Fabrication and characterization of CeO$_2$/rGO conducting electrodes

A DISSERTATION

SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE AWARD OF THE DEGREE

OF

MASTER OF TECHNOLOGY

in

POLYMER TECHNOLOGY

Submitted by

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CANDIDATE'S DECLARTION

I **Shimul Chakma, 2K19/PTE/05** student of M.Tech hereby declare that the project Dissertation titled **"Fabrication and characterization of CeO_2/rGO conducting electrodes"** which is submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in the partial fulfillment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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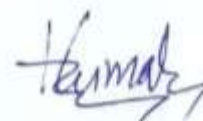**Shimul Chakma**

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CERTIFICATE

I hereby certify that the Project Dissertation titled "**Fabrication and characterization of CeO$_2$/rGo conducting electrodes**" which is submitted by **Shimul Chakma, 2K19/PTE/05**, Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the Master of Technology, is a record of the project work carried out by the student under my supervision. To the best of our knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

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Date: July 2021

Prof. D Kumar

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ACKNOWLEDGEMENT

ABSTRACT

Fabrication of advanced electrode material is highly desired for novel electrochemical sensor development. In this work, cerium oxide (CeO_2) nanoparticles were successfully loaded on reduced graphene oxide (RGO) by one-step hydrothermal synthesis approach, and this nanocomposite (CeO_2/ rGO) was used as novel electrode material for urea detection. Herein, efforts have been made to fabricate a conducting paper based sensor comprising of CeO_2/rGO nanocomposite and PEDOT: PSS. The conductivity of the PEDOT: PSS coated paper significantly increases from 6.9 x 10^{-5} S/cm to 1.1 x 10^{-4} S/cm on treatment with ethylene glycol. Further, the modification of conducting paper with synthesized CeO_2/rGO nanocomposite shows better electrochemical properties.

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LIST OF ABBREVIATIONS

Symbol	Notation
CeO_2	Cerium Oxide
CP	Conducting paper
CrGOC	Ceria reduced Graphene Oxide Composite
CV	Cyclic Voltammetry
DSC	Differential scanning calorimetry
DW	Distilled water
FTIR	Fourier transform infrared spectroscopy
GOCC	Graphene Oxide-Ceria Composite
PEDOT: PSS	Poly(3, 4-ethylenedioxythiophene):poly (4-styrenesulphonate)
rGO	Reduced graphene oxide
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV-Vis	UV visible spectroscopy
XRD	X-ray diffraction

CHAPTER 1: INTRODUCTION

Urea is an important biomarker for medical diagnosis as it is involved in several biological activities like metabolism and neurotransmitters synthesis as well as the essential amino acids which are very important for the human health. The normal range of urea in human body is 15-40 mg/dl [1] but it causes problems, if varies beyond this range. Therefore, a clinical estimation of urea is very necessary for maintaining the same because less urea concentration causes liver failure, cachexia and nephritic syndrome. On the other hand, an excessive urea concentration in blood and urine causes kidney failure, renal failure, dehydration, gastrointestinal bleeding, headaches, lethargy and human schizophrenia [2]. In addition to the above, the concentration of urea in food products is also a crucial issue considering the food safety measures because it is noticed that many food products have been adulterated these days for the sake of monitory benefits.

Considering the above aspect, it is extremely essential to develop a rapid, cheap, easy to use and reliable method for urea detection in food and biological samples. Though, several analytical methods are reported in the literature but among these enzymatic methods offer an advantage over others in terms of specificity, selectivity, response time, repeatability and smaller size. Therefore, due to the high sensitivity and selectivity, low cost and simplicity, an electrochemical technique has attracted considerable interest among the researchers for the determination of amino acids [3]. In these electrochemical techniques, the conventional electrodes show the poor sensing performance toward the urea detection. Therefore, the fabrication and use of better quality electrode is highly demanded. Further, the performance of electrochemical sensor is strongly depends on the physical and chemical properties of the electrode materials [4]. An excellent electrical conductivity and large surface area of graphene oxide have also created a lot of interests for its use as a promising electrode material in electrochemical sensors [5-7].

Presently, there are many urea detecting devices used for the detection of urea concentration such as IR spectroscopy, florescence spectroscopy, Raman spectroscopy, polarimetry [8-12] but these instrumental techniques are not only complicated, time taking and expensive but also require skilled manpower. Thus, it is necessary to develop a simple device which can be used at the point-of-care for the detection of urea concentration in the human body. Focusing on this aspect, the biosensor is found to be a suitable, simple and precise device for this purpose.

In recent years, conducting paper (CP) has also been evolved as an ideal platform for the desired analytical and clinical biosensing applications. Since, the CP provides large surface to volume ratio which enhances its utility as a suitable substrate for the chemical and biological analysis [13]. Further, the CP requires a small quantity of samples and possesses a porous structure that facilitates immobilization of sensing materials by suitable surface modification [14]. In comparison to other traditional substrates like glass, ceramic and polymer, the paper-based substrate is easy to develop, cheaper, biocompatible, portable, flexible, disposable, and environment friendly substrate [15]. For making this paper substrate conducting, various inorganic and organic materials have been widely used for this purpose. The cerium oxide (CeO_2), a rare earth metal oxide has been reported as an electrode material for electrochemical sensor as well as biosensor [16] but iits low electrical conductivity hinders the use of CeO_2 nanomaterial. However, this problem was sorted out by loading the metal oxide nanoparticles on support materials like graphene oxide for boosting the desired properties and achieved the hybrid composite electrode materials, with improved selectivity and sensitivity for numerous applications including biosensing application [17-18].

Polymers with π electrons are said to be conducting polymers and delocalization of these π electrons with rapid electron transfer and solution processing facility leads to the promising applications of conducting polymer to obtain conducting paper for biosensing application. The conducting polymer, poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), has been used for the fabrication of conducting paper electrode

for biosensing application. Moreover, the solvent treatment with particular dopant significantly enhances the conductivity of PEDOT:PSS and further improves its electrochemical performance in terms of sensitivity and stability [19]. The doping of conducting polymer with particular dopants or the reinforcement of graphene, metal or metal oxide nanoparticles, enhances its chemical, physical, optical, electrical and electrochemical properties. In the present project work, CeO_2/rGO nanocomposite (CrGOC) has been fabricated for biosensing application.

CHAPTER 2: LITERATURE REVIEW

2.1 Biosensor

Biosensor is a device which is used for the detection of the analyte or chemical substances on combining with a biological component with a physicochemical detector [4]. This biological sensing element along with a physiochemical transducer helps to measure the sensitivity and also specificity of biochemical system. Thus, biosensors are having two following important parts, namely, bioreceptor and transducer.

Bioreceptor: In biosensor, the bioreceptor component is a biological material which may be virus, enzymes, nucleic acid, tissue, antibodies and bacteria etc. The binding process between bioreceptor and target biomolecule is very specific. Analyte or target biomolecule is a simple compound such as glucose, urea, DNA, RNA etc.

Transducer: It converts the biochemical interactions outcome into the measurable electronic signals.
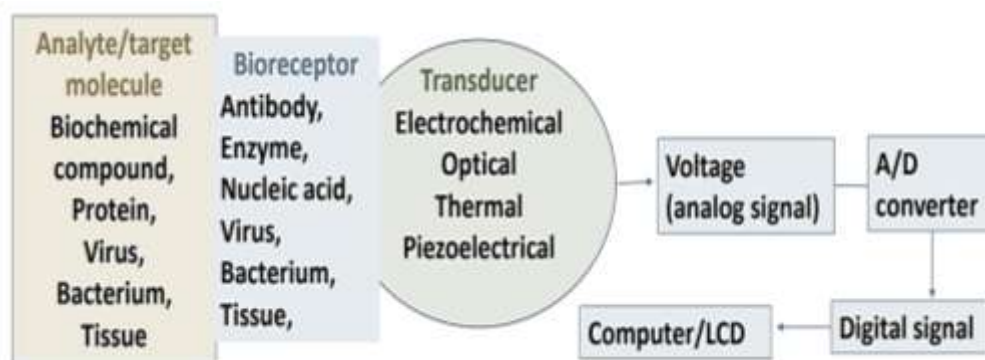
Fig 2.1: Schematic representation of a typical biosensor [15]

Transducer is helpful to convert the electronic energy to measurable data. In sensors, transducers convert physical energy into electrical energy. The main types of transducers are electrochemical, piezoelectric, optical and magnetic etc. Electrochemical biosensors measure change in electric distribution and have been widely used in biosensor fabrication as they show excellent selectivity, sensitivity, stability, reproducibility, and

quick maintenance with minimum cost. Electrochemical biosensors are of four types, i.e., potentiometric, condutometric, amperometric and impedance [20].

