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REVIEW ARTICLE

Polymeric Innovations Driving Sensitivity in Electrochemical Analysis

Reena Kushwaha,* Auwalu Abdullahi Shehu, Preeti Pandey Department of Chemistry, Kalinga University, Nava Raipur-402101, Chhattisgarh, India

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Abstract: One significant family of organic functional materials is conducting polymers (CPs). In the development of electrochemical sensors, polymer composite materials have emerged as a key component, providing an optimal blend of properties to ensure stability, sensitivity, and selectivity. These materials utilize the electrical conductivity of polymers along with the mechanical performance and functional diversity of composite materials, enabling a broad range of applications from biological diagnostics to environmental monitoring. Electrochemical sensors capitalize on the conversion of chemical information into detectable electrical signals, and polymeric composite materials have dramatically improved sensor efficiency. Common conductive polymers, such as polyaniline, polypyrrole, and polythiophene, are frequently combined with nanomaterials like graphene, carbon nanotubes, and metal nanoparticles to form composites. To meet the stringent requirements for high-precision analyte trace detection, these hybrid compounds must have a large surface area, rapid electron transfer kinetics, and biocompatibility. To further enhance CP performance, additional composite components have been developed, including carbon-based composites, metal oxides, and metals. This study thoroughly examines the various applications of CPs and their composites. The current work aims to provide a comprehensive analysis of electrochemical detectors based on CPs and composite materials, with future research focusing on increasing the production and functionalization of polymeric composites as well as enhancing the sensor sensitivity and specificity.

Keywords: azulene (PZ), polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), poly (3,4-ethylenedioxythiophene) (PEDOT), polyactylene (PA).

UNSDG GOALS: UNSDG 3: Good Health and Well-being, UNSDG 6: Clean Water and Sanitation, UNSDG 9: Industry, Innovation and Infrastructure, UNSDG 12: Responsible Consumption and Production, UNSDG 13: Climate Action, UNSDG 14: Life Below Water, UNSDG 15: Life on Land

1. INTRODUCTION

Polymer composite materials that emerged as considered a new range of substances used in electrochemical sensors, with extraordinary promise to address today's technological challenges. A material comprising the beneficial properties of polymers and functional properties of other materials such as metals, ceramics, carbon-based materials, or nanomaterials has introduced revolutionary advances in sensor performance, sensitivity, and stability. They are suitable for use in a wide range of diagnostics that include industrial quality control, food safety, environmental monitoring, and health due to their inherent flexibility, light weight, and molecular engineering capabilities. Electrochemical sensors take advantage of the detection and measurement of electrical signals generated by chemical reactions, and hence they become an indispensable tool for the fast and reliable analysis of analytes of interest for diverse applications. Conventional electrochemical sensors are useful, but have limitations such as poor stability, fouling susceptibility, and inadequate sensitivity for trace-level analyte detection. Polymeric composite materials provide a solution to these limitations by simplifying the fabrication of sensors with improved chemical specificity, mechanical durability, and electrochemical properties. Secondary additives such as conducting fillers or catalytic particles greatly improve the electrochemical functionality of composite materials, even though the incorporation of polymer matrix adds processability, flexibility, and cost-effectiveness. For example, conducting polymers (CP) provide a great electron transport platform for the production of sensors; however, by adding nanostructures such as metal nanoparticles or graphene, the surface area and catalytic activity of the sensing platforms are improved. It enables the attainment of a greater number of sensing capabilities, selectivity, and miniaturization while designing sensors, which combined properties by polymeric composites make them unique. This type of material can be tuned for many other properties, including hydrophobic, biocompatibility, and stability against the environmental factors to be applied in the sensing requirement. For example, biosensors made by enzyme-or molecularly imprinted polymer-based polymeric composites are capable of acting extremely selectively, and those that incorporate carbonbased nanomaterials, such as carbon nanotubes, may detect very tiny chemical species with good precision.

Over the past several years, advances in nanotechnology and material science have accelerated the development of polymeric composite materials for electrochemical sensors with wearable sensors, real-time monitoring sensors, and handheld diagnostics. These developments position polymers not only as sensing materials but also as building blocks behind the next wave of smart, multifunctional sensors. With the ongoing need for sensors that are more efficient, more reliable, and more sustainable, the investigation of polymeric composite materials in electrochemical sensors continues to be an active and promising field of study.

