, for the C2 adsorption configuration, the COCl₂ adsorption lowers the ionization potential to 2.09eV and increases the electron affinity to 0.98 eV. These results implies that efficient charge transfer took place in case of B2 and C2 configurations respectively. Furthermore, to examine the chemical reactivity of the surface sensing material, we have calculated electrophilicity which describes the electron-accepting tendency of the adsorbent. From Table 5, we found that pristine hBN has the lowest electrophilicity value of about 1.31eV, and this property increases by 3.81 % and 21.37 % upon substitutional doping and Cu adsorption respectively. These findings imply that the incorporation of the Cu atom enhances the electrophilicity character in Cu-doped hBN and Cu-hBN systems by losing electrons to the nearby highly electronegative N atoms. However, upon COCl₂ adsorption, we found that the B2 (8.54eV) configuration exhibits the highest electrophilicity among the various configurations. In addition, to determine the chemical stability, we have calculated the chemical hardness and softness factor for all these adsorption configurations because it describes the resistance and willingness of the material to undergo any change in its electronic properties. The chemical hardness factor for the pristine hBN, Cu-doped hBN, and Cu-hBN systems was found to be 2.15eV, 1.55eV, and 1.21eV, whereas the corresponding chemical softness factor was found to be 0.23eV, 0.32eV, and 0.41eV, respectively. We found that Cu-doped hBN has a high hardness and a low softness compared to Cu-hBN. These findings suggest that Cu-hBN would exhibit significant variation in the energy gap upon incorporating Cu atom onto hBN, consistent with our HOMO-LUMO gap results. We also observed that upon COCl₂ adsorption, there was a 39.47 % increase in softness and a 39.06 % decrease in hardness factor for the A4 adsorption configuration. In contrast, for the B2 and C2 adsorption configurations, there was a 72.41 % and 54.44 % increment in the softness factor, whereas 72.25 % and 53.71 % decrement in the hardness factor, respectively. The observed high softness and low hardness imply that both B2 and C2 configurations are more likely to undergo significant variations in the electronic properties. Hence, the above-discussed quantum descriptors suggest that Cu-doped hBN and Cu-hBN exhibit excellent chemical reactivity towards COCl₂ compared to pristine hBN.

3.13. Sensitivity analysis of the pristine hBN, Cu-doped hBN and Cu-hBN

Sensitivity is considered an important parameter in determining the sensing performance of chemical gas sensors, and it is primarily judged by the variation in electrical conductivity upon gas adsorption. According to equation (15), the electrical conductivity of the sensing material depends exponentially on the negative of the band gap at a certain temperature. This implies that a reduction in the band gap leads to an enhancement in the electrical conductivity of the sensing material. Therefore, to analyze the sensitivity of the A4, B2, and C2 adsorption configurations, we have utilized DOS to calculate the changes the band gap underwent upon COCl₂ adsorption.

$$\sigma = A e^{\left(\frac{E_g}{2k_B T}\right)} \quad (15)$$

where σ is electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and k_B is the Boltzmann constant in eV/K. The resulting DOS plot shown in Fig. 13(a) revealed that the COCl₂ adsorption onto hBN introduces an impurity state near the conduction band, reducing the band gap from 4.29eV to 2.62eV. In contrast, COCl₂ adsorption onto the Cu-doped hBN and Cu-hBN creates an impurity state

Table 4
Adsorption energies reported previously for some of the various systems upon COCl₂ adsorption.

Systems	Adsorption energy (eV)	Reference
B ₁₃ N ₁₃ nanocage	−0.097	[36]
Cu-decorated B ₁₂ N ₁₂ nanocage	−0.175	
B ₁₃ P ₁₂	−0.271	[57]
Cu-decorated B ₁₂ P ₁₂	−1.233	
BN nanotubes	−0.943	[37]
Sc doped BN nanotubes	−0.182	
Li-decorated B ₁₂ C ₆ N ₆ nanocage	−0.790	[35]
Cu-graphene	−0.719	[58]
BN nanoflake	−0.141	[59]
B ₂₄ N ₂₄ nanocage	−0.943	[60]
Al-B ₂₄ N ₂₄ nanocage	−0.236	
BN nanocages	−0.254	[61]

Table 5

Calculated HOMO-LUMO energies, HOMO-LUMO gaps (E_g), ionization potential (IP), electron affinity (EA), chemical potential(μ), electrophilicity (ω), chemical softness(S) and chemical hardness(η) respectively for the pristine hBN, A4, Cu-doped hBN, B2, Cu-hBN, and C2 systems respectively. All the reported values are in eV.

Adsorption Configurations	HOMO	LUMO	E_g	μ	IP	EA	S	η	ω
Pristine hBN	-4.51	0.22	4.29	-2.37	4.51	0.22	0.23	2.15	1.31
A4	-4.35	-1.73	2.62	-3.04	4.35	1.73	0.38	1.31	3.53
Cu-doped hBN	-3.60	-0.50	3.10	-2.05	3.60	0.50	0.32	1.55	1.36
B2	-3.14	-2.28	0.86	-2.71	3.14	2.28	1.16	0.43	8.54
Cu-hBN	-3.17	-0.75	2.42	-1.96	3.17	0.75	0.41	1.21	1.59
C2	-2.09	-0.98	1.11	-1.54	2.09	0.98	0.90	0.56	2.14

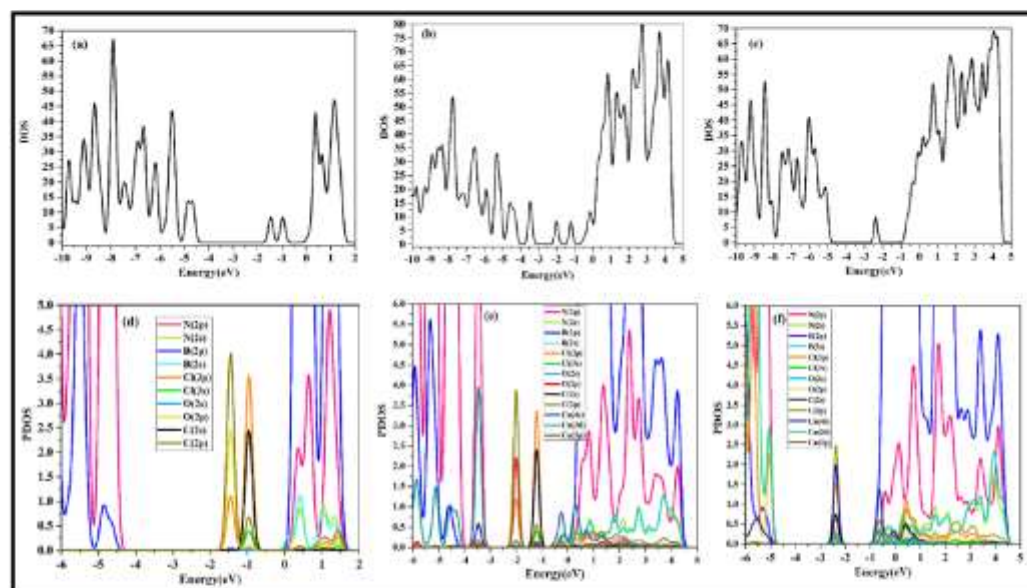


Fig. 13. Plotted DOS for (a)A4, (b)B2, and (c) C2 adsorption configurations and plotted PDOS for (d)A4, (e)B2, and (f) C2 adsorption configurations, respectively.

in the energy range -2to-1eV and -3to-2eV reduces the band gap from 3.10eV to 0.86eV, and from 2.42eV to 1.11eV as shown in Fig. 13(b) and (c) respectively. The calculated band gap indicates that the B2 and C2 configurations exhibit better electrical conductivity than the A4 configuration due to the 72.25 % and 54.13 % reduction in the energy gap. Further, to gain additional insights regarding the contribution of the different atomic orbitals to the impurity state, we have calculated PDOS for all these configurations. The resulting PDOS plot in Fig. 13(d) revealed that the impurity states in case of A4 configurations were due to the contribution from the 2p-B, 2p-C, 2p-O, 3p-Cl atomic orbitals. However, the contribution from the 2p-B atomic orbital was weak, resulting in weak hybridization between the B and O atoms, accounting for the weak interaction between the COCl_2 gas and hBN. Conversely, the PDOS plot in Fig. 13(e) revealed that the impurity states in the case of A4 configurations were due to the contribution from the 2p-C, 2p-O, 3p-Cl, 2s-C, and 3d-Cu atomic orbitals. Similarly, for the C2 configuration, 3d-Cu and 2p-C atomic orbitals contribute to the impurity states lying in the energy range from -3eV to -2eV, as shown in Fig. 13(f). These findings suggest that impurity states lying very close to the conduction band facilitate easy pathways for the charge transfer during the interaction of the COCl_2 with the sensing material. Therefore, it was due to the reduction in the band gap, there was a strong charge transfer in the case of B2 and C2 configurations, which is responsible for the observed

enhancement in the electrical conductivity of the Cu-doped hBN and Cu-hBN upon COCl_2 adsorption. Hence our findings suggest that both the Cu-doped-hBN and Cu-hBN systems exhibit better sensitivity than pristine hBN, making them a promising sensing material to detect COCl_2 gas molecules.

3.14. Recovery time analysis of the hBN, Cu-doped hBN and Cu-hBN systems

To analyze the reusability of the gas sensor, we have calculated the recovery time (τ) using equation (16) for the A4, B2, and C2 adsorption configurations, respectively.

$$\tau = \frac{1}{\nu} \exp\left(\frac{E_{ad}}{k_B T}\right) \quad (16)$$

where T is the testing temperature measured in Kelvin (K), and k_B is the Boltzmann constant whose value is 8.62×10^{-5} eV/K. E_{ad} is the potential barrier for the desorption of gas molecules, which can be substituted with adsorption energy (E_{ad}) because adsorption and desorption are reverse processes to each other, and ν represents the attempt frequency, which is 10^{12} Hz for the visible radiation. The recovery time calculated for the A4, B2, and C2 adsorption configurations

at 300K under visible light was found to be 8.937×10^{-6} sec, 3.661×10^{-20} sec, and 2.495×10^{-7} sec, respectively. The reported too-high recovery time for the B2 and C2 adsorption configurations can be attributed to the calculated high adsorption energy for these configurations. This result implies that the too-high recovery time limits the reusability of both the Cu-doped hBN and Cu-hBN systems as gas sensing material in chemical gas sensor to detect COCl_2 gas at room temperature. According to equation (16) we can improve the recovery time either by increasing the temperature, attempt frequency, or both if the adsorption energy is kept constant. Recently, Li et al. also validated that ultraviolet (UV) radiation assists quick recovery time of the gas sensor [62]. Therefore, to examine the effect UV radiation and increased temperature had on the recovery time of the B2 and C2 configurations. We have calculated the recovery time value at different temperatures under visible and UV light exposures for these configurations. The reported value in Table 6 suggests that the recovery time for the B2 and C2 configurations reduces from 3.661×10^{-20} s to 5.876×10^{-3} s and from 2.495×10^{-7} s to 6.593×10^{-10} s, respectively, as the temperature increases from 300K to 1000K under UV radiations respectively. This happened because both high temperatures and UV radiation facilitate additional high input energies required for the desorption of the COCl_2 gas from the surface of Cu-doped hBN and Cu-hBN. These findings suggest that annealing at high temperatures under UV radiation effectively improves the recovery time of the Cu-doped hBN and Cu-hBN systems. Hence, the recovery time analysis validates that Cu-doped hBN and Cu-hBN systems can be used as a sensing material at elevated temperatures to detect COCl_2 gas.

4. Conclusion

In the present work, we have systematically investigated the adsorption behavior of COCl_2 gas onto the pristine hBN and Cu-decorated hBN using first principle calculations. The adsorption of COCl_2 onto pristine hBN was a physisorption due to their small adsorption energy. The physisorption of COCl_2 onto pristine hBN resulted in poor sensitivity and recovery time. Therefore, the Cu atom was adsorbed onto hBN and substitutional doped into hBN at N and B vacancy. The formation and binding energy suggest that the Cu atom doped at B vacancy is the most stable configuration. On the other side, the Cu atom adsorbed at the N site was the most stable configuration. Further, the adsorption energy upon COCl_2 adsorption onto Cu-doped hBN and Cu-hBN was found to be high, indicating that the adsorption process was a chemisorption and there exists strong chemical interaction between the COCl_2 and Cu-doped hBN and Cu-hBN. The RDG analysis revealed that there exists a weak vdW interaction between the COCl_2 and pristine hBN. In contrast, for the B2 and C2 adsorption configurations, it was the electrostatic interaction that caused the COCl_2 to orient with the O atom facing toward the Cu atom. This resulted in the strong electron transfer from the Cu atom to the COCl_2 verified from the Hirshfeld and charge density difference methods revealed. As a consequence, there was a shift in the impurity state towards the conduction band and a reduction in the band gap upon COCl_2 adsorption, indicating an enhancement in the sensitivity of the B2 and C2 adsorption configurations. The corresponding PDOS plot revealed that strong hybridization exists between the 3d-Cu atom and 2p-O atom, accounting for the strong interaction between the gas and the adsorbate. Furthermore, the calculated recovery time for the B2 and C2 adsorption configurations at 300K was found to be too high. Therefore, annealing at high temperatures under UV exposure improves the recovery time of the B2 and C2 adsorption configurations. Hence, the improved recovery time, better sensitivity, adsorption energy, and enhanced electrical conductivity upon COCl_2 adsorption validate that Cu-doped hBN and Cu-hBN are promising sensing materials at elevated temperatures for sensing COCl_2 .

CRediT authorship contribution statement

Anurag Bhandari: Writing – original draft, Software, Investigation,

Table 6

Calculated the recovery time for the Cu-doped hBN and Cu-hBN systems upon COCl_2 adsorption at different temperatures under visible light and UV radiation.

Temperature (K)	B2		C2	
	recovery time visible light	recovery time UV	recovery time visible light	recovery time UV
300 K	3.661×10^{-20} s	3.661×10^{-20} s	2.495×10^{-7} s	2.495×10^{-7} s
400K	2.647×10^{-12} s	2.647×10^{-12} s	3.530×10^{-7} s	3.530×10^{-7} s
500K	3.453×10^{-7} s	3.453×10^{-7} s	4.347×10^{-1} s	4.347×10^{-1} s
600K	1.913×10^{-6} s	1.913×10^{-6} s	4.995×10^{-3} s	4.995×10^{-3} s
700K	9.033×10^{-5} s	9.033×10^{-5} s	2.056×10^{-6} s	2.056×10^{-6} s
800K	1.626×10^{-4} s	1.626×10^{-4} s	1.879×10^{-6} s	1.879×10^{-6} s
900K	7.154×10^{-2} s	7.154×10^{-2} s	2.992×10^{-9} s	2.992×10^{-9} s
1000K	5.876×10^{-3} s	5.876×10^{-3} s	6.593×10^{-10} s	6.593×10^{-10} s

Conceptualization, Piyush Dua: Writing – review & editing, Validation, Supervision, Software, Methodology, Investigation. Mukhtiyar Singh: Writing – review & editing, Visualization. Kamal Upreti: Writing – review & editing, Visualization. Shubham Mahajan: Writing – review & editing, Data curation. S.S. Askar: Writing – review & editing, Visualization, Data curation. Mohamed Abouhewash: Writing – review & editing, Visualization, Formal analysis. Nitin K. Puri: Writing – review & editing, Supervision, Software, Resources.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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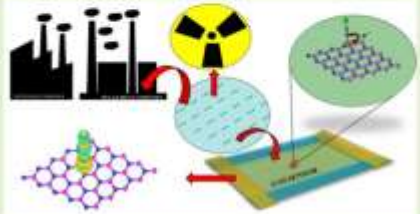
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Adsorption of Cyanogen Chloride Gas onto the Pristine and Copper-Decorated hBN Monolayer: A Comparative DFT Study

Anurag Bhandari, Nitin K. Puri, and Piyush Dua, *Member, IEEE*

Abstract—The adsorption of toxic gas such as Cyanogen Chloride (CNCI) onto the pristine and Cu-decorated hexagonal boron nitride (hBN) was investigated using Density Functional Theory (DFT). The adsorption of CNCI gas molecules onto pristine hBN was a physisorption resulted in poor recovery time. However, Cu decoration onto hBN modifies the electronic properties of hBN. Further CNCI adsorption onto Cu-hBN resulted in three structures abbreviated as B1, B2, and B3 structures. The calculated adsorption energies suggest that the adsorption of CNCI gas onto Cu-hBN was physisorption with enhanced adsorption energy and B3 was the most stable configuration. Further various parameter such as DOS, charge density differences, ELF were calculated for the most stable adsorption configuration. The DOS result revealed that CNCI adsorption enhances the conductivity by reducing the band gap. It was due to the charge transfer from CNCI gas to the Cu-hBN verified from charge density difference. The reduction in the band gap resulted 31.54% variation in the work function indicating highly sensitive behavior of the Cu-hBN system. Additionally, RDG analysis suggest that non covalent interaction between CNCI and Cu-hBN was responsible for the physisorption. Finally, the recovery time for CNCI adsorbed onto Cu-hBN was found to be 1.596×10^{-6} sec, 2.525×10^{-7} sec, and 2.098×10^{-8} sec at 300K, 400K, and 500K respectively. Hence, based on our DFT results, Cu-hBN system can be used as a practical sensor to detect CNCI gas at 300K

Index Terms—DFT, Copper, hBN, CNCI, Adsorption



I. Introduction

CNCI[1], being a colorless gas volatilizes into toxic gas upon exposure to air is primarily used in rubber, plastic, fumigants, and pesticides industries. Acute exposure to CNCI gas causes sleepiness, sore throat, cough, dizziness, and nausea[2]. In contrast, prolonged exposure causes respiratory failure, metabolic obstruction, and irreversible damage to the red blood cells and central nervous system[3]. Therefore, looking at the detrimental effects CNCI gas has on human health, there is a need to monitor, capture, and remove toxic gas for a safer and cleaner environment. In this regard, gas sensors capable to exhibit high selectivity, sensitivity, stability, and rapid recovery time in harsh environments are required. Two-dimensional (2D) materials such as graphene[4], black phosphorene[5], germanene[6], silicene, aluminum nitride (AlN)[7], Indium nitride (InN)[8], and transitional metal dichalcogenides (TMDs)[9, 10] have been extensively explored as sensing material due to their high surface to volume ratio, tunable optical and electronic properties, and structural diversities. However, due to certain limitation like absence of a dangling group, zero band gap in graphene[11], and low carrier mobility in TMDs hinder the practical application of these material as a sensing material in gas sensor. Moreover poor selectivity and sensitivity at elevated temperatures is also considered as bottleneck problems for these 2D materials [12]. Therefore, there is an inevitable need to explore alternative 2D

materials capable of exhibiting high sensitivity, selectivity, fast recovery time, stability, and reliable operation at high temperatures. In this regard, hBN, widely known as 'white graphene,' can be considered a suitable sensing material in harsh environments due to its unique properties, like high thermal conductivity and better structural stability at high temperatures[13, 14]. However, there have been numerous reports regarding the utilization of hBN as a sensor[15-17]. In contrast it was also concluded from the literature that pristine hBN-based gas sensors exhibit instantaneous recovery time, slower response, and poor selectivity[18]. This can be attributed to the weak adsorption ability of hBN due to its inherent chemical inertness. Therefore, to overcome the issue of weak adsorption ability and poor sensing performance of hBN, researchers have adopted the method of surface activation method by doping[19, 20] and substrate engineering[21, 22]. It has been well proven that metal atom decoration onto hBN enhance the adsorption ability and sensing performance of hBN. Recently, Kalwar et al. studied the adsorption of harmful toxic gases such as CO₂, CO, H₂S, HF, and NO onto a Ti-doped hBN monolayer[23]. Their study revealed that CO₂, CO, H₂S, HF, and NO got adsorbed onto Ti-doped hBN with adsorption energies -1.32eV, -1.66eV, -1.20eV, -0.81eV and -1.82eV respectively. Additionally, Ti decoration onto hBN resulted transitions from semiconductor to narrow band semiconductor and metal upon CO₂, H₂S, NO, and CO, HF adsorption,

Anurag Bhandari is with the Nanomaterial Research Laboratory, Department of Applied Physics, Delhi Technological University 110042, New Delhi, India (email: anurag9412131447@gmail.com).
Nitin K. Puri is with the Nanomaterial Research Laboratory, Department of Applied Physics, Delhi Technological University 110042, New Delhi, India (email: nitinkumar.puri@dtu.ac.in).

Piyush Dua associated with the Department of Applied Sciences, DBS Global University, Mi-122, behind Pharma City, Selakui, Central Hope Town, Dehradun, Uttarakhand (email: dua.piyush@gmail.com).

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respectively. The reported variation in the electronic properties and adsorption energy upon Ti decoration onto hBN lead to high sensitivity and better recovery time than pristine hBN. In another study Khan et al. reported that the adsorption of CO, COS, CH₂N₂ and CF₃O onto Fe-decorated hBN was chemisorption, whereas the adsorption of CO₂ and CH₄O onto Fe-decorated hBN was physisorption [24]. There exists various reports regarding the adsorption of CNCl gas onto metal-doped graphene quantum dots[25], Al and Ga-doped BN nanotubes[26], and phosphorene nanosheets[27]. However, there have been no reports regarding adsorption of CNCl gas onto Cu-decorated hBN monolayer has served as a motivation for this work. Therefore, in this work, we have investigated the adsorption of CNCl gas onto Cu-decorated hBN monolayer using DFT. Adsorption energy and adsorption distances were calculated in order to determine the strength of interaction during the adsorption of CNCl gas onto hBN and Cu-decorated hBN system. Moreover, to analyze the effect Cu decoration on hBN and CNCl gas adsorption had on the electronic properties, DOS and PDOS were calculated, respectively. Charge transfer during the interaction was analyzed quantitatively and qualitatively using charge density difference and Hirshfield calculation. RDG and ELF calculations were also performed to determine the existence of any non-covalent interaction and distribution of electron density around the interacting atoms. Finally, the sensitivity and recovery time of the Cu-decorated hBN and pristine hBN upon CNCl adsorption was evaluated utilizing the work function and adsorption energy, respectively. The outcome of the DFT study provides a deep insight into the adsorption mechanism and sensing performance of hBN and Cu-decorated hBN towards CNCl gas detection, which would be helpful for the experimentalist to design Cu-decorated hBN-based gas sensor.

II. COMPUTATIONAL DETAILS

All the computational calculations were carried out within the framework of DFT using the QUANTUM ESPRESSO[28] software package. To describe the correlation between the electrons, we have used Generalized Gradient Approximation (GGA)[29] with Perdew Burke-Ernzerhof (PBE)[30] as an exchange-correlation (XC) function. A Plane wave basis was implemented within the framework of the projector augmented wave (PAW) method. Ultra-soft pseudopotential [31] was used to represent the electron-ion interaction. For the proper convergence of the self-consistent field (SCF) calculation, we have performed a convergence test to determine the optimized cut-off energy and K points. From Fig.1(a) and Fig.1(b), we found 55Ry and 7x7x1 as the optimized cut-off energy and K points for the SCF calculation. Further, the hBN monolayer was grown along the X-Y plane by repeating the unit cell 5 times along the X and Y axes, resulting in a 5X5 supercell containing 25 B and 25 N atoms. A vacuum layer of 20Å applied along the z-axis to obstruct the interaction between the periodic replicas. To consider the weak vanderwaal (vdW) interaction in the total energy calculation, we have implemented the "Grimme DFT-D2" [32] approach. All the structures were fully optimized until the energy, pressure, and force convergence were less than 10⁻⁴ Ry, 0.5 kbar, and 10⁻³ Ry/Bohr, respectively, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme. Finally, VESTA software was used to visualize the adsorption distance, bond

angle, charge gain, and lost regions in the optimized structures. The RDG scatter and RDG isosurface plots were visualized using Multiwin and VMD software.

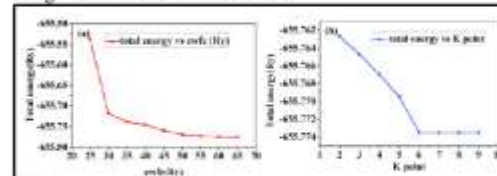


Fig. 1 Variation of (a) total energy with cut off energy (b) total energy with K points respectively.

