CeO_2 grafted Polyaniline matrix-based biosensor for the detection of 17β-Estradiol

A PROJECT REPORT

SUBMITTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF

MASTER OF SCIENCE

in

CHEMISTRY

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CANDIDATE’S DECLARATION

We, **Aditya Dam, 2K21/MSCCHE/02** and **Tanu Rajput, 2K21/MSCCHE/44**, students of M.Sc. (Chemistry), hereby declare that the project Dissertation titled **“CeO_2 grafted Polyaniline matrix-based biosensor for the detection of 17β-Estradiol”** which is submitted by us to the Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science, 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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CERTIFICATE

I hereby certify that the Project Dissertation titled **"CeO_2 grafted Polyaniline matrix-based biosensor for the detection of 17β-Estradiol"** which is submitted by **Aditya Dam, 2K21/MSCCHE/02** and **Tanu Rajput, 2K21/MSCCHE/44,** Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi **Prof. D Kumar**

Date: 16/05/23 **(SUPERVISOR)**

ACKNOWLEDGEMENT

The success and final outcome of this project required a lot of guidance and assistance from many people, and we are extremely fortunate to have got all this along with the completion of this project work.

We wish to express our gratitude to our project supervisor, **Prof. D Kumar, Department of Applied Chemistry, Delhi Technological University**, who provided us with a delightful opportunity to work under his guidance. His academic guidance and wise suggestions helped us to complete the project on time.

We wish to thank **Prof. Anil Kumar, Head of the Department of Applied Chemistry, Delhi Technological University** and **Prof. Ram Singh, coordinator of the Master of Science in Chemistry program, Department of Applied Chemistry, Delhi Technological University** for their constant support.

We are thankful and fortunate enough to get constant motivation, support, encouragement and guidance from all the research scholars of our lab and teaching staffs of Department of Applied Chemistry, who helped us in successfully completing our Dissertation. Moreover, we are obliged and thankful to Sakshi Verma, PhD scholar, Delhi Technological University for her time, support and motivation.

Finally, yet importantly, we would like to express our heartfelt thanks to our beloved family and friends who have endured our long working hours and whose motivation kept us going on the right path.

Aditya Dam

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Abstract

We present a non-enzymatic biosensing platform using polyaniline (PANI) as conducting polymer matrix grafted with CeO_2. The one-pot synthesized nanocomposite has been used for the detection of 17β-Estradiol (E2). The homogeneous distribution of CeO_2 onto PANI matrix leads to an increase in surface area and conductivity of synthesized nanocomposite PANI@CeO_2. The PANI@CeO_2 nanocomposite was characterized using structural and morphological techniques. Further, the electrode fabrication was performed by electrophoretically depositing of PANI@CeO_2 nanocomposite onto ITO. The PANI@CeO_2/ITO showed enhanced electrochemical behaviour as compared to PANI/ITO. The developed biosensor has been found to be stable and selective towards E2 and has been successfully utilized for the detection of E2 in real samples like tap water and human urine sample, encouraging its use for further application in clinical diagnosis and biomedical sciences. Further, we discussed over an overview of conducting polymers and its applications broadly.

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List of Abbreviations

WFD	Water Framework Directive
PCOD	Polycystic Ovary Disease
HPLC	High Pressure Liquid Chromatography
GC-MS	Gas Chromatography Mass Spectrometry
PEDOT	poly(3,4-ethylenedioxythiophene)
PANI	Polyaniline
eEDC	Estrogen-like endocrine disrupting chemicals
SPR	Surface Plasmon Resonance
SERS	Surface Enhanced Raman Spectroscopy
PPy	Polypyrrole
PPV	Poly (Para vinylene)
PPP	Poly (Para phenylene)
ROMP	Ring Opening Metathesis Polymerisation
ADMET	Acyclic diene metathesis
RCM	Ring Closing Metathesis
MBL-PPV	Poly [lithium 5-methoxy-2-(4-sulfobutoxy)-1,4-phenylenevinylene]
MWCNT	Multi-walled carbon nanotubes
DFAFC	Direct formic acid fuel cells
DMFC	Direct methanol fuel cell
CPE	Carbon Paste Electrode
PSS	Poly styrene sulfonate
OLED	Organic Light Emitting Diode

DSSC	Dye-sensitized Solar Cell
PEO	Polyethylene Oxide
P4VP	Poly(4vinylpyridine)
RHEED	Reflection High Energy Electron Diffraction
ITO	Indium Tin Oxide
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
CV	Cyclic Voltammetry
DPV	Differential Pulse Voltammetry
EPD	Electrophoretic Deposition
PBS	Phosphate Buffer Saline
LED	Light Emitting Diode
PUF	Polyurethane foam
E2	17-β Estradiol
PT	Polythiophene
PA	Polyacetylene
PLED	Polymer Light Emitting Diode
PET	Polyethylene terephthalate
IC	Ion Chromatography
GCE	Glassy Carbon Electrode
E2mAb	Estradiol monoclonal antibody
BSA	Bovine Serum Albumin solution
MIP	Molecularly Imprinted Polymers
RGO	Reduced Graphene Oxide

GQD	Graphene Quantum dots
PMTA	Poly (m-phenylene terephthalamide)
CNT	Carbon Nanotube

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Estradiol, which is naturally present in all mammals, is the most powerful estrogen variant. It contains 18-C atoms. Its production is mainly done in the female gonads (ovaries). Apart from the ovaries, a small amount of this hormone is also produced in the adrenal cortex and the testes. It is primarily produced by females that aids in growth and also increases milk yield in cows. This increasing demand has led to a surge in the use in animal husbandry in recent years [1]. The WFD of the European Union has reported the presence of estradiol (E2) in water samples. E2 may enter the environment from a variety of sources, the most common of which are animal as well as human urine, either naturally excreted or caused by the widespread use of synthetic hormonal contraceptives or the large-scale production of milk in the dairy industry [2]. Toxicological studies have concluded that even if a small amount of E2 residue enters an organism's body via the food chain, it can disrupt the working of the endocrine system, resulting in medical issues like male infertility, damage to the blood-brain barrier, increased chances of obesity, causes polycystic ovary disease (pcod), breast and testicular cancer [3]. Excessive or unregulated levels of E2 can have harmful impacts on the body's growth, reproductive processes, and developmental stages. It has also been found responsible for endangering the health of the offspring. Therefore, in order to ensure public and environmental health is controlled, there is a need for a rapid and convenient analytical method that can characterize E2 with high sensitivity. Some of the instrumental analytical methods were utilised to detect E2 with high precision and sensitivity include HPLC and GC-MS. However, introduction of biosensors for monitoring and managing E2 have shown drastic rapid, sensitive, selective and efficient results in monitoring E2 over the last decade. Biosensors can detect and measure biological signals [4]. One most promising method for the detection of this hormone could be using a substrate that can be flexible along with a potent sensing material based on polymers. Polymers with good conducting capabilities like PEDOT, PANI and polypyrrole have gained significant attention for biosensor development due to their great electrical conductivity, easily prepared, quick response, and cost-effectiveness [5,6]. Currently, the detection of hormone based on enzyme immobilization mobility is gaining popularity due to high specificity, easy fabrication and rapid feedback, despite of this popularity, this technique comes with various limitations like high cost, thermal and chemical instability, low sensitivity caused by enzyme leakage from the transducer interface [7,8].