2.1.1 Electrochemical Biosensor

Electrochemical biosensors have received substantial attention as they are cost-effective, sensitive and selective. Electrochemical sensing system requires a working electrode, reference electrode and auxiliary or counter electrode for the detection of analytes. Working electrode comprises of transduction element in the electrochemical system dictates the importance of sensing electrode material as the biochemical reaction takes place on the working electrode. An auxiliary electrode is fabricated from electrochemically inert material such as platinum, gold or carbon. Ag/AgCl is being used as reference electrode in three components cell system. This reference electrode is used for maintaining a desirable and stable potential in the cell [21] during the measurements.

The basic principle of urea concentration measurement depends on the interaction of urease enzyme with urea during its hydrolysis. The bio-specificity is the key parameter in this enzymatic reaction [22]. During the biochemical reaction, an increase in current is measured with respect to time using urea biosensor device. The reaction between urea and urease enzyme results in products like ammonium and bicarbonate ions which facilitate the enhancement of the conductivity. The number of NH_4^+ ions transfers at electrode surface is directly related to the number of urea molecules available in the blood/environment and thus easily measured.

The enzymatic reaction of urea with urease is shown in the following reaction:

$$NH_2CONH_2 + 3H_2O \xrightarrow{\text{Urease}} 2NH_4^+ \, HCO_3^- + OH^-$$

Three ions are produced in the above reaction such as two NH_4^+ and one CO_3^- ions which are responsible for an increase in the conductivity [23]. In case of CrGOC material, a reaction between ammonium ions and CrGOC will develop an electromotive force (EMF) change which can be studied by cyclic voltammetry (CV). The

immobilization techniques used for the fabrication of urea biosensor are shown in the Fig. 2.2 [24]. while Fig. 2.3 shows the pictorial representation of the working model urea detecting biosensor [25].
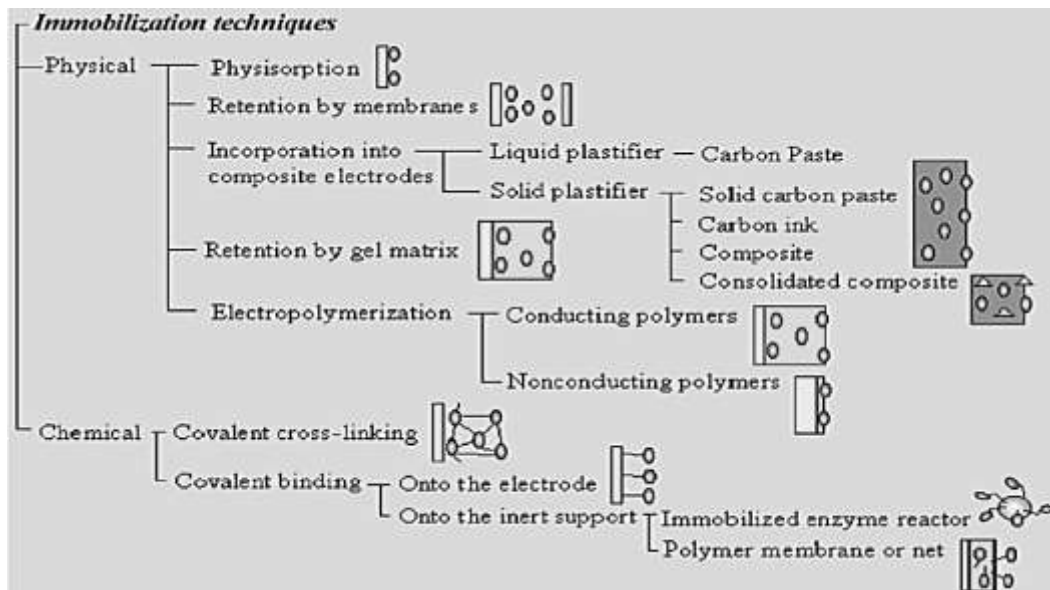
Fig 2.2 Immobilization techniques used for the development of urea biosensors
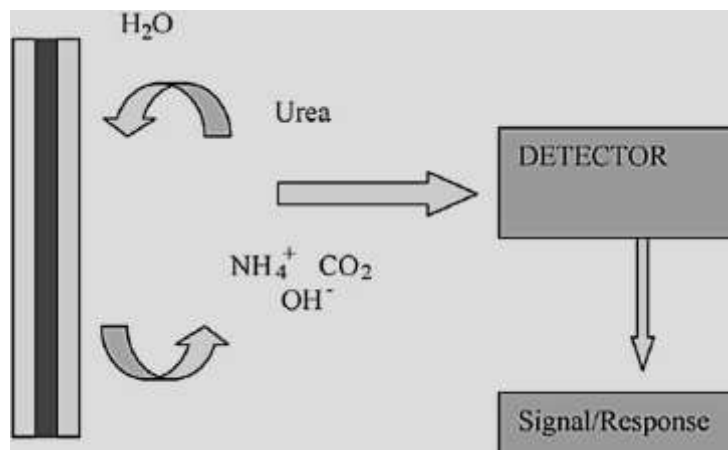
Fig 2.3 Schematic of a typical urea biosensor

For detecting the urea content, an electrochemical technique having biological enzyme with nanoparticles has been primarily used, but still there is a need of a non-invasive method, using highly flexible and reproducible with resistant to interferential material device. Though, urea detection has been carried out by numerous researchers using various methods and technologies but still improvements are required for its commercialization [26] point of view. Fabrication should be feasible with economical device showing rapid assay time. Therefore, conducting nanoparticles have been utilized for the acceleration of electron transfer systematically on the surface of electrodes.

Earlier studies have been mentioned direct attachment of nanoparticles onto the graphene oxide for the electrode fabrication and their corresponding electrochemical characteristics to determine the analyte concentration [27]. It has been well described in the latest studies that incorporation of nanoparticles has significantly improved the analyte detection with improvement in electron transfer efficiencies when compared those electrode without nanoparticles [23] use.

2.2 Fabrication of Conducting Paper (CP)

For biosensing application, the fabrication of CP can impact the sensing behavior. At present, conducting papers (CPs) have received great attention in the electronic world as highly desirable electronic materials. Conducting papers are expected to be used in a variety of applications, including electromagnetic shielding and electrodes. By altering the surface characteristics of cellulose fiber we can modify that paper by chemical processing or physical adsorption for biosensing application in particular. There are few methods used for the fabrication of CP include dip coating, inkjet printing, photolithography and wax printing etc. These methods are elaborated in the following sections.