III. RESULTS AND DISCUSSION

A. Structure and electronic properties analysis of hBN monolayer

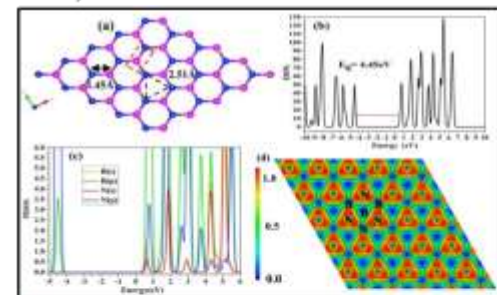


Fig. 2 (a) Optimized hBN monolayer (b) DOS (c) PDOS and (d) ELF. The atoms in blue and pink colors represent the N and B atoms, respectively. To investigate the structural properties of the hexagonal boron nitride (hBN) structure. For this purpose, we have optimized the structure. After optimization, the resulting structure, as shown in Fig.2(a), revealed that the B-N bond length and bond angle between B-N-B were 1.45 Å and 120°, respectively[33]. In contrast, the atomic distance between the nearest B-B and N-N atoms was 2.51Å, consistent with the previous theoretical and experimental studies[34, 35]. Further, to investigate the electronic properties of the hBN structure, we have calculated the Density of States (DOS). The plotted DOS, as shown in Fig.2(b), revealed that hBN is a wide gap insulator with an energy band gap (E_g) of about 4.45 eV, which agrees with the previous theoretical studies[36, 37]. Moreover, the projected density of states (PDOS) was also calculated to determine the contribution of different atomic orbitals to the DOS. The PDOS plot shown in Fig.2(c) revealed that significant contributions to the valence band (VB) and conduction band (CB) were from the 2p orbitals of the B and N atoms, respectively. We have utilized the Electron Localization Function (ELF) to visualize the electron density distribution between the atoms. The resulting ELF plot, shown in Fig.2(d), illustrated a region of high and low electron densities around the N and B atoms identified by red and blue-colored regions, respectively. The observed variation in the electron density was due to the difference in the electronegativity. Being highly electronegative, the N atom withdrew electrons from the B atom, making the N-site electrons rich and the B-site electrons deficient. Thus, ELF confirmed the behavior of N and B atoms as electron donors

and acceptors, respectively. Hence, the observed structural and electronic properties suggest that the resulting optimized hBN structure is a monolayer.

B. Adsorption of CNCl gas onto pristine hBN monolayer

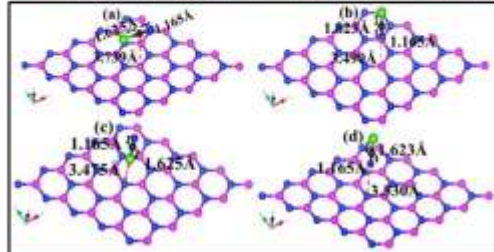


Fig. 3 Side view of the different optimized structures (a) A1, (b) A2, (c) A3, and (d) A4, respectively. The pink, blue, black, and green atoms correspond to B, N, C, and Cl atoms.

TABLE I
CALCULATED ADSORPTION ENERGIES, HEIGHTS, FOR THE DIFFERENT OPTIMIZED STRUCTURES

systems	Adsorption heights (Å)	Adsorption Energy (eV)
A1	3.739	-0.191
A2	3.490	-0.141
A3	3.475	-0.189
A4	3.530	-0.094

To analyze the interaction of CNCl gas with the hBN monolayer, we have considered the B site (on top of the B atom) and the N site (on top of the N atom) as the adsorption sites. This is because the gas molecules can easily interact with the electron-deficient (B site) or electron-rich (N site) sites. For the adsorption study, we have considered different orientations of CNCl gas at N and B sites as the input geometries for optimization. Upon optimization, we obtained four different optimized structures abbreviated as A1, A2, A3, and A4. As shown in Fig.3, the resulting optimized structures revealed that the C-Cl and C-N bond lengths underwent no significant variation upon adsorption. This indicates weak interaction between the CNCl gas and the hBN layer. In A1 and A2 geometries, the CNCl gas molecule got adsorbed at a distance of 3.739 Å and 3.490 Å in a direction perpendicular and parallel to the z-axis with the C and N atoms orientating towards the B sites, as shown in Fig. 3(a) and 3(b), respectively. In A3 and A4 geometries, the CNCl gas molecule got adsorbed at a distance of 3.475 Å and 3.530 Å in a direction perpendicular to the z-axis with the Cl and N atoms orientating towards the N sites, as shown in Fig. 2(c), and 2(d), respectively. Further adsorption energies (E_{ad}) for the optimized structures were calculated using equation (1) where $E_{hBN-CNCl}$, E_{hBN} , and E_{CNCl} represent the total energies of the CNCl gas adsorbed onto hBN complexes, pristine hBN, and isolated CNCl gas molecule, respectively.

$$E_{ad} = E_{hBN-CNCl} - (E_{hBN} + E_{CNCl}) \quad (1)$$

From Table 1, the adsorption energies for the A1, A2, A3, and A4 geometries were found to be -0.191 eV, -0.141 eV, -0.189 eV and -0.094 eV respectively. The reported negative value in Table 1 suggests that the adsorption process was exothermic. Based on energy minimization, we found A1 to be the most stable among the various optimized structures[38]. We have referred A1 configuration as 'CNCl-hBN' for the rest of the

study. The calculated adsorption energy suggests that the adsorption of the CNCl gas molecule onto the hBN monolayer was a physisorption. Moreover, the reported adsorption distance in Table I was larger than the sum of the atomic radii of B, N, C, and Cl atoms, confirmed weak interaction between the CNCl gas molecule and the hBN layer. Hence, from the perspective of the adsorption study, we found that pristine hBN has a weak adsorption ability for CNCl gas molecules.

C. Analysis of the recovery time for the CNCl gas adsorbed onto the hBN monolayer

To analyze the gas sensing performance of the CNCl-hBN, we have calculated recovery time (τ), defined as the time required by the gas molecule to desorb entirely from the surface of the sensing material using equation (3).

$$\tau = \nu^{-1} e^{\left(\frac{E_{ad}}{k_B T}\right)} \quad (3)$$

Where T is the testing temperature measured in Kelvin (K), k_B is the Boltzmann constant whose value is 8.26×10^{-5} eV/K. E_{ad} is the potential barrier for desorption of gas molecules, which can be substituted with E_{ad} , because adsorption and desorption are reverse processes to each other, and ν represents the attempt frequency, which is 10^{12} Hz[39] for the visible radiation. According to equation (3), the recovery time for the CNCl-hBN system was found to be 2.225×10^{-6} s under visible light exposure at 300K, which is too small to produce any variation in the electronic property of the hBN. Hence, based on the recovery time analysis, we found that the hBN sheet cannot be utilized as a gas sensor to detect CNCl gas at room temperature.

D. Adsorption of Cu atom onto the hBN monolayer

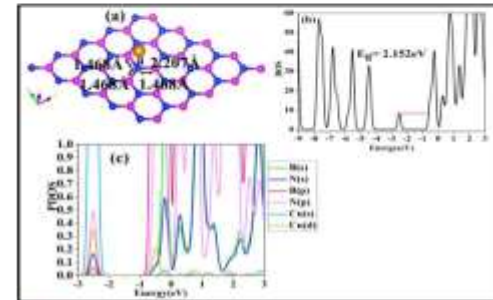


Fig. 4 (a) optimized structure, (b) DOS, and (c) PDOS of the Cu-hBN, respectively.

In the previous section, we observed that pristine hBN exhibits poor gas adsorption ability and sensing performance towards CNCl gas. The decoration of Transition metal (TM) atoms onto 2D material enhances the gas adsorption capability of 2D material. Therefore, we decorated the Cu atom onto the hBN layer by placing the Cu atom above the N site. Among the various TM metal atoms, we have selected the Cu atom because it is inexpensive, abundant in nature, and does not get poisoned by analyte[40]. Based on previous theoretical studies, we have selected the N site as the most preferential adsorption site for the Cu atom[41, 42]. Upon optimization, the resulting optimized structure is abbreviated as Cu-hBN. The optimized structure revealed that the B-N bond length increased from

1.450Å to 1.468Å, and the CNCl gas got adsorbed at a distance of 2.207Å with adsorption energy -0.33eV. The observed increment in the B-N length indicates that the B-N ring undergoes expansion to incorporate the Cu atom. Further, cohesive energy ($E_{coh}/atom$) was calculated using equation (4) to determine the thermodynamic stability of the Cu-hBN system.

$$E_{coh} = \frac{E_{hBN-Cu} - (x \cdot E_B + y \cdot E_N + z \cdot E_{Cu})}{n} \quad (4)$$

where E_{hBN-Cu} , E_B , E_N , E_{Cu} , x , y , and z represent the total energies of the Cu-hBN system, isolated B, N, Cu atoms, number of B, N, and total atoms within the unit cell, respectively. According to equation (4), the $E_{coh}/atom$ for the Cu-hBN system was found to be -1.40eV/atom. The negative value of the $E_{coh}/atom$ indicates that the structure remained thermodynamically stable, which is consistent with the other theoretical calculations[43-45]. Additionally, we have performed DOS calculations to investigate the electronic properties of the Cu-hBN system. From Fig.4(b), we observed that the impurity state within the energy range -3 to -2eV reduces the band gap from 4.45eV to 2.152eV upon Cu decoration. It was confirmed from the PDOS study that the impurity state is a result of the hybridization between the 4s-Cu and 2p-N orbitals, as shown in Fig.4(c). The observed reduction in the band gap indicates an enhancement in the electrical conductivity of the hBN layer. This might occur due to the charge transfer from the Cu atom to the hBN layer. Hence, the observed structural and electronic properties suggest that Cu atom decoration onto hBN modifies the structural and electronic properties of the hBN layer.

E. Adsorption of CNCl gas onto the Cu-decorated hBN monolayer

TABLE II
CALCULATED ADSORPTION ENERGIES, HEIGHTS, AND BOND LENGTHS FOR THREE DIFFERENT OPTIMIZED ADSORPTION CONFIGURATIONS

systems	Adsorption heights (Å)	C-N bond length (Å)	C-Cl bond length (Å)	Adsorption Energy (eV)
B1	3.881	1.166	1.623	-0.204
B2	2.960	1.167	1.672	-0.126
B3	1.859	1.172	1.650	-0.411

To analyze the interaction of the CNCl gas with the Cu-hBN system, we have considered different orientations of the CNCl gas at the dopant site as the input geometry for optimization. The dopant site is selected as the adsorption site because the CNCl gas molecule can readily be adsorbed at the dopant site. After optimization, we got three optimized structures abbreviated as B1, B2, and B3, respectively as shown in Fig.5. The optimized structure shown in Fig.5(a), Fig.5(b) and Fig.5(c) suggests that the C-Cl bond lengths are 1.166Å, 1.167Å, and 1.172 Å for the B1, B2, and B3 configurations. In contrast, the C-N bond lengths are 1.623Å, 1.672Å, and 1.650Å for the B1, B2, and B3 configurations. We found on the comparison that the C-Cl and C-N bond lengths of CNCl gas upon adsorption vary from that of the isolated CNCl molecule in all the optimized structures. The observed variation in the bond length was due to the catalytic effect of Cu atom. Further, adsorption energies were calculated using equation (5) and reported in Table II to determine the interaction strength between the CNCl gas and Cu-decorated hBN monolayer.

$$E_{ads} = E_{hBN-Cu-CNCl} - (E_{hBN-Cu} + E_{CNCl}) \quad (5)$$

Where E_{CNCl} , $E_{hBN-Cu-CNCl}$ and E_{hBN-Cu} represents the total energies of the isolated CNCl gas molecule, Cu-decorated hBN with and without CNCl gas molecule, respectively. Table II shows the adsorption energies for the B1, B2, and B3 structures were found to be -0.204eV, -0.126eV, and -0.411eV, respectively. The negative value of the adsorption energies suggested that the adsorption process was exothermic. We found that the B3 structure was the most stable among the various optimized structures because of its lowest adsorption energy. For the rest of the study, we have referred to B3 as "CNCl-Cu-hBN". The reported adsorption energy in Table II suggests that the adsorption process was a physisorption. Moreover, the reported adsorption energy in Table II was more enhanced than the adsorption energy in Table I on comparison. This indicates that the Cu-hBN system has better adsorption affinity than the pristine hBN for CNCl gas. Hence, the adsorption study suggests that the decoration of the Cu atom onto hBN is an effective way to enhance the gas adsorption ability of the hBN sheet towards the CNCl gas.

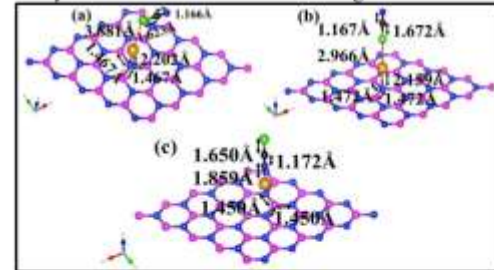


Fig. 5 Side view of the different optimized structures (a) B1, (b) B2, and (c) B3, respectively. The orange color corresponds to the Cu atom.

F. Electronic properties analysis

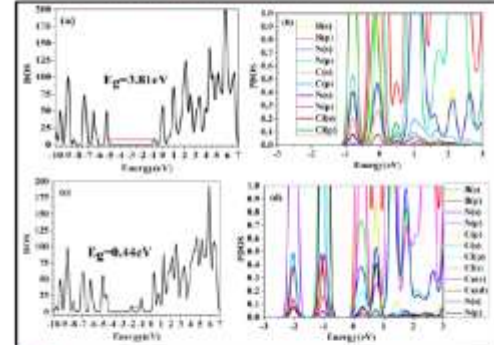


Fig. 6 (a) DOS and (b) PDOS plots for the CNCl-hBN system. (c) DOS and (d) PDOS plot for the CNCl-Cu-hBN system, respectively.

To analyze the effect CNCl gas had on the electronic properties of hBN and Cu-hBN systems, we have performed DOS and PDOS calculations for CNCl-hBN and CNCl-Cu-hBN systems. The DOS results shown in Fig.6(a) revealed that CNCl gas introduces an impurity state in the energy range -1 to 0eV, thereby reducing the band gap from 4.45eV to 3.81eV in the case of the CNCl-hBN system. In the case of the CNCl-Cu-hBN system, CNCl gas introduces a new impurity state at -1eV

adjacent to the impurity state created upon Cu decoration at -2eV, as shown in Fig.6(c). The new impurity state facilitates easy charge transfer from the Cu atom to the CNCl gas during the interaction, reducing the band gap from 2.152eV to 0.44eV. Further, the PDOS plot in Fig.6(b) indicates hybridization between the 3p-N and 2p-C atomic orbitals of hBN and CNCl gas responsible for creating an impurity state in the energy range -1to0eV. From Fig.6(d), we found that hybridization between the 3p-N and 4s-Cu atomic orbitals of CNCl and Cu-hBN was responsible for the observed impurity state in the energy range -2to-1eV. On comparison, we found that CNCl produces significant variation in the band gap of Cu-hBN, thereby enhancing the conductivity of the Cu-hBN system. This might be due to the significant charge transfer during the interaction. Hence, based on the observed variation in the electronic properties of CNCl-hBN and CNCl-Cu-hBN systems, we found that the Cu-hBN system can be used as an electronic sensor.

G. Non-Covalent Interaction (NCI) analysis

To determine the existence of non-covalent interaction between the CNCl gas molecules and adsorbent, we have performed the reduced density gradient (RDG) analysis proposed by Johnson and co-workers. The results obtained from the RDG analysis were visualized using the RDG scatter plot and RDG isosurfaces, as shown in Fig.7. The RDG scatter plot represents the relationship between the RDG function $s(r)$ and $\text{sign}(\lambda_2) \rho(r)$, where λ_2 represents the second eigenvalues of the Hessian matrix interaction and $s(r)$ defines a relation between the electron $\rho(r)$ and its gradient $(\nabla \rho(r))$ as follows:

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho|}{\rho(r)^{4/3}} \quad (6)$$

The function $\text{sign}(\lambda_2) \rho(r)$ is of great significance as it provides information about the nature of the interaction. If $\text{sign}(\lambda_2) \rho(r) < 0$, $\text{sign}(\lambda_2) \rho(r) = 0$, and $\text{sign}(\lambda_2) \rho(r) > 0$, it indicates strong attractive hydrogen bonding, weak van der Waals (vdW), interaction, and strong repulsive steric effects. In Fig. 7(a), the RDG scatter plot illustrated a sharp decline in the RDG function value around $\text{sign}(\lambda_2) \rho(r) = 0$ for the CNCl-hBN system. Further, the corresponding RDG isosurface plot in Fig. 7(b) illustrated green patches between the CNCl gas and hBN layer, indicating vdW interaction between the CNCl gas and hBN layer. These findings confirmed that the adsorption of CNCl gas onto hBN was physisorption. The RDG scatter plot in Fig.7(c) illustrated a fluctuation in the RDG value around $\text{sign}(\lambda_2) \rho(r) > 0$ and $\text{sign}(\lambda_2) \rho(r) = 0$ upon CNCl adsorption onto Cu-hBN systems. From Fig.7(d), the corresponding RDG isosurface plot illustrated blue patches between the CNCl gas and hBN layer and green patches between the Cu atom and hBN layer. The observed blue patches indicate that the interaction of CNCl gas with the Cu atom is purely electrostatic and responsible for the observed enhancement in the adsorption energy. These findings suggest that Cu-hBN binds CNCl more effectively than pristine hBN. This proved that Cu-hBN system has better adsorption affinity for CNCl gas than pristine hBN. Hence, based on our RDG analysis, we found that non-covalent interaction exists, which strongly influences the adsorption of CNCl gas and sensitivity of the hBN and Cu-hBN systems.

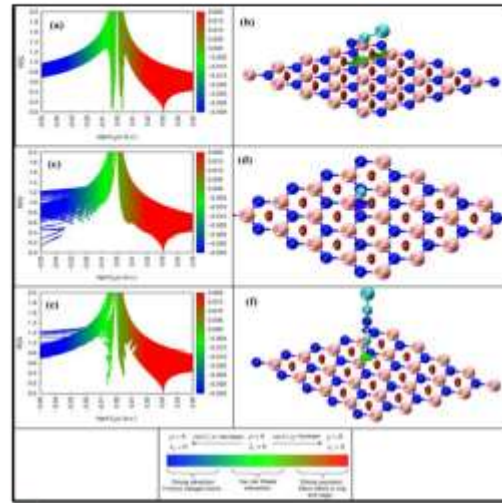


Fig. 7 RDG scatter plot for the (a) CNCl-hBN, (c) Cu-hBN, and (e) CNCl-Cu-hBN systems. Isosurface plot for the (b) CNCl-hBN, (d) Cu-hBN, and (f) CNCl-Cu-hBN systems, respectively.

H. Charge Density Difference analysis

TABLE III
CALCULATED CHARGE TRANSFER FOR CNCL-HBN AND CNCL-CU-HBN ADSORPTION CONFIGURATIONS

Configuration	CNCL-hBN	CNCL-Cu-hBN
Charge transfer	0.067e	0.142e

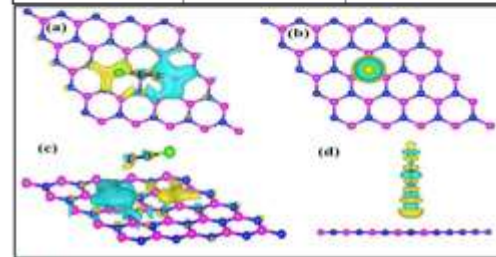


Fig. 8 (a) DOS and (b) PDOS plots for the CNCl-hBN system. (c) DOS and (d) PDOS plot for the CNCl-Cu-hBN system, respectively

To investigate the charge transfer during the interaction of CNCl gas with the sensing material, we have utilized charge density difference and Hirshfield methods to visualize the charge transfer. The charge density difference ($\Delta \rho$) was calculated using equation (7).

$$\Delta \rho = \rho_{AB} - \rho_A - \rho_B \quad (7)$$

Here, ρ_{AB} , ρ_A , and ρ_B represent the charge density of the complex with gas molecule, complex and gas, respectively. From Hirshfield charge analysis, we found that 0.067e was transferred between CNCl and hBN, whereas 0.142e was transferred between CNCl and Cu-hBN. It was on comparison of the reported charge transfer in Table III we found that significant charge transfer took place in the case of CNCl-Cu-hBN. This was verified from the charge density difference diagram shown in Fig.8. From Fig.8(a) and 8(c), we observed a

small region of charge loss and gain around the N and C atoms of the CNCl gas molecule identified by the cyan and yellow color, respectively. This indicates weak charge transfer from hBN to CNCl. Further, Fig.8(b) and 8(d) illustrate significant charge loss and gain regions around the Cu and N atoms. This indicates that a significant charge was transferred from the Cu atom to the CNCl gas. The observed charge transfer can be attributed to the difference in the electronegativity between the Cu and N atoms. Being highly electronegative, the N atom withdraws electrons from the highly electropositive Cu atom during the interaction. Hence our charge density difference results agreed with the Hirshfeld charge analysis.

I. Electron Localization Function analysis

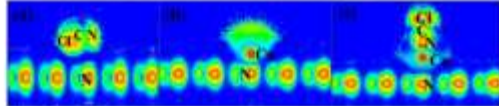


Fig. 9 ELF plot for (a) CNCl-hBN, (b) Cu-hBN, and (c) CNCl-Cu-hBN systems, respectively.

We have performed ELF calculations to analyze the distribution of electrons around the interacting atom during the adsorption of CNCl onto sensing material. The ELF plot shown in Fig.9(a) illustrates high electron density around N and Cl atoms, indicating the highly reactive sites of CNCl gas identified by red. Moreover, a large region of low electron density exists in the interacting region identified by the blue color. This indicates a weak interaction between CNCl gas and the hBN layer. However, upon Cu decoration, we found a large red color region around the N atom compared to the Cu atom, as shown in Fig.9(b). This happens due to the electron transfer from the Cu atom to the nearby N atom, making the Cu atom electropositive and the N atom electron-rich. Further upon CNCl adsorption, we observe a large red-colored region around the CNCl gas compared to the Cu atom, as shown in Fig.9(c). This indicates that electrons were transferred from the Cu atom to the CNCl gas, confirming the interaction of CNCl gas with the Cu atom is purely electrostatic. These findings were consistent with our RDG result that a strong, attractive interaction exists between the CNCl gas and Cu-hBN layer upon CNCl adsorption. Hence, our ELF results were in agreement with the RDG analysis.

J. Sensitivity analysis

TABLE IV
CALCULATED ELECTRICAL CONDUCTIVITY FOR CNCL-HBN AND CNCL-CU-HBN AT DIFFERENT TEMPERATURES

Configuration	σ ($\Omega^{-1} m^{-1}$) at $T=300K$	σ ($\Omega^{-1} m^{-1}$) at $T=400K$	σ ($\Omega^{-1} m^{-1}$) at $T=500K$
CNCl-hBN	1.017×10^{-12}	1.012×10^{-14}	6.373×10^{-10}
CNCl-Cu-hBN	2.019×10^{-4}	1.694×10^{-5}	6.069×10^{-3}

The sensitivity of the semiconducting material is judged mainly by its electrical conductivity, which undergoes a variation with the adsorption of the gas molecule. Therefore, we utilized equation (8) to calculate the electrical conductivity of the CNCl-hBN and CNCl-Cu-hBN systems.

$$\sigma = A e^{\frac{-E_g}{2k_B T}} \quad (8)$$

where σ is electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and k_B is the Boltzmann constant in eV/K. The calculated data in Table IV indicates that the electrical conductivity of the CNCl-hBN and

CNCl-Cu-hBN systems increases with temperature and upon CNCl adsorption. The observed increase in the electrical conductivity with temperature indicates the semiconductor behavior of the CNCl-hBN and CNCl-Cu-hBN systems. On comparison, we found that the CNCl-Cu-hBN system exhibits better electrical conductivity than the CNCl-hBN system. This can be attributed to the large reduction in the band gap upon gas adsorption. The DOS calculation verified that the CNCl adsorption reduces the band gap by 14.38% and 79.58% in the case of CNCl-hBN and CNCl-Cu-hBN systems. Significant variation in the band gap of the CNCl-Cu-hBN system leads to efficient charge transfer between the interacting species, leading to measurable changes in the electrical signal. This indicates that the CNCl-Cu-hBN system exhibits sensor properties and can be used as an electronic sensor. Hence, all these findings suggest that Cu decoration onto hBN improves the sensitivity of the hBN layer toward CNCl gas.