^{*}Corresponding Author: Reena Kushwaha, Department of chemistry, Kalinga University, Naya DOI:10.70130/RCS.2025.0201003 Raipur-402101, Chhattisgarh, India. E-mailLreenakushwaha714@gmail .com. © RSYN RESEARCH LLP https://pubs.rsyn.org/rcs



Integration into contemporary sensor technologies holds the key to the rethinking of our methods of monitoring and analyzing intricate chemical and biological systems, paving the way for pioneering advances in science and technology.

2. PROPERTIES OF CP'S

2.1 Magnetic Behavior of Conducting Polymers

The doping levels, manufacturing conditions, and chemical composition of CPs significantly influence the magnetic properties that such materials possess. The parameters include paramagnetism, ferromagnetism, and diamagnetism, which are the possible properties of such materials influenced by the doping agent and polymer used. Certain polymer chains, such as doped polyaniline (PANI) and polypyrrole (PPy), contain localized unpaired electrons, and hence are paramagnetic in nature. These CPs can be rendered magnetically active by doping them with transition metals, such as iron (Fe) or cobalt, that enhance their magnetic properties. These CPs have shown tremendous potential for use where magnetic properties are key, for instance, in data storage, sensors, and electromagnetic shielding. These are also attributes that determine the magnetic properties; for the most part, CPs with an organized structure respond more magnetically to their amorphous structures (Correa et al., 2020; Namsheer & Rout, 2021). The ability to modulate the magnetic behavior of CPs through the change in the doping level has also opened new possibilities for the development of functional materials with designed magnetic behavior for various applications (Elizalde et al., 2022; Oladipo et al., 2023).

2.2 Optical Behavior of Conducting Polymers

The conjugated molecular structure of CPs is the key concept behind their ability to absorb and emit light in the visible, UV, and infrared regions. Optoelectronic devices such as organic light-emitting diodes, photovoltaic cells, and sensors are based on conducting polymers because their optical behaviors are absorption, fluorescence, and electroluminescence. The extent of conjugation in the polymer structure, whenever it is a matter of CP absorption spectra and bandgap, is vital. In the ultraviolet–visible range, for example, polymers such as polyaniline (PANI) and poly (3, 4-ethylenedioxythiophene) (PEDOT) have different absorption bands, and the optical properties of these materials are extremely sensitive to doping and environmental factors. Devices that need adjustable optical properties could benefit significantly from doping, which changes the emission properties and the absorption spectra. Strong photoluminescence and electroluminescence are also features of CPs that qualify them for application in displays and LEDs. Morphology is also responsible for their interaction with light; materials with more crystalline or organized morphologies (Kaloni et al., 2017; Ghomi et al., 2022) were found to possess improved optical properties. With tunable optical properties, electrical and mechanical flexibility, and growing prevalence in next-generation optoelectronic devices, CPs have found increasingly diverse applications.

2.3 Mechanical Behavior of Conducting Polymers

The mechanical properties of CPs are similar to those of normal polymers but with significant dependence on the chemical structure and doping level. Changes in chemical composition or doping make undoped CPs more valuable and practical, but they are generally rigid and brittle. PPy and PANI are two metals of moderate tensile strength when they are fiber- or film-formed but without mechanical toughness or endurance. Flexible electronics, wearable devices, and soft robotics exploit a three-way trade-off between mechanical flexibility and conductivity. The mechanical properties of CPs are dependent on the structural organization of the monomers. Amorphous polymers are rigid and short-lived compared to crystalline polymers (Matysiak et al., 2020; Franciszczak et al., 2019). The research has now focused on the promising brilliant future of mechanically flexible and microwave-absorbing CPs; this can be responsible for the recent surge in their usage (Pratap et al., 2024).