Recently, on account of its high sensitivity, reliability, and cost-effectiveness, Polyaniline (PANI) has been extensively researched as an excellent sensing materials [9]. However, pure PANI materials have some limitations:

- Their long-term stability is poor
- Their response and recovery time is also long

As a result, in order to enhance the performance of flexible PANI-based biosensors, PANI-based nanocomposites, particularly those made with PANI-carbon series nanomaterials, are being suggested as a viable option. PANI-based nanocomposites are being utilised for the detection of biomolecules, gas sensing, medical diagonstics [10]. Nanocomposites reinforced in polymer matrix can be Carbon nanotube composites, graphene, metal-oxide nanocomposites and many more. Nanocomposites which have organic polymers and inorganic metal oxide nanoparticles in nano-scale regimes give rise to a new category of materials that possess distinctive properties. It has been documented that nano-structured composites of conducting polymers along with inorganic nanoparticles exhibit synergetic effects with regards to electrical and mechanical properties. The inclusion of semiconductor metal oxide nanoparticles into polymer matrices has been shown to enhance the mechanical, thermal, dielectric, also the optical properties of polymers, enabling high carrier mobilities [11]. In this regard, Cerium oxide (CeO_2) nanoparticles have several advantages for the development of biosensors, including electrocatalytic behaviour, oxygen storage capacity, and optical transparency [12]. After considering the characteristics of PANI@CeO_2 nanocomposite and its significant potential as biosensor in order to detect 17β-estradiol, the contribution of this work can be summarised as-

a) This work provides valuable insights into the properties of β-estradiol and offers novel sensing techniques for the detection of this hormone.
b) This work outlines new synthetic methods of conducting polymers.
c) This work explores novel applications of PANI@CeO_2 nanocomposites.

d) This work examines the structure property relationships of PANI@CeO_2 nanocomposites, utilizing various techniques such as XRD, FTIR spectroscopy, TGA, and SEM.

e) This work elucidates the characterization of the sensing properties of PANI@CeO_2 nanocomposites, employing techniques such as CV and DPV.

f) This work tells us how the incorporation of CeO_2 in the conducting polymer PANI to form PANI@CeO_2 is a sensing platform with superior efficiency for detecting E2. PANI matrix grafted with CeO_2 results in increase in surface area, density, electrical conductivity, and sensitivity of the nanocomposite.

g) For better evaluation, the performance of PANI@CeO_2 composite as a sensing platform is being conducted by using real samples such as human urine and tap water.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. 17β- ESTRADIOL

Estradiol (E2) is a naturally occurring steroid hormone that belongs to the class of estrogens. As a female hormone, it is essential for regulating and maintaining female reproductive tissues and secondary sexual characteristics [13]. It increases milk production and helps to promote animal growth and so it is widely used in animal husbandry [14]. Moreover, this compound is referred to as estrogenic endocrine-disrupting chemicals (eEDCs) which owns the potential to harm the stability of ecosystem [15]. Many reports claimed that even an entrance of minimal concentration of residue of E2 in organisms through food chain results in interference with normal endocrine system, homeostasis, agonistic behavior, and offspring health growth, leading to injurious outcomes such as infertility in male, blood-brain barrier damage, rise in the prevalence of obesity and breast and testis cancers [16,17,18]. The adverse and harmful biological and physiological effects on living organisms including aquatic animals and humans could be caused even with a low exposure of E2 residue of concentration in range (1-10 ng/L) [19]. The development of a quick, sensitive, and uncomplicated technique for detecting E2 and other (eEDCs) in biological, food, and environmental samples analysis is extremely important.

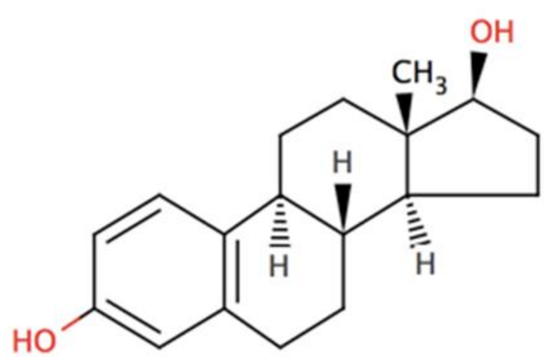

Figure 2.1- Chemical structure of 17β estradiol

2.2. METHODOLOGY FOR 17β- ESTRADIOL DETECTION

The detection of beta-estradiol (E2) can be achieved through several methodologies, including, electrochemical sensors, and chromatographic methods.

1. <u>Chromatographic methods</u>

HPLC and GC-MS are chromatographic techniques capable of detecting E2 with great sensitivity and precision. These methods involve separating E2 from other components in a sample and then detecting it using a suitable detector. HPLC is commonly used for detecting E2 in biological fluids like serum and urine, and it can detect very low concentrations of E2. GC-MS is a highly accurate method for both qualitative and quantitative analysis of E2 [20,21].

2. <u>Aptamer sensor</u>

An aptamer sensor for the detection of beta-estradiol (E2) is a type of biosensor that utilizes aptamers, that are single-stranded DNA or RNA molecules which binds to specific target molecules with high affinity and selectivity. The target molecule binds to the aptamer causing a conformational change that can be detected and quantified [22,23].

3. <u>Surface plasmon resonance (SPR) sensor</u>

SPR sensors are widely adopted for detecting the small molecules because of their high sensitivity and specificity. A SPR sensor for detecting beta-estradiol (E2) has been developed using a gold-coated sensor chip functionalized with an E2-specific antibody. The SPR sensor demonstrated high selectivity as well as sensitivity for E2 detection, making it a promising tool for environmental and clinical applications [24,25,26].

4. **Surface enhanced Raman spectroscopy (SERS)**

Using silver nanoparticle-deposited silicon substrates functionalized with an E2-specific aptamer, a SERS-based detection method for beta-estradiol (E2) has been developed. This method utilizes the sensitivity and versatility of SERS for the detecting small molecules, including E2. The high sensitivity also the specificity of this method for detecting E2 suggests its potential as a valuable tool in environmental and clinical applications [27,28,29].

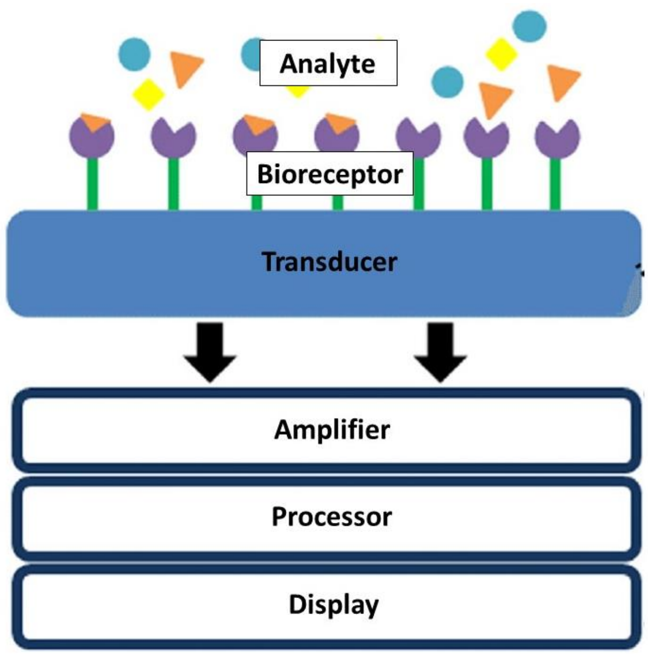

Figure 2.2- Working mechanism of a biosensor

5. **Electrochemical biosensor**

A biosensor based on electrochemical detection is an effective, moreover convenient way to detect small molecules on account of its simplicity, affordability, and highly sensitive property. The detection of beta-estradiol (E2) has been achieved by developing a biosensor using an E2-specific aptamer functionalized carbon nanotube-modified electrode. This biosensor exhibits high specificity and selectivity for detecting E2, leading it to a potential tool in clinical and environmental usage [30,31].