K. Work function analysis

The sensitivity of the sensing material in a work function-based gas sensor is generally determined by the work function (ϕ). Since any variation in the work function ($\Delta\phi$) causes changes in the emitted electron current densities, this can be inferred from equation (9), which shows the exponential dependence of emitted electron current densities on ϕ .

$$j = A T^2 e^{\left(\frac{-\phi}{k_B T}\right)} \quad (9)$$

where j is the emitted electron current densities (A/m^2), A is a Richard constant ($A/m^2 K^2$), ϕ is the work function of the material in eV, T is the temperature in K, and k_B is the Boltzmann constant in eV/K respectively. Therefore, we have analyzed qualitatively variation in the work function ($\Delta\phi$) of hBN and Cu-hBN systems upon CNCl adsorption. For this purpose, the work function for these systems was calculated using equation (10).

$$\phi = E_{inf} - E_F \quad (10)$$

E_{inf} and E_F represent the electrostatic potential at infinity and Fermi level energy. The electrostatic potential at infinity is assumed to be zero. In contrast, variation in the value of $\Delta\phi$ was calculated by subtracting the work function of the sensing material without gas molecules from that of the sensing material with gas molecules. The computed value of ϕ for the pristine hBN with and without gas molecules was found to be 2.44eV and 2.12eV, respectively. In contrast, for the Cu-hBN system, the value of ϕ with and without gas molecules was found to be 1.154eV and 0.790eV, respectively. Further, on comparison, we found a large negative variation in the work function of the Cu-decorated hBN sheet. The large negative variation can be attributed to the significant charge transfer between the CNCl and Cu-hBN, validated by our charge density difference calculations. Hence, from the perspective of work function analysis again, we found that the Cu-hBN system exhibits better sensitivity towards CNCl gas than the pristine hBN.

L. Recovery time analysis

TABLE V
CALCULATED RECOVERY TIME AT THREE DIFFERENT TEMPERATURES FOR CNCL-CU-HBN

Visible light exposure		Ultraviolet exposure	
Temperature	Recovery time	Temperature	Recovery time
300 K	1.596×10^{-5} sec	300K	1.596×10^{-5} sec
400K	2.525×10^{-5} sec	400K	2.525×10^{-5} sec
500K	2.098×10^{-5} sec	500K	2.098×10^{-5} sec

Recovery time is considered a key indicator in evaluating the reusability of a gas sensor. Therefore, we have calculated the recovery time for the CNCI-Cu-hBN system to investigate its practical utility as a gas sensor. The calculated recovery time for the CNCI-Cu-hBN system at 300K under visible light was found to be 1.596×10^{-5} sec, which is better than the reported recovery time for the CNCI-hBN system. This was due to the better adsorption affinity of the Cu-hBN system for CNCI gas. According to equation (3), increasing the temperature, attempt frequency, or both can reduce recovery time if adsorption energy is kept constant. Recently, Li et al. reported that ultraviolet (UV) radiation assists quick recovery time of the gas sensor[46]. Therefore, to analyze the effect annealing and exposure to UV radiation had on the recovery time of the CNCI-Cu-hBN system. We have calculated and reported the recovery time in Table V at 400K and 500K under visible and UV light exposure. The reported data in Table V indicate that the recovery time reduces from 1.596×10^{-5} sec to 2.525×10^{-5} sec and 2.098×10^{-5} sec upon annealing and exposure to UV light at 400K and 500 K, respectively. Hence, the reported data suggest that annealing above 500K under UV radiation makes recovery time too short to reuse as a gas sensor to detect CNCI gas.

IV. CONCLUSION

In this study, we have systematically investigated the sensing performance of hBN and Cu-hBN systems towards CNCI gas using DFT. From the adsorption study, the adsorption of CNCI gas onto hBN was physisorption involving weak vanderwaal interaction between them. However, upon Cu adsorption, the adatom creates new electronic states within the band gap region due to the strong hybridization between the 4s-Cu and 2p-N atomic orbitals verified from the DOS and PDOS calculation. This facilitates the easy charge transfer from the adsorbed Cu atom to the nearby N atom. As a consequence, the Cu atom enhances the nucleophilic nature by becoming a highly electropositive atom, whereas the surrounding N atoms become an electron-rich species verified from the ELF calculation. This makes the Cu-decorated hBN surface highly reactive towards the adsorption of the gas molecule containing electrophilic species. Further, upon CNCI adsorption Further, as the CNCI gas approaches the adsorbed Cu atom, the adatom tries to orient the CNCI in such a way that the nucleophilic part of the CNCI gas faces toward the Cu atom to maximize the electrostatic interaction and charge transfer between. This causes an increment in the adsorption energy thereby validating that Cu decorated hBN binds CNCI gas effectively than hBN due to the involvement of the electrostatic interaction. Finally, the recovery time analysis revealed that the Cu-hBN system exhibits better recovery time than the pristine hBN, which can be further reduced by annealing under UV radiation. Hence, based on our DFT results, we conclude that the Cu-hBN system can be used as a gas sensor to detect CNCI gas.

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8

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Anurag Bhandari is currently working at the Nanomaterial Research Laboratory and pursuing his PhD degree from Delhi Technological University, Delhi, India. His research area of interest includes investigating the potential of 2D material as a gas-sensing material for toxic gases.



Prof. Nitin K. Puri is currently working as an Executive Director at the National Institute of Electronics and Information Technology (NIELIT), Patna. He obtained his Ph.D. degree in 2004 from the Cyclotron Laboratory, Punjab University, Chandigarh, India. After completing his doctoral studies, he pursued post-doctoral research at Hong Hua Co. Ltd, Sichuan, China. Since 2010, Prof. Puri has been a faculty member at DTU, where he is also the lab in charge of the Advanced Sensor Lab (ASL) and the Nanomaterials Research Laboratory (NRL). His research interests lie in the areas of gas sensors, biosensors, nanotechnology, ion-beam modification of materials, thin films, and 2D nanomaterials, with a focus on sensing applications, particularly in gas and biosensing technologies. Prof. Puri is also an active member of several renowned scientific societies,

including the Indian Science Congress Association (ISCA), the Indian Society for Technical Education (ISTE), and the Indian Society of Radiation Physics (ISRP). He has held significant leadership roles, including serving as Chairman of the Working Group (WG-III) at the International Atomic Energy Agency (IAEA) in Vienna, Austria, in 2017 and as Vice Chairman of the same group in 2015. He was also a member of the National and International Advisory Board for the Electrical Energy: Safety and Conservation conference at the University of Delhi in 2016.



Dr. Piyush Dua obtained a Ph.D. degree from the Indian Institute of Technology (IIT), Roorkee, India, in 2005. Presently, he is working as a Professor at DSS Global University, Dehradun. He had worked as a Post-Doctoral Scientist at POSTECH, Pohang, Korea. He had published 40+ papers in refereed journals of international repute. He has various awards and credentials to his credit. He was selected as a category 'A' speaker by DST, Government of India. He has received the Asia award from Blackboard Company for innovation and excellence in the Blackboard global community of practice for the faculty development program. Dr. Dua has contributed as an Expert Speaker at the India International Science Festival, 2020 and 2021, organized by the Government of India, and as an Expert Speaker at Azadi Ka Amrit Mahotsav and 80 Years of CSIR in 2021, Organized by AMPRI, Bhopal (CSIR Lab).



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A deep insight into the adsorption mechanisms of lithium-ion battery thermal runaway gases onto Cu-decorated hBN for gas sensing applications using DFT

Anurag Bhandari,^a Nitin K. Puri,^{b,*} Piyush Dua^{b,c} and Rishu Chaujar^{b,a}

Lithium-ion batteries, due to their environmental friendliness and high energy capacity, are extensively used in the field of transportation and energy storage. However, the problem of thermal runaway in lithium-ion batteries has become a serious threat to humans. Therefore, considering these issues, we have investigated the adsorption mechanism of thermal runaway gases (C_2H_4 , CO, CO_2 , H_2 , and CH_4) onto pristine hBN and Cu-doped hBN using Density Functional Theory (DFT). The adsorption of C_2H_4 , CO, CO_2 , H_2 , and CH_4 gas molecules on pristine hBN occurs via physisorption, resulting in poor recovery time, charge transfer, selectivity and sensitivity. However, substitutional doping of Cu atoms at the B vacancies causes thermal runaway gases to be adsorbed chemically. DOS calculations showed that the adsorption of C_2H_4 , CO, CO_2 , H_2 , and CH_4 gas molecules reduces the band gap of Cu doped hBN, indicating the chemoresistive behaviour of Cu-doped hBN. Furthermore, various other calculations, such as charge density differences, showed that C_2H_4 , CH_4 , CO, CO_2 and H_2 gases act as electron donors and Cu-doped hBN acts as an electron acceptor, whereas RDG calculations confirmed that weak vdW and strong attractive non-covalent interactions exist in the case of pristine hBN and Cu-doped hBN, respectively. Finally, our DFT results confirmed that Cu-doped hBN exhibits enhanced sensitivity and recovery time towards thermal runaway gases, thereby making Cu-doped hBN a potential candidate for use as a sensing material in gas sensors to detect thermal runaway gases.

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1 Introduction

Fossil fuels have been the primary source of energy in industrialisation, transportation, and domestic heating.^{1–3} Due to globalisation, there has been a rapid increase in the consumption of fossil fuels, causing depletion of natural resources, a rise in environmental pollution, and global warming, which has become the most important issues human race is facing today.^{4–6} Therefore, there is an inevitable need to develop clean and sustainable green energy, which is challenging without the help of energy storage technologies.⁷ In response to these challenges, researchers are actively working towards the development of electrochemical energy storage systems. Among the various electrochemical energy storage systems such as lead-acid,⁸ lithium-ion,^{9,10} sodium-ion,¹¹ and nickel-cadmium¹² batteries, it is lithium-ion batteries that have attracted significant attention due to their high energy density,

long cycling time, and lack of memory effects.^{13,14} As a consequence, they are finding their utility as an energy storage system in Electric Vehicles (EVs),^{15,16} portable electronics,^{17,18} aerospace,¹⁹ power grids, and other fields. However, due to electrical,²⁰ thermal and mechanical abuse,^{21–23} lithium-ion batteries undergo thermal runaway conditions generating heat that doesn't get dissipated from the battery, thereby causing a rapid increase in the pressure and temperature, which accelerates the reaction rate, ruptures the cells, and releases highly flammable gases like C_2H_4 , CO_2 , CO, CH_4 and H_2 . The continuous production of these flammable gases causes lithium-ion batteries to explode, leading to major accidents. According to a report, a total of 357 incidents related to thermal runaway of lithium-ion batteries were reported from 2006 to 2022, and in the year 2020, over 100 cases of self-burning of electric vehicles were reported.²⁴ Since the thermal runaway condition in lithium-ion batteries is unavoidable, there is a necessary and urgent need to monitor thermal runaway gases in order to ensure the safety of the environment and human civilization. Currently, various gas detection techniques such as gas chromatography and mass spectrometry exist, but these detection techniques are expensive, time-consuming, and require a skilled operator for their operation²⁵ whereas

^aDepartment of Applied Physics, Delhi Technological University, Delhi, 110042, India.
E-mail: nitinkumarpari@delhi.ac.in

^bNational Institute of Electronics & Information Technology (NIELIT), Patna, India.
E-mail: dir-patna@nielit.gov.in

^cDepartment of Applied Sciences, DBS Global University, Setaqui, Central Hope Town, Dehradun, Uttarakhand, 248011, India

techniques like infrared thermography and acoustic are also expensive and difficult to implement in portable devices due to their large volume.²⁶ In response to these issues, gas sensors can be considered as an optimal detection technique because of their low cost, ease of operation and simple preparation methods.²⁷ For this purpose, researchers are extensively exploring various layered structures such as graphene, Transition Metal Dichalcogenides (TMDs),^{28,29} blue phosphorene,^{30,31} Transition Metal Chalcogenides (TMCs),^{32,33} Gallium Nitride (GaN),^{34,35} Aluminium Nitride (AlN),^{36,37} MXene,³⁸ and metal oxides^{39,40} due to their high surface-to-volume ratio, tunable band gap, good compatibility with modern electronics.⁴¹ Despite having such unique properties, these materials in their pristine form are practically immature to meet the current requirements as sensing materials. In order to overcome these issues, researchers have adopted various methods such as surface functionalization through transition metal (TM) doping,^{42–44} substrate engineering,^{45,46} and defect engineering.⁴⁷ Previous studies have proved that doping TM atoms into 2D materials significantly improves the gas sensing characteristics. For example, Yu *et al.* investigated the adsorption of CNCl, HCN, and NH₃ on metal-doped diamane.⁴⁸ He observed that the introduction of the metal atom improves the adsorption capacity and sensitivity of the diamane. Mohammadi *et al.* reported that the adsorption of H₂S, Cl₂, NH₃, and COCl₂ gases onto B₁₂C₆N₆ occurs via physisorption, whereas Li-decorated B₁₂C₆N₆ exhibits excellent sensitivity towards Cl₂ and COCl₂ gas molecules.⁴⁹ Hussain *et al.* studied the adsorption of COCl₂ onto Cu-decorated B₁₂N₁₂ nanocages. Their findings indicate that Cu atom decoration onto B₁₂N₁₂ nanocages enhances the adsorption strength, stability, and chemical reactivity of B₁₂N₁₂, and Cu-decorated B₁₂N₁₂ nanocages can be used as efficient gas sensors for the detection of COCl₂ gas molecules.⁵⁰ Xiao *et al.* prepared Pt-BiVO₄ nanosheets *via* a two-phase method. He observed that the Pt-BiVO₄-based gas sensor exhibits high sensitivity, excellent stability, and a low detection limit towards acetone compared to BiVO₄.⁵¹ Beheshtian *et al.* emphasised that doping of Sc atoms into boron nitride nanotubes (BNNTs) enhances the adsorption capability and electrical conductivity of BNNTs upon COCl₂ adsorption, thereby making Sc-doped BNNTs a potential candidate for use as electronic sensors to detect COCl₂ gas molecules.⁵²

There exists a plethora of literature reporting the utilisation of 2D materials as sensing materials to detect thermal runaway gases. Wu *et al.*⁵³ investigated the adsorption and gas sensing properties of Cu_n and Pd_n (*n* = 1–3) cluster-modified MoSe₂ for lithium-ion battery thermal runaway gases. Their results revealed that Cu_n-MoSe₂ and Pd_n-MoSe₂ have potential applications as sensing materials towards thermal runaway gases. Li *et al.* also investigated the adsorption and gas sensing properties of Cu-embedded HfS₂ (Cu-HfS₂) and Cu-decorated HfS₂ (Cu@HfS₂) using DFT.⁵⁴ Their studies revealed that Cu@HfS₂ has a strong adsorption capability towards CO, C₂H₄, and H₂, whereas Cu-HfS₂ has a strong adsorption capability towards CH₄ and CO₂. In another study, Xue *et al.* studied the gas sensing properties of precious metal (Ag and Au) modified Janus MoSeTe for lithium-ion thermal runaway gases.⁵⁵ Their

findings revealed that the introduction of Ag and Au significantly improved the adsorption capacity and charge transfer of Ag-MoTeSe₂ towards CH₄. Recently, Qin *et al.* investigated the adsorption capabilities of Pd₄/hBN, Rh₄/hBN, and Ru₄/hBN structures towards thermal runaway gases like CH₄, CO₂, CO, and H₂ using DFT.⁵⁶ Their DFT results revealed that metal modification significantly enhances the adsorption capability of hBN towards all these gases. Hou *et al.* developed a Ce-doped MoS₂-based gas sensor with high humidity resistance for detecting H₂, which is generated during thermal runaway of lithium-ion batteries.⁵⁷ It exhibited excellent H₂ selectivity in the presence of CO, C₂H₆O, CH₄, and C₂H₆O, maintaining its stability under high humidity conditions ranging from 30% to 85%, demonstrating a fast response to H₂, making it ideal for monitoring H₂ levels under thermal runaway conditions. Chen *et al.* analysed the sensing characteristics of Ag-CdS, Pd-CdS, and Pt-CdS towards H₂ and CO₂.⁵⁸ They found that Pd-CdS and Pt-CdS show potential for room temperature H₂S sensing, while the CdS monolayer displays potential for H₂ and CO₂ cleaning. The sensitivity of Pt-CdS and Pd-CdS towards H₂ at 300 K is 78.61% and 98.17%, respectively, while their sensitivity towards CO₂ is 99.99%. Similarly, Zhai *et al.* studied the physicochemical properties of Rh-doped PdS₂ and Rh-PdS₂ and their sensing performance towards the thermal runaway gases in lithium-ion batteries.⁵⁹ He found that the adsorption of CO and C₂H₄ onto Rh-doped PdS₂ and Rh-PdS₂ occurs *via* chemisorption, whereas the adsorption of H₂, CO₂, and CH₄ occurs *via* physisorption. Furthermore, work function analysis suggested that both systems can be utilized as work function-based gas sensors with comparable performance. Yang *et al.* investigated the sensing performance of BC₃-based gas sensors for organic and inorganic gases using DFT.⁶⁰ Their DFT results indicated that BC₃ is very sensitive to the adsorption of CO, NH, NO, NO₂, C₂H₂, C₂H₄, and HCHO, thereby validating that the BC₃ monolayer can be used as a sensing material in gas sensors. Liu *et al.* investigated the gas sensing capabilities of TM (Fe, Co, and Pd) doped MoTeSe monolayers in detecting thermal runaway gases generated by lithium-ion batteries.⁶¹ They reported that adding TM atoms as dopants enhances the electrical conductivity and adsorption capacity of MoTeSe, thereby confirming that the Pd-MoTeSe monolayer has the best sensing performance, followed by Co-MoTeSe and Fe-MoTeSe monolayers. However, to the best of the author's knowledge, there have been no previous reports regarding the adsorption behaviour of thermal runaway gases from lithium-ion batteries onto Cu-doped hBN. This lack of prior research motivated us to investigate the adsorption behaviour of thermal runaway gases from lithium-ion batteries onto pristine hBN and Cu-doped hBN. Therefore, in this study, we have used DFT as a tool to calculate the adsorption energy and distances of the thermal runaway gases onto pristine hBN and Cu-doped hBN. In addition to analysing the effect of adsorption of thermal runaway gases on the electrical conductivity of pristine hBN and Cu-doped hBN, we calculated DOS and PDOS for these systems, respectively. For the quantitative analysis of the charge transfer during the interaction of thermal runaway gases with all these systems, we calculated the charge density difference. Furthermore, RDG analysis was performed

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to examine the presence of non-covalent interactions between the adsorbate and adsorbent. Finally, the recovery time sensitivity and selectivity were also calculated to examine the performance of Cu-doped hBN upon the adsorption of thermal runaway gases.

2 Computational details

All the computational calculations in this work were performed using DFT as implemented in the Quantum ESPRESSO⁶² software package. The electronic exchange and correlation interactions were treated using the Generalized Gradient Approximation (GGA)^{63,64} along with the Perdew–Burke–Ernzerhof (PBE)⁶⁵ functional. To model the electron–ion interactions, we have employed the Projector Augmented Wave (PAW) method with ultrasoft pseudopotentials.⁶⁶ Furthermore, the Grimme DFT-D3 (ref. 67 and 68) dispersion correction was incorporated to account for weak van der Waals (vdW) forces, which are significant in layered materials. A cutoff energy of 55 Ry and a Monkhorst–Pack grid $7 \times 7 \times 1$ k -points were used for the plane-wave basis and Brillouin zone sampling. The hexagonal boron nitride (hBN) monolayer was modelled using a 5×5 supercell, created by repeating the primitive unit cell five times along the X and Y directions. A vacuum layer of 20 Å was applied along the z -axis in order to prevent the interlayer interactions between periodic images. Structural optimizations were carried out using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm until the total energy, pressure, and forces converged to within 10^{-8} Ry, 0.5 kbar, and 10^{-3} Ry bohr⁻¹, respectively.

Finally calculation of the bond lengths of the optimized geometries and visualisation of charge density difference plots were performed using VESTA,⁶⁹ whereas RDG scatter plots and isosurfaces were generated using Multiwfn⁷⁰ and VMD⁷¹ software.

3 Results and discussion

3.1. Analysis of the geometric structure and electronic properties of pristine hBN

In this section, we have examined the structural and electronic properties of the pristine hBN in order to analyze the structural and electronic property variations it undergoes upon substitutional doping of a Cu atom and adsorption of thermal runaway gases. Geometry optimization revealed that the resulting structure consists of a periodically alternating arrangement of boron and nitrogen atoms, each bonded to three neighbouring atoms, forming a planar honeycomb lattice with sp^2 hybridization, as depicted in Fig. 1(a). The optimized B–N bond length was found to be 1.45 Å, with a bond angle of 120° between B–N–B, and atomic separation between the nearest B–B or N–N atoms was 2.51 Å.^{72,73} These structural parameters are in good agreement with previously reported experimental data. To explore the electronic behaviour of the optimized structure, we performed density of states (DOS) calculations. The resulting DOS plot as shown in Fig. 1(b), indicates that the structure exhibits insulating behaviour with an energy band gap of approximately 4.29 eV, which closely aligns with the 4.30 eV gap reported by Kim⁷⁴ *et al.*, thereby affirming the reliability of our DFT-based

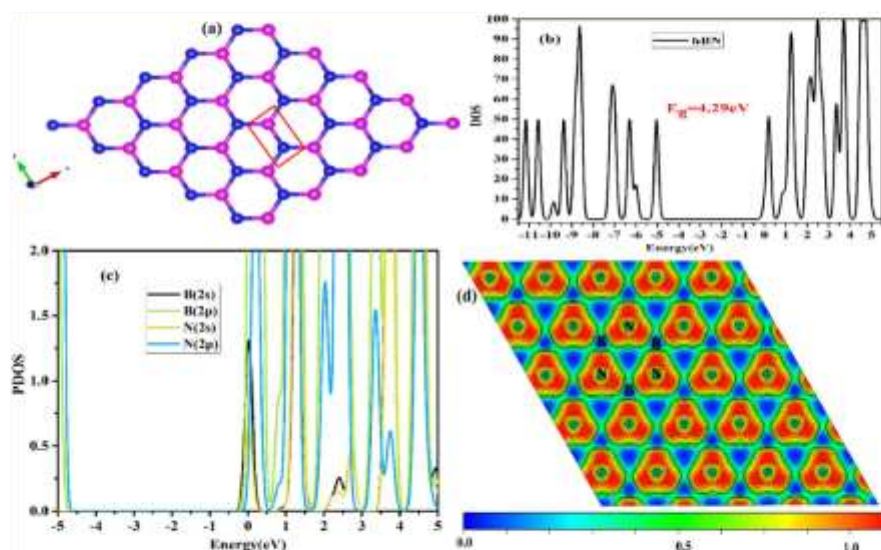


Fig. 1 (a) Optimized hBN monolayer, with the unit cell outlined in red. B and N atoms are represented by pink and blue spheres, respectively. (b) DOS and (c) PDOS. (d) Electron localization function (ELF) map, where red, green, and blue regions correspond to highly localized, partially localized, and delocalized electronic states, respectively.

approach. Furthermore, we performed projected density of states (PDOS) calculations to examine the orbital contributions to the total DOS (TDOS). The PDOS plot in Fig. 1(c) demonstrates that the valence band (VB) is mainly composed of filled 2p orbitals of N atoms, whereas the conduction band (CB) is mainly composed of empty 2p orbitals of boron (B) atoms. These findings indicate that B and N atoms act as electron-rich and deficient sites, respectively, which is consistent with our ELF study. The resulting ELF plot, as shown in Fig. 1(d), demonstrated regions of high and low electron density around the N and B atoms identified by the red and blue regions, respectively. The observed variation in electron density can be attributed to the difference in electronegativity between B–N atoms, causing the highly electronegative N atom to withdraw electrons from adjacent B atoms thereby making N and B sites electron-rich (donor) and electron-deficient (acceptor) sites, respectively. Overall, the structural and electronic analysis confirmed that the resulting optimized structure behaves as a hBN monolayer.