2.4 Electrical Behavior of Conducting Polymers

Indistinguishably, with the more common insulating polymers, CPs possess distinct electrical properties. The explanation for CPs conducting electricity is that they possess conjugated networks that contain delocalized π -electrons. Doping, which is the process of adding charge carriers such as electrons or holes to the polymer system, significantly increases the electrical conductivity of CPs. There exists a significant relationship between the electrical conductivity of CPs and doping level, dopant species, and manufacturing conditions. Some examples of CPs that have been the subject of much study are PANI and PPy, which can accommodate a wide range of doping levels to modulate their conductivities. Flexible electronics, sensors, and organic semiconductors can potentially all take advantage of CPs because of their electrical properties, and these can be tailored. Although CPs could achieve metal-like conductivity under optimal doping conditions, they cannot yet surpass the electric performance of Standard metal conductors (Yoon et al., 2020). Found that the electric performance of CPs is influenced by their shape, crystallinity, and defects within the polymer core, which could enhance or deter electron mobility. Another important use of CPs for energy storage devices such as batteries and supercapacitors is due to their electrochemical properties (Le et al., 2017).

2.5 Environmental Sensitivity

Several CP traits, such as electrical conductivity and mechanical flexibility, are environmentally sensitive, indicating that they show changes toward their environment such as humidity, temperature, and gas exposure. Although CPs are capable of recognizing changes in their environment, such as an abundance of gas or changes in temperature, their sensitivity is useful in sensors (Kim et al., 2016).

3. CONDUCTIVE POLYMERS

In general, substances made up of polymer chains are called polymers. These compounds usually have relative molecular weights between a few thousand and a few million. Both natural and synthetic polymers exhibited very little electrical conductivity at first, and it was not until the 1970s that CPs were synthesized with any real progress. Their conjugated main electron system, which allows doping to conductivity values greater than 1,000 S*cm-1, is the feature that distinguishes CP. Because these materials include alternating single and multiple bonds (double or triple bonds), they exhibit resistivity whenever oxidized (both positive doping and p-doping) or reduced (negative doping or n-doping), as illustrated in Figure 1. The polymer is vulnerable to doping methods that decrease or oxidize it due to the delocalization of π electrons associated with numerous bonds in the extended region of the conjugated structure. Doping with π -conjugated systems improves conductivity from the semiconductor/insulator boundary to metallic behavior by removing physical and morphological disorder, leading to an increase in conductivity (Tsukamoto et al., 1990). In their neutral state, the conductivity of CPs usually falls between 106 and 105 S * cm -1, but when doped, it can rise as high as 105.

Figure 1. Polyacetylene structure, showing the conjugated double bonds in the main chain.

CPs can be synthesized using a variety of techniques. Oxidative coupling, the most widely used synthetic principle, is the process of oxidizing monomers to produce cationic free radicals, which then proceed through coupling reactions to form cations, repeatedly forming polymers. Because of its simplicity and reliability, electrochemical production has become the predominant and preferred technique for synthesizing CPs. Another advantage of electrochemical polymerization is that it may be performed at room temperature while precisely controlling the thickness of thin films by varying the voltage or current profiles. CPs are usually electrochemically polymerized using one of the following techniques: (1) a specific voltage or steady potential, (2) variable current or fixed current density, or (3) cyclic voltammetry or potential scanning/cycling processes. Glass plates coated with indium tin oxide are prevalent anode materials, as are electrolytes coated in platinum, chromium, gold, nickel, palladium, or titanium. Additionally, semiconductor materials such as n-doped silicon, cadmium sulfide and semimetallic graphite (Aguilar-Bolados et al., 2017) are employed in the electrochemical generation of CP films. This synthetic approach enables the creation of autonomous, homogenous, and self-doped thin films, as well as copolymerization and grafting reactions. Some of the conducting polymers (CP) used are mentioned in Figure 2.



Figure 2. Recognizing their multiple advantages, conducting polymers (CPs) are widely used in a variety of fields (Youheng et al., 2024).