2.1.1 Dip Coating

This is the simplest method for the fabrication of CP, where there is no necessity of other techniques or instruments. For this technique, Whatman filter paper is used. This paper is cut into small pieces and these strips of Whatman papers are dipped in the solution of PEDOT:PSS with nanomaterial for 30-60 min and dried in an oven. This process was repeated several times and this thickness of the coating layer is proportional to the number of dipping on the paper substrate. Pre-treatment on paper using tween-20 or any other surfactant helps to enhance the overall efficiency of coating [27].
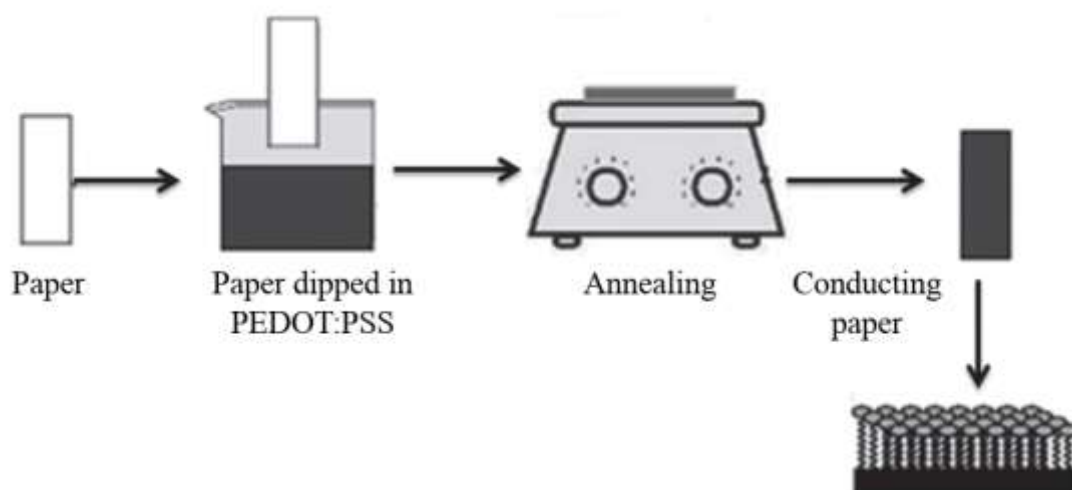
Fig 2.4 Pictorial representation of dip coating method [3]

2.2.2 Conductive Inkjet Printing

There is no need of additional instrumentation in case of inkjet printing. It is widely used because of its reduced cross contamination between samples and reagents and non-contact operation. There are some commercially available modified inkjet printers and ink cartridges that are being used to print biomolecules for sensors. However, for this fabrication technique either a modified inkjet printer or an expensive bio-ink printer is necessary [28].

2.2.3 Photolithography

Photolithography technique has been used for paper-based sensors with high resolution in large scale production. It involves the use of photoresist, which is poured onto the paper and baked. Further, the paper is irradiated with UV light and that paper should be a patterned transparent film. Then with the help of acetone, un-polymerized photoresist is removed and dried. To create hydrophilic area, this paper is exposed to air plasma. This procedure involves long and complex steps and requires the use of expensive processing equipment. However, the formed sensors may damage when it is bent or folded [29].

2.2.4 Wax Printing

Wax printing technique is simple, non-toxicity, and low cost compared to other technique. Paper-based microfluidics devices have been fabricated using the wax printing technique [29]. This process occurs by controlling the flow of fluid and wax patterns are directly printed on the paper which includes the samples and the reagents on the paper. This process is not suitable as the wax melts at high temperature.

2.3 Conducting Paper (CP) in Biosensor

CPs are being widely used in the field of biosensors for diagnostics of diseases, for water and food quality maintenance and detection of pathogens and environmental agents. It can be considered as pocket laboratory and has been widely studied as per the sensitivity and reliability. A comparison between conventional electrode and conducting paper based biosensor electrode suggests that the conducting paper electrode will be cost effective, flexible, light weight and disposable [30]. Kumer et al. used a composite of PEDOT:PSS and carbon nanotubes for the development of conducting paper electrode by a simple coating using dip method. It was reported that the conductivity of the paper electrode was found increased during the measurements. The fabricated CP based electrochemical biosensor was found to be flexible, efficient conductive, and disposable too. In another work, the CNT was replaced with rGO resulting in better electrochemical performance. Such biosensor electrode materials are very useful in the various analytes detection. Therefore, an electrochemical detection of analytes like glucose, urea, and uric acid may be carried out using above sensing electrodes in the biosensors.

In recent advances, the paper-based microfluidic devices which are low-cost, flexible, easy-to-use, and portable diagnostic platforms have been made easily by wax printing technique. Further, these platforms have been used to detect various environmental reagents and biological analytes [31].

2.4 Importance of conducting materials in biosensors

Mostly polymers are chemically inert and electrically insulating materials and therefore mainly used for packaging application based on their mechanical properties [13]. But, nowadays conducting polymers have also attained more interest in the field of biosensor fabrication. Moreover, the conducting polymers can efficiently transport the electric charges developed in a biological activity. They are suitable matrix for enzyme bioreceptors. Conducting polymers can be synthesized directly on the working electrode using electrochemical polymerization method. An immobilization of biomolecules may also be done electrochemically during the polymerization process simultaneously. By modifying the polymer state, the spatial distribution of the immobilized enzyme, the film thickness, and the enzyme activity are adjustable. The doping process is used to modify the electronic conductivity of these polymers by several orders of magnitude. Conducting polymers are compatible with biological molecules in neutral aqueous solution.
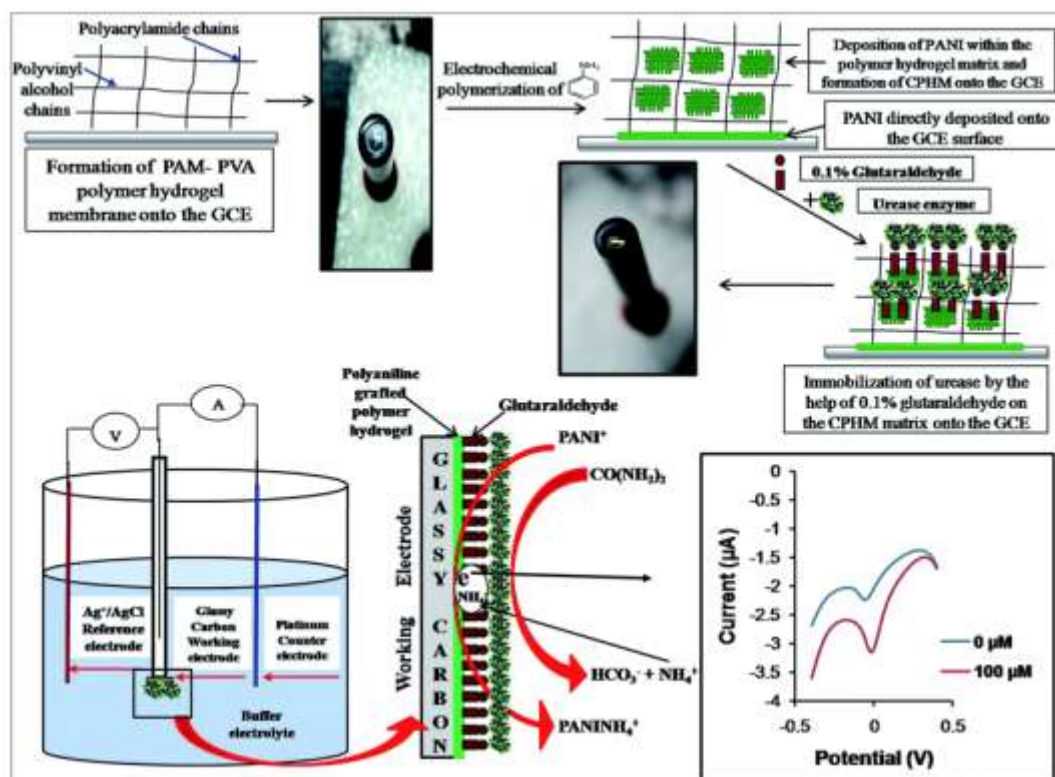

Fig 2.5: Pictorial representation of polyaniline based enzymatic electrochemical biosensor for urea detection [22]

For the detection of important analytes during diagnostics, the conducting polymers are useful for enhancing the performance of the biosensors. That's why the use of conducting polymers is increasing in diagnostics medical reagents [32]. Different size, shape and geometry electrodes may be used easily for the deposition or immobilization of biologically active molecules by different techniques. These techniques are more appropriate for the design of poly-analytes electrochemical biosensor. Electrically conducting polymers may also be modified in terms of electrical and mechanical properties as per our requirement. Moreover, for binding the protein molecules, the conducting polymer can itself be modified as and when required. Significance of conducting polymer also reflects for getting enhanced sensitivity, speed and versatility of biosensors in diagnostics of diseases by measuring vital analytes. More importantly, conducting polymers are being deposited directly on the electrode surface or paper during the electrochemical polymerization [33]. Thus, the enzyme activity is tuned by changing the state of the polymer according to our requirement.