3.2. Adsorption of thermal runaway gases onto pristine hBN

To study the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules onto pristine hBN (on top of the B atom) and N sites (on top of the N atom) as the active sites for adsorption due to their electron deficient and electron rich behaviour which is also suggested by our ELF calculations. Therefore, we considered different orientations of the thermal runaway gases at the B and N sites as the initial structures for optimization. Upon geometry optimization we obtained sixteen different adsorption configurations abbreviated as A1, A2, A3, A4, B1, B2, C1, C2, C3, C4, D1, D2, D3, and E1, E2, E3 as shown in Fig. 2(a)–(p) respectively. For the A1, B1, D1 and E1 adsorption configurations, we observed that the C_2H_4 , CH_4 , CO_2 and H_2 gas molecules oriented themselves in a direction parallel to the Z axis at distances of 4.285 Å, 4.036 Å, 3.330 Å and 3.00 Å from the B sites as shown in Fig. 2(a), (e), (k) and (n) respectively whereas for the A2 and D2 adsorption configurations we observed that the C_2H_4 and CO_2 gas molecules oriented themselves in a direction perpendicular to the Z axis at distances of 4.055 Å and 3.871 Å, from the B sites as shown in Fig. 2(b) and (l) respectively. In the case of A3, B2 and E2 adsorption configurations, we observed that the C_2H_4 , CH_4 and H_2 gas molecules oriented themselves in a direction parallel to the Z axis at distances of 4.275 Å, 3.616 Å and 2.998 Å from the N sites as shown in Fig. 2(c), (f) and (o) respectively. Similarly, in the case of C1, C2, and C3, C4 adsorption configurations, the CO gas molecules were adsorbed at distances of 3.375 Å, 3.534 Å and 3.480 Å, 3.656 Å from the N sites in a direction parallel to the Z axis as shown in Fig. 2(g)–(j) respectively. We also observed that in the case of A4, D3 and E3 adsorption configurations, C_2H_4 , CO_2 and H_2 gas molecules were adsorbed at distances of 4.249 Å, 3.600 Å and 3.328 Å from the N sites in a direction perpendicular to the Z axis as shown in Fig. 2(d), (m) and (p) respectively. The reported B–N, C–H, C–C, C–O, and H–H bond lengths in Table 1 didn't vary too much from those of pristine hBN and the isolated C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules. These

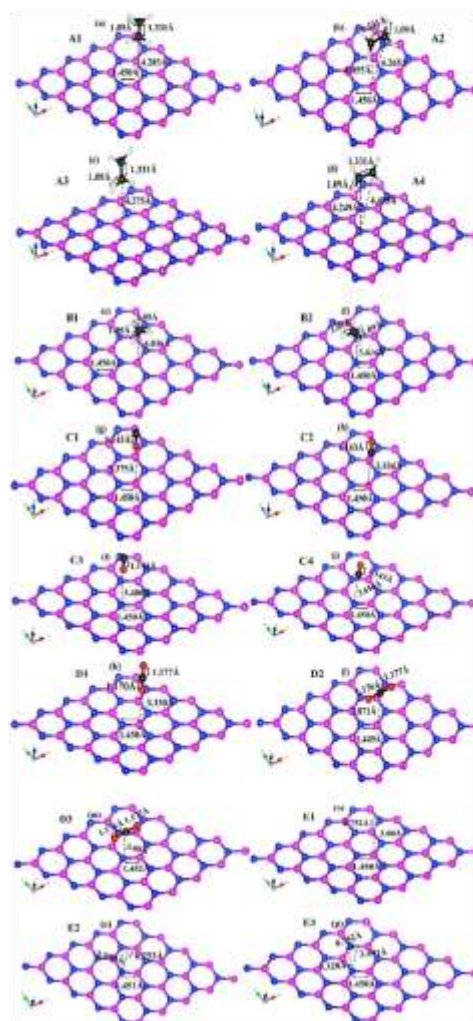


Fig. 2 Optimized different adsorption configurations of (a)–(d) C_2H_4 , (e)–(h) CH_4 , (i)–(j) CO , (k)–(m) CO_2 , and (n)–(p) H_2 gas molecules onto pristine hBN, respectively.

findings suggest that weak interactions exist between thermal runaway gases and pristine hBN. Furthermore, to verify the above findings we calculated adsorption energy (E_{ads}) for all these adsorption configurations using eqn (1) in order to determine the most stable adsorption configurations and the strength of the interaction between the gas molecule and hBN.

$$E_{ads} = E_{A/gas} - E_A - E_{gas} \quad (1)$$

Table 1 The adsorption energy (E_{ads}), adsorption distances (D_{ads}), B–N and C–H bond lengths upon the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules onto pristine hBN

System	E_{ads} (eV)	D_{ads} (Å)	B–N (Å)	C–H (Å)	C=C (Å)	H–H (Å)	C–O (Å)
A1	–0.140	4.285	1.450	1.09	1.331	—	—
A2	–0.191	4.055–4.265	1.450	1.09	1.331	—	—
A3	–0.140	4.275	1.450	1.09	1.331	—	—
A4	–0.184	4.249–4.455	1.450	1.09	1.331	—	—
B1	–0.108	4.036	1.450	1.09	—	—	—
B2	–0.134	3.616	1.450	1.09	—	—	—
C1	–0.085	3.375	1.450	—	—	—	1.143
C2	–0.089	3.534	1.450	—	—	—	1.143
C3	–0.077	3.480	1.450	—	—	—	1.143
C4	–0.077	3.656	1.450	—	—	—	1.143
D1	–0.323	3.330	1.450	—	—	—	1.170–1.177
D2	–0.357	3.871	1.449	—	—	—	1.176–1.177
D3	–0.383	3.600	1.452	—	—	—	1.176–1.177
E1	–0.054	3.000	1.450	—	—	0.752	—
E2	–0.053	2.998	1.451	—	—	0.753	—
E3	–0.049	3.328–3.491	1.450	—	—	0.752	—

where $E_{\text{A}^{\text{gas}}}$, E_{A} , and E_{gas} represent the total energy of the gas adsorbed onto the sensing material, energy of the pristine sensing material, and energy of the isolated gas molecules, respectively. The calculated adsorption energies for the A1, A2, A3, A4, B1, B2, C1, C2, C3, C4, D1, D2, D3 and E1, E2, and E3 adsorption configurations were found to be –0.140 eV, –0.191 eV, –0.140 eV, –0.184 eV, –0.108 eV, –0.134 eV, –0.085 eV, –0.089 eV, –0.077 eV, –0.077 eV, –0.323 eV, –0.357 eV, –0.383 eV and –0.054 eV, –0.053 eV and –0.049 eV, respectively. The low values confirm that the adsorption of thermal runaway gases onto pristine hBN occurs via physisorption, and weak interactions exist between C_2H_4 , CH_4 , CO , CO_2 , and H_2 gases and hBN. Based on the minimization of the adsorption energies, we found that A2, B2, C2, D3, and E2 were the most stable adsorption configurations among the different optimized C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas-adsorbed hBN configurations. For the rest of the study, we considered A2, B2, C3, D2, and E2 as the final adsorption configurations and referred to them as C_2H_4 -hBN, CH_4 -hBN, CO -hBN, CO_2 -hBN, and H_2 -hBN, respectively.

3.3. Analysis of the geometric structure and electronic properties of Cu-doped hBN

In the previous section, we observed that pristine hBN demonstrates weak adsorption capability towards thermal runaway gases. Therefore, to address this limitation, we adopted substitutional doping of Transition Metal (TM) atoms into hBN, which is an effective method to enhance the gas adsorption capability and sensing performance of hBN. Among the various TM atoms, we selected the Cu atom as a dopant based on our previous theoretical studies.^{74–77} In this study, we have considered two different substitutional doping configurations abbreviated as Cu-V_{B} -hBN (Cu atom substituted at a B vacancy) and Cu-V_{N} -hBN (Cu substituted at an N vacancy) as input geometries for optimization. For Cu-V_{B} -hBN and Cu-V_{N} -hBN, single B and N atoms were removed from the hBN lattice to create vacancy sites, respectively. After relaxation, both

structures exhibited distortion in the hexagonal ring due to the larger atomic radius of Cu (1.28 Å) compared to B (0.85 Å) and N (0.65 Å), causing the ring to expand around the dopant site. From Fig. 3(a) and (b), we found that the Cu atom forms bonds with three adjacent nitrogen atoms in Cu-V_{B} -hBN and with three boron atoms in Cu-V_{N} -hBN. The corresponding Cu–N and Cu–B bond lengths were 1.739 Å and 1.763 Å, respectively. Both Cu–N and Cu–B bonds were found to be longer than the typical B–N bonds in pristine hBN, suggesting that the Cu atom protrudes slightly from the surface, potentially making it a favourable site for gas adsorption. Additionally, the average B–N bond lengths in the doped Cu-V_{B} -hBN and Cu-V_{N} -hBN (1.445 Å) structures were slightly shorter than those in pristine hBN, indicating minor corrugation introduced by the dopant. To further assess the structural stability and bonding nature of the doped systems, the binding energy (E_{b}) and formation energy (E_{f}) were computed using the following equations.

$$E_{\text{b}} = E_{\text{Cu-hBN+gas}} - (E_{\text{V}} + E_{\text{Cu}}) \quad (2)$$

$$E_{\text{f}} = E_{\text{Cu+hBN}} - E_{\text{hBN}} - \mu_{\text{Cu}} + \mu_{\text{X}} \quad (3)$$

where $E_{\text{Cu+hBN}}$, E_{V} , E_{Cu} , μ_{Cu} and μ_{X} represent the total energies of the substitutionally doped Cu atoms into hBN, total energies of the defective hBN, total energies of the isolated Cu atom, and chemical potentials of the isolated Cu atom and ejected atoms from the hexagonal lattice, respectively. The calculated binding and formation energies for Cu-V_{B} -hBN were –5.048 eV and 5.379 eV, respectively, while those for Cu-V_{N} -hBN were 1.31 eV and 9.42 eV. The lower formation energy of the Cu-V_{B} -hBN structures indicates that the Cu atom preferentially occupies the B site over the N site, consistent with previous theoretical studies reporting that TM doping is energetically more favourable at B vacancies.⁷⁸ Based on the minimisation of the binding and formation energies, we found that Cu-V_{B} -hBN is a thermodynamically more stable structure than Cu-V_{N} -hBN. As a consequence, for the rest of the study, we have considered Cu-

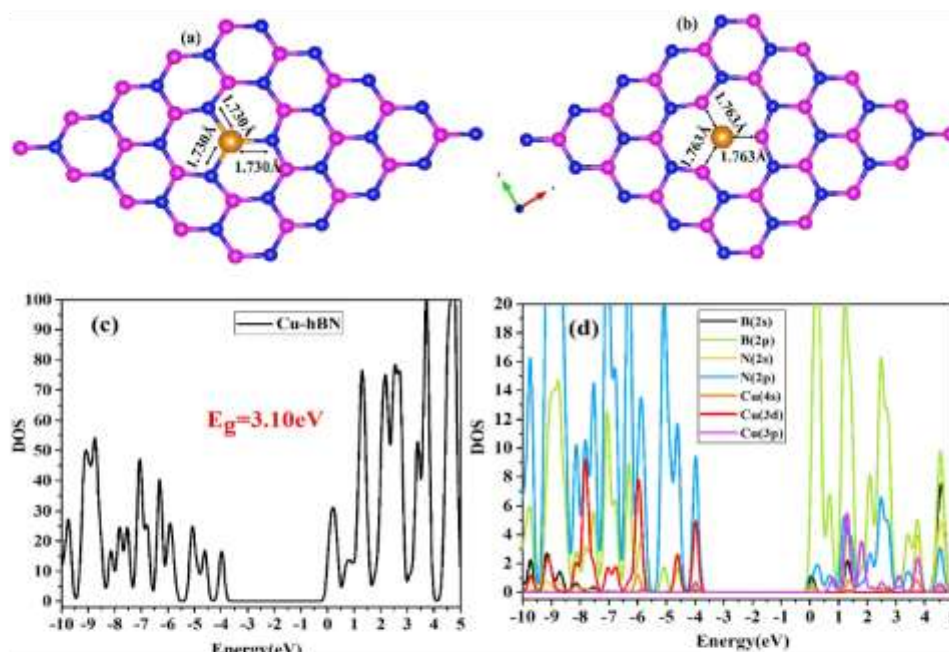


Fig. 3 Optimized (a) Cu-VB-hBN and (b) Cu-VN-hBN substitutionally doped structures, respectively. (c) DOS and (d) PDOS for the Cu-doped hBN structures, respectively.

V_N-hBN as the final structure and referred to it as “Cu-doped hBN”. Furthermore, to examine the thermal stability of Cu-doped hBN, we performed *ab initio* molecular dynamics simulations at 300 K. Our *ab initio* molecular dynamics simulations (SI-1) showed that the substitutionally doped Cu atom vibrates about the equilibrium position. This can be attributed to the fact that the substitutionally doped Cu atom tries to escape from the crystal structure as it gains thermal energy from the surrounding, but the electrostatic interaction between the substitutionally doped Cu atom and the nearby neighbouring N atom tries to pull back the substitutionally doped Cu atom. As a result the substitutionally doped Cu atom remains an integral part of the crystal structure thereby validating the thermal stability of Cu-decorated hBN. To analyze the effect of Cu doping on the electronic properties of hBN, we calculated the DOS and plotted it, as shown in Fig. 3(c). The DOS plot showed the emergence of an impurity state at -4 eV, causing the transition from an insulator to a wide band gap semiconductor as the band gap reduces from 4.29 eV to 3.10 eV. The reduction of the band gap indicates that electrons can easily transfer from the VB to the CB just by applying a suitable external electric field. These findings confirmed that doping Cu atoms causes an increase in the electrical conductivity. Furthermore, the PDOS plot in Fig. 3(d) shows significant overlapping between the 3d-Cu and 2p-N atomic orbitals within the energy range of -4 eV

to -10 eV, confirming the existence of the strong hybridization between the 3d and 2p atomic orbitals and formation of a strong bond between the doped Cu atom and the nearby N atoms. Hence, our structural and electronic property analyses confirmed that substitutional doping of Cu atoms creates active sites for the gas molecules and modifies the electrical conductivity of hBN.

3.4. Adsorption of thermal runaway gases onto Cu-doped hBN

To investigate the adsorption of C₂H₄, CO, CO₂, CH₄, and H₂ gas molecules onto Cu-doped hBN, we considered the dopant sites as the most preferential adsorption sites; because of the protrusion of Cu atoms from the hBN surface, incoming gas molecules are more likely to interact with the dopant atom than with the B and N atoms. Therefore, we have considered different orientations of the thermal runaway gases at the dopant sites as the initial structure for optimization. Upon optimization we obtained two different optimized adsorption configurations each in the case of C₂H₄, H₂, CO, and CO₂ gas molecules adsorbed onto Cu-doped hBN, abbreviated as F1, F2, F3, F4, F5, F6, F7, and F8 and one different optimized adsorption configuration for CH₄ adsorbed onto Cu-doped hBN abbreviated as F9, as shown in Fig. 4(a)–(i) respectively. For the F1, F5, F7 and F9 adsorption configurations, we observed that the C₂H₄, CO₂,

Paper

Journal of Materials Chemistry A

H₂ and CH₄ gas molecules oriented themselves in a direction parallel to the Z axis at distances of 2.948 Å, 2.590 Å, 2.141 Å and 2.865 Å from the dopant sites as shown in Fig. 4(a), (e), (g) and (i) respectively whereas for the F2, F6 and F8 adsorption configurations we observed that the C₂H₄, CO₂ and H₂ gas molecules oriented themselves in a direction perpendicular to

the Z axis at distances of 2.260 Å, 4.092 Å and 2.214 Å from the dopant sites as shown in Fig. 4(b), (f) and (h) respectively. On the other hand, in the case of F3 and F4 adsorption configurations, we observed that the CO gas molecules adsorbed at distances of 2.841 Å and 1.964 Å from the dopant sites in a direction parallel to the Z axis with C and O atoms facing

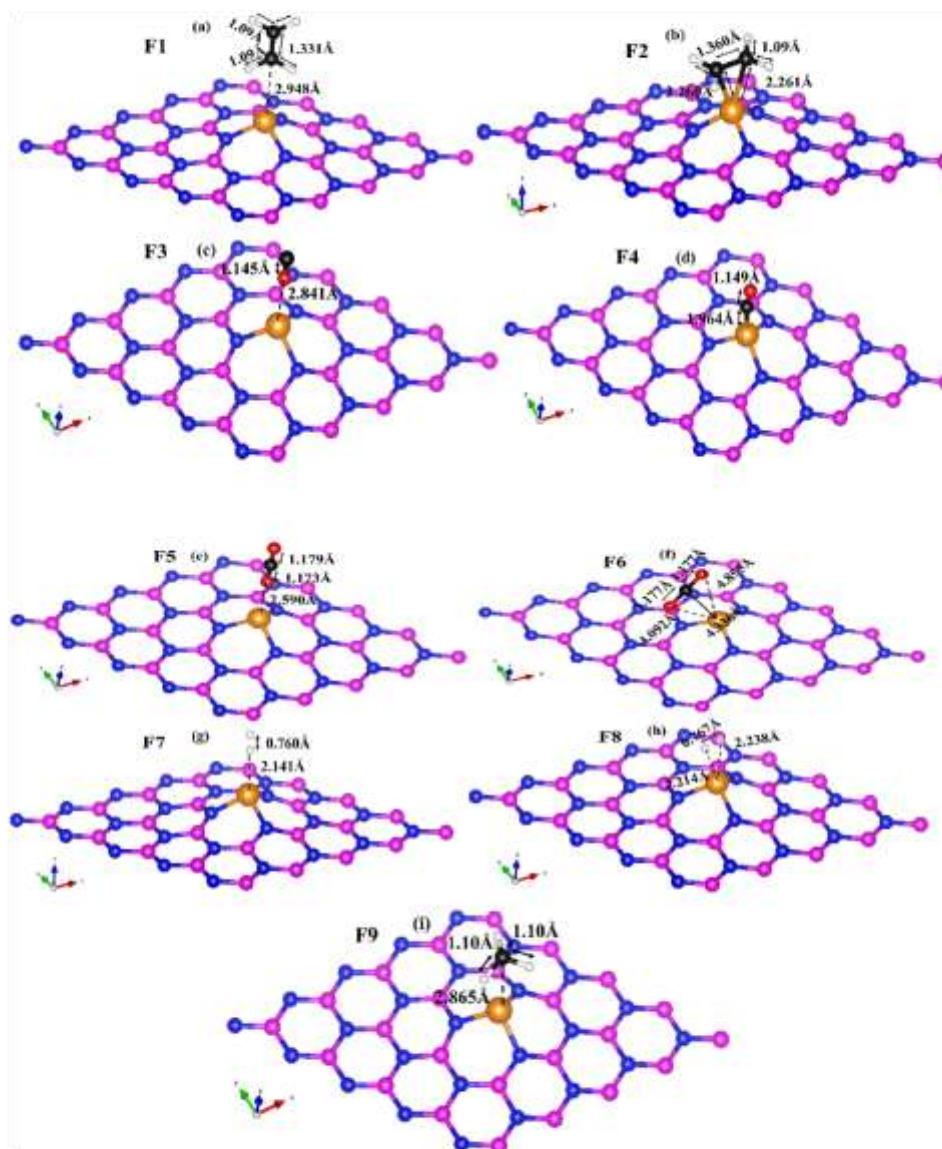


Fig. 4 Optimized adsorption configurations of (a) and (b) C₂H₄, (c) and (d) CO, (e) and (f) CO₂ (g) and (h) H₂ and (i) CH₄ onto Cu-doped hBN.

Table 2 The adsorption energy (E_{ads}), adsorption distances (D_{ads}), C–C, C–O, C–H, and H–H bond lengths upon the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules onto Cu-doped hBN

System	E_{ads} (eV)	D_{ads} (Å)	C–H (Å)	C–C (Å)	C–O (Å)	H–H (Å)
F1	−1.429	2.948	1.09	1.331	—	—
F2	−2.028	2.260	1.09	1.360	—	—
F3	−1.341	2.841	—	—	1.145	—
F4	−1.986	1.964	—	—	1.149	—
F5	−1.625	2.590	—	—	1.173–1.179	—
F6	−1.528	4.092	—	—	1.177	—
F7	−1.386	2.141	—	—	—	0.760
F8	−1.330	2.214	—	—	—	0.767
F9	−1.440	2.865	1.10	—	—	—

towards the Cu atom, as shown in Fig. 4(c) and (d), respectively. Furthermore, the reported C–H and C–C bond lengths in Table 2 for the F1 and F2 adsorption configurations increased from 1.06 Å to 1.09 Å and from 1.20 Å to 1.331 Å and 1.360 Å respectively whereas for the F7, F8 and F9 configurations, the H–H and C–H bond lengths increased from 0.751 Å to 0.760 Å, 0.767 Å and from 1.09 Å to 1.10 Å respectively. For F3 and F4 adsorption configurations, we observed that the length of the triple-bonded C–O increases from 1.128 Å to 1.145 Å and 1.149 Å, respectively. On the other hand, the length of the two double-bonded C–O increases from 1.160 Å to 1.173 Å and 1.179 Å in the case of F5, whereas for the F6 system, the C–O bond length increases from 1.160 Å to 1.177 Å. The observed variation in the bond length upon the adsorption of the thermal runaway gases indicates weakening of the bond, resulting in activation of gas molecules towards bond formation with the doped Cu atom. These findings indicate the catalytic behaviour of the Cu atom. The calculated adsorption energies for the optimized F1, F2, F3, F4, F5, F6, F7, F8 and F9 adsorption configurations were found to be −1.429 eV, −2.028 eV, −1.341 eV, −1.986 eV, −1.625 eV, −1.528 eV, −1.386 eV, −1.330 eV, and −1.440 eV, respectively. The high values of the adsorption energies suggested that the adsorption of C_2H_4 , CH_4 , CO , CO_2 , and H_2 gas molecules onto Cu-doped hBN occurs via chemisorption, verifying that strong interactions exist between the adsorbed thermal runaway gases and Cu-doped hBN. Based on the minimization of the adsorption energies, we found that F2, F4, F5, F7, and F9 were the most stable adsorption configurations. For the rest of the study, we have considered F2, F4, F5, F7, and F9 as the final adsorption configurations and referred to them as C_2H_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN, H_2 -Cu-doped hBN, and CH_4 -Cu-doped hBN, respectively.

3.5. Electronic property analysis upon adsorption of thermal runaway gases onto pristine hBN and Cu-doped hBN

To analyze the electronic properties of the hBN and Cu-doped hBN systems upon the adsorption of thermal runaway gases, we calculated and plotted the DOS for C_2H_4 -hBN, CH_4 -hBN, CO_2 -hBN, CO -hBN, H_2 -hBN, C_2H_4 -Cu-doped-hBN, CH_4 -Cu-doped-hBN, CO_2 -Cu-doped-hBN, CO -Cu-doped-hBN and H_2 -Cu-doped-hBN adsorption configurations as shown in Fig. 5. From Fig. 5(a), (c), (g) and (i), we observed that C_2H_4 , CH_4 , CO_2 ,

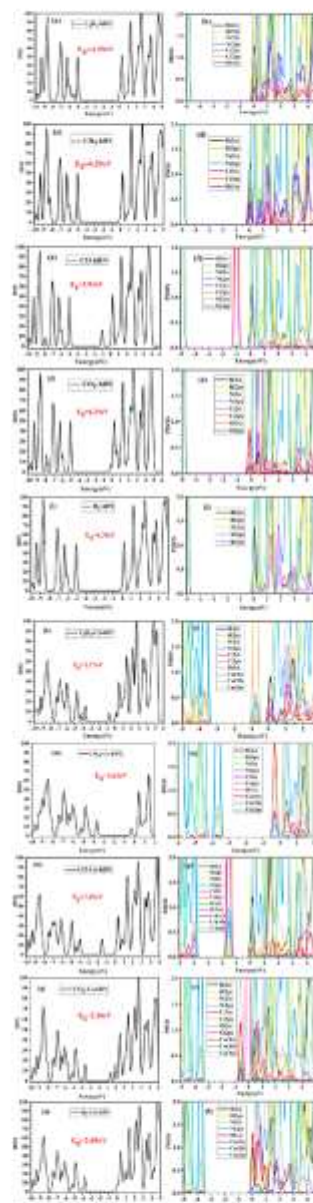


Fig. 5 DOS and PDOS for the (a) and (b) C_2H_4 -hBN, (c) and (d) CH_4 -hBN, (e) and (f) CO -hBN, (g) and (h) CO_2 -hBN, (i) and (j) H_2 -hBN, (k) and (l) C_2H_4 -Cu-doped hBN, (m) and (n) CH_4 -Cu-doped hBN, (o) and (p) CO -Cu-doped hBN, (q) and (r) CO_2 -Cu-doped hBN, and (s) and (t) H_2 -Cu-doped hBN systems.