3.1 Polythiophene (PTh)

Pth, its doped form, and its derivatives have been the center of extensive attention for sensing because of their excellent capacity for adsorption and selective barrier properties toward specific compounds. The electronic properties of the pitch can be altered by incorporating complementary groups or drugs with a 3 to 1 eV band gap (Kaloni et al., 2017). However, due to the high oxidation potential of Pth, polymerization and deposition on vast insulating surfaces pose considerable problems. Furthermore, doping in its oxidized state rapidly returns to its intrinsic state and is extremely unstable in air. Several methods, such as electrochemical oxidation, solution chemical oxidation, oxidative chemical vapor deposition, and electrospinning, can be employed to produce polymer films. P₃ATs, which involve poly (3-hexylthiophene) (P₃HT), poly (3-amylthiophene) (P₃PT), and poly (3-butylthiophene) (P₃BT), have been considered one of the most vital forms of Pth due to its more accurate electrical conductivity, thermal conductivity, and processing stability. The gradual increase in the degree of phase separation due to the longer alkyl chains within these polymer structures adds to the enhanced equilibrium of hole and electron transport (Gadisa et al., 2009; Razzell-Hollis et al., 2017; Wang et al., 2013). The SEM characterization and chemical structural diagram of Pt are shown in Figure 3.



Figure 3. Chemical structure diagram of Pth.



Figure 4. Chemical structure diagram of polypyrrole (PPy).

3.2 Poly(p-phenylenevinylene) (PPV)

The chemical structure of PPV consists of a benzene ring and an ethylene monomer. The conjugated double bonds hold the benzene ring together as a conjugated π -electron system. The chemical structure of PPV consists of multiple π -conjugated bonds, which contribute to a conjugated system that favors the mobility of free electrons within the molecule. Because the polymer is conjugated, electrons are possible to pass through the chain with increased ease. Second, planarity in the form of PPV further adds conductivity through enhancing the flow of electrons from molecules to molecules while prompting the development of conjugated units. Although its conductivity, although regulated through a redox process, can be changed by adding dopants for extra charge carriers (Van der Zee et al., 2022). These characteristics give PPV a broad array of possible uses in areas such as organic light-emitting diodes and optoelectronic devices.

3.3 Polyacetylene (PA)

A polyene chain may include up to polyactylene (PA), a linear conjugated polymer. The structure of PA, one of the most basic organic polymers, has an important impact on electrical conductivity. The conductive properties of trans- and cis-polyacetylene are 10-6 and 10-9 S*cm⁻¹, respectively. However, p or n doping treatments can increase PA conductivity to metallic levels (104-105 S*cm⁻¹). Due to its high instability and difficult processing properties, PA has few practical uses. Precursor-assisted synthesis, catalytic polymerization, and noncatalytic polymerization are the techniques used to prepare PA (K & Rout, 2021). High solubility and selectivity catalysts are required for the production of PA or oligomers, which are frequently achieved by catalytic polymerization processes. Since PA can also be made without the use of catalysts or solvents by radiant polymerization methods such as glow discharge, ultraviolet light, or gamma rays, there is a lot of potential for future advancements in this area. To increase its conductivity, PA is frequently hybridized or doped with other materials, for example, hexamethylene phosphate, cellulose nanoparticles of quaternary ammonium salt, or gold nanoparticles (Hu et al., 2010; Li et al., 2012; Tsou et al., 2012). The catalyst can then be used in bioelectrodes and electrochemical biosensors.

3.4 PPy

The fundamental structure of PPy consists of repeated pyrrole units containing nitrogen atoms and benzene rings (**Figure 4**). The ease with which PPy can be oxidized, its water solubility, commercial viability, lightweight nature, affordability, and biocompatibility distinguish PPy from other CPs. Furthermore, PPy is characterized by very high conductivity, flexibility, redox properties, and ecological hardness. Accordingly, it has found extensive application in various forms of biochemical and electrochemical devices (Thadathil et al., 2022; Xia et al., 2011; Yang & Mai, 2014). Higher specific surface area and electrical conductivity in composite materials can be achieved by mixing PPy with other materials, including metal oxides and carbon-based materials. PPy possesses special properties that make it an excellent alternative to the apparatus used in electrochemical sensors.