It is well known that conducting polymers based sensing electrodes are compatible with biological molecule and capable to detect the analytes easily. These electrodes can be doped or undoped reversely due to their unique redox behavior resulting in conductivity change and other properties [34].

2.4.1 PEDOT: PSS

PEDOT: PSS is made by blending the poly(3,4-ethylenedioxythiophene) with poly(styrene sulfonate) and widely used in numerous applications. This is a blend of PSS polyanion with cataionic polythiopene derivative. PEDOT:PSS is conducting in nature where the hydrophobic PEDOT-rich chain is encapsulated by hydrophilic and insulating PSS chain [35]. Kim et al. reported that the conductivity of PEDOT: PSS enhances after adding the polar organic solvents like dimethyl sulfoxide (DMSO), N, N-dimethylformamide (DMF) or tetrahydrofuran (THF) into PEDOT:PSS aqueous solution. In the previous studies, it was also found that higher boiling point polar organic solvents

such as ethylene glycol, glycerol, nitro methanol can significantly enhance the conductivity of PEDOT:PSS about 200 S/cm [36]. The chemical structure of PEDOT:PSS is shown in the following figure.
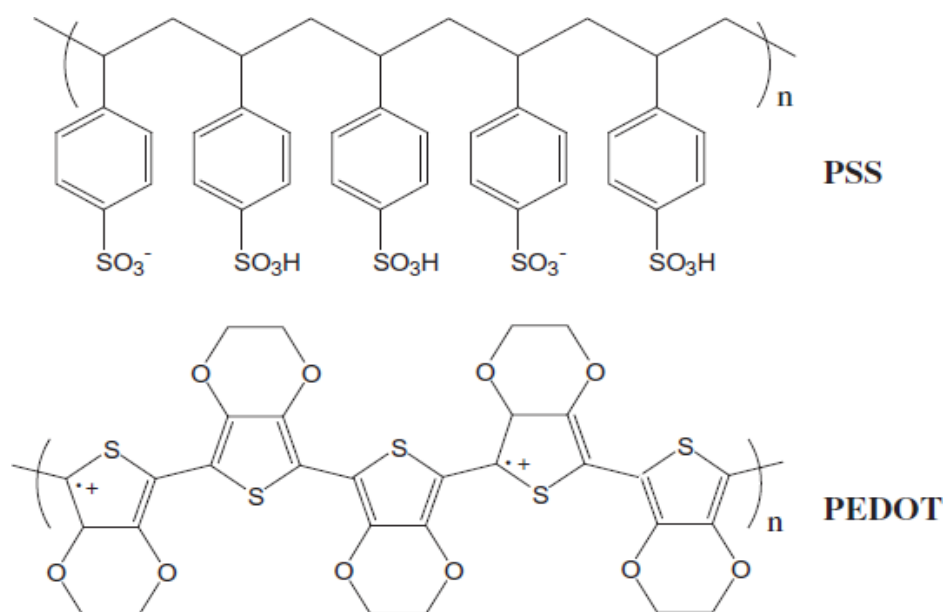
Fig 2.6: Chemical structure of PEDOT: PSS

2.5 Enzyme Immobilization

Immobilization of enzyme is an important parameter for the development of good performance biosensor with enhanced sensitivity, high selectivity, excellent operational and storage stability, high reproducibility and short response time. To retain the biological activity of the immobilized biomolecule after immobilization they have to maintain the structure, function etc. [22]. The immobilization technique should be easy and effective and it should not affect the recognition probe's functioning during use. The mostly used methods for immobilization are well reported in the literature. An immobilization process may be performed by means of physical adsorption, covalent coalition, electrochemical entrapment, and affinity interactions [24] etc. In literature different matrices are reported which are being used to enhance the performance of the immobilized enzymes. Among these nanomaterials matrices attracted much attention of the researchers worldwide due to their unique physico-chemical properties. The nanoparticles have the ability to equilibrate key components that determine the efficiency

of biocatalysts, mass transfer resistance, specific surface area and enzyme loading [3].

2.6 Graphene

Graphene is a 2D layer of carbon atoms placed in a hexagonal lattice which is extremely thin. In the graphene sheet, every atom is connected to its three nearest neighbors with a σ-bond. Each atom contributes one electron to a conduction band which delocalize over the whole sheet. In a graphene sheet, three outer-shell electrons out of four occupy three sp^2 hybrid orbital forming σ-bonds with bond lengths about 0.142 nm as shown in the following figure.
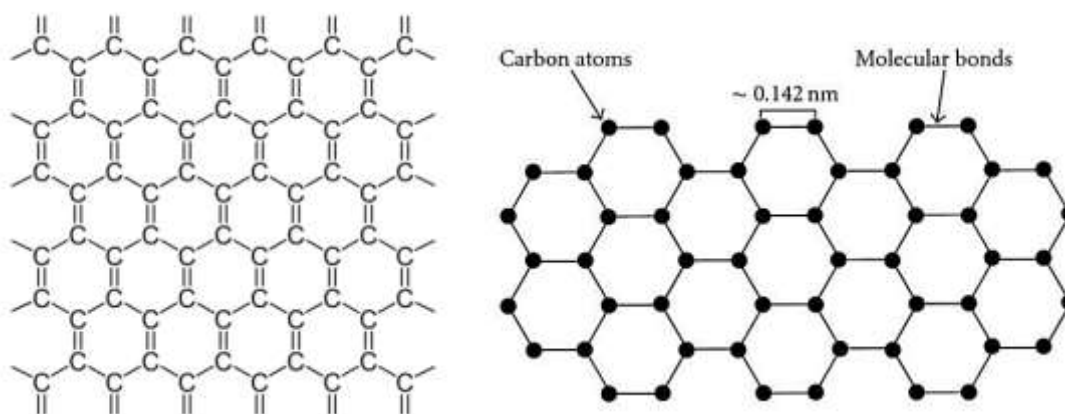
Fig 2.7: Chemical structure of graphene

It has remarkable and unique biophysical and chemical property with excellent mechanical, optical, electronic and thermal properties. As they are not reactive, therefore these are functionalized to graphene oxide (GO) forming hydroxyl, carboxyl, ethyl functional groups on the graphene plane, but those are insulated in nature. To attain the conjugated network and electrical conductivity of pure graphene, it requires the reduction of GO to rGO (fig 2.7). The electrical transport can be affected, if the carboxyl, hydroxyl or epoxy groups bonded on graphene sheet [37].
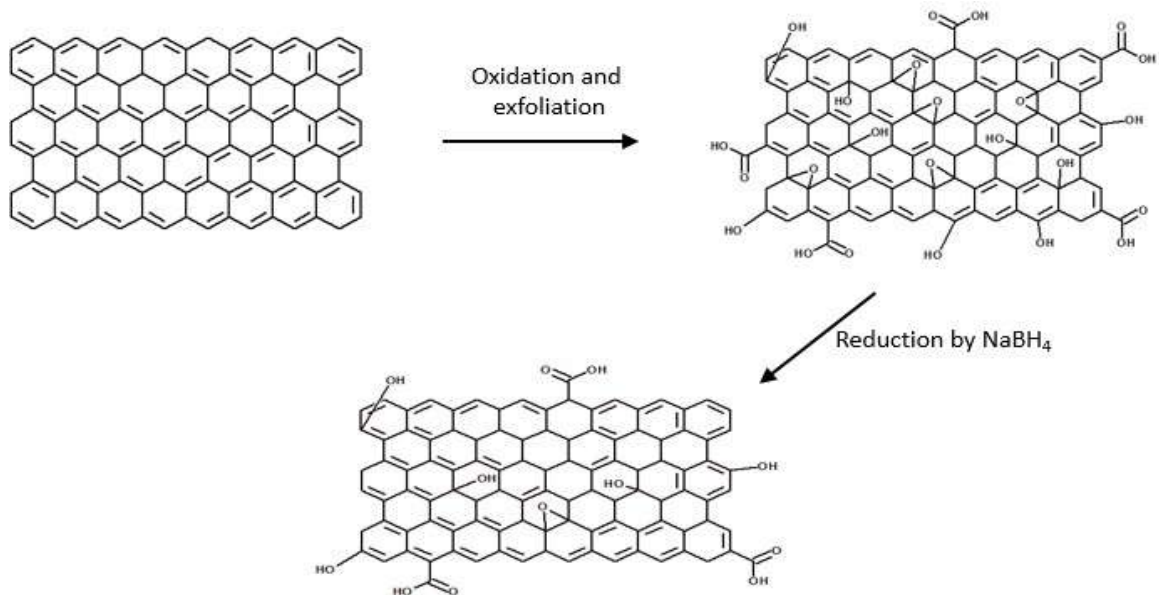
Fig 2.8 Schematic showing the conversion of graphene to reduced graphene oxide