Paper

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Journal of Materials Chemistry A

and H₂ gas molecules upon adsorption onto hBN do not introduce any impurity states within the band gap region; as a consequence, the band gap of pristine hBN remained unchanged. These findings confirm the existence of weak interactions between C₂H₄, CH₄, CO₂, H₂ gases and hBN, which might be due to weak charge transfer between them. In contrast, the adsorption of CO gas onto hBN introduces a new impurity state at -1 eV, causing the band gap to reduce from 4.29 eV to 3.01 eV as shown in Fig. 5(e). However the adsorption of C₂H₄ and CO gas molecules onto Cu-doped-hBN creates impurity states at -1 eV and within the energy range of -2 to -1 eV, causing the Fermi level to shift towards the CB, thereby reducing the band gap from 3.10 eV to 2.17 eV and 1.69 eV as shown in Fig. 5(k) and (o) respectively whereas the adsorption of CH₄, CO₂ and H₂ gas molecules onto Cu-doped hBN creates impurity states within the energy range of -1 to 0 eV and also causes the Fermi level to shift towards the CB thereby reducing the band gap from 3.10 eV to 2.63 eV, 2.26 eV and 3.05 eV as shown in Fig. 5(m), (q) and (s) respectively. Based on the comparison we found that Cu-doped hBN exhibits better variation in the electronic properties than pristine hBN upon the adsorption of thermal runaway gases. This might be due to the strong charge transfer between the thermal runaway gases and Cu-doped hBN. Furthermore, to analyse the contribution from the atomic orbitals of the thermal runaway gases, pristine hBN and Cu-doped hBN, we calculated PDOS for the above-mentioned adsorption configurations. From Fig. 5(b) and (d), we observed that in C₂H₄-hBN and CH₄-hBN systems, the 2s and 2p atomic orbitals of C and 1s atomic orbitals of H atoms contribute weakly to the DOS within the energy range of 1 to 5 eV. Similarly, in the CO₂-hBN and H₂-hBN systems, we observed that the 2s and 2p atomic orbitals of C and O and 1s atomic orbitals of H atoms also contribute weakly within the energy range of 1 to 5 eV, as shown in Fig. 5(g) and (i), respectively. On the other hand, for the CO-hBN systems, we observed from Fig. 5(f) that the impurity state at -1 eV existed due to the weak hybridization between the 2s, 2p, and 2p atomic orbitals of C and B atoms. The existence of weak hybridization between the atomic orbitals confirmed the formation of weak bonds between the thermal runaway gases and hBN. However, for the C₂H₄-Cu-doped-hBN systems, we observed from Fig. 5(l) that the impurity state at -1 eV results from the significant contribution of the 2p and 3d atomic orbitals of C and Cu atoms indicating sharing of electrons between these atomic orbitals to form covalent bonding between the C₂H₄ gas and Cu-doped hBN. For the CH₄-Cu-doped-hBN system we observed from Fig. 5(n) that the impurity state within the range arises from the contribution of 4s and 2s atomic orbitals of Cu and C atoms indicating that electrons are shared between these atomic orbitals to form covalent bonds between CH₄ gas and Cu-doped hBN whereas for the CO₂-Cu-doped-hBN system we observed from Fig. 5(r) that the 3p, 4s and 2s atomic orbitals of Cu and O atoms are involved in the sharing of the electrons and contribute to the creation of impurity states within the energy range of -1 to 0 eV. For the CO-Cu-doped-hBN system, we observed from Fig. 5(p) that the 2s, 2p and 3d atomic orbitals of C and Cu atoms contribute to the creation of impurity states

within the energy range of -2 to -1 eV. On comparison we found that the Cu-doped hBN system exhibits better variation in the electronic properties compared to pristine hBN upon the adsorption of thermal runaway gases, clearly indicating that Cu-doped hBN can be utilized as a chemoresistive gas sensor.

3.6. Charge density difference analysis

To understand the charge transfer mechanism between the thermal runaway gas and the sensing materials, we calculated the charge density difference using eqn (4) and plotted it, as shown in Fig. 6.

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B \quad (4)$$

where ρ_{AB} , ρ_A and ρ_B represent the charge densities on the sensing material upon gas adsorption, charge densities on the sensing material without gas molecules, and the charge densities of the isolated gas molecules, respectively. The yellow and cyan coloured regions in the charge density difference diagrams represent the electron accumulation and electron depletion regions, respectively. From Fig. 6(a) and (b), we observe that the electron density around the C and H atoms increases and decreases upon the adsorption of C₂H₄ and CH₄ gases onto hBN, identified by the yellow and cyan coloured regions around the C and H atoms of the C₂H₄ and CH₄ gas molecules whereas upon the adsorption of CO₂ onto hBN, the C atom loses electrons to the nearby highly electronegative O atom, identified by the yellow and cyan coloured regions around the O and C atoms of the CO₂ gas as shown in Fig. 6(c). We also observed that in C₂H₄-hBN, CH₄-hBN and CO₂-hBN systems electrons are uniformly accumulated and depleted within the layer. All these findings indicate that the atoms of the layer and gas molecules are primarily involved in charge transfer among themselves. On the other hand upon H₂ adsorption, we observed that the H atoms lose electrons to the N atoms, as indicated by the cyan colour around H atoms whereas upon CO adsorption, the C atoms gained electrons from the B atoms identified by the yellow-coloured region as shown in Fig. 6(e) and (e) respectively. However, upon substitutional doping of the Cu atom, we found that the Cu atom loses electrons to the nearby electronegative N atom identified by the cyan and yellow coloured regions around the Cu and N atoms as shown in Fig. 6(f). These findings confirmed the nature of the Cu atom and hBN as electrons donors and acceptors respectively. Furthermore, upon the adsorption of C₂H₄ and CH₄ gas molecules onto Cu-doped hBN, we observed that the electron rich C atom loses electrons to the electron deficient Cu atom identified by the large cyan coloured region between them as shown in Fig. 6(g) and (h) respectively thereby confirming the nature of Cu-doped hBN and C₂H₄, CH₄ as electron acceptor and donor. For the CO-Cu-doped hBN system, we observed from Fig. 6(i) that high electron density exists around the O atoms identified by the yellow colour, but the lone pair on the C atom readily available for covalent bonding with the Cu atom makes the C site partially electron rich and highly reactive toward the electron-deficient Cu atom. As a consequence, the C atom loses electrons to the Cu atom, identified by the yellow-coloured region in the interaction zone

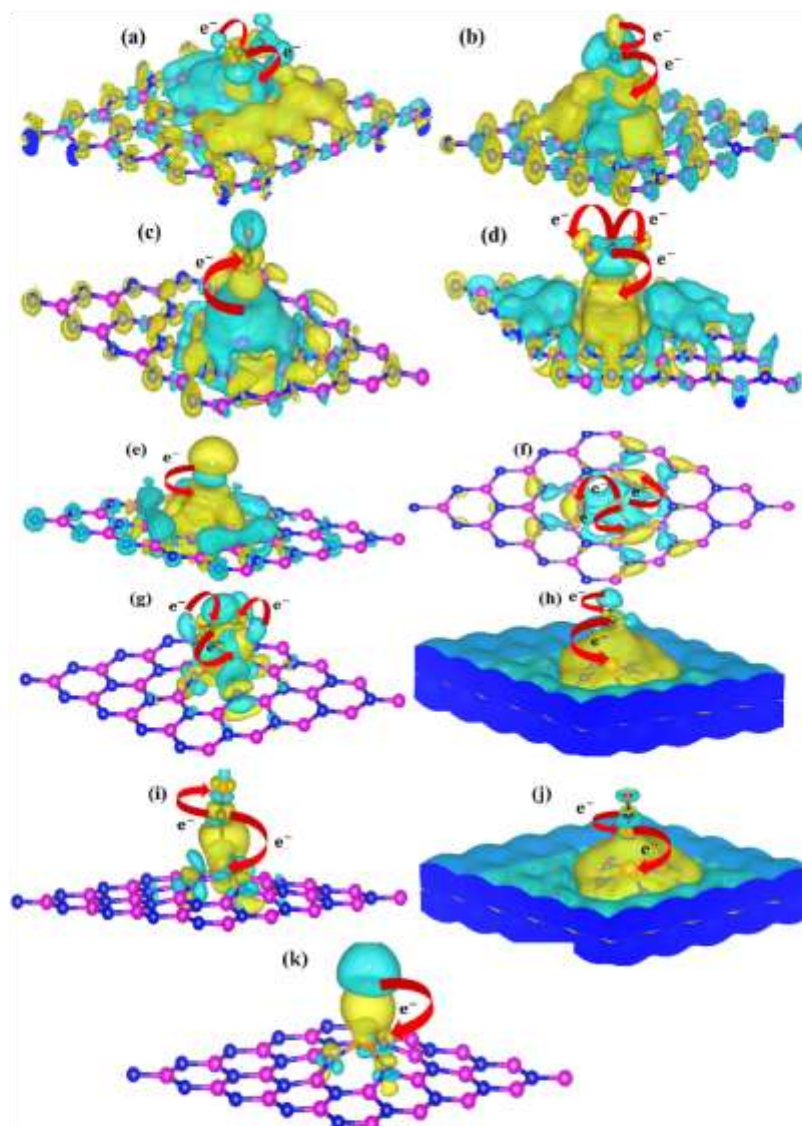


Fig. 6 Charge density difference of (a) C_2H_4 -hBN, (b) CH_4 -hBN, (c) CO -hBN, (d) CO_2 -hBN, (e) H_2 -hBN, (f) Cu-doped hBN, (g) C_2H_4 -Cu-doped hBN, (h) CH_4 -Cu-doped hBN, (i) CO -Cu-doped hBN, (j) CO_2 -Cu-doped hBN, and (k) H_2 -Cu-doped hBN.

between Cu and CO_2 gas. For the CO_2 -Cu-doped hBN system, we observed from Fig. 6(j) that upon CO_2 adsorption, that electrostatic interactions cause the electron rich O atom to lose electrons to the electron deficient Cu atom. For the H_2 -Cu-doped hBN system, we found that the Cu atom, being more electronegative than H atom, withdraws electrons from it,

identified by the large yellow-coloured region between the Cu and H atoms, as shown in Fig. 6(k). Based on the comparison of the charge accumulation/depletion areas in the interaction regime we found that a large electron accumulation/depletion area exists in the interaction region for Cu-doped hBN upon the adsorption of thermal runaway gases.

Paper

View Article Online
Journal of Materials Chemistry A

These findings indicate that significant charge transfer takes place between the doped Cu atom and thermal runaway gases which is the reason behind the larger variation in the band gap of Cu-doped hBN compared to pristine hBN upon the adsorption of thermal runaway gases. Hence, our charge density difference analysis confirmed that substitutional doping of Cu atoms is an cost-effective method to improve the charge transfer between the thermal runaway gases and the hBN layer.

3.7. Noncovalent interaction analysis

Noncovalent interactions (NCIs) such as hydrogen bonding, van der Waals (vdW), and steric effects play a significant role in the adsorption of the gas molecules onto the sensing materials, thereby influencing the adsorption capabilities and recovery time of the sensing materials. Therefore, to understand the nature of the non-covalent interactions between pristine hBN, Cu-doped hBN, and gas molecules, we calculated the reduced density gradient (RDG) function using eqn (5) and plotted it against $\text{sign}(\lambda_2)\rho(r)$ as shown in Fig. 7.

$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{[\rho(r)]^{4/3}} \quad (5)$$

Here $\rho(r)$, $\nabla\rho(r)$, and λ_2 represent the electron density, gradient electron density, and second eigenvalues of the Hessian matrix, respectively. The quantity $\text{sign}(\lambda_2)\rho(r)$ is of great importance as it describes the fluctuation in the electron density near the critical points, which can be used to determine the nature of the non-covalent interactions. If $\text{sign}(\lambda_2)\rho(r) < 0$, $\text{sign}(\lambda_2)\rho(r) \approx 0$, and $\text{sign}(\lambda_2)\rho(r) > 0$, it indicates strong attractive, weak, and strong repulsive interactions, respectively. The RDG scatter plots show a sharp decline in the RDG value around $\text{sign}(\lambda_2)\rho(r) \approx 0$, for the C_2H_4 -hBN, CH_4 -hBN, CO -hBN, CO_2 -hBN, and H_2 -hBN adsorption configurations as shown in Fig. 7(a)–(e), respectively. These results indicate that weak vdW interaction exists upon the adsorption of thermal runaway gases onto pristine hBN, which can be verified from the corresponding RDG isosurface plot displaying green patches between the adsorbed gas molecules and pristine hBN as shown in Fig. 8(a)–(e). However, upon substitutional doping of the Cu atom, we observed that there is a decline in the RDG value around $\text{sign}(\lambda_2)\rho(r) < 0$, as shown in Fig. 7(f). The corresponding RDG isosurface plot in Fig. 8(f) displays a strong attractive electrostatic interaction between the doped Cu atom and the neighbouring N atoms, identified by blue patches between them. Furthermore, upon C_2H_4 adsorption onto Cu-doped hBN, we observed that the RDG value in the RDG scatter plot undergoes variation around $\text{sign}(\lambda_2)\rho(r) < 0$ as shown in Fig. 7(g). The corresponding RDG isosurface plot reveals strong attractive electrostatic interactions with steric effects between the Cu atom and C_2H_4 , identified by a blue-red patch between them as shown in Fig. 8(g). The observed steric effect arose due to the repulsion between the nearby C-C atoms of the C_2H_4 gas molecule. For the CO -Cu-doped-hBN and H_2 -Cu-doped-hBN systems, we observed that the RDG value undergoes deviation around $\text{sign}(\lambda_2)\rho(r) < 0$, as shown in Fig. 7(i) and (k), whereas the corresponding RDG isosurface plot revealed that CO and H_2

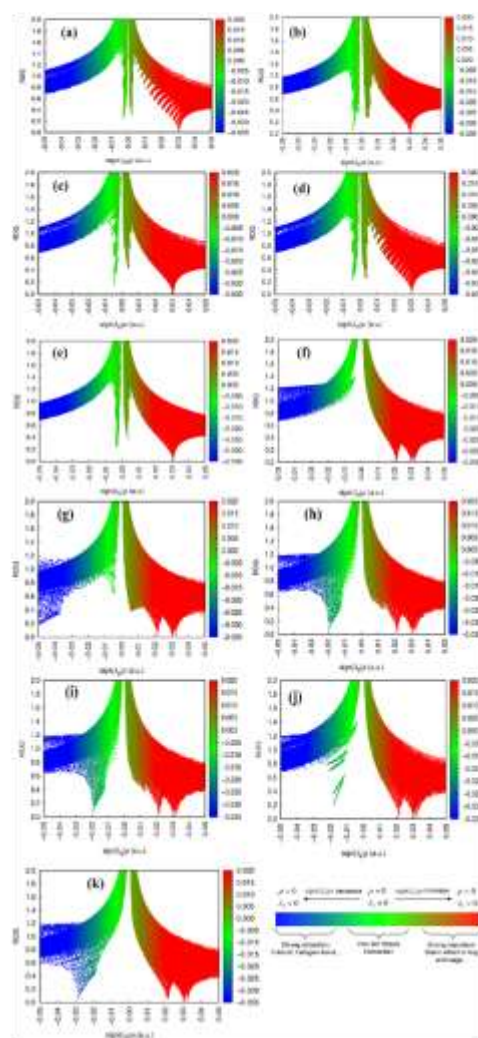


Fig. 7 Reduced density gradient plot for (a) C_2H_4 -hBN, (b) CH_4 -hBN, (c) CO -hBN, (d) CO_2 -hBN, (e) H_2 -hBN, (f) Cu-doped hBN, (g) C_2H_4 -Cu-doped hBN, (h) CH_4 -Cu-doped hBN, (i) CO -Cu-doped hBN, (j) CO_2 -Cu-doped hBN, and (k) H_2 -Cu-doped hBN.

gas interact electrostatically with the Cu atom. On the other side, in the case of CH_4 and CO_2 adsorption onto Cu-doped hBN, we found from the RDG scatter plot that there was a relatively large deviation in the RDG value around $\text{sign}(\lambda_2)\rho(r) < 0$ compared to $\text{sign}(\lambda_2)\rho(r) \approx 0$, as shown in Fig. 7(h) and (j), respectively. These results indicate that electrostatic interaction dominates over vdW interaction, which can be verified from the corresponding RDG isosurface plot as shown in Fig. 8(h) and (j)

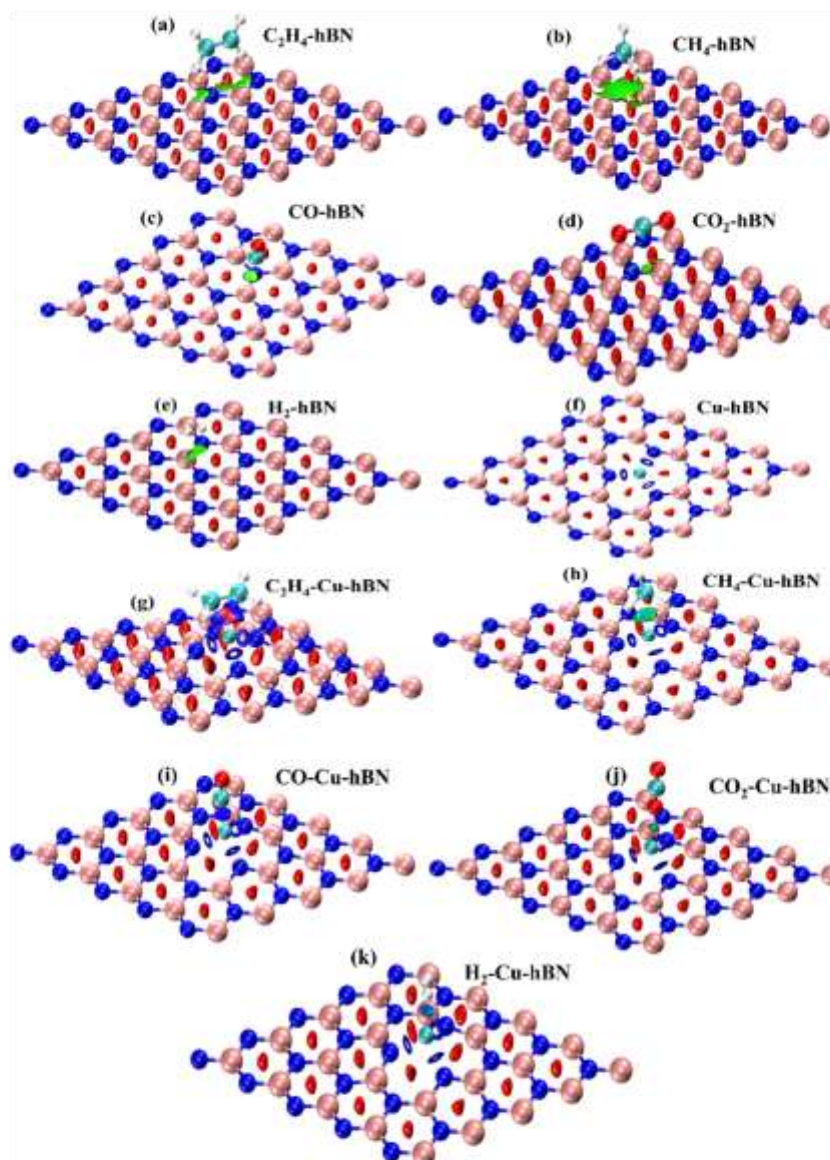


Fig. 8 Reduced density gradient isosurface plot corresponding to (a) C_2H_4 -hBN, (b) CH_4 -hBN, (c) CO-hBN, (d) CO_2 -hBN, (e) H_2 -hBN, (f) Cu-doped hBN, (g) C_2H_4 -Cu-doped hBN, (h) CH_4 -Cu-doped hBN, (i) CO-Cu-doped hBN, (j) CO_2 -Cu-doped hBN, and (k) H_2 -Cu-doped hBN respectively. The blue, red, and green color schemes shown in the RDG isosurface correspond to attractive strong hydrogen bonding, repulsive steric effect, and weak vdW interaction, respectively.

respectively. In addition, we observed that within the hexagonal ring, there exists a repulsive steric effect between the nearby B-B or N-N atoms identified by the red patches. Hence, based on

our RDG analysis, we found that the electrostatic interaction contributes to the adsorption energy in the case of Cu-doped hBN, whereas the vdW interaction contributes to the

Paper

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Journal of Materials Chemistry A

adsorption energy in the case of hBN upon the adsorption of thermal runaway gases.