3.5 Polyaniline (PANI)

PANI is among the most promising CP conjugates, because of its superior optical characteristics, great processability, reversible conductivity of electricity, and environmental stability. Like **Figure 5** shows, MacDiarmid's 1987 suggestion of the universally accepted structural formula for conductive PANI is grounded in the coexistence idea of a "benzene-benzene" chain-reducing unit and a "benzene-quinone" alternate oxidation unit. The electrical conductivity, hues, and interconvertible oxidation states of PANI vary according to the composition of these two structural units. The compound can be doped chemically or electrically to neutralize its charge on the polymerization main chain and the incorporated ions in the polymer skeleton due to the simple fact that conjugated polymer compounds easily undergo REDOX reactions. PANI can transition from an insulating state to a conducting state quickly and reversibly. The imine nitrogen atom on the molecular chain is protonated when PANI is doped with protonic acid because positive charges move and delocalize onto the linear conjugate structure (Li et al., 2015). As a result, PANI exhibits exceptional conductivity and a unique three-dimensional bridging structure (**Figure 5**).



Figure 5. Chemical structure diagram of PANI's.

4. BASIC PRINCIPLE OF ELECTROCHEMICAL SENSORS

The creation of electrochemical sensors is the primary focus of increasing interest in using and constructing electrochemical tools for the observation, measurement, and identification of specific chemical substances. According to analytic chemistry, electrochemical sensors are the kind of chemical sensors that are developing the fastest. 'A device that provides uninterrupted information on its surrounding environment' is the definition of an electrochemical sensor. More precisely, the quantity of chemical species is instantly revealed by the quantitative reaction produced by electrochemical sensors. The transducer and a sensor or catalyst are common components of electrochemical sensors. The transducer, also known as the electrode, turns chemical energy into electrical energy, while the sensing element produces the electrical impulses of the discovered analyte and displays them on the instrument for future investigation (Stetter et al., 2003). An electrochemical sensor schematic diagram is shown in Figure 6. Electrochemical sensors are classified into three main groups: amperometric, voltammetric/potentiometric, and impedimetric. These categories are based on the observable conductivity change of the medium (impedimetric), detectable potential (potentiometric detection), and measurable current (amperometric detection). There are three electrodes in an electrochemical sensor: the working electrode, the reference electrode, and the auxiliary or counter electrode. Additionally, the working electrode can be made of carbon, indium-doped tin oxide, platinum, gold, or fluorine-doped tin oxide. An example of a reference electrode is silver chloride or Ag/AgCl. In addition, reference electrodes may be saturated calomel electrodes or reverse hydrogen electrodes. The auxiliary or counter electrode can be made of graphite rod, platinum foil, platinum wire, or platinum mesh, among other materials (Hitchman & Berlouis, 1995).

By establishing a voltage between the reference and working electrodes, a voltammetric sensor produces an electrical current that oxidizes or reduces the target analyte. Electromechanical alterations of the surface at electrical electrodes and their connections to the electrolytes are the primary sources of the generated current. Practical voltammetric techniques include linear sweep, hydrodynamic, differential pulse, square wave, and cyclic. Voltammetric sensors have low detection thresholds and a wide dynamic range. On the contrary, amperometric sensors apply a constant voltage to the working electrode, which causes the analyte to oxidize or reduce. First, the voltammetric technique is used to determine the oxidation or reduction potential. This sensor records the generated current in relation to time. It is possible to conclude that the primary distinction between voltammetric and amperometric sensors is that the former use the current step instead of the potential sweep. Furthermore, the current produced varies on the basis of the concentration of the desired analyte. The oxidation and reduction potential of the analyte of concern can clarify whether these sensors were significantly more sensitive and selective. Potentiometric sensors measure the electrical potential variance between the standard and working electrodes. This potential difference offers details on the targeted analyte. On the basis of the type of electrode, potentiometric sensors can be categorized into three main types: ion-selective electrodes, field-effect transistors with effects (FETS), and coated wire electrodes. Electrodes that are specifically ion-selective have the lowest detection limit among the many potentiometric sensor types. The pH electrode is the most widely used ion-selective electrode, due to its unquestionable benefits, including its nondestructive nature, low cost, easy construction, simplicity of utilization, and compatibility with a broad range of concentrations. Conductometric or impedometric sensors, which measure conductivity over a range of frequencies, are the third kind of electrochemical sensor (Bobacka et al., 2008; Rahman et al., 2008).