6. Non-enzymatic electrochemical biosensor

The detection of beta-estradiol (E2) can be achieved by following these steps –

(a) Preparation of electrode- A working electrode is prepared by coating a conductive substrate, such as glassy carbon, with a layer of the detection material, for instance Pd/N-doped reduced graphene oxide material can be used, the electrode would be formed through the process of depositing a material layer onto the substrate.

(b) Calibration of the electrode: The electrode is calibrated using a known concentration of beta estradiol. This is typically done by exposing the electrode to a solution containing a known concentration of beta estradiol and measuring the resulting current or potential.

(c) Detection of beta estradiol: The electrode is then exposed to the sample containing beta estradiol, and the measurement of resultant current and potential is done. The amount of beta estradiol in the sample can be ascertained by comparing the measured value to calibration curve generated in step b [32].

TABLE-2.1: Limit of Detection and method of detection for different biosensors for the detection of 17β-Estradiol

Sl. No.	Immobilized matrix	Detection technique	Linear range	LOD/LOQ	References
1.	clopidogrel concentration	HPLC	0.25-30 μg/mL	0.45μg/mL	[20]
2.	Serum (mouse)	HPLC		3-5 pg/mL	[21]
3.	Aptamer/AuNPs/VS2/ GCE	DPV	1.0×10^{-11} to 1.0×10^{-8}M	1.0×10^{-12}M	[22]

4.	Split aptamer	Absorbance	1µM−100 µM		[23]
5.	E2mAb/MNPs	SPR	3.906-1000ng/mL	3.24ng/mL	[24]
6.	11-MUA/E2-BSA conjugate on Au sensor chip vs. Ab-E2	SPR	0.036– 3.6 pM	0.0036 pM	[25]
7.	Au@TiO2	SERS	0-100 µM	1nM	[27]
8.	Zn/Au-Ag/Ag	SERS	0.1-10 ppm	0.1 ppm	[28]
9.	Au@Ag/CS/NPs	SERS	10^{-4}- 10 nM	0.05 pM	[29]
10.	MIP Hybrid	CV	1×10^{-7} M to 8×10^{-7} M	6.86×10^{-7} M	[30]
11.	MIPs-AuNPs-GCE	CV, EIS	1×10^{-7} to 1×10^{-12} mg/mL	1.28×10^{-12} mg/mL	[31]
12.	Pd/N-RGO/GCE	DPV	(0.1–2 and 2–400 µM)	1.8 nM	[33]
13.	Gold/GQDs/Laccase	CV	5-120 µM	1.51 µM	[34]
14.	Pt/MWNTs/GCE	SWV	15-50 µM	1.8 µM	[35]

2.3. BIOSENSORS AND ITS TYPES

An electrochemical biosensor utilizes the chemical interactions between biological molecules and electrodes to detect and quantify the amount of a specific substance in a sample. It usually comprises of a biological recognition element (such as an enzyme or antibody), a transducer (typically an electrode), and a signal processing unit. Electrochemical biosensors offer numerous benefits over conventional analytical methods, including exceptional sensitivity, specificity, and selectivity. They are also fast, user-friendly, and portable. As a result, they find applications in diverse fields for instance medical diagnostics, environmental monitoring, and food safety [36,37].

Electrochemical biosensor is being classified into enzymatic biosensor and non-enzymatic biosensor-

a. <u>Enzymatic biosensor</u>

Enzymatic biosensors are biosensors that make use of enzymes as the biological recognition element to detect and evaluate the analyte's concentration in a sample. These biosensors usually include an immobilized enzyme, a transducer (typically an electrode), and a signal processing unit [38]. The interaction among the target analyte and the enzyme in the enzymatic biosensor leads to a reaction that generates a detectable signal. The transducer then converts this signal into an electrical one that is subsequently processed by the signal processing unit to determine the concentration of the analyte [39].

b. <u>Non-enzymatic biosensor</u>

Non-enzymatic biosensors are biosensors that use molecules other than enzymes, such as antibodies, aptamers, or nucleic acids, as the biological recognition element used for detection and measurement of the concentration of an analyte in a sample. They do not rely on enzymes as the recognition element [40]. A biosensor typically comprises three principal components, namely a sensing element, a transducer, and a signal processing unit.

The sensing element of a biosensor interacts with the target analyte and generates a signal that is subsequently transformed into an electrical signal by the transducer. Finally, the signal processing unit analyzes the electrical signal to determine the concentration of the analyte [41].

2.4. CONDUCTING POLYMERS

Conducting polymers are a type of macromolecules which conducts electricity because of the π electron delocalization. These conducting polymers are a subject of considerable curiosity in the domain of research due to cost-effectiveness, environmental stability along with mechanical properties [42]. Some of the conducting polymers are described below-

i) Polyaniline

Henry Lethe discovered Polyaniline (PANI) in 19th century while studying the chemical and electrochemical oxidation products of aniline in acidic media. Polyaniline is believed to be octameric in nature and present in four different oxidation states [43]. The general formula of Polyaniline is the repeating units of its reduced and oxidized form which is shown below-

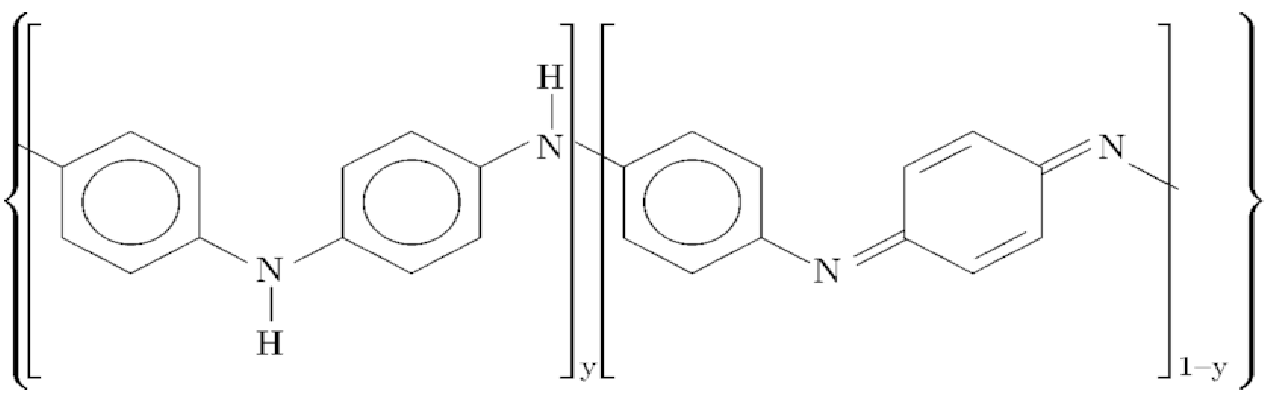

Figure 2.3- General formula of the chemical structure of Polyaniline; if y=1, then it will be completely reduced form, Leucoemeraldine; if y=0, then it will be completely oxidized form, Pernigraniline.