3.8. Global reactivity descriptors

To analyze the effect of the adsorption of thermal runaway gases onto the stability and chemical reactivity of pristine hBN and Cu-doped hBN, we calculated various types of global reactivity descriptors such as ionization potential (IP), HOMO–LUMO gaps (E_g), electron affinity (EA), electrophilicity (ω), chemical softness (S), and hardness (η) using eqn (6)–(9) described below and reported in Table 3

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (6)$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (7)$$

$$S = \frac{1}{2\eta} \quad (8)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (9)$$

Here the ionization potential and electron affinity represent the electron donating and accepting capability of the sensing material, which are equal to the negative values of the HOMO and LUMO energies, respectively. The values reported in Table 4 suggest that hBN is chemically inert in nature due to its highest ionization potential (4.52 eV) and lowest electron affinity (0.22 eV), whereas the ionization potential and electron affinity of

pristine hBN remained unaltered upon the adsorption of C_2H_4 , CH_4 , CO_2 , and H_2 gas molecules; however the adsorption of CO gas molecules onto pristine hBN, causes the ionization potential to decrease from 4.51 eV to 4.40 eV and electron affinity to increase from 0.22 eV to 1.40 eV. These findings indicate that the C_2H_4 -hBN, CH_4 -hBN, CO_2 -hBN, and H_2 -hBN systems exhibit poor electron-donating and accepting capacity compared to CO-hBN which is the reason behind the observed poor charge transfer between the C_2H_4 , CH_4 , CO_2 , H_2 and hBN during the adsorption process. However, upon substitutional doping of Cu atoms the ionization potential decreases from 4.51 eV to 3.60 eV and the electron affinity increases from 0.22 eV to 0.50 eV. Furthermore, upon the adsorption of C_2H_4 , CH_4 , CO, and CO_2 gases onto Cu-doped hBN the ionization potential decreases from 3.60 eV to 3.28 eV, 3.29 eV, 3.56 eV, and 3.21 eV and the electron affinity increases from 0.50 eV to 1.11 eV, 0.66 eV, 1.87 eV, and 0.95 eV whereas upon the adsorption of H_2 onto Cu-doped hBN the ionization potential and electron affinity both decreases from 3.60 eV and 0.50 eV to 3.36 eV and 0.31 eV, respectively. Based on the variation in the ionization potential and electron affinity we found that the band gap of the hBN underwent 0% and 30.06% variation upon the adsorption of C_2H_4 , CH_4 , CO_2 , H_2 and CO gases. On the other hand, the band gap of Cu-doped-hBN underwent 30%, 15.16%, 45.48%, 27.09%, and 1.61% variation upon the adsorption of C_2H_4 , CH_4 , CO, CO_2 , and H_2 gases. The variation in the band gap is directly related to the increase in the conductivity of the sensing materials. Based on the comparison we found that the Cu-doped hBN system underwent large variation in the band gap

Table 3 Calculated HOMO–LUMO energies, HOMO–LUMO gaps (E_g), ionization potential (IP), electron affinity (EA), electrophilicity (ω), chemical softness (S), and chemical hardness (η), respectively, for the pristine hBN, C_2H_4 -hBN, CH_4 -hBN, CO-hBN, CO_2 -hBN, and H_2 -hBN, Cu-doped hBN, C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems. All the reported values are in eV

Adsorption configurations	HOMO	LUMO	E_g	IP	EA	S	η	ω
Pristine hBN	−4.51	−0.22	4.29	4.51	0.22	0.23	2.15	1.31
C_2H_4 -hBN	−4.51	−0.22	4.29	4.51	0.22	0.23	2.15	1.31
CH_4 -hBN	−4.51	−0.22	4.29	4.51	0.22	0.23	2.15	1.31
CO_2 -hBN	−4.51	−0.22	4.29	4.51	0.22	0.23	2.15	1.31
CO-hBN	−4.40	−1.40	3.00	4.40	1.40	0.33	1.50	2.80
H_2 -hBN	−4.51	−0.22	4.29	4.51	0.22	0.23	2.15	1.31
Cu-doped hBN	−3.60	−0.50	3.10	3.60	0.50	0.32	1.55	1.36
C_2H_4 -Cu-doped hBN	−3.28	−1.11	2.17	3.28	1.11	0.46	1.085	2.22
CH_4 -Cu-doped hBN	−3.29	−0.66	2.63	3.29	0.66	0.38	1.315	1.48
CO-Cu-doped hBN	−3.56	−1.87	1.69	3.56	1.87	0.59	0.845	4.36
CO_2 -Cu-doped hBN	−3.21	−0.95	2.26	3.21	0.95	0.44	1.13	1.91
H_2 -Cu-doped hBN	−3.36	−0.31	3.05	3.36	0.31	0.33	1.525	1.10

Table 4 Variation in the sensitivity of the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN at 300 K, 500 K, 700 K, and 900 K temperatures, respectively

Temperature	C_2H_4 -Cu-doped hBN	CH_4 -Cu-doped hBN	CO-Cu-doped hBN	CO_2 -Cu-doped hBN	H_2 -Cu-doped hBN
300 K	99.99%	99.98%	100%	99.99%	61.96%
500 K	99.99%	99.57%	99.99%	99.99%	44.01%
700 K	99.95%	97.96%	99.99%	99.90%	33.92%
900 K	99.75%	95.16%	99.98%	99.55%	27.54%

upon the adsorption of thermal runaway gases, thereby validating that the Cu-doped hBN exhibits better variation in conductivity than hBN making it a potential candidate for use as chemoresistive sensors. The electrophilicity index is calculated to examine the chemical reactivity of the sensing surface. From Table 4, we found that there is no change in the electrophilicity index of pristine hBN upon the adsorption of C_2H_4 , CH_4 , CO_2 , and H_2 , except for CO, where the electrophilicity index increases from 1.31 eV to 2.80 eV whereas, the electrophilicity index of pristine hBN increases from 1.31 eV to 1.36 eV upon substitutional doping of the Cu atom. However, upon the adsorption of C_2H_4 , CH_4 , CO, and CO_2 , the electrophilicity index of Cu-doped hBN increases by 63.23%, 8.82%, 220.58%, and 40.44%, respectively; in contrast for H_2 -Cu-doped hBN, the electrophilicity factor decreases by 19.11%. These findings suggest that Cu-doped hBN exhibits better sensitivity and adsorption capability towards C_2H_4 , CH_4 , CO, and CO_2 due to its higher chemical reactivity than pristine hBN. In addition, to determine the chemical stability of the sensing material, we calculated the chemical hardness and softness factors because they describe the resistance and willingness of the material to undergo any change in its electronic properties. We found from the data reported in Table 4 that the chemical hardness for C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN and H_2 -Cu-doped hBN systems decreased by 49.53%, 38.83%, 43.66%, 47.44% and 29.06% compared to the C_2H_4 -hBN, CH_4 -hBN, CO-hBN, CO_2 -hBN, and H_2 -hBN systems. On the other hand, the chemical softness for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems was found to increase by 50%, 39.47%, 47.27%, 44.06%, and 3.03% relative to the C_2H_4 -hBN, CH_4 -hBN, CO-hBN, CO_2 -hBN, and H_2 -hBN systems. The observed variations in the chemical hardness and softness factor validate that Cu-doped hBN is more likely to show significant variations in the electronic properties compared to pristine hBN which is consistent with our band gap calculations. Hence, the above-discussed global indices of reactivity descriptors suggest that Cu-doped hBN can be utilized as an efficient gas sensor to detect thermal runaway gases.

3.9. Sensitivity and selectivity analysis of hBN and Cu-doped hBN

Sensitivity is considered to be an important parameter for assessing the gas sensing performance of the semiconducting

materials, as it describes how rapidly the sensing materials respond to any change in the concentration of the gas molecules. For semiconducting materials, sensitivity was determined from their electrical conductivity (σ), which undergoes variation upon gas adsorption. According to eqn (10), the electrical conductivity of the semiconducting materials was found to be exponentially dependent on the band gap.

$$\sigma = AT^{3/2}e^{\left(\frac{E_g}{2k_B T}\right)} \quad (10)$$

where σ is the electrical conductivity, A is a constant, T is the temperature in K, E_g is the band gap in eV, and k_B is the Boltzmann constant in eV K⁻¹. This indicates that large variations in the band gap led to an enhancement in the electrical conductivity, thereby affecting the sensitivity of the sensing materials. Therefore, we performed DOS calculations to analyze the variation in the band gap upon adsorption of thermal runaway gases onto pristine hBN and Cu-doped hBN. From our DOS calculations, we found that the adsorption of C_2H_4 , CH_4 , H_2 , and CO_2 gas molecules onto pristine hBN produces 0% variations in the band gap, whereas the adsorption of the CO gas molecule onto pristine hBN produces only 30.06% variations in the band gap with respect to pristine hBN. On the other hand, Cu-doped hBN underwent 30%, 15.16%, 27.09%, 44.19%, and 1.61% variation in the band gap upon C_2H_4 , CH_4 , CO_2 , CO, and H_2 adsorption, respectively. Based on the comparison of the variations in the band gap, we found that Cu-doped hBN exhibits better sensitivity than pristine hBN upon the adsorption of these thermal runaway gases. Furthermore, to determine the capability of the sensing material to distinguish the specified target gas from other gases in the environment, we calculated the sensing response (S) at 300 K, 500 K, 700 K, and 900 K using eqn (11) and reported the results in Table 4 for Cu-doped hBN upon adsorption of thermal runaway gases.

$$S = \left| \frac{\sigma_{gas}^{-1} - \sigma_{pure}^{-1}}{\sigma_{pure}^{-1}} \right| \times 100 = e^{\left(\frac{\Delta E_g}{2k_B T}\right)} - 1 \quad (11)$$

where σ_{gas}^{-1} and σ_{pure}^{-1} represent the electrical conductivity of Cu-doped hBN with and without gas molecules, respectively. The reported sensing response at 300 K for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN configurations was found to be 99.99%, 99.98%, 100%, 99.99% and 61.96% respectively. Moreover, as the temperature increases from 300 K to 900 K, the

Table 5 Calculated recovery time for the adsorption of C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems at different temperatures under visible light

Adsorption systems	τ under visible light at 500 K	τ under visible light at 700 K	τ under visible light at 800 K	τ under visible light at 900 K
C_2H_4 -Cu-doped hBN	2.722×10^6 s	3.948×10^2 s	5.914 s	2.253×10^{-1} s
CO-Cu-doped hBN	1.027×10^5 s	1.968×10^2 s	3.216 s	1.311×10^{-1} s
CO_2 -Cu-doped hBN	2.367×10^4 s	4.964×10^{-1} s	1.713×10^{-2} s	3.202×10^{-3} s
H_2 -Cu-doped hBN	3.807×10^2 s	2.598×10^{-1} s	5.354×10^{-4} s	5.739×10^{-5} s
CH_4 -Cu-doped hBN	3.236×10^2 s	2.313×10^{-2} s	1.171×10^{-3} s	1.151×10^{-4} s

Paper

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Journal of Materials Chemistry A

sensing responses of the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN configurations decrease by 0.25%, 4.82%, 2%, 0.44% and 55.55% respectively. Upon comparison we found that CO-Cu-doped hBN systems exhibit the highest sensing response, and H_2 -Cu-hBN systems exhibit the lowest sensing response. The high and low sensing responses of Cu-doped hBN towards CO and H_2 gas molecules can be attributed to the 44.19% and 1.61% variations in the band gap, as suggested by our DOS calculations. There exists a significant difference in the sensing response of Cu-doped hBN upon the adsorption of H_2 gas. These findings indicate that Cu-doped hBN-based gas sensors can easily differentiate C_2H_4 , CH_4 , CO, and CO_2 from H_2 , whereas it is difficult for the Cu-doped hBN to differentiate between C_2H_4 , CH_4 , CO, and CO_2 . Hence, the sensitivity and selectivity analyses suggest that Cu-doped hBN holds potential to be used as a gas sensor under thermal runaway conditions.

3.10. Recovery time analysis of Cu-doped hBN

Recovery time is considered to be an important parameter for a gas sensor, as it tells us about the capability of the gas sensor to restore to its original resistance states after the desorption of the gas molecule from the sensing surface. Through a literature survey, we found that thermal runaway occurs above $300^\circ\text{C} = 573\text{ K}$ in lithium-ion batteries.^{79,80} Therefore, we calculated the recovery time (τ) for the Cu-doped hBN system upon the adsorption of thermal runaway gases at temperatures above 500 K using transition state theory and the van't Hoff-Arrhenius equation as mentioned in eqn (12) below:

$$\tau = \tau_0 e^{\left(\frac{E_{\text{bp}}}{k_B T}\right)} \quad (12)$$

where T is the testing temperature measured in kelvin (K), τ_0 is the attempted frequency factor, and k_B is the Boltzmann constant, whose values are 10^{12} Hz for visible radiation and $8.62 \times 10^{-5}\text{ eV K}^{-1}$ respectively. E_{bp} is the potential barrier for the desorption of gas molecules, which is equivalent to adsorption energy (E_{ads}) because adsorption and desorption are reverse processes of each other. The recovery time for the C_2H_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, H_2 -Cu-doped hBN, and CH_4 -Cu-doped hBN configurations at 500 K under visible light was found to be 2.722×10^3 , 1.027×10^3 , 2.367×10^3 , 3.807×10^3 , and 3.236×10^3 s, respectively. The above-reported recovery times in Table 5 suggested that the desorption time at 500 K for C_2H_4 -Cu-doped hBN, CO-Cu-

doped hBN, and CO_2 -Cu-doped hBN is too slow, making the desorption of the thermal runaway gases difficult, indicating poor reusability or potential use of Cu-doped hBN as a gas adsorbent. According to eqn (12), the recovery time was found to be exponentially dependent on adsorption energy and temperature, implying that if adsorption energy is kept constant, then by increasing the temperature or the attempt frequency, we can improve the recovery time of Cu-doped hBN. Furthermore, we calculated the recovery times under UV radiation at elevated temperatures for the C_2H_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, H_2 -Cu-doped hBN, and CH_4 -Cu-doped hBN configurations. The reported data in Table 6 suggest that the recovery time for the C_2H_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, H_2 -Cu-doped hBN, and CH_4 -Cu-doped hBN configurations reduces from 2.722×10^3 to $2.253 \times 10^{-1}\text{ s}$, 1.027×10^3 to $1.311 \times 10^{-1}\text{ s}$, 2.367×10^3 to $3.202 \times 10^{-6}\text{ s}$, 3.807×10^3 to $5.739 \times 10^{-8}\text{ s}$, and 3.236×10^3 to $1.151 \times 10^{-7}\text{ s}$, respectively, as the temperature increases from 500 K to 900 K under UV radiation. The observed reduction in the recovery time can be attributed to the fact that both high temperatures and UV radiation provide additional input energies required for the desorption of thermal runaway gases from the surface of Cu-doped hBN. All these findings indicate that annealing at high temperatures under UV radiation effectively improves the recovery times of the Cu-doped hBN systems. Hence, our recovery time analysis confirmed that above 500 K Cu-doped hBN systems can be used as a sensing material to detect thermal runaway gases.

3.11. Comparison of the adsorption energies, band gap variations, and sensitivity

In this section, we have compared the adsorption energies, band gap variations, and sensitivity at 300 K for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems with respect to previously reported theoretical studies. From the adsorption energies reported in Table 7, we found that Cu-doped hBN exhibits better adsorption capabilities than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ systems towards thermal runaway gases. In addition, we also observed that Cu-doped hBN exhibited better variation in the band gap than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ upon the adsorption of CO, CO_2 gas molecules, whereas Rh@PdS₂ exhibited the highest variation in the band gap upon the adsorption of C_2H_4 and CH_4 . On the other hand, C_2H_4 /Rh@PdS₂, C_2H_4 /Rh-PdS₂, H_2 /Rh@PdS₂, and H_2 /Rh-PdS₂, exhibited 100% variation in the

Table 6 Calculated recovery time for the adsorption of C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO-Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems at different temperatures under UV radiation

Adsorption systems	τ under UV at 500 K	τ under UV at 700 K	τ under UV at 800 K	τ under UV at 900 K
C_2H_4 -Cu-doped hBN	$2.722 \times 10^3\text{ s}$	$3.948 \times 10^{-1}\text{ s}$	$5.914 \times 10^{-3}\text{ s}$	$2.253 \times 10^{-1}\text{ s}$
CO-Cu-doped hBN	$1.027 \times 10^3\text{ s}$	$1.968 \times 10^{-1}\text{ s}$	$3.216 \times 10^{-3}\text{ s}$	$1.311 \times 10^{-1}\text{ s}$
CO_2 -Cu-doped hBN	$2.367 \times 10^3\text{ s}$	$4.964 \times 10^{-6}\text{ s}$	$1.713 \times 10^{-3}\text{ s}$	$3.202 \times 10^{-6}\text{ s}$
H_2 -Cu-doped hBN	$3.807 \times 10^{-1}\text{ s}$	$2.598 \times 10^{-6}\text{ s}$	$5.354 \times 10^{-7}\text{ s}$	$5.739 \times 10^{-8}\text{ s}$
CH_4 -Cu-doped hBN	$3.236 \times 10^{-1}\text{ s}$	$2.313 \times 10^{-5}\text{ s}$	$1.171 \times 10^{-6}\text{ s}$	$1.151 \times 10^{-7}\text{ s}$

Table 7 Comparison of the adsorption energies, change in the band gap, and sensitivity at 300 K for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems with respect to previously reported theoretical studies

Systems	Adsorption energy (eV)	ΔE_g (eV)	Sensitivity	Reference
Pt-SnSe/ C_2H_4	-0.920	16.3%	97.10%	81
Pt-SnSe/ CO	-1.170	24.7%	99.50%	
Pt-SnSe/ CO_2	-0.130	0.4%	10%	
C_2H_4 /Cu@HfS ₂	-0.947	6.36%	—	
CH_4 /Cu@HfS ₂	-0.234	1.10%	—	54
CO /Cu@HfS ₂	-0.984	9.66%	—	
CO_2 /Cu@HfS ₂	-0.250	1.44%	—	
H_2 /Cu@HfS ₂	-0.229	4.49%	—	
C_2H_4 /Cu-HfS ₂	-0.858	22.88%	99.70%	59
CH_4 /Cu-HfS ₂	-0.304	5.49%	—	
CO /Cu-HfS ₂	-0.750	22.06%	99.60%	
CO_2 /Cu-HfS ₂	-0.311	19.65%	99.20%	
H_2 /Cu-HfS ₂	-0.159	6.04%	—	59
C_2H_4 /Rh@PdS ₂	-1.340	100%	-99.99%	
CH_4 /Rh@PdS ₂	-0.160	18.95%	81.58%	
CO /Rh@PdS ₂	-1.510	29.19%	92.61%	
CO_2 /Rh@PdS ₂	-0.150	24.18%	88.45%	
H_2 /Rh@PdS ₂	-0.450	100%	-99.99%	—1
C_2H_4 /Rh-PdS ₂	-0.610	100%	—	
CH_4 /Rh-PdS ₂	-0.300	4.05%	50.34%	
CO /Rh-PdS ₂	-1.940	26.35%	97.26%	
CO_2 /Rh-PdS ₂	-0.230	4.62%	54.94%	Present work
H_2 /Rh-PdS ₂	-0.610	100%	—	
C_2H_4 -Cu-doped hBN	-2.173	30%	99.99%	
CO -Cu-doped hBN	-2.097	44.19%	100%	
CO_2 -Cu-doped hBN	-1.594	27.09%	99.99%	Present work
H_2 -Cu-doped hBN	-1.447	1.61%	61.96%	
CH_4 -Cu-doped hBN	-1.545	15.16%	99.98%	

band gap because upon the adsorption of C_2H_4 and H_2 gas molecules, Rh@PdS₂ and Rh-PdS₂ undergo a transition from semiconductor to metal. Furthermore, Rh@PdS₂ exhibited the highest sensitivity towards the adsorption of H_2 gas molecules. In contrast, the sensitivity of Cu-doped hBN was found to be better than that of Cu@HfS₂, Cu@HfS₂, Rh@PdS₂, and Rh-PdS₂ upon the adsorption of CH_4 , CO , and CO_2 gas molecules. Hence, the comparative analysis suggested that Cu-doped hBN is a more efficient sensing material than Pt-SnSe, Cu@HfS₂, Cu-HfS₂, Rh@PdS₂, and Rh-PdS₂ towards the detection of CO and CO_2 gas molecules.

4 Conclusions

In this work, we have systematically investigated the adsorption mechanisms of thermal runaway gases onto pristine hBN and Cu-doped hBN using *ab initio* calculations. From our adsorption energy calculations, we found that the adsorption of C_2H_4 , CH_4 , CO , CO_2 and H_2 gas molecules onto pristine hBN occurs *via* physisorption due to poor charge transfer and low adsorption energy. This leads to poor variation in electrical conductivity, sensitivity, selectivity and very low recovery time, confirming that pristine hBN cannot be used as a gas sensor to detect thermal runaway gases. Therefore, to enhance the gas sensing performance of hBN, we substituted Cu atoms at N and B vacancies. Based on the formation and binding energy, the Cu

atom doped at the B vacancy was found to be the most stable configuration. After doping Cu atoms, the adsorption energy for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN and H_2 -Cu-doped hBN systems was found to be high, resulting in chemisorption. DOS plots confirmed that the band gap reduces to 2.17 eV, 2.63 eV, 1.69 eV, 2.26 eV and 3.05 eV respectively upon the adsorption of C_2H_4 , CH_4 , CO , CO_2 and H_2 gas molecules onto Cu-doped hBN whereas the PDOS plots confirmed that the hybridization of the 3d atomic orbitals of the Cu atom with the atomic orbitals of C_2H_4 and CO gas molecules is responsible for the stronger interaction of C_2H_4 and CO gas molecules with Cu-doped hBN. The RDG results revealed that weak vdW-type non-covalent interaction exists between the thermal runaway gases and pristine hBN, whereas electrostatic interaction exists due to the charge transfer between C_2H_4 , CO , CO_2 , and H_2 gases, and Cu-doped hBN due to the charge transfer, as verified by the charge density difference calculations. Such a large variation in the band gap indicates that Cu-doped hBN is highly sensitive towards the adsorption of all these gases. However, the sensing response for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN, CO -Cu-doped hBN, CO_2 -Cu-doped hBN, and H_2 -Cu-doped hBN systems indicates that Cu-doped hBN is unable to differentiate between C_2H_4 , CH_4 , CO , and CO_2 but it can differentiate H_2 from the rest of the gases. Furthermore, the recovery time calculated for the C_2H_4 -Cu-doped hBN, CH_4 -Cu-doped hBN,

Paper

CO-Cu-doped hBN, CO₂-Cu-doped hBN, and H₂-Cu-doped hBN systems at 300 K was found to be too high. But we also found that annealing within the temperature range of 500 K to 900 K under UV exposure improves the recovery time of all the configurations. Hence, we conclude from our DFT results that substitutional doping of Cu is a cost-effective method to improve the recovery time, sensitivity, selectivity, and adsorption capability of hBN upon the adsorption of thermal runaway gases, making it a promising sensing material at elevated temperatures for the early detection of thermal runaway gases.

Author contributions

All the authors contributed significantly to the development of this research and approved the final manuscript.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

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Effect of Substitutional Doping and Cu Adsorption on MoS₂ Nanowire: A Comparative DFT Study

Anurag Bhandari,^[a] Piyush Dua,^[b] and Nitin K. Puri^{*[a, c]}

In this study, we have investigated the effect of substitutional doped (Cu-doped MoS₂NW) and surface-adsorbed Cu atom (Cu-MoS₂NW) on the electronic properties of MoS₂ nanowire (NW) using Density Functional Theory (DFT). Our adsorption study revealed that the adsorption of the Cu atom was a chemisorption. Electron Localization Function (ELF) analysis indicates that the Cu atom formed a covalent and ionic bond with MoS₂NW upon adsorption and substitutional doping, respectively. These findings indicate that a charge transfer occurred between the Cu atom and MoS₂NW during the interaction, confirmed by the Bader charge method. Further, the work function calculation indicates that Cu-doped MoS₂NW exhibits a large negative

variation in the work function, indicating enhanced electron emission capability of the Cu-doped MoS₂NW systems. All of our systems are thermodynamically stable based on our cohesive energy calculations. Overall, the DFT results suggest that Cu-doped MoS₂NW systems exhibit superior electrical conductivity, enhanced charge transfer, and larger variation in the work function compared to pristine MoS₂NW and Cu-MoS₂NW. These findings confirmed that substitutional doping is an effective way to modify the electronic properties of MoS₂NW. Therefore, Cu-doped MoS₂NW systems hold potential for applications in field emission and nanoelectronics devices.