5. ELECTROCHEMICAL SENSORS

When creating electrochemical sensors, PNCs are a prevalent component. Electrochemical sensors are based on three different types of PNCs. Some examples of conductive materials are polymers, carbon nanotubes, graphene, and inorganic nanoparticles. Following the interaction between the target analyte and the PNC-based electrochemical sensors, the transduction system detects an electrical signal.

5.1 Polymer nanocomposites consisting of graphene and conductive polymers

With its unique electrical conductivity and two-dimensional existence qualities, graphene (Grp), an allotrope of carbon, has drawn interest as a novel material and has been extensively used in sensor research since the beginning of this millennium. Grp-PNC-based electrochemical detectors are utilized to electroanalytically detect target substances with high selectivity and sensitivity. They exhibit outstanding detection limits over a wide range. An electrochemical sensor designed with PANI-Grp-GCE was used to detect 4-aminophenol (4-AP). Its sensitivity was $604.2 \,\mu\text{AmM}^{-1}$ and its detection limit was $6.5 \times 10-8$ M. To create a sensor with a sensitivity limit of 0.15 mA ng/ml, a PANI-Grp-based PNC was applied to an indium-doped tin oxide sheet containing immobilized horseradish peroxidase. A PANI-Grp-GCE-based PNC sensor was used to extract the mineral antagonist lercanidipine from pharmaceutical formulations meant for medical use. The detection limit range was 5 to 125 ng / ml (Jain et al., 2014). A further advantage came from detecting the nitazoxanide chemical using the same PANI-GrpGCE-based PNC sensor. Because of their specialized applications in the overoxidized state of PPy, PPy-based PNC-based electrochemical sensors are becoming more common. Concurrent detection of adenine and guanine using an electrodeposition approach was made possible by the formation of polypyrrole-graphene (PPyox/Grp). The pyrrole was electrochemically reduced after being electropolymerized with graphene oxide using the PPy-Grp composite. The unique structure of the nanocomposite allows the electrochemical sensor to detect adenine and guanine more effectively. Adenine and guanine exhibited significant relationships between and cationic selectivity (Zhang et al., 2012). When it came to the detection of PNC, dopamine (DA), a major neurotransmitter involved in neurological diseases such as schizophrenia and Parkinson's disease, was the gold standard in neurochemical research. A polypyrrole-graphene oxide (PIL-PPy-GO)-functionalized PNC electrochemical sensor was created by polymerizing 1-vinyl-3-ethyl-imidazolium bromide on PPy-GO films that had been treated with N-vinyl imidazolium. The PILs helped detect DA by altering the surface charge and dispersibility of the PIL-PPy-GO composite (Wang et al., 2014). DA may be detected by an electrodeposition-made poly (3,4-ethylenedioxythiophene)-graphene oxide (PEDOT-GO) sensor based on PNC, which showed remarkable sensing capabilities. A one-step electrochemical redox synthesis technique of PEDOT-Grp PNC film was carried out using concurrent PEDOT electrodeposition and electrochemical reduction of graphene oxide on a glassy carbon electrode (GCE) with better ascorbic acid molecule detection sensitivity. PEDOT-Grp thin film PNC enabled electron transit between the AO and electrode interface, significantly increasing the electrocatalytic activity and sensitivity of ascorbic acid molecules in this sensor (Jain & Shrivastava, 2014). To increase the effectiveness of detectors used in pharmaceutical products for electrocatalytic etodolac oxidation, Jain et al. coupled Grp with a conducting PANI-Bi2O3 PNC.



Figure 6. Electrochemical sensor circuit diagram (Rahman et al., 2008).