Properties of graphene

Some properties of graphene are given as below:

- Nearly transparent and thinnest material

- sp^2 carbon atom

- Excellent electrical conductivity

- Good specific surface area

- High mechanical strength

- Excellent electron mobility

- Exceptional biocompatibility

- Easy functionalization

- Cost-effective

- Better sensing performance

- Can absorb light of all visible wavelengths

Various properties data of graphene are also tabulated in Table 2.1 as given below:

Table 2.1: Various Properties Data of Graphene

Specific density	2.26 g/cm^3
Elastic modulus	1 TPa (in-plane)
Resistivity	50 μΩ cm (in-plane)
Thermal conductivity	3000 W m^{-1} K^{-1} (in-plane) 6 W m-1 K-1 (c-axis)
Thermal expansion	-1 x 10^{-6} K^{-1} (in-plane) 29 x 10^{-6} K^{-1} (c-axis)
Thermal stability	450-650°C

2.7 CeO$_2$

CeO$_2$ is commonly known as *ceria* a rare earth material. Rare earth material is also known as *industrial vitamin* and *treasury* of new materials. Rare earths have an important role in technical progress and the development of traditional industries. It is widely applied in the "HI-TECH" industries like information and biotechnological industries [38]. CeO$_2$ nanoparticles have significant properties for biomedical, sensing and drug delivery applications. These nanoparticles are unique because of the cerium presence in two oxidation states (Ce^{3+} or Ce^{4+}), that enables them to be useful in redox catalysts.

Some properties of CeO$_2$ nanoparticles are listed below:

- unique chemical and electronic configurations

- mechanical stability

- Biocompatibility

- High oxygen mobility

- Enhance catalytic activity and selectivity

- Superior thermoelectric property

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials Used

For synthesizing the graphene oxide, the graphite powder (99.9%), chemicals used for the electrodeposition of the CeO_2 nanostructures were cerium (III) nitrate hexahydrate $(Ce(NO_3)_3 \cdot 6H_2O$, 99% trace metals basis, CAS 10294-41-4) which were procured from Sigma Aldrich (France). The chemicals used for cleaning purposes were acetone (100%), and hydrochloric acid (HCl) which were purchased from Central Drug House (Pvt). Other chemicals used including ascorbic acid (AA), were procured purchased from Sigma-Aldrich (USA). PEDOT: PSS (2.8 wt%), H_2SO_4, $NaNO_3$, $CaCl_2$, ethylene glycol, $NaBH_4$, methanol, ethanol and H_2O_2 were procured from Thermofischer Scientific, India.

3.2 Synthesis of graphene oxide

The graphene oxide has been synthesized using the modified Hummer's method. This method involves oxidation and exfoliation of graphite sheet because of thermal treatment of the solution [5,39].

The steps of the synthesis are as follows-

i. 1.5 gm graphite powder and 1.5 gm of sodium nitrate were mixed in 80 ml of 98% sulphuric acid in a 1000 ml beaker with continuous stirring. The temperature was maintained 0-5°C using ice bath.

ii. The mixture was stirred using magnetic stirrer for 4 h at 350 rpm rotation rate and temperature was also maintained at 0-5°C.

iii. 7gm of potassium permanganate was added slowly to the suspension by keeping the temperature below 15°C for 1 h.

iv. The solution was diluted by the addition of 150 ml DW slowly and kept under stirring for 2 h.

v. After removing the ice bath, the solution was stirred for 2 h at 35°C.

vi. 20 ml solution of 30% H_2O_2 was then added drop wise. Color of the suspension appears bright yellow.

vii. The resulting mixture was washed with 10% HCl and then with DW several times by using centrifuge at 5000 rpm for 15 min each.

After centrifuging the paste like substance was dried in oven for 24 h at $80^{\circ}C$.

Fig 3.1: Pictorial view of the synthesis of graphene oxide

3.3 Synthesis of Ceria-reduced Graphene Oxide Composite (CrGOC)

The CrGOC was prepared by one-pot synthesis method [40-41] as given in the following steps.

i. 25 mg of GO was dissolved in 50 ml distilled water and stirred using sonication for 120 min.

ii. 1.5 mMol of Cerium (III) nitrate hexa-hydrate was added into the above GO suspension and stirred well.

iii. 1.5 mL of $NH_3.H_2O$ was added to the mixture.

iv. The mixture was stirred for 30 min.

v. Then the mixture was transferred to the Teflon-lined Stainless steel autoclave (120 mL) and heated up to $180^{\circ}C$ for 24 h in an oven.

vi. The autoclave was left to cool at room temperature.

vii. The above product so obtained was washed several times with distilled water and then with ethanol for removing an excessive ammonium hydroxide.

viii.　　Finally, the obtained CrGOC was dried at 60$^{\text{o}}$C for 48 h.

Fig 3.2: Synthesis of Ceria-reduced Graphene Oxide Composite (CrGOC)

3.4 Fabrication of PEDOT:PSS paper electrode

For the fabrication of PEDOT:PSS paper electrode Whatman filter paper was cut into 10mm × 3 mm dimension. This paper was dipped into ethyl alcohol solution and ultrasonicated for 15 min. Further, the paper was rinsed with distilled water and dried at 60$^{\text{o}}$C. Finally, dipped in aqueous suspension of PEDOT:PSS for 60 min and dried at dried at 60$^{\text{o}}$C in oven.

3.5　Electrophoretic deposition (EPD)

Electrophoretic deposition was carried out by using GX300C (Genetix Brand) electrophoretic unit with Pt as the counter electrode. Here CrGOC composite deposited on ITO coated glass electrode. For that operation, 5mg of CrGOC was mixed with 20 ml of DW and then ultrasonicated for an hour. Then, the prepared suspension and ethanol was mixed in 1:1 ratio in a 10 ml glass beaker for deposition. The EPD process for stable suspensions was conducted at constant voltages of 12 V by DC power supply and optimized at 9 s. After the EPD, the electrode was taken out from the suspension, washed with distilled water, dried and kept in refrigerator for further use [30].