1. Introduction

Two-dimensional (2D) materials such as graphene,^[1] hexagonal boron nitride(hBN),^[2] Transition metal dichalcogenides (TMDs),^[3] and black phosphorene^[4] have attracted considerable attention for both the theoretician and experimentalists due to their wide range of application in the various nanoelectronics and optoelectronics devices. Therefore, among the various 2D materials, MoS₂ which is a layered transition metal dichalcogenide formed by the vertical stacking of weakly coupled S-Mo-S layers has attracted considerable interest of the researchers due to their unique physical, catalytic, optical, and electronic properties they are finding their applications in the field of hydrogen evolution reaction (HER),^[5] storage,^[6] gas sensors,^[7] catalysis, energy conversion,^[8] photodetectors,^[9] photocatalysis, photoelectrochemical and stretchable electronics. Contrary to graphene zero band gap limitations, MoS₂, in its bulk form, is an indirect band semiconductor with a band gap value of 1.2 eV, whereas an atomically thin layer of MoS₂ is a direct band semiconductor with a band gap value of 1.8 eV.^[10] As a consequence, MoS₂ exhibits basic properties like gate control, wide band gap, high

current capability, and good electrical transport. All these findings suggest that MoS₂ can serve as an alternative to graphene for the application of nanoelectronics and optoelectronics. Currently, the trend in the research is primarily focused on utilizing 2D materials to their maximum potential in various applications. However despite such advances MoS₂ also exhibit low electron mobility compared to graphene^[11] which hinder their practical implementation in various nanoelectronics devices like transparent electrode etc. Therefore, there is a need to modulate the intrinsic properties of MoS₂ to make them fit for practical use. In this regard, researchers have adopted various effective methods to modulate the intrinsic properties of materials, such as defect engineering,^[12] substitutional doping,^[13] adatom adsorption,^[14] and substrate engineering.^[15] Among the various methods, it has been well proven that the adsorption of transition metal (TM) atoms onto 2D material effectively modulates the intrinsic properties of 2D materials. For example- Xu et al. studied the adsorption of various alkali metals (Li, Na), alkaline earth metals (Be, Mg), 3d TM atoms (Ti, V, Cr, Mn, Fe, Co), and precious metals (Ag, Au, Pt) onto dumbbell C₄N.^[16] Their study revealed that the adsorption of the above-mentioned metals opens the zero-band gap of dumbbell C₄N, making it a promising candidate for electronic devices. Similarly, Zhang et al. studied the structural, electronic, magnetic, and optical properties of 4d TM atoms adsorbed onto blue phosphorene.^[17] Their study revealed that adsorbing 4dTM onto blue phosphorene effectively modifies blue phosphorene's structural, electronic, magnetic, and optical properties. On the other side, there have been various reports regarding the adsorption of various TM atoms onto the MoS₂ monolayer for various applications. Kadioglu et al. investigated the adsorption of Au, Cu, and Au₂Cu₂ nanoclusters on MoS₂ monolayer for sensing CO and H₂O.^[18] Their results revealed that the adsorption of Au, Cu, and AuCu nanoclusters onto the

[a] A. Bhandari, Prof. N. K. Puri
Department of Applied Physics, Delhi Technological University, New Delhi 110042, India
E-mail: nitinkumar@dtu.ac.in

[b] Dr. P. Dua
Department of Applied Sciences, DSS Global University, MI-122, behind Pharma City, Selakui, Central Hope Town, Dehradun, Uttarakhand 248071, India

[c] Prof. N. K. Puri
National Institute of Electronics & Information Technology (NIELIT), Patna 801306, India

MoS₂ monolayer enhanced the chemical activity and sensitivity towards CO and H₂O molecules. Sharma et al. investigated the catalytic activity of Cu-embedded MoS₂ monolayer for CO.^[19] They found that the basal plane of the MoS₂ sheet gets activated upon substitutional doping of the Cu atom at S vacancy, which catalyzes the oxidation of CO effectively without poisoning. Rawal et al. studied the effects of defect on the catalytic activity of the 29 adatoms of Cu, Ag, and Au nanoparticles (NP) onto MoS₂ monolayer towards CO.^[20] Wang et al. investigated the structural, electronic, and magnetic properties of adsorbed transition metal from Sc to Zn onto MoS₂ monolayer using DFT. They conclude that all the TM atoms got adsorbed chemically except Zn, whereas the electronic and magnetic properties of the MoS₂ monolayer can be effectively modified by adsorbing different TM atoms. Thus, TM adsorbed MoS₂ monolayer can be utilized for spintronics.^[21] In another study, Li et al. emphasized that the adsorption of alkali metal, alkaline earth metals, 3d TM, noble metal, and non-metal atoms induce magnetic moments and transforms the band gap from semiconductor to metallic, semi-metallic, making them promising candidates for spintronics and electronic devices.^[22] Moreover, Joseph et al. synthesized Cu-doped MoS₂ hydrothermally to analyze the effect of Cu doping on the thermoelectric properties of MoS₂.^[23] Recently, Zhou et al.^[24] reported a method for selectively exposing and activating the inert basal planes of 2H-MoS₂ for CO₂ hydrogenation to methanol, achieved through the physically constrained sulfidation of ultrafine MoO₃ nanocores into hollow, few layer MoS₂ spheres within a mesoporous silica framework. The spherical curvature of MoS₂ induces strain and sulfur vacancies (S_v) on the typically inactive basal planes. This increases the exposure of in-plane sulfur vacancies while minimizing the exposure of edge vacancies, significantly enhancing its catalytic performance in synthesizing CH₃OH from the hydrogenation of CO₂. In contrast, the adsorption of the Cu atom onto MoS₂ facilitated the activation of H₂, delivering a remarkable CH₃OH production rate of 6.11 mol·molMo⁻¹·h⁻¹ and a high CH₃OH selectivity of 72.5% under reaction conditions of 260 °C, 5 MPa, and 24000 mL·gcat⁻¹·h⁻¹. They conclude that the Cu/MoS₂/SiO₂ catalyst demonstrates excellent stability, maintaining its silica-encapsulated hollow core-shell structure throughout the reaction process. Wang et al. studied the electrocatalytic activity of the Cu-decorated MoS₂ monolayer paving the way for application in electronics and energy storage.^[25] The above literature survey suggests that there exists a plethora of literature regarding the Cu decoration onto various MoS₂ nanostructures. However, to the best of the author's knowledge, there have been no reports regarding the effect of substitutional doping (Cu-doped MoS₂NW) and surface-adsorbed Cu atom (Cu-MoS₂NW) on the electronic properties of MoS₂ NW. This reported gap in the research motivated us to investigate the electronic properties of MoS₂ NW upon substitutional doping and surface-adsorption of Cu atom. Therefore, in this work, we have extensively investigated the effect of substitutional doping and surface-adsorption of Cu atoms onto electronic properties of MoS₂ NW using DFT. We have selected the Cu atom as a dopant for this study because it has been well proved experimentally that it has good chemistry

with MoS₂. The adsorption of the Cu atom was analyzed by calculating the adsorption energy and distances. In addition, the electronic properties and conductivity of the Cu-decorated MoS₂ NW were calculated through DOS, PDOS, and work function. Further, the structure stability of the optimized Cu-decorated MoS₂ NW structures nature of the bond formation, and the charge transfer mechanism during the Cu interaction with MoS₂ NW were analyzed utilizing cohesive energy, ELF, and the Bader charge method. Finally, we have compared our calculated DFT results for both the systems.

2. Methodology

2.1. Computational Details

We have used the Linear Combination of Atomic Orbital (LCAO) calculator in the Quantum ATK^[26] package to ensure accuracy while calculating the electronic properties of the various optimized structures. To approximate the nucleus and valence electrons interaction, the Fritz-Haber-Institute (FHI) pseudopotential was implemented. For transition metals (TM) atoms such as Cu and Mo, the Double Zeta Polarized (DZP)^[26] basis set was considered to ensure accuracy during the calculation. To consider the electron-electron interaction effectively, we have considered Generalized Gradient approximation (GGA)^[29] with the predefined function Perdew Burke Ernzhoeof (PBE)^[30] as an exchange-correlation function (XC). Further, we have selected 200 Ha (400 eV) and 10⁻⁶ eV as the cutoff energy and energy convergence criteria for the ground state energy calculation. According to the Monkhorst-Pack grid scheme, we have implemented 1 × 1 × 51 K points for calculating the density of states (DOS). For the adsorption study, MoS₂ NW was grown along the Z axis by continuously repeating the 1 × 1 unit cell of MoS₂ monolayer four times along the X and Y directions, resulting in 4 × 4 supercells. The 4 × 4 supercells contain 16 Mo and 32 S atoms with a vacuum layer of 10 Å was applied along the X and Y directions to prevent interactions between the adjacent periodic replicas. Equations (1) and (2) were used to determine the strength of the interaction during the adsorption of the Cu atom onto the surface of MoS₂ NW and the thermodynamic stability of the various adsorption configurations, respectively.

$$E_{\text{ads}} = E_{\text{Total}} - E_{\text{(MoS}_2\text{)}} - E_{\text{(Cu)}} \quad (1)$$

$$E_{\text{coh}} = \frac{E_{\text{(MoS}_2\text{)}} - [n_{\text{Mo}}E_{\text{Mo}} + n_{\text{S}}E_{\text{S}}]}{N} \quad (2)$$

where E_{Total} represents the total energy of the Cu adsorbed MoS₂ NW, $E_{\text{(MoS}_2\text{)}}$ represents the energy of the MoS₂ NW, $E_{\text{(Cu)}}$ represents the energy of the isolated copper atom, $E_{\text{(S)}}$ represents the energy of the isolated sulfur atom, $E_{\text{(Mo)}}$ represent the energy of the isolated Mo atom, $n_{\text{(Mo)}}$, $n_{\text{(S)}}$, represents the number of Mo and S atoms, and N represents the total atoms within the system, respectively.

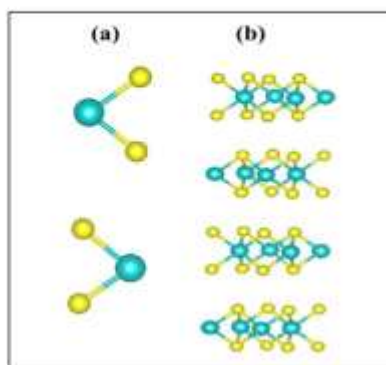


Figure 1. Optimized (a) MoS₂ monolayer and (b) MoS₂ NW structure. The atoms in yellow and cyan colors represent the S and Mo atoms, respectively.

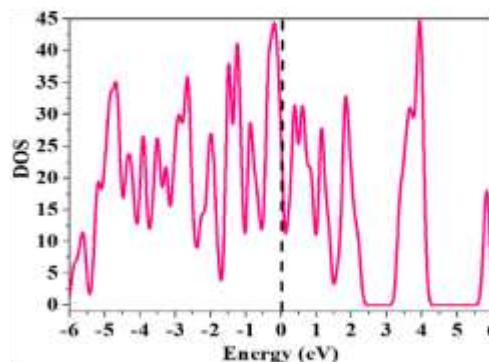


Figure 3. DOS plot for the MoS₂ NW. The black dotted line represents the Fermi level set to zero for reference.

3. Results and Discussion

3.1. Structure and Electronic Properties Analysis of MoS₂ Monolayer and MoS₂ NW

To investigate the differences in the geometrical and electronic properties of the MoS₂ monolayer and MoS₂ NW. For this purpose, initially, we optimized the geometry. After optimization, the resulting optimized lattice parameters for the optimized MoS₂ monolayer were $a = 3.244$ Å and $c = 12.880$ Å with a c/a ratio of 3.97, consistent with the previous theoretical calculation.^[36] Further, the band structure was plotted for the optimized MoS₂ monolayer. The resulting band structure in Figure 2a illustrates that the MoS₂ monolayer exhibits a

direct band gap of about 1.56 eV, verified from the DOS plot in Figure 2b and agreed with the previously reported theoretical studies.^[37] In the optimized MoS₂ NW shown in Figure 1b, each S atom is coordinated with multiple Mo atoms, resulting in a distorted octahedral arrangement of atoms within the layer, confirming the existence of 1T phase in MoS₂ NW. This type of structural arrangement of atoms within the layer facilitates high tensile strength and significant overlapping between the d orbitals of Mo atoms, facilitating a pathway for efficient electron movement, which is advantageous for the application of field effect transistor,^[38] energy storage,^[34] and as a catalyst in electrochemical reactions.^[35] The diameter, height, and Mo–S bond length for the optimized MoS₂ NW were 7.44 Å, 20 Å, and 2.35 Å, respectively. Moreover, the resulting DOS plot in Figure 3 illustrates the existence of continuous impurity states near the Fermi

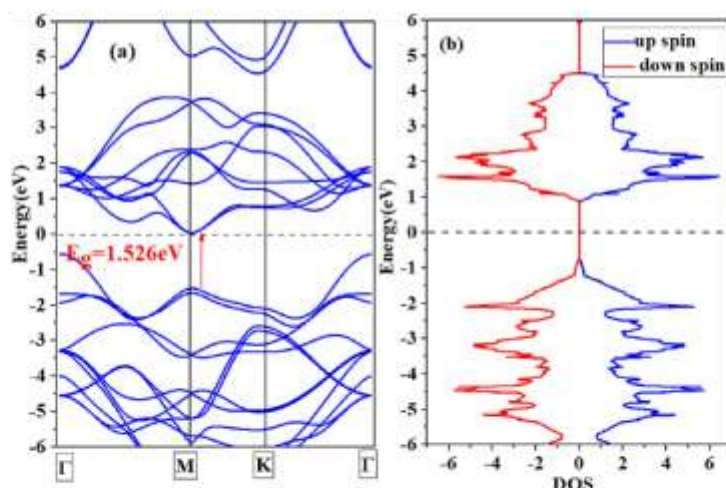


Figure 2. Plotted (a) Band structure and (b) DOS for the MoS₂ monolayer respectively.

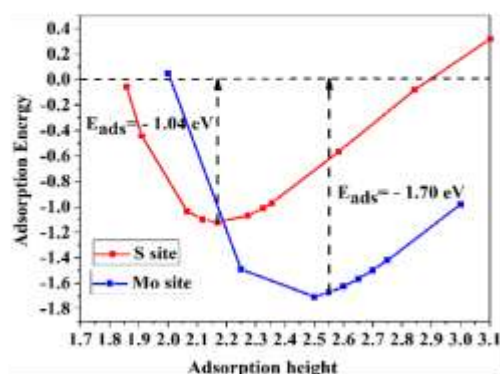


Figure 4. The plotted red and blue curves represent the variation of the adsorption energy with adsorption heights for Cu adsorbed onto MoS₂ NW at S and Mo sites, respectively.

level (E_F), reduces the band gap from 1.56 eV to zero, confirming the metallic behavior of the 1T phase of MoS₂ NW, consistent with the study performed by Selvane et al.^[36] The observed transition from the semiconductor to a metallic was due to the quantum confinement effect. Hence, the complete agreement of the calculated band gap value proved the validity and reliability of our computational procedure.

3.2. Adsorption of Cu Atom Onto the MoS₂ NW

To analyze the interaction of the Cu atom with MoS₂ NW, we have considered the S site (on top of the S atom) and the Mo site (on top of the Mo atom) as the preferential adsorption sites for the Cu atom. This is because both Mo and S atoms contain vacant d and p orbitals that can readily accept electrons from the Cu atom through charge transfer during the interaction. Therefore, we have considered different orientations of the Cu atom at the Mo and S sites, as shown in 4a–s as the input geometries for the adsorption study. Further, adsorption energies were calculated using Equation (1) and reported in Table 1 for all these different adsorption configurations. From the reported value in Table 1, we found that the adsorption energies gradually decrease, attain minima, and then increase with increased adsorption heights. On plotting the adsorption energy as a function of adsorption height, the resulting curve was found to be a U-shaped curve, as shown in Figure 5. The minima of the adsorption energy curve correspond to the minimum adsorption energies and optimized adsorption height. From Figure 5, we found that the Cu atom preferred to be adsorbed at a height of 2.10 Å and 2.50 Å with the adsorption energies –1.04 eV and –1.70 eV at the S and Mo sites, respectively. It was based on energy minimization; we found that the Cu atom preferred to be adsorbed at the Mo site. Therefore, the Cu atom adsorbed at the Mo site was referred to as “Cu-MoS₂NW” and selected for the rest of the calculation. The reported negative value of the adsorption energies in Table 1 indicates that the adsorption pro-

Table 1. The calculated adsorption energies and heights for the Cu atom adsorbed onto MoS₂ NW at Mo and S sites.

Adsorption Height (Å) ^a	Adsorption Energy(eV) ^b	Adsorption Height (Å) ^c	Adsorption Energy(eV) ^d
1.80	–0.03805	2.0	0.04943
1.85	–0.40184	2.25	–1.49111
2.0	–0.9630	2.50	–1.70622
2.05	–1.02261	2.55	–1.67339
2.10	–1.04492	2.60	–1.62624
2.20	–0.99535	2.65	–1.56628
2.25	–0.9423	2.70	–1.4974
2.28	–0.89945	2.75	–1.42075
2.50	–0.51971	3.0	–0.97992
2.75	–0.06315	–	–
3.0	0.31902	–	–

^a Calculated adsorption height at S site.

^b Calculated adsorption energy at S site.

^c Calculated adsorption height at Mo site.

^d Calculated adsorption energy at Mo site.

Table 2. Comparison of the calculated adsorption energies for the Cu-MoS₂NW with previously reported adsorption energies for TM adsorbed onto various 2D materials.

Systems	Adsorption Energy (eV)	Reference
Cu-SnO monolayer	1.342 eV	[37]
Cu-GaN monolayer	1.07 eV	[38]
Cu-hBN monolayer	0.407 eV	[39]
Cu-MoS ₂ monolayer	1.307 eV	[21]
Cu-graphene monolayer	0.228 eV	[40]
Cu-MoS ₂ NW	1.70 eV	Present work

cess was exothermic, spontaneous, and energetically favourable. Additionally, the calculated sum of the corresponding atomic radii for the Cu-Mo atoms (2.73 Å) was larger than the reported adsorption height (2.50 Å) on the comparison. This indicates that covalent interaction exists between the Cu atom and MoS₂ NW during the adsorption. Hence, the calculated high adsorption energy and the existence of covalent interaction between the Cu atom and MoS₂NW suggest that the adsorption of the Cu atom onto MoS₂ NW was a chemisorption.

3.3. Comparison of the Calculated Adsorption Energies for the Cu-MoS₂ NW

In this section, we have compared our calculated adsorption energy for the Cu-MoS₂NW with the previously reported adsorption energies for TM adsorbed onto various 2D materials by different authors. From the reported adsorption energies in Table 2, we found that the Cu atom got adsorbed onto the,SnO monolayer, GaN monolayer, hBN monolayer, MoS₂ monolayer,

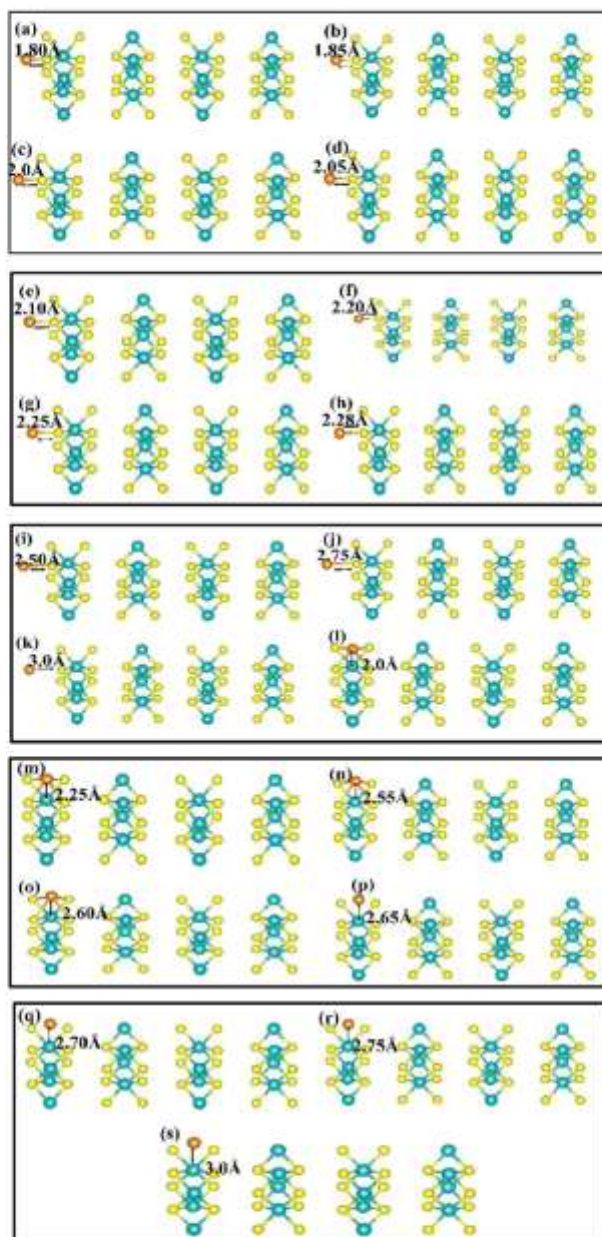


Figure 5. Top view of the different optimized adsorption configurations (a)–(k) at the S site and (l)–(s) at the Mo site, respectively.

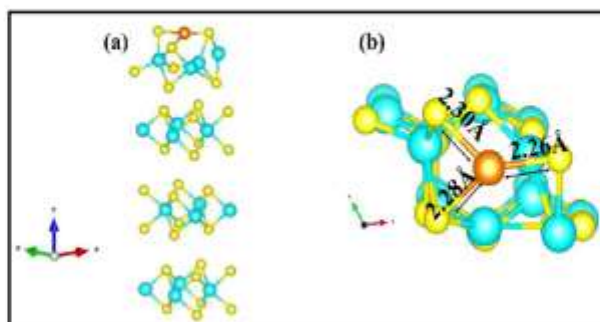


Figure 6. (a) Side view and (b) top view of the optimized Cu-doped MoS₂ NW structures.

and graphene monolayer, with adsorption energies 1.342 eV, 1.07 eV, 0.407 eV, 1.307 eV, and 1.13 eV respectively. The comparison showed that the adsorption energy for the Cu-MoS₂NW was higher than the Cu atom adsorbed onto the SnO monolayer, GaN monolayer, MoS₂ monolayer, and graphene monolayer. This indicates that MoS₂NW has a better adsorption affinity for Cu atoms than SnO monolayer, GaN monolayer, MoS₂ monolayer, and graphene monolayer.

3.4. Structure Analysis of the Cu-doped MoS₂ NW

In this section, we have analyzed the structural properties of the substitutional doped structure. For this purpose, we replaced one of the atoms of MoS₂ NW from the lattice with the Cu atom and optimized the doped structure. After optimization, we found that the doped Cu atom was displaced and occupied the interstitial sites where it bonded with the neighboring three S atoms, as shown in Figure 6. From Figure 6b, we found that the three Cu–S bond lengths in the optimized structure were found to be 2.30 Å, 2.26 Å and 2.28 Å which is shorter than the Mo–S (2.35 Å) bond length of the pristine MoS₂ NW. This indicates that the dopant atom causes the overall structure to be somewhat corrugated due to the protrusion of the Cu atom away from the surface of MoS₂ NW. Moreover, the Mo–S bond lengths in the resulting optimized structure no longer remained a fixed value and underwent variations from 2.36 Å–2.63 Å. On comparison, we found that the variations in the Mo–S bond lengths upon substitutional doping were more significant than the Mo–S (2.35 Å) bond length of the pristine MoS₂ NW. This indicates that the surface of the MoS₂

NW undergoes expansion to accumulate the large atomic radius Cu atom (1.28 Å) within the lattice. These findings suggest that substitutional doping of the Cu atom causes structural distortion within the lattice. For the rest of the study, we have abbreviated the optimized substitutional doped structure as “Cu-doped MoS₂ NW”. To determine the bonding strength of the Cu atom with the MoS₂ NW and the stability of the Cu-doped MoS₂ NW structures, we have calculated the binding energy (E_b) and formation energy (E_f) using Equation (3) and Equation (4)

respectively.

$$E_b = E_{\text{Cu-MoS}_2\text{NW}} - (E_{\text{Cu}} + E_{\text{MoS}_2}) \quad (3)$$

$$E_f = E_{\text{Cu-MoS}_2\text{NW}} - E_{\text{MoS}_2} - \mu_{\text{Cu}} + \mu_{\text{S}} \quad (4)$$

where $E_{\text{Cu-MoS}_2\text{NW}}$, E_{Cu} , E_{MoS_2} , μ_{Cu} , and μ_{S} represents the total energies of the substitutional doped Cu atom into MoS₂ NW, total energies of the defected MoS₂ NW, total energies of the isolated Cu atom, and chemical potentials of the isolated Cu and ejected atoms from the MoS₂ NW, respectively. According to Equations (3) and (4), the binding and formation energies for the Cu-doped MoS₂ NW were –11.326 eV and –5.662 eV, respectively. The calculated high formation and binding energy suggests that the Cu atom binds strongly with the MoS₂ NW, and the Cu-doped MoS₂ NW structures are stable.

3.5. Thermodynamic Stability of the Cu-MoS₂NW and Cu-doped MoS₂NW Systems

To analyze the thermodynamic stability of the substitutionally doped and Cu-adsorbed optimized structures, we have calculated the cohesive energy/atom (E_{coh} /atom) using Equation (2).^[25] And reported in Table 4. According to Equation (2), we found that the cohesive energy for the MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂NW systems was found to be –5.22 eV/atom, –5.15 eV/atom, and –eV/atom respectively. The calculated negative value of the cohesive energy suggests that all our systems are thermodynamically stable. On comparison, we found that the increasing order of thermodynamic stability is Cu-doped MoS₂NW < Cu-MoS₂NW < MoS₂NW. The observed low cohesive energy of Cu-doped MoS₂NW and Cu-MoS₂NW systems with respect to MoS₂ NW can be attributed to the strong interaction of the Cu atom with the surface atoms, thereby reducing the interaction of the surface atoms with the bulk atom. As a consequence, it reduces the overall cohesive energy of the systems. From Table 3 and Table 4, we found that various computational studies suggest that generally, on doping the cohesive energy decreases as observed in the different 2D and 1D nanostruc-

Table 3. Reported calculated cohesive energies for the various 2D materials from various previous computational studies.