It has been found that the protonation of emeraldine base of PANI leads to the formation of poly semiquinone radical cation having polaronic conduction band which is confirmed by Raman spectra [44].

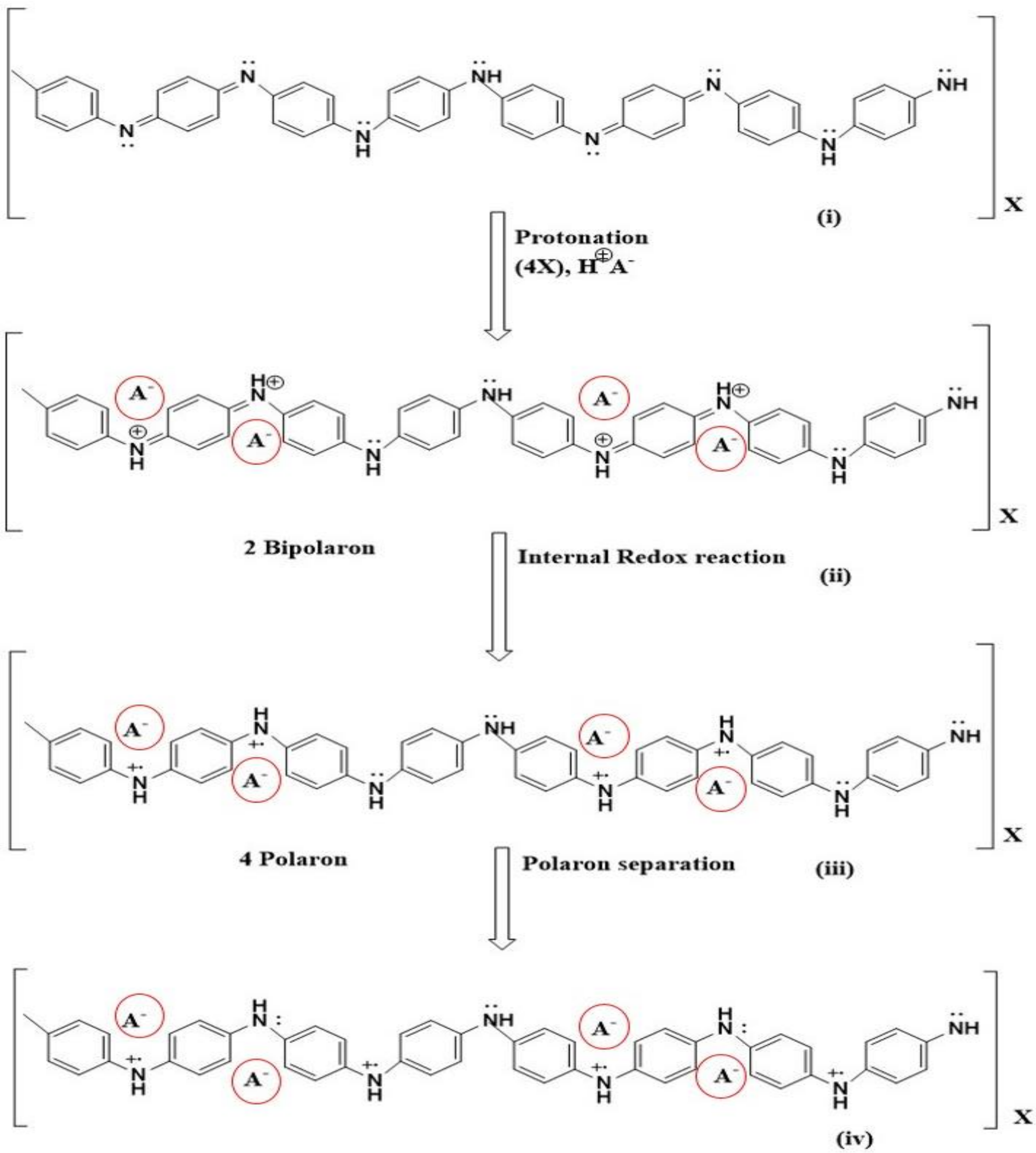

Figure 2.4- Conduction mechanism of Polyaniline.

Polyaniline shows conductivity of about 4.4 S Cm^{-1} [45]. It is observed that at room temperature this conductivity increases in the presence of water vapor and decreases reversibly in vacuum [46].

PANI is of great interest among the conducting polymers due to its light weight, corrosion resistant, and thermally stable nature.

ii) <u>Polyacetylene</u>

Polyacetylene is the first known polymer which conducts electricity made up of repeating units of acetylene [47]. The conductivity of PA films increases when exposed to vapors of p-type dopants. Polyacetylene doped with p-type dopants are stable in air whereas those films doped with n-type dopants are tremendously sensitive to air [48].

iii) <u>Poly(thiophene)</u>

Polythiophene has put up a very large interest in third order NLO properties. These are the conducting polymers of repeating units of thiophene linked through its 2^{nd} and 5^{th} carbon atom. Polythiophene films show good temperature and potential stimuli properties via changing its colour [49]. PT is an excellent material in the development of optical sensors.

iv) <u>Polypyrrole</u>

Polypyrrole is extensively used in making conducting nanowires obtained via oxidative polymerization of pyrrole [50]. PPy are naturally yellow but become darken in the present of air. All the types of doped and undoped films of PPy are insoluble in solvents but due to its crosslinking nature, it is swellable. They are stable in air up to 150°C.

Polypyrrole along with another conducting conjugated polymer such as polyaniline used as artificial muscles[51].

v) Others

Poly (3,4ethylenedioxythiophene) (PEDOT), Poly (phenylene vinylene), Polyphenylene and Polyparaphenylene are some other examples of conducting polymers. PEDOT is severely used in antistatic coating of polymers and glass. PPV is used in PLED due to its electroluminescence property [52]. PPP is highly stable at higher temperatures. Apart from these polymers, there are a lot of conducting polymers which were or are being studied.