3.6 Characterization

X-ray diffraction studies were performed using Brukers XRD D8 discover instrument. Zeta potential distribution was done using Malvern Zetasizer Ver. 7.13. Thermogravimetric analysis was performed using TGA 4000, Perkin Elmer and all the studies were carried out in N_2 atmosphere. Differential scanning calorimetry was performed using TA Instrument (Model Q20), USA. Scans were performed on materials weighing about 2 mg and heated at a heating rate of 10°C/ min from room temperature to 300°C. FTIR of CrGOC, GO and CeO_2 was carried out using Perkin Elmer FTIR spectrometer, model- Spectrum Two. The UV analysis was performed by Cary Series UV-Vis spectrophotometer model- Cary 300 UV-Vis at 600 nm/min scanning rate. Cyclic voltammetry was carried out on Autolab Galvanostat/Potentiostat (Eco Chemie, Netherlands) by using the conventional three-electrode cell with the platinum as auxiliary electrode, Ag/AgCl as reference electrode and EPD ITO of CrGOC as working electrode in PBS (100 mM, pH 7.0) buffer.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 UV-Vis Spectroscopy

The optical properties of nanomaterials can be observed by using UV visible spectroscopy technique. Fig 4.1 shows UV visible spectra of GO, CeO_2 and CrGOC dispersed in DW and ultrasonicated. The spectra of GO, the peaks at 233 and 302 nm shows π-π* and n-π* transitions respectively. The peaks in absorption spectrum for CeO_2 nanoparticle are at 209 and 320 nm where valence band is 2p of 'O' and conduction band corresponds to 5d of Ce element. However, the CrGOC nanocomposite verifies peaks at 204 and 264 nm. Charge transfer from 2p of 'O' to 4f of Ce is responsible due to the reduction of GO to CrGOC. The peak has been shifted towards higher wavelength.
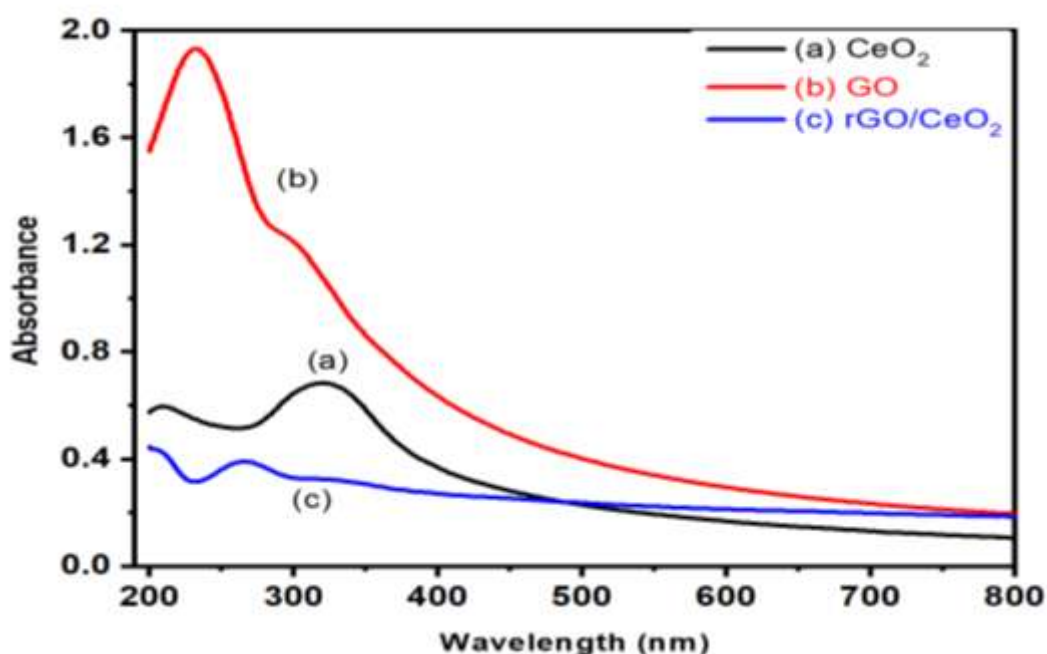

Fig 4.1: UV absorption spectra of (a) CeO_2, (b) GO and (c) CrGOC Composite

4.2   FTIR Analysis

Fig 4.2 depicts the FTIR spectra of GO, CeO_2 and CrGOC. The absorption band in the range 3400-3500 cm^{-1} indicates water absorbed on surface of synthesized sample. The peaks at 1733, 1629, 1401, 1224 and 1058 cm^{-1} illustrate C=O, C=C stretching, O-H bending, C-O-C of epoxy and C-O stretching, respectively. The peak at 1733 cm^{-1} in CrGOC spectra vanishes, this

signifies the reduction of Oxygen-bearing functional group.

The absorption bands at 1635 and 1307 cm^{-1} are characteristic peaks of graphene and the Ce-O stretching vibration is depicted by absorption band at 450 cm^{-1}. These results illustrate the formation of CrGOC using hydrothermal method effectively.
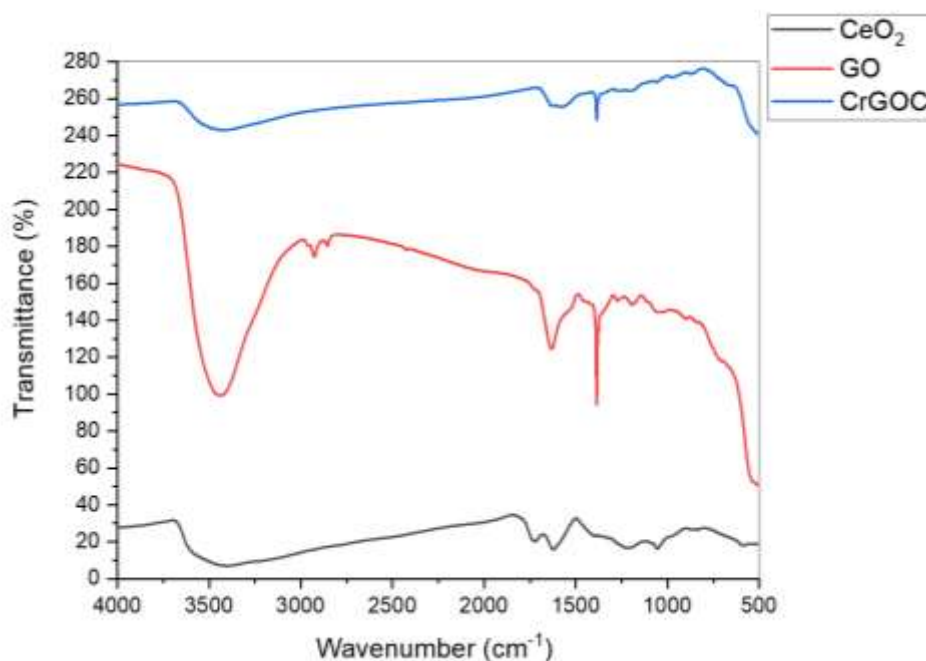
Fig 4.2 FT-IR spectra of CeO$_2$, GO and CrGOC

4.3   Cyclic voltammetry (CV)

Figure 4.3 represents the CV curves for the CrGOC composite electrode under different scan rates (10–300 mVs^{-1}) at potential range of -0.5 to 0.5 V. The well-defined CV curves show that the synthesized material is efficient for electrochemical sensing application in future.
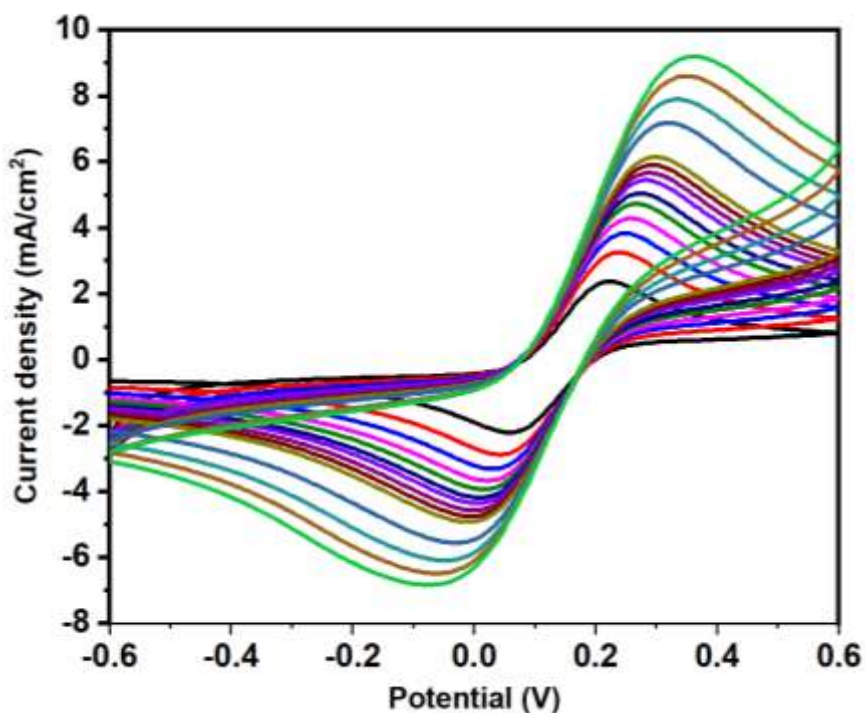
Fig 4.3 CV characteristics of CrGOC