System	Cohesive Energy (eV)	Reference
Aluminene(Planar)	−1.96 eV/atom	[41]
Aluminene(P6mmm)	−2.32 eV/atom	
Aluminene(Buckled)	−3.47 eV/atom	
Aluminene(P3m1)	−3.27 eV/atom	
Aluminene(TriangularPmmn)	−2.76 eV/atom	
Aluminene(TriangularPmmn)	−3.27 eV/atom	
Aluminene(4-layerslab, 8-Pmmn)	−3.16 eV/atom	
Gallenene (Puckered)	−2.32 eV/atom	
Indiene (Planar)	−1.81 eV/atom	
Indiene (Buckled)	−1.83 eV/atom	
Indiene (Pucker, sw)	−1.88 eV/atom	
Silicene (Buckled)	−4.57 eV/atom	[42]
Silicene (P3m1)	−3.91 eV/atom	[43]
Germanene (Buckled)	−3.24 eV/atom	[43]
Germanene (P3m1)	−2.93 eV/atom	[44]
Stanene (Buckled)	−3.31 eV/atom	[45]
Stanene (P3m1)	−2.73 eV/atom	[43]
Plumbene (Buckled)	−2.28 eV/atom	[46]
SiGe (Buckled)	−4.81 eV/atom	[47]
SiGe (P3m1)	−2.56 eV/atom	[48]
SnSi (Buckled)	−3.61 eV/atom	[49]
SnSi (P3m1)	−2.28 eV/atom	[50]
SnGe (Buckled)	−3.79 eV/atom	[49]
SnGe(P3m1)	−2.25 eV/atom	[50]
Cu-graphene	2.490eV	[51]
α -CuC	4.99eV	[52]
β -CuC	4.97eV	
α -LiC	4.66eV	
β -LiC	4.66eV	
Cu ₂ Si ₃	3.45eV	
Bulk MoS ₂	4.95 eV/atom	[53]
MoS ₂ monolayer	4.96 eV/atom	

tures like Aluminene (Planar), Aluminene(P6mmm), Aluminene (4-layers slab, 8-Pmmn), Aluminene (Triangular, Pmmn), Indiene, Cu-graphene, SnGe, SnSi, Stanene, Mo₅Se₆ NW, Mo₅S₂Se₃ NW, Mo₅S₄I₂ NW, Mo₅S₂Se₃ NW, Mo₅S₂Se₃ NW, Mo₅S₂Se₃ NW, and Mo₅S₂Se₃ NW respectively. A similar trend was observed for the MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂ NW systems. Also, the calculated high cohesive energy suggests that MoS₂NW, Cu-doped MoS₂NW, and Cu-MoS₂ NW systems can be synthesized experimentally via high energy methods such as Chemical Vapour Deposition (CVD) and molecular beam epitaxy (MBE). This finding was consistent with the Ding et al. results that SiX and XS₃ (where X = B, C, N, Al, and P atoms) could be synthesized via CVD and MBE methods based on cohesive energy calculations.^[56]

Table 4. Reported cohesive energies for the various 1D materials along with MoS₂NW, Cu-doped MoS₂NW, and Cu-MoS₂NW.

System	Cohesive Energy (eV)	Reference
Mo ₅ Se ₆ NW	−4.97 eV/atom	[54]
Mo ₅ S ₂ Se ₃ NW	−5.15 eV/atom	
Mo ₅ S ₄ I ₂ NW	−4.93 eV/atom	
Mo ₅ S ₂ I ₂ NW	−4.69 eV/atom	
Mo ₅ S ₂ Se ₃ I ₂ NW	−4.81 eV/atom	
Mo ₅ S ₂ Se ₃ NW	−4.88 eV/atom	
Mo ₅ S ₂ Se ₃ NW	−4.57 eV/atom	
Mo ₅ S ₂ I ₂ NW	−3.86 eV/atom	
Mo ₅ S ₂ I ₂ NW	−3.73 eV/atom	
Mo ₅ S ₂ Se ₃ NW	−3.67 eV/atom	
MoS ₂ NW	−5.22 eV/atom	Present work
Cu-doped MoS ₂ NW	−3.20 eV/atom	Present work
Cu-MoS ₂ NW	−5.15 eV/atom	Present work

3.6. Electron Localization Function (ELF) Analysis

We have utilized ELF as an effective tool to visualize electron density distribution, lone pairs, and bonding pairs of electrons around the interacting atom. Therefore, we have performed an ELF calculation for the Cu-MoS₂ NW and Cu-doped MoS₂ NW systems. The ELF plot shown in Figure 6 illustrates that the ELF value varies between 0 and 1, with red, blue, and green colors corresponding to the ELF value 1, 0, and 0.5, respectively. The ELF value close to 1 corresponds to a region where electrons are fully localized or have a high electron density. In contrast, the ELF values close to 0 and 0.5 correspond to areas with low electron density and partially delocalized electrons. From Figure 7a, we found a large region of high electron density around the S atoms identified by sizeable red color spherically symmetric rings with a small area of partially delocalized electrons between the Mo-S atoms identified by green spherically unsymmetrical rings. These findings suggest that covalent interaction with a partially ionic nature exists between the Mo and S atoms in the case of the Cu-MoS₂NW system. Additionally, a region of partially delocalized electrons exists between the Cu and Mo atoms, indicating that the Cu and Mo atoms mutually share transferred electrons during the interaction. This confirms that strong covalent bonding exists between the Cu and Mo atoms during the Cu adsorption, which is consistent with our adsorption study. Similarly, for the Cu-doped MoS₂ NW, we found a large spherically red color region around the S atoms rather than Cu atoms, as shown in Figure 7b. These findings suggest that electrons are strongly localized around the S atom compared to the Cu atom, indicating that the Cu atom loses electrons to the nearby S atom, thereby increasing the electron density around the S atom. All these findings confirmed that the interaction of the Cu atom with the nearby S atoms is purely electrostatic. Moreover, a green colored region exists between the Mo-S atoms, indicating that electrons are mutually shared between the Mo-S atoms, again confirming that covalent bonding exists between Mo-S atoms. Hence, our ELF result suggests that covalent and electrostatic

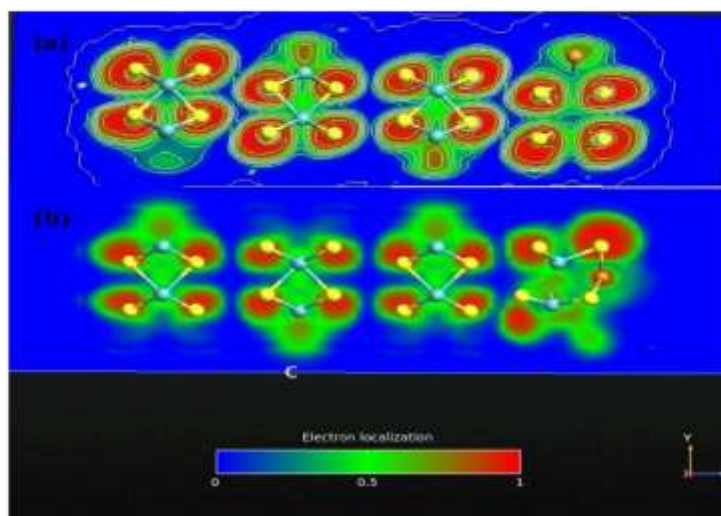


Figure 7. ELF plot for (a) Cu-MoS₂ NW system and (b) Cu-doped MoS₂ NW system, respectively. The ELF magnitude is given in a color scheme in which red, blue, and green correspond to high electron density, low electron density, and free electrons, respectively.

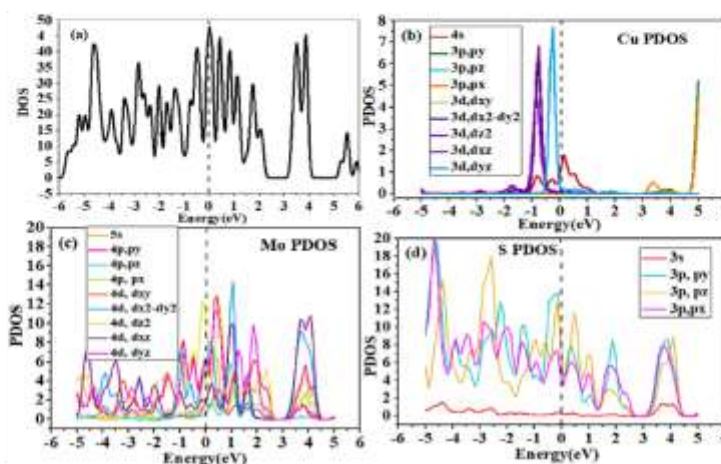


Figure 8. Calculated (a) DOS for the Cu adsorbed MoS₂ NW. PDOS for (b) Cu, (c) Mo, and (d) S atoms, respectively. The black dotted line represents the Fermi level.

Interaction exists between the Cu atom and MoS₂ NW in the case of Cu-MoS₂ NW and Cu-doped MoS₂ NW systems.

3.7. Effect of Cu Adsorption on the Electronic Properties of MoS₂ NW

To analyze the effect of introducing the Cu atom as a foreign atom onto MoS₂ NW, we have calculated DOS and PDOS for the

Cu-MoS₂ NW and Cu-doped MoS₂ NW systems. From Figures 8a and 9a, we found that continuous impurity states exist around the Fermi level (E_F) for both systems. This indicates that the metallic nature of the MoS₂ NW remained preserved even upon substitutional doping and Cu adsorption onto MoS₂ NW. We also found an increase in the peak intensity for both systems. This indicates that charge transfer occurs during the interaction of the Cu atom with the MoS₂ NW. On comparison, we found that the peak intensity of Cu-doped MoS₂ NW was higher than that

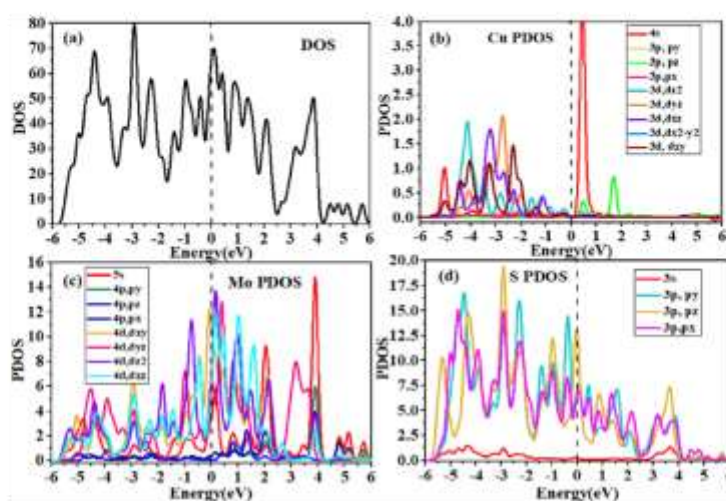


Figure 9. Calculated (a) DOS for the Cu-doped-MoS₂ NW. PDOS for (b) Cu, (c) S, and (d) Mo atoms, respectively.

of Cu-MoS₂ NW, indicating that significant charge transfer occurs in the case of Cu-doped MoS₂ NW. Significant charge transfer indicates better electrical conductivity of the Cu-doped MoS₂ NW than Cu-MoS₂ NW and pristine MoS₂ NW, making the Cu-doped MoS₂ NW a promising candidate for nanoelectronics. We also observed a shift in the Fermi level towards the conduction band, indicating that the Cu atom has an n-type doping effect. Further, PDOS was calculated to determine the contribution of the atomic orbital to the DOS. The PDOS plot in Figure 8c,d illustrates there exists multiple overlapping between the 4d(d_{xy}) and 3p(p_z)-S atomic orbitals in the energy range from -1 eV to 2 eV leading to the strong hybridization between the atomic orbitals to form molecular orbitals responsible for the formation of a covalent bond. Similarly, from Figure 8(b) and 8(c) we found that the 4s-Cu and 4d(d_{xy})-Mo atomic orbitals overlap in the energy range 0 eV–1 eV, indicating strong hybridization and charge was transferred from the 4s orbital of Cu atom to 4d(d_{xy}) orbital of Mo atom during the interaction. In contrast, for the Cu-doped MoS₂ systems, the PDOS plot in Figure 9c,d illustrated that multiple overlapping exists between the 5s-Mo and 3p(p_z)-S atomic orbitals in the energy range from 0 eV to 1 eV, indicating strong hybridization between the atomic orbitals to form molecular orbitals involved in the formation of the strong covalent bond between them. From Figure 9b,c we found that electron transferred from the 4s-Cu atomic orbital to the 3p(p_z)-S atomic orbitals was responsible for the formation of the ionic bond between the Cu and nearby S atoms during the interaction. This type of hybridization indicates that the electronic states are not isolated but are aligned with the existing electronic states of MoS₂ NW. Consequently, these electronic states act as effective charge carriers, facilitating easy charge transfer from the Cu atom to the MoS₂ NW. These findings indicate that the Cu atom-induced electronic states are less likely to trap charge carriers for

long periods, reducing the probability of acting as recombination centers. Moreover, we also noted that the contribution from the Cu atom to the DOS was considerably more significant in the Cu-doped MoS₂ NW compared to the Cu-MoS₂ NW system. This is consistent with our observation that a substantial charge was transferred from the Cu atom to MoS₂ NW in the case of Cu-doped MoS₂ NW, which is consistent with our DOS calculation. Hence, our DOS and PDOS results were in good agreement with each other.

3.8. Bader Charge and Electron Density Difference Analysis

We have performed the Bader charge method and Electron density difference for the Cu-MoS₂ NW and Cu-doped MoS₂ NW systems to analyze the charge transfer mechanism during the interaction. The positive and negative values of the Bader charge indicate charge loss and gain during the interaction. According to the Bader charge method, we found that the Cu atom loses 0.047e to the MoS₂NW in the case of Cu-MoS₂NW, whereas the surface Mo atoms lose 0.692e, 1.344e, 1.414e, and 1.880e to the adjacent S atoms, as shown in Figure 11a. In contrast, for the Cu-doped MoS₂ NW system, we found that the Cu atom loses 0.371e, whereas the nearby neighbouring S atoms gain -0.586e, -0.848e, and -0.745e, as shown in Figure 11b. In comparison, we found that significant charge transfer was observed from the Cu atom in the case of Cu-doped MoS₂NW. These findings validate that the Cu-doped MoS₂NW system exhibits better electrical conductivity than the Cu-MoS₂ NW system. Further, to validate our findings, we have described the charge transfer qualitatively using the electron density difference diagram for the Cu-doped MoS₂NW and Cu-MoS₂NW. The red and blue regions indicate the charge gained and loss region in Figure 10. The electron den-

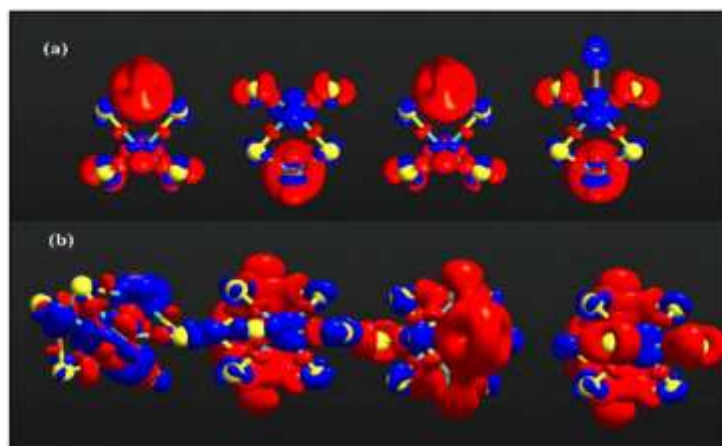


Figure 10. Electron density difference diagram for (a) Cu-MoS₂ NW and (b) Cu-doped MoS₂ NW systems. The red and blue regions indicate charge gain and charge loss regions, respectively.

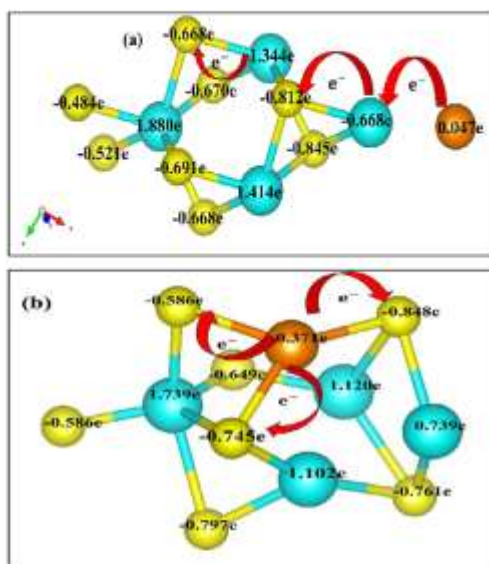


Figure 11. Calculated Bader charge distribution for the surface atoms of (a) Cu-MoS₂ NW and (b) Cu-doped MoS₂ NW, respectively. The red arrows represent the directions of electron transfer from the Cu atom to the MoS₂ NW.

sity difference diagram in Figure 10a illustrates the blue-coloured region around the Cu and Mo atoms, whereas the red-coloured region around the S atom. The red and blue region indicates that the S atom gains electrons, whereas the Mo and Cu atoms lose electrons in the case of Cu-MoS₂NW. In contrast to the Cu-doped MoS₂NW, Figure 10b illustrates a large red region around

the S atom and a large blue region around the Mo and Cu atoms. Large blue and red areas indicate that a substantial charge was gained by the S atom and lost by the Mo and Cu atoms during the interaction. This again suggests that substantial charge transfer occurs from the doped Cu atom to the MoS₂ NW during the interaction. The observed charge lost and gained can be attributed to the difference in the electronegativity between the interacting atoms. According to the Pauling scale, the electronegativity of Mo(χ_{Mo}), S(χ_{S}), and Cu(χ_{Cu}) differ by 13.68% and 35.78% with respect to χ_{Cu} . Slight differences in the electronegativity make Cu and Mo atoms partially positive and negative. This creates a local weak electric field between the Cu and surface atoms, resulting in a weak charge transfer from the Cu atom to the MoS₂NW in the case of Cu-MoS₂NW. Consequently, valence electrons are mutually shared, confirming that the Cu atom interacts with MoS₂ NW via covalent interaction, which agrees with our ELF study. Conversely, considerable differences in the electronegativity between the S—Cu atoms make Cu and nearby S atoms electrons deficient and electrons rich species. This creates a strong electric field between the interacting S—Cu atoms, causing substantial charge transfer from the Cu atom to the nearby S atom. This is why, upon geometry optimization, the Cu atom got occupied at the interstitial sites where the Cu atom got bonded with the three S atoms to maximize the electrostatic interaction. Hence, our Bader charge analysis agrees with electron density difference results.

3.9. Effect of Cu Adsorption on the Work Function of MoS₂ NW

The work function is considered an essential parameter for nanoelectronic devices because any variation in the work function influences the charge injection capability of the material,

thereby significantly impacting the performance of nanoelectronic devices. It is observed that the adsorption of transition metal atoms strongly influences the work function. For example, Chi et al. studied the variation in the work function of GaN NW and GaN monolayer upon the alkali metal adsorption using the first principle calculation. They reported that the work function of the GaN monolayer changes from 4.21 eV to 2.47 eV, 1.88 eV, 1.49 eV, 1.29 eV, and 0.84 eV upon the adsorption of Li, Na, K, Rb, and Cs metal atoms onto GaN monolayer.^[57] In contrast, they also observed that the work of the pristine GaN NW changes from 4.11 eV to 2.45 eV, 2.32 eV, 2.06 eV, 1.81 eV, and 2.38 eV upon the adsorption of Li, Na, K, Rb, and Cs metal atoms onto GaN NW.^[58] In another study, Sahin et al.^[59] reported that the work function of the silicene changes from 4.77 eV to 4.39 eV, 4.25 eV, 4.09 eV, 4.68 eV, 4.81 eV, 4.47 eV, 4.77 eV, 4.84 eV, 4.65 eV, 4.73 eV, 4.81 eV, 5.0 eV, 4.97 eV, and 4.90 eV upon the adsorption of Li, Na, K, Be, Mg, Ca, Ti, V, Cr, Mn, Fe, Co, Mo and W onto silicene. Therefore, based on the above findings, we have also evaluated the variation in the work function of the MoS₂ NW upon substitutional doping and adsorption of the Cu atom. For this purpose, the work function of the pristine MoS₂ NW and Cu-doped MoS₂ NW and Cu-MoS₂ NW systems was calculated using Equation (5).

$$\phi = E_{\text{ref}} - E_F \quad (5)$$

where E_{ref} and E_F represent the electrostatic potential at infinity and Fermi level energy, the electrostatic potential at infinity is assumed to be zero in the present work. Further, the variation in the work function ($\Delta\phi$) for the Cu-doped MoS₂ NW and Cu-MoS₂ NW was calculated by subtracting the work function of the Cu-doped MoS₂ NW and Cu-MoS₂ NW from that of the pristine MoS₂ NW. The computed work function values for the pristine MoS₂ NW, Cu-doped MoS₂ NW, and Cu-MoS₂ NW were found to be 4.99 eV, 3.792 eV, and 3.845 eV, respectively. These findings indicate that the value of the work function decreases and undergoes negative variation to 24% and 22.9% upon substitutional doping and adsorption of Cu atom onto MoS₂NW. A similar trend in the work function was observed by Ouma et al.^[60] While studying the effect of substitutional doped and adatoms 3d TM onto the TcS₂ monolayer. The observed variation in the work function of Cu-doped MoS₂ NW and Cu-MoS₂ NW was due to the existence of a strong electric field between the substitutional doped Cu atom and MoS₂NW that facilitates redistribution of electron density around the dopant site and substantial charge transfer from the Cu atom to MoS₂NW. According to Equation (6), an exponential relationship exists between the emitted electron current densities and variation in the work function.

$$j = AT^2 e^{-\frac{\Delta\phi}{K_B T}} \quad (6)$$

where j is the emitted electron current densities (A/m²), A is a Richard constant (A/m² K²), ϕ is the work function of the material in eV, T is the temperature in K, and K_B is the Boltzmann constant in eV/K respectively. Therefore, a significant variation in the work function of Cu-doped MoS₂NW than Cu-MoS₂NW indi-

cates better electron emission capability of Cu-doped MoS₂NW. Hence, the work function analysis suggests that the Cu-doped MoS₂NW system can be utilized in field emission devices.

4. Conclusion

In this study, we have systematically investigated the structural and electronic properties of substitutional doping and adsorption of Cu atom onto MoS₂ NW using first principles calculation. According to the adsorption study, the Cu atom prefers to be adsorbed at the Mo site with an adsorption energy of about -1.70 eV. This results in the chemical bond formation between the Cu atom and MoS₂NW during the interaction. In contrast, substitutional doping of the Cu atom distorts the structure to accommodate the Cu atom and exhibits strong covalent bonding with the Cu atom. According to the Bader charge method, the Cu atom loses 0.047e and 0.371e to the MoS₂ NW in the case of Cu-MoS₂NW and Cu-doped MoS₂NW, respectively. Significant charge transfer leads to enhancement in the conductivity and variation in the work function. The DOS results suggest that the Cu atom induces an electronic state near the Fermi level, facilitating easy charge transfer from the Cu atom to MoS₂NW. There was also a shift in the fermi level towards CB, indicating that the Cu atom has an n-type effect on substitutional doping and adsorption. From the work function calculation, we found that the work function of the Cu-doped MoS₂ NW and Cu-MoS₂NW systems undergo 24% and 22.9% with respect to that of pristine MoS₂NW. Further from the PDOS study, we found that in case of Cu-MoS₂NW strong hybridization exists between the 4d(d_{xy})-Mo and 3p(p_z)-S atomic orbitals responsible for the formation of covalent bond whereas for the Cu-doped-MoS₂ systems, hybridization between the 4s-Cu atomic orbital to the 3p(p_z)-S atomic orbitals was responsible for the formation of the ionic bond between the Cu and nearby S atoms during the interaction. Moreover, our calculated cohesive energy suggests that the pristine MoS₂NW, Cu-MoS₂NW, and Cu-doped MoS₂NW systems are thermodynamically stable. Finally, our DFT result suggests that substitutional doping is an effective way to modulate the electronic properties of MoS₂NW as Cu-doped MoS₂ NW systems exhibit better electrical conductivity than pristine MoS₂NW and Cu-MoS₂NW due to better charge transfer and variation in the work function. Thus, the Cu-doped MoS₂NW system is a promising candidate for nanoelectronics and field emission device applications.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Adsorption · Copper · DFT · MoS₂ · Nanowire

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