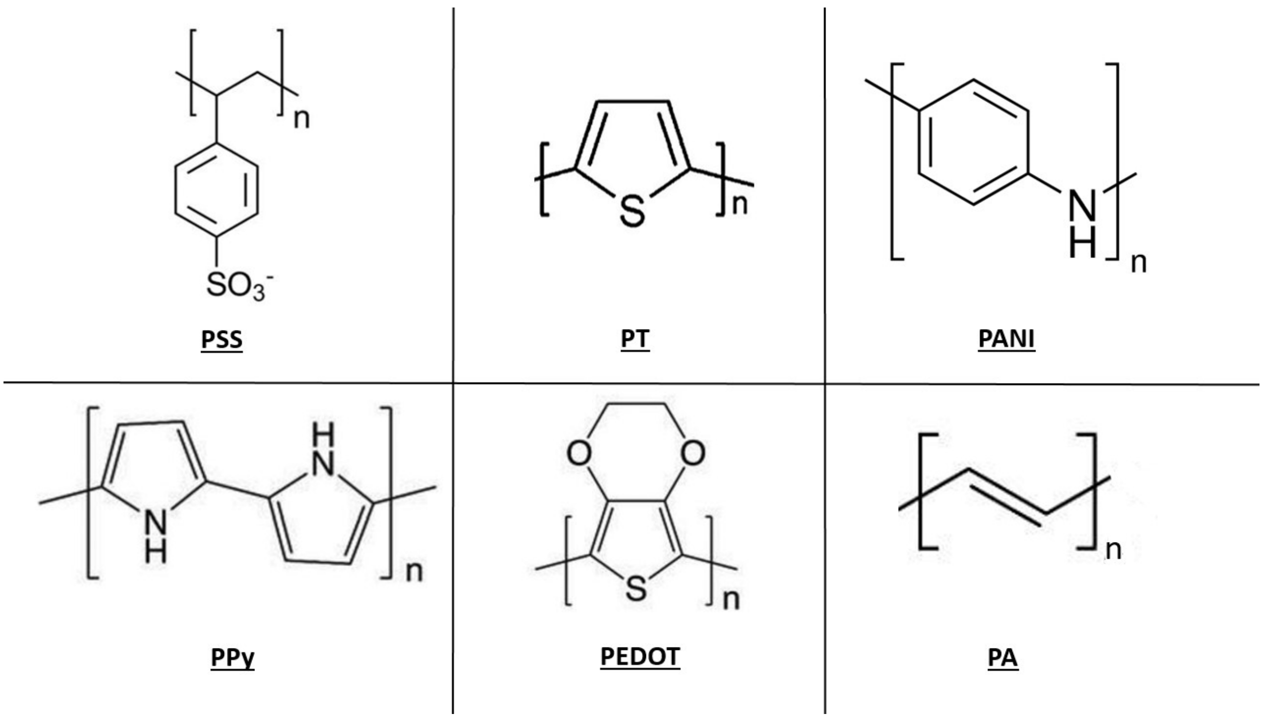

Figure 2.5- Chemical structures of various conducting polymers.

2.5. SYNTHESIS OF CONDUCTING POLYMERS

Either of the following methods which could be employed for synthesizing conducting polymers:

1. Chemical polymerization

Chemical polymerization is the prevalent technique used for synthesizing conducting polymers. It is being widely used because it is of minimal cost, involves facile processing, and can be utilized for synthesizing majorly all classes of conjugated polymers. There is no requirement of electrodes in this method [53]. Chemical polymerization is initiated by oxidation of monomer using an oxidant (dopant ion) or a catalyst to generate a reactive species called cation radical which undergo coupling to form di cations and polymer is being generated on repeating this process. The major limitation of this technique is its inability to form thin films [54].

2. Electrochemical polymerization

Among the different reported techniques, it is very important method for the synthesis of conducting polymers because it is cost effective, reproducible, no polymerization initiator, UV light, heating is required and the films of the conducting polymers produced are uniform and thick in nature which is controlled by the amount of charge transferred during this method [55]. Electrochemical polymerization is carried out by using three electrode configurations which are working, counter and reference electrode in an electrolyte both dissolved in appropriate solvent. The commonly used electrode as anode is chromium, gold, platinum, titanium, palladium etc. Monomers generally used in electrochemical polymerization have low anodic potential and is feasible to electrophilic substitution. The appropriate solvent and electrolyte are chosen based on the stability of the anodic potential of the monomer providing conductive medium in this method. Moreover, it can also be carried out potentiometrically by potentiostatgalvanostat where in potentiostatic conditions having constant potential are used to obtain thin films and galvanostatic conditions having constant current are addressed for thick films. The disadvantages are the difficulty to remove films from surface of electrode and the post- covalent modification of bulk conducting polymer is difficult [56].

3. Photochemical polymerization

Photopolymerization involves utilizing light energy to trigger and advance polymerization reactions through the use of a photosensitizer or photoinitiator. Free-radical and cationic are the two main types of photopolymerization. Compared to conventional polymerization, photopolymerization offers benefits such as reduced energy consumption, lower reaction temperatures, faster curing, and less waste. However, the technique's limited light penetration depth and the fact that polymerization ceases when the light source is removed restricts it to thin film applications. Photopolymerization finds numerous applications, including coatings, adhesives, electronic materials, and biomedical devices. It has been used to fabricate dental restorations, contact lenses, drug delivery systems, and in 3D printing technologies [57,58].

4. Concentrated emulsion method

Emulsion polymerization is a method of heterophase polymerization that involves three segments: the water segment, the latex particle segment, and the monomer droplet segment. The main mechanism involved is radical polymerization, and the method typically involves a micelle-forming surfactant, a water-soluble initiator, and a water-insoluble monomer. Polymerization occurs primarily in the monomer swollen micelles and latex particles, resulting in a distribution of latex particles as the final product. Microemulsion polymerization involves small monomer droplets as the site of polymerization, and inverse emulsion polymerization involves an organic continuous segment mixed with a water-soluble monomer in small water droplets. The use of emulsion polymerization is limited to the production of modacrylic masterpieces in the acrylic fiber industry [59,60].

5. Inclusion method

Inclusion polymerization is a process that produces composite materials at the atomic or molecular level, offering potential for creating unique low-dimensionality composite materials. For example, the inclusion of an electroconductive polymer can result in a molecular wire. Composites of these polymers with organic hosts have been synthesized based on the inclusion method. Miyata.et.al have pointed out that this type of polymerization should not be viewed solely from the perspective of stereoregular polymerization but rather as a space-dependent polymerization [61].

6. Pyrolysis method

Pyrolysis is a process that involves the heating of organic materials at high temperatures to cause chemical degradation. It has proven to be useful in identifying organic polymeric substances in various fields, such as plastic and rubber production, dentistry, environmental protection, and failure testing. This technique allows for the direct analysis of small sample sizes without the need for time-consuming sample preparation. While spectroscopic methods can detect the presence of monomeric species, pyrolytic degradation is crucial in determining the structure of the polymer. Pyrolysis gas chromatography is commonly used for the analysis of both synthetic and natural polymers [62].

7. Plasma polymerization

Plasma polymerization is a contemporary method employed for producing thin films from diverse organic and organometallic substances. These films possess exceptional attributes, including high crosslinking, thermal stability, chemical inertness, and mechanical strength, which makes them highly desirable for a wide range of applications. Furthermore, they exhibit strong adherence to various surfaces, such as polymers, metals, and glass. Consequently, they have been extensively utilized for manufacturing perm-selective membranes, biomedical materials, protective coatings, electronic and optical devices, and adhesion promoters in recent years [63].

8. Solid state polymerization

Solid state polymerization is a technique that involves heating polymer chains in the absence of oxygen and water to increase their length. The process is controlled by temperature, pressure, and the diffusion of by-products from the core of the pellet to the shell and is typically performed in simple and inexpensive apparatus. This method is often employed after melt-polymerization to enhance the mechanical and rheological properties of polymers before injection blow molding and is widely used in the production of bottle-grade PET, films, and advanced industrial fibers. The key advantages of solid-state polymerization in industrial applications are the avoidance of some of the issues associated with conventional polymerization methods [64].

9. Metathesis polymerization

Metathesis refers to a chemical reaction that involves the exchange of one part of each of two compounds to produce two different compounds. There are three categories of metathesis polymerization: ROMP, ADMET, and RCM polymerization. Metathesis polymerization provides several benefits compared to conventional polymerization techniques including the ability to produce polymers with restricted molecular weight distribution, high stereo- as well as regioselectivity, and ability to use renewable monomers [65,66].