5.2 Polymer nanocomposites consisting of carbon nanotubes and conductive polymers

Conductive polymer-based poly(vinyl chloride) (PNC)s increased the sensitivity and dependability of their electrochemical sensors, hence expanding their sensing capacity. Recently, several renowned CNT-based PNCs have been described in the literature. The sensor was developed using PPy multiwalled carbon nanotubes (MWCNTs) and toluene sulfonic acid as its substrate and demonstrated excellent sensitivity in detecting cholesterol with a response time of 9 s. Xu et al. produced a carbon paste electrode (carbon paste electrode El). The nine-second response time sensor showed great sensitivity to detect cholesterol and was developed using PPy-MWCNTs and toluene sulfonic acid as its substrate. Xu et al. created a PEDOT-CNT nanocomposite carbon paste electrode. Pemetrexed, an anticancer drug, was found by combining sodium dodecyl sulfate-doped PPyox with carboxylic acid-enhanced MWCNT-modified GCE. Ecofriendly biosensors with a PEDOT-CNT nanocomposite. The anticancer drug pemetrexed was discovered using carboxylic acid-enhanced MWCNT-modified GCE and sodium dodecyl sulfate-doped PPyox. They analyzed nitrobenzene, DA and hydroquinone using this electrode (Xu et al., 2014).

5.3 Conducting polymer compounds that contain metals

In recognition of their superior electrical, catalytic, and optical qualities, metals have drawn a great deal of study interest. As a result, metals have numerous applications in technologies, energy conversion and retention, and sensing technologies. Nanoscale metals have been widely used in the past 20 years to investigate property enhancement, particularly in the electrochemical field, since their large surface area efficiently improves the electron transfer rate and catalytic capabilities. However, the propensity of metal nanoparticles to agglomerate at the nanoscale reduces their catalytic potential. For the reason that to prevent aggregation and to get around the drawbacks of pure metal nanoparticles, they are commonly incorporated into polymer matrices. Composites are frequently created by combining noble metals such as Ag, Au, Pt, and Pd with conducting polymers. Furthermore, as fillers, Ni and Cu have also been studied (Hangarter et al., 2013). The electrical, catalytic, and increased sensitivity of MCPs make them highly promising for use in sensing devices. These sensing devices use metal-conducting polymer composites to detect a wide range of chemical species of concern, such as volatile organic compounds, alcohols, humidity, and hazardous gases. The CP's in the composites both directly interact with the analytes and transduce the nanoparticles' electrical reaction. There has been a great deal of research on metal-conducting polymer combinations as biosensors because of their ability to immobilize biomolecules. Dopamine is an essential catecholamine neurotransmitter prevalent in the central nervous system for message transmission. To detect it, sensors based on metal-conducting polymer composites have been created. Additionally, electrocatalytic oxidation of NADH has been found to enhance these composites (Duraisamy et al., 2012; Manesh et al., 2008).

5.4 Conducting polymer composites with carbonaceous fillers

Graphene and CNTs are the most common types of carbon-based materials. CNTs were first discovered in 1991 and have since found widespread application in electrochemical sensing owing to their beneficial electrical conductivity, the ability to catalyze the redox reaction of the target analyte, and the suitable size, mechanical strength, and positioning for immobilization on the outermost layer of electrodes. Because CNTs have low sensitivity and selectivity, they are rarely used alone. Since the response mechanism depends on the electron affinity and density ratio of the target analyte in relation to the CNT transducer, minimal selectivity is seen (Mehmood Shahid et al., 2017). Composites can be created by combining CNT with CP. Compared to CPs or CNTs alone, these composites offer a variety of advantages. The components of CNT-conducting polymer composites are combined to produce a strong, flexible, and highly conductive material ideal for sensing applications such as the detection of biological compounds and pollutants in water. Ding et al. studied the electrocatalytic reduction of a water contaminant, bromate, applying an altered GCE and an in situ chemical oxidation approach with (PANI)/multi-walled carbon nanotube. CPs improve the adhesion of the active layer to the substrate, while CNTs increase the rigidity and electrical conductivity of the composites. Electrochemical performance was good in the composite. While bromate was electrochemically reduced, PANI was transformed from emeraldine to leucoemeraldine in an acidic solution (Ding et al., 2012). The results indicated that the maximum current of the bromate reduction gradually increased. A different study used a carbon ionic liquid electrode that had been modified with a composite of polythionine and MWCNTs to detect a decrease in the amount of nicotinamide adenine din (NADH). The electrode may enable NADH oxidation using an excess potential as low as 0.03 V, according to cyclic voltammetric studies, while an amperometric test demonstrated a sensitive and reliable reaction to NADH in less than 5 s, according to the latter. The range to measure NADH ranged from 0.8 to 422 μ mol/L, and the detection limit was 0.26 μ mol/L (S/N = 3). The creation of NAD⁺ dependent enzyme-based biosensors may benefit from the wide linearity, reduced detection limit, and faster reactivity to NADH.