4.4   TGA Analysis

Thermogravimetric analysis (TGA) shows the weight loss study of GO, CeO_2 and CrGOC nanocomposite with respect to temperature. The weight loss nearly 100 ^{0}C attributed to the evaporation of moisture contents in all synthesized materials. The TGA plot (curve c) of GO suggests that the weight loss takes place in three steps. Initial weight loss occurs below 150 ^{0}C about 35% which is due to the desorption of moisture content in GO. In the second and third stages, the weight loss occurs around 180-280^{0}C due to decomposition of the labile oxygen containing functional groups, yielding CO & CO_2, and around 520^0-600^{0}C suggesting GO to be thermally unstable as shows in figure 4.4. Whereas, a negligible weight loss is observed in standard TGA thermogram (curve a) of CeO_2 which corresponds to the loss of the surfaced absorbed water around 100-120 ^{0}C (5% only). And same as in CrGOC nanocomposite case, no abrupt weight loss is observed while 4% weight change is due to the moisture loss. The difference in weight loss of GO, CeO_2 & CrGOC suggests that the synthesized CrGOC is thermally more stable than Pristine GO & CeO_2.
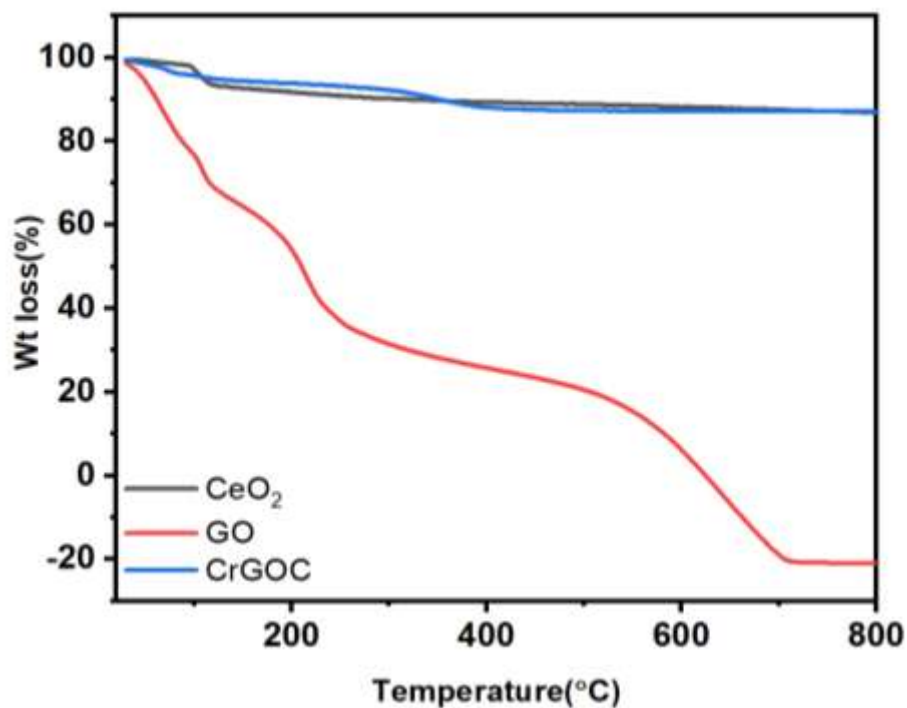
31

Fig. 4.4 TGA of CeO$_2$, GO and CrGOC composites

4.5 DSC Analysis

The DSC curve of CeO$_2$/rGO exothermic peak was observed around 80°C, indicating the crystallization temperature (T$_c$). As the temperature increases, CeO$_2$/rGO go through the glass transition (T$_g$). While the temperature increases, it didn't show the endothermic peak mentioning melting point, which means the melting point increases by the incorporation of CeO$_2$ and rGO because of its structural property. The DSC thermograms are shown in Fig. 4.5 (a & b).
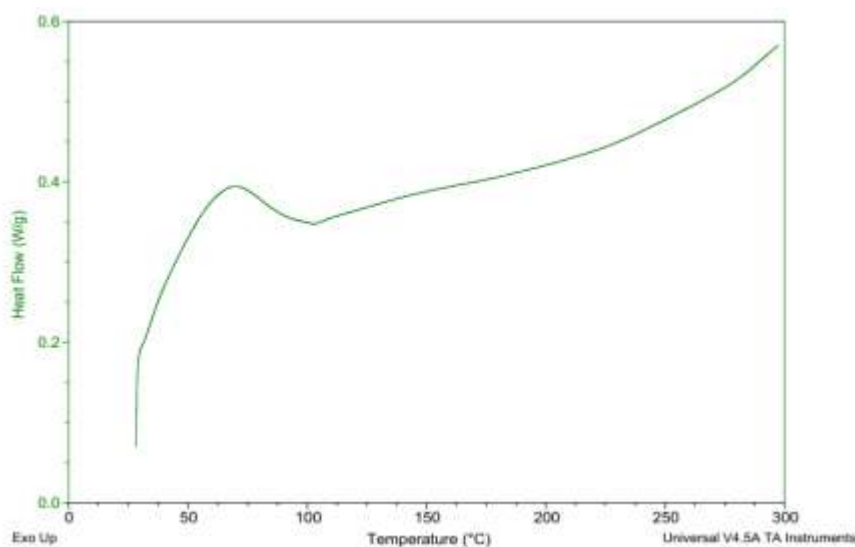

Fig 4.5 (a) DSC plot of CeO$_2$/rGO
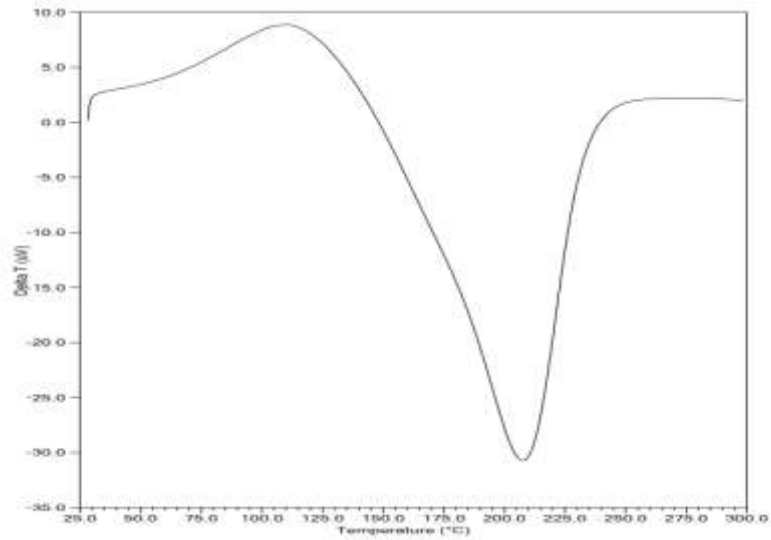
Fig 4.5 (b) DSC plot of GO