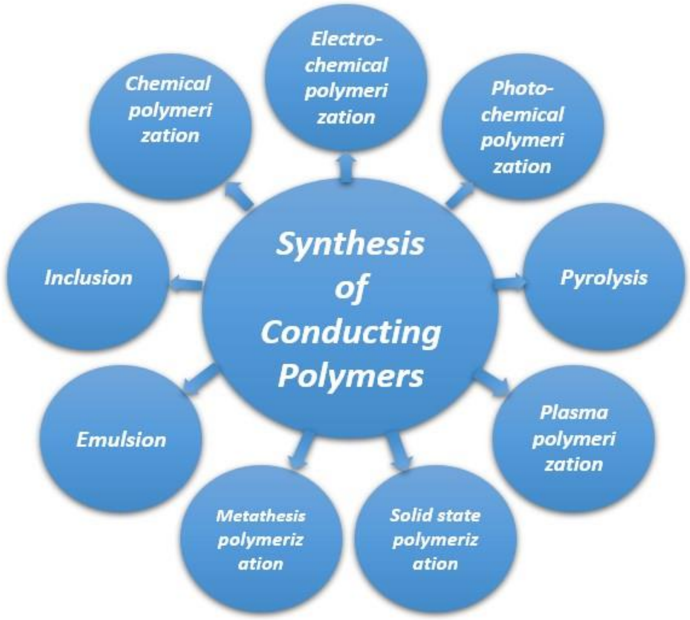

Figure 2.6- Schematic diagram of synthesis of conducting polymers.

2.6. IMPORTANCE OF CONDUCTING POLYMERS

Conducting polymers are broadly utilized nowadays in numerous fields like biosensors, electrical nanodevices, optical sensors, energy storage, catalysis etc., because of their distinct multifunctional properties. However, these applications of conducting polymers depend on their processing properties [67]. The importance of CPs in different aspects is illustrated under-

i) <u>Biosensors</u>

For many years, conducting polymers is being deployed as a material for use in biosensing purposes because of their fast electron transport properties, furthermore they also provide low costing rate. On attaching functional groups to the chains of conducting polymers result in increase in its surface area [68]. There are different types of methods used in a biosensor such as adsorption, entrapment, cross-linking etc. By the cross-linking method biosensor loses its enzyme activity with time, whereas enzyme is not used in adsorption method. These biosensors are employed in applications such as health diagnostics, environmental pollution monitoring, DNA sensors, food analysis etc. [69]

In enzymatic type of sensors, hydrogen peroxide is often found as a product. So, it is important to detect H_2O_2. PANI based composites are severely applied in sensors to detect this H_2O_2 [70]. For the determination of glucose PANI based nanocomposites are often employed after doped with glucose oxidase enzyme. Camphor sulfonic acid doped polyaniline/polystyrene nanofibers have been used in the determination of both peroxide and glucose. It was observed that electro-copolymerization of pyrrole and aniline in organic acid medium doesn't gave a mixture of PPy and PANI, instead a copolymerization occurred between them [71]. Apart from PANI, polypyrrole-coated glassy carbon electrode has been utilized in the determining DNA. Poly(azure B) film prepared by electrochemical method was used in the determination of phenols [72].

ii) **Other sensors**

Polypyrrole is the first CP which is applied as gas sensor, but the sensitivity of PPy towards gases is found to be low. Later, PANI based CPs have been approved for better choice for the sensing of gases [73]. There are many known ammonia sensors derived on polyaniline films that is being studied due to their fast response and higher sensitivity [74]. Polystyrene sulfonic acid doped polyaniline films are incorporated in the sensing of NO_2 [75]. Platinum electrodes altered with poly(1,8-diaminonaphthalene) used in the determination of NO_X in water [76]. Polypyrrole doped with calcion was used as a potentiometric sensor for the determination of calcium. Soluble films polyaniline has also been investigated in the sensing purposes of calcium [77]. PANI/In_2O_3 composite nanofibers are used in the determination of H_2, CO and NO_2 at room temperature. For the detection of hydrogen sulfide gas, PANI/$CuCl_2$ composite films have been used [78].

Reversible electrochemical doping on conducting polymer changing its optical properties and this phenomenon is applied for optical sensors. Ozone detection using polyaniline film optically has been discovered. Both polypyrrole and polyaniline films are used in optical pH determination [79]. MBL-PPV has been used in detecting cytochrome C optically [80].

iii) Energy storage

Conducting polymers on account to its high energy density and minimal costing is used as an alternate in energy storage industries. This energy storage can be controlled through different doping agents. PANI demonstrates specific energy of 10 W h kg^{-1} whereas carbon-based capacitor exhibits a energy of about 5 W h kg^{-1} [81]. Wang et al. Developed PEDOT paper which provide higher energy capacitance owning large surface area, low sheet resistance properties. It can be synthesized in 30 minutes [82]. Latest PANI derivative, poly (2-methyl thio aniline)-coated MWCNTs (PMTA@CNT) grafted onto graphene has been recently introduced in this field. These materials show much higher energetic properties than those simple polyaniline composites [83]. Another polymer-based capacitor made with pristine carbon and PPy has been developed which doesn't lose its ionic mobilities [84]. Conducting polymers grafted with TiO_2 are believed to be an excellent candidate in the development of solar cells due to their electron migration capability. poly(3-hexylthiophene) films without any dopants are used in perovskite solar cells [85]. Platinum NPs dispersed on PANI is used in DFAFCs has been recently studied and found out that it is better than direct methanol fuel cells DMFC, because of its good catalytic activity [86]. Cu_2O/PPy/CPE is used to oxidize ethanol in fuel cells [87].

A novel PTh-coated silicon composite, PANI/tin dioxide/MWCNT material is being used as anode in Lithium-ion batteries to improve rate capacity [88,89]. PANi-TiO_2 composite is used in AA dimension batteries as cathode. Poly(phenylene) derivative, V_2O_5 blended with poly(3-hexylthiophene)-block-poly(ethylene oxide), PEDOT/PSS, poly(azulene) derivatives is utilized in Li-ion batteries [90].

iv) **Electronic and electrochromic devices**

Owing high electrical properties and environmentally friendly nature of conducting polymers, nowadays CPs are preferred over carbon nanotubes, metals in making electrical devices. Field effect transistor based on polyaniline/polyethylene oxide nanofiber has been employed recently, another ultra short transistor with 2 nm width based on poly (3-hexylthiophene) has also been reported. Many more transistors based on polyaniline nanowires, polypyrrole derivatives have also been developed [91]. Gold microelectrodes on the SiO_2/Si substrate grafted with poly (p-phenylene ethynylene) are used as micro junction. PANI and PT based nanofibers doped with gold nanoparticles are used in storing the data as a replacement of silicon memory [92].