4.6 Zeta Potential Distribution of GO and CeO₂/rGO

The Zeta Potential distribution for both GO and CrGOC samples were done at 25° C in DW. Whereas the dispersant RI, viscosity (cP), dispersant dielectric constant are 1.330, 0.8872 and 78.5, respectively. GO shows the Zeta Potential value -34.6 mV whereas CrGOC shows – 14.5mV. The high Zeta potential of GO was due to the presence of negatively charged –OH and –COOH groups. The lesser value of zeta potential in CrGOC shows successful dispersion of CeO₂ in GO.
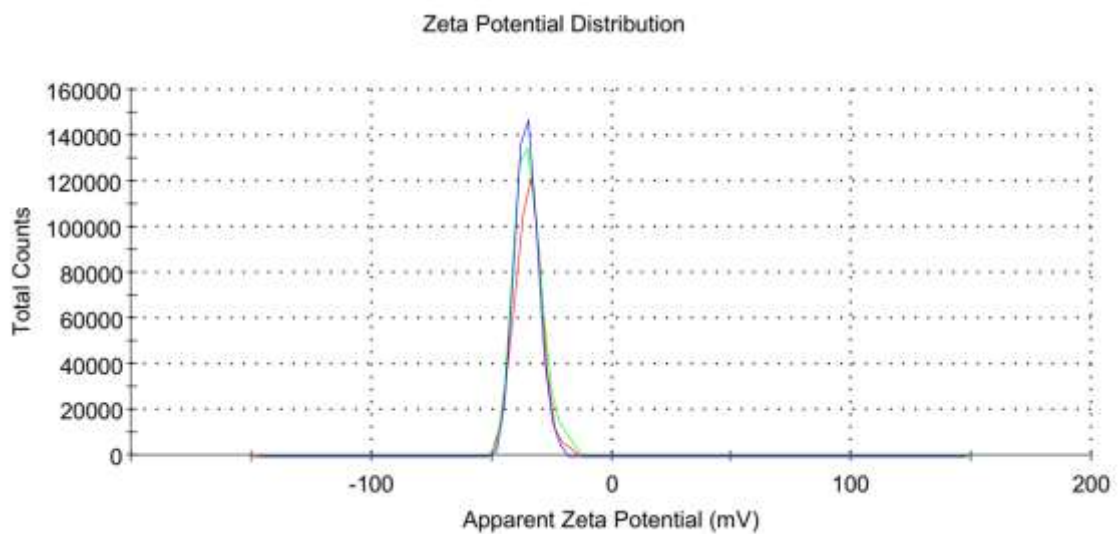
Fig 4.6 (a) Zeta Potential of GO

Zeta Potential Distribution
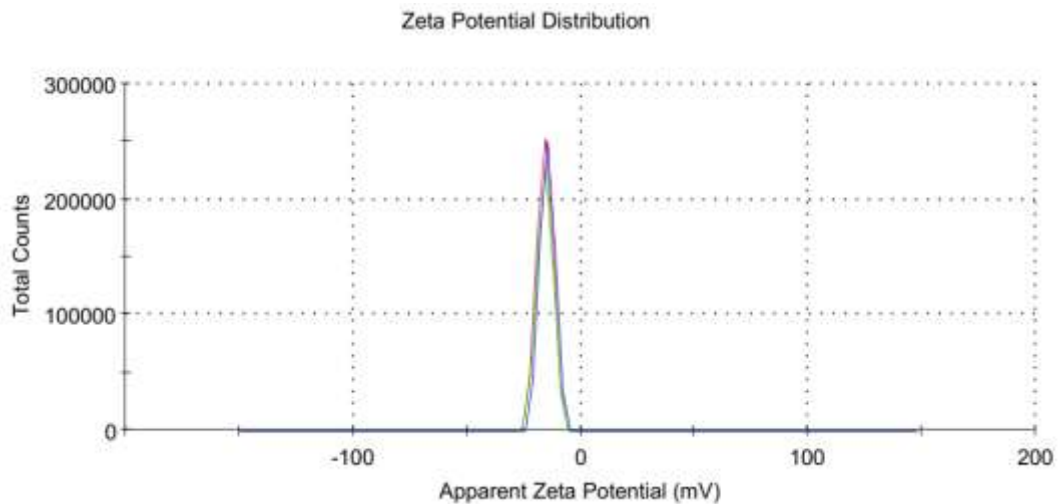
Fig 4.6 (b) Zeta Potential of CrGOC

4.7 XRD Analysis

Fig 4.7 shows the X-ray diffraction of graphite, GO and CrGOC composite. A sharp peak at 20-26.5° corresponds to a typical structure of graphite (curve a). And after using modified Hummer's method, the crystalline plane of chemically synthesized GO was very evident at $2\theta = 10.7°$ which is typical for GO (curve c). On incorporation of CeO_2 in GO, the peak at $10.7°$ has been disappeared as GO converted into a reduced form due to the removal of O_2 containing group. And new peaks at $2\theta = 28.6°$, $33.2°$, $47.3°$ and $56.2°$ corresponding to 111, 200, 220 and 222 crystal planes, respectively, indicate the formation of CrGOC as shown in figure 4.7 (curve b).
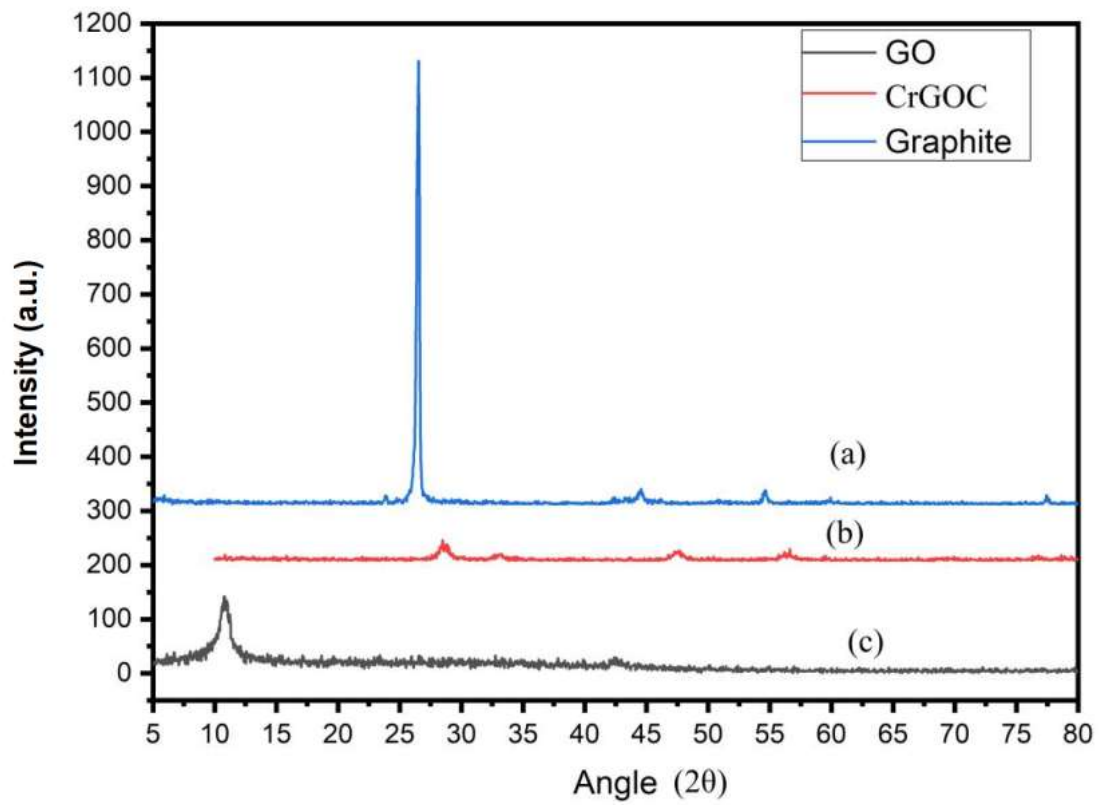
Fig. 4.7 XRD patterns of graphite, CrGOC and GO composites

CHAPTER 5: CONCLUSION

The CrGOC nanocomposite was successfully prepared by using an environment friendly one-pot hydrothermal method. It was characterized by using various techniques considering as novel electrode material for sensing application. This nanocomposite exhibits good dispersabilty of CeO_2 in graphene oxide. The CrGOC may ideal for enzyme immobilization due to the presence of functional groups in rGO. In the future, a biosensor could be fabricated using the CrGOC electrode with electrically appended covalent connection with biomolecules.

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