Some of the conducting polymers also possess electrochromic properties, the ability to change color with applied current. PEDOT nanowires are used in making field emission displays such as smart windows [93].

v) **Surface protection and EMI shielding**

Polyaniline microtubes, polyaniline-multiwalled carbon nanotube are used as electromagnetic frequency absorbers in wireless systems, space science etc. [94] There are three methods of coating using CPs- coating the metal, chemical conversion coatings and cathodic protection coating. The third method is more effective out of these three. PANI and poly(thiophene) derivatives used in protecting steels in marine and space equipment. PANI with mixture of poly(o-phenetidine) is observed to have better corrosion protecting efficiency than PANI [95]. PPy-clay with low concentration (1%) nanocomposites are also useful in anti-corrosion purposes.

vi) Wastewater treatment

Conducting polymers are known for their mechanically stable, good adsorbing, versatile properties. Thus, they are used in wastewater treatment to remove heavy metal ions, hazardous chemicals, waste coming from the industries etc. PANI based derivatives are used in removing hexavalent chromium (Cr (VI)) as polyaniline contains '–NH' in their chains [96]. Various polypyrrole based derivatives are also employed in removing heavy metals like Ni (II), Zn (II), Pb (II), Cu (II) etc. [97] PANI/FeO nanocomposite are used in adsorbing arsenate ions due to good complexation between them [98]. PPy/K-birnessite is used in the photodegradation of Bisphenol in water with 90 % capacity [99]. PANI doped with $BiVO_4$ nanocomposite is used in the removal of ethyl orange dye from water with 99% effectivity [100].

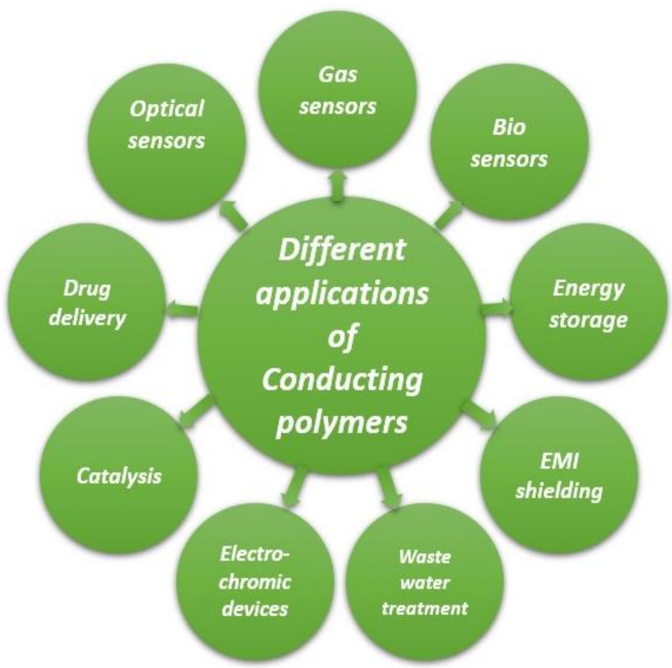

Figure 2.7- Schematic diagram of various applications of conducting polymers.

vii) <u>Other applications</u>

- Conducting polymer can be used as catalysts in many organic and inorganic reactions such as Suzuki coupling reaction, where PANI/Pd composite is used.
- Nowadays conducting polymers is being studied as a component of Electrorheological fluids which are used in hydraulic valves, disk brakes etc. [101]
- In the field of biomedical applications, CPs are being extensively used in drug delivery, in the development of actuators, tissue engineering etc. [102]
- Conducting polymers are useful in making stationary phases in chromatography techniques such as HPLC, GC, IC etc., as well as they are used in detectors.

2.7. APPLICATIONS OF POLYANILINE

Polyaniline possesses broad spectrum of properties, that makes it suitable for a variety of applications across various fields. Here are some potential applications that can leverage its unique properties:

The special features of PANI make it an adequate material for various applications. One of its applications is in smart or electrochromic glass, where it changes color or opacity when an electrical current is passed through it [103]. PANI must be coated with SnO_2 or ITO glasses via film formation to make it a smart material, and film thickness can be controlled using electro polymerization methods. PANI can also be fine-tuned for use in electrochemical devices such as displays and smart windows by combining it with organic/inorganic hybrid materials or modifying it by bonding it with substrates such as ITO or FTO [104]. Additionally, PANI can be combined with other materials such as clay or graphene oxide to exhibit higher current density and multicolor electrochromism [105]. Techniques such as spin coating or hydrothermal synthesis can be used to obtain uniform layers of PANI, and PANI-WO_3 exhibits stability and faster switch compared to PANI due to the creation of a donor-acceptor system [106].

PANI (polyaniline) is not only used in smart or electrochromic glass, but also for corrosion protection. It has been found to efficiently protect against oxidation in stainless steel and proton exchange membrane fuel cells. The effectiveness of PANI act as a protective coating may depend on the type of metal and presence of other materials. Recent research suggests that PANI sulfate coats are more effective than PO_4^{3-} polyaniline coats in preventing stainless steel corrosion, and PANI sultanate coats have been found to provide avoidance of anode for stainless steel substrates. PANI tungstate has also been proven effective in protecting steel against corrosion [107].

Electroluminescence, which occurs when an electrical current or field is induced, is the fundamental process behind LEDs and OLEDs that produces light emission, where a conducting polymer such as PANI-PPS is used as the hole injection layer to enhance efficiency and lower voltage operation. Doping PPS with self-doped PANI can improve film quality and dissolution for mobile/panel displays [108]. Self-doped PANI can be utilized as a hole injection layer in double-layer electroluminescence, resulting in orange electroluminescence [109]. Additionally, PANI can be combined with ZnO nanowires to create an organic/inorganic LEDs emitting blue light [110].

Compared to inorganic battery materials, PANI exhibits superior specific energies, conductivity, and a rapid redox reaction, which make it a suitable choice for capacitive applications. However, the lifespan of pure PANI-based capacitors is incompatible with the material, resulting in contractions during charge and discharge cycles [111]. To address this, PANI-based compounds such as PANI-CNT and PANI-graphene are being synthesized to improve capacitive properties. PANI films with a porous vermicular structure have been prepared by Kim on flexible ITO substrates, as revealed by the morphological analysis. The utilization of thin PANI films as capacitive electrodes can enhance the energy density, stability, and robustness of the system. Furthermore, the remarkable characteristics of PANI make it a promising material for application in supercapacitors [112].

PANI's unique structures and morphologies make it an appealing material for sensors, including chemical and biosensors [113]. PANI has been utilized in gas sensors because of its large surface area and gas diffusion potential [114]. Researchers have developed PANI sensors for detecting a wide range of substances including H_2S, HCl, NH_3, hydrazine, $CHCl_3$, and CH_3OH. Hydrogen sensors use doped PANI where hydrogen interaction affects PANI conductivity through the amine nitrogen site. NH_3 detection is easier because it has high electron affinity. TiO_2/PANI sensors can detect NH_3 at room temperature without requiring high temperature or platinum doping, unlike TiO_2 sensors. Cu-PANI can detect chlorinated hydrocarbons, and Au-PANI can detect NO_2. PANI's biocompatibility, environmental stability, and ability to mediate electron transfer make it suitable for biosensor applications, such as glucose biosensors for diabetes management. PANI-based biosensors can be used for enzymatic and bio affinity detection, with PANI serving as a self-contained electron transfer mediator. Enzyme-based sensors utilize enzyme reactions to detect and identify substances.

DSSCs uses a semiconductor and electrolyte for conversion of sunlight into electricity, and the expensive Pt counter electrode in DSSCs can be replaced with cost-effective carbon-based materials like PANI [115]. Microporous PANI has more electrocatalytic activity than Pt electrodes, and for the I_3^-redox reaction, PANI-SO_4 exhibits the lowest charge transfer resistance and the highest reduction current among all porous media, owing to its high porosity. . It can also be electrodeposited on graphene surfaces to improve its electrocatalytic activity. Dual-functional PANI plays a significant role in solid-state perovskite-sensitized solar cells by acting as a p-type hole-transport material and a sensitizer. This enhances carrier mobility and light absorbance per unit surface area, resulting in improved performance of the solar cell. Alignment of PANI nanowires can enhance solar cells efficiency, whereas the use of transparent PANI enables the cost-effective fabrication of bifacial DSSCs having high efficiency.

For Li batteries, $LiPF_6$ doped electro-sprayed PANI on aluminum foil is used as cathode material at atmospheric temperature through the electrospinning method, resulting in high discharge ability and approaching the high theoretical capacity as per researchers [116]. After 50 cycles, the capacity decreases to 61%. Additionally, PANI polysulfide has been used in cathodes with high energy density for Li/S batteries. Recent research has focused on using PANI compound materials in rechargeable batteries.

2.8. POLYANILINE BASED NANOCOMPOSITES

Polyaniline has received adequate attention in the field of conducting polymers because of its suitable characteristics, however it has many disadvantages as well such as low processability, solubility in common solvents, decreased conductivity with time etc. [117] To diminish these disadvantages research based on copolymerization, blending and nanocomposites of PANI has been made. Polyaniline based nanocomposites have an excellent mechanical matrix that prevents the structural corrosion of PANI. These nanocomposites with improved conductivity, better morphology, solvent processability are suitable candidates in the field of biomedicine. Current research on PANI based nanocomposites is extensively focused on metal oxides and carbon nanotube materials.

In industrial and biomedical applications, rheological properties of PANI are too important. According to Bilal et al. studied PANI-PEO and their composites with KNO_3 and $NaNO_3$ for rheological property measurements and found out that Pyridine is the best solvent for the measurement [118]. PANI/zinc−aluminum layered double hydroxide nanocomposite show antibacterial activity which is prepared through the free radical emulsion polymerization. PANI/Ag NPs are also a good candidate in showing antibacterial activities, but silver based PANI nanocomposites are also comparatively used as biosensor for antibacterial drugs determination. Some of the nanocomposites of PANI such as PANI/strach show an increase in antioxidant properties with a higher ratio of PANI. PANI/polyxanthonetriazole/Fe3O4 also shows antioxidant properties dure to presence of large number of hydrogen and electrons. PANI-polyurethane foam (PANI/PUF) is used in wound healing purposes prepared in the presence of dopant called usnic acid. PANI with the grafting of magnetic Fe3O4 is used in chemotherapy. The TiO_2/PANI based nanocomposite and NiO NPs/PANI nanowire/graphene oxide nanosheet composites used as biosensor for glucose detection. These PANI based glucose sensors are known to have a shelf life of 30 days. Apart from these glucose sensor PANI/carbon nanotube composites is used in the detection of cholesterol. Gold NPs/PANI based nanocomposite used as Geno sensor with a detection limit 0.01 fM. For detecting prostate specific antigen, Peptide nanotube-Au nanoparticles-PANI immobilized pencil graphite electrode has been used as immunosensor.

There are known PANI involved nanocomposites used for electromagnetic shielding applications as well. PANI grafted with graphene aerogel show microwave absorption properties of about -42.3 dB in 3 mm with 11.2 GHz frequency range (about 0.12 in) thickness [119]. PANI/carbon nanotube coated fabric also show excellent shielding of 23 dB in between 4-6 GHz.

Polyaniline blended with carbon materials used as electrodes in supercapacitors due to their higher interface interactions. PANI-activated carbon-based electrodes which are used in supercapacitors are known to have an energy density of 18 Wh kg^{-1} [120]. Later, It was reported ordered mesoporous carbon/PANI nanocomposites having specific capacitance of 336 F g^{-1} at 0.1 A g^{-1}. Due to the enhanced conductivity of some polyaniline based CNTs such as PANI coated with P4VP as dopant, the core shell structured electrode capable of having specific capacitance of 1065 F g^{-1} at 0.5 A g^{-1}. Graphene modified PANI are also an emerging candidate in this field. water-dispersible graphene/sulfonated PANI composite shows high volumetric energy density of 1.51 mWh cm^{-3}. Apart from these applications, PANI based nanocomposites are also used as gas sensors and humidity sensors as well.

2.9. CeO_2 NANOPARTICLES

Cerium oxide or *ceria* is recently grown as a nanoparticle in the use of catalytic processes due to its self-regeneration surface activity. It is also useful as a ROS scavenger for its oxygen storage capacity. RHEED provides us with the information that the surface lattice of this nanoparticle is aligned in a consistent manner with the bulk region of the nanoparticle. Cerium oxide has a structure of fluorite in which O atoms are present in the corners of a simple cubic lattice and Ce atoms are present in the face centered position. CeO_2 (111) and CeO_2 (110) surfaces are known to have low energy as compared to CeO_2 (100) surface. The stability of these surfaces follows the order- (111)>(110)>(100) [121].

The characteristics of CeO_2 nanoparticles are mentioned as follows [122]:

- High catalytic activity.

- Large surface area.
- High mechanical strength.
- Non-toxicity to living cells.
- Oxygen transfer and capacitive ability.
- Switchable redox reactivity of modulating oxidation states.

2.10. PANI@CeO_2 BASED NANOCOMPOSITES

Cerium oxide employed as a dopant to PANI is of great interest in recent years for researchers because cerium oxide consists of good optical and electrical properties. Researchers also found out that PANI@CeO_2 nanocomposite shows higher thermal stability and better conductivity than pure polyaniline [123]. Several synthesize methods like in situ polymerization, microwave assisted solution method, sol-gel synthesis, hydrothermal method has been employed earlier to make this nanocomposite. From the UV vis spectra of PANI@CeO_2 nanocomposite, a blue shift phenomenon is observed because of the size quantization effect. Also, the band gap of this nanocomposite is higher than the CeO_2 NPs. In the CeO_2 grafted polyaniline nanocomposite, CeO_2 distributed in the polyaniline chain blocking the movement of charge carriers and thus increasing the conductivity which is also been proved by AC conductivity analysis. These PANI@CeO_2 nanocomposites are extensively used as sensors, biosensors, optical sensors, photovoltaics etc.

CHAPTER 3

CONCLUSION

3. CONCLUSION

In this work, an approach for the detection of E2 has been performed by using non-enzymatic approach. For that, PANI@CeO_2 nanocomposite has been synthesized, characterized and electrophoretically deposited onto ITO. Electrochemical behaviour of PANI@CeO_2 and PANI modified electrode has been studied. This study depicts that PANI@CeO_2 persist higher current as compared to PANI modified electrode. Better diffusion of redox ions by the PANI@CeO_2 modified ITO has been shown through the results. The experiments showed good results which confirm the good repeatability, stability and reproducibility as a non-enzymatic biosensor, which highlights the predominance of our developed biosensor over other non-enzymatic biosensor for detecting E2. Additionally, a real sample analysis was also verified in human urine and tap water to showcase the applicability of this biosensor.

CHAPTER 4

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4. REFERENCES

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