5.5 Compounds of CPs with metal oxides

Metal oxide nanoparticles are an effective substitute for carbon- and metal-based materials in electrochemical systems. Metallic oxides are abundant, cheap, and environmentally friendly. Also, there are many methods that have been described in the past 20 years to make metal oxide nanoparticles, so it is not particularly hard to create them. Among the many outstanding properties of these materials are their small particle size, high surface reaction activity, high surface-to-volume ratio, enormous adsorption capacity, and high electron transfer rate. These properties of metal oxide nanoparticles make them ideal for sensors. However, the active area and catalytic potential of metal oxide nanoparticles are reduced when they aggregate, making it challenging to employ them in sensors. Metal oxide-based sensors use a lot of energy and operate at high temperatures. However, CPs have attracted a lot of attention as useful materials for sensors that operate at ambient temperature. Limited temperature stability, long

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response time, and limited response are some of the drawbacks of CPs. These drawbacks prevent them from being widely used in sensors. On the contrary, CPs and metal oxides cooperate to stop nanoparticles from clumping together, increasing their catalytic potential and active surface area. When conductive polymers are combined with metal oxides, their thermal stability and response time are also greatly enhanced. The improved performance of metal oxide-conducting polymer composites is what makes them useful for a variety of sensing applications. These compounds are great options for immobilizing and biocatalyzing biomolecules such as dopamine, ascorbic acid, NADH, uric acid, hydrazine, epinephrine, and others in sensors (Tsele et al., 2017; Yang et al., 2017). These compounds are excellent for catalytic combustion and reduction of organic compounds such as 4-nitophenol and bisphenol A, due to the catalytic properties of metal oxides. Natural materials such as blood, serum, and flesh may have their chemical components detected by these composites. Sensors based on metal oxide CPs have enough potential to remove harmful organic pollutants from the air and water. These compounds have the potential to remove heavy metal ions $(Pb^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Hg, Cu^{2+}, etc.)$ and dyes from drinking water due to their extremely low parts per billion detection ability. The best use of these secomposites in sensors is for the detection and measurement of pharmaceutical formulations. Furthermore, the detection of glucose in meals is studied using modified electrodes in electrochemical sensors made of non-enzymatic metal oxide-conducting polymer composites, additionally, gas sensing (NH₃, H₂S, CO, CO₂, H₂, NO₂, etc.) is a specialty of these composites. Because metal oxides have an innate capacity to absorb and desorb gases, the metal oxide component of composites is responsible for its gas-sensing capabilities (Dey, 2018). TiO₂-MWCNTs-PANI and RuO₂-MWCNTs-PANI composites were described by Tsele et al. as altered gold electrodes for catalytic oxidation of the epinephrine biomolecule. Epinephrine was detected using the cyclic voltammetry technique in buffer solutions with a pH of 1.0 to 7.0, as well as real adrenaline injection samples. The gold electrodes that were modified with TiO_2 -MWCNTs-PANI have a detection limit of 0.16 μ M, while the gold electrodes that were modified with RuO2-MWCNTs-PANI have a detection limit of 0.18 µM. Yang et al. also created Fe₃O₄/graphene oxide/polypyrrole composites to detect hydrazine. Composites were made by combining coprecipitation with chemical oxidative polymerization. The compounds produced were placed onto the transparent carbon electrode. The sensor showed remarkable sensitivity to dissolved hydrazine within a concentration ranging from 5.0 µM to 1.3 mM. It showed a resolution of 449.7 μ A m·M⁻¹ cm⁻² and a minimum detectable concentration of 1.4 μ M (with a signal-to-noise ratio of 3). Unlike saturated calomel electrodes, it was most effective at 0.2 V.

6. APPLICATIONS

Electrochemical sensors based on CPs have a wide range of biomedical applications, including biomolecular detection, cancer marker identification, drug screening, and delivery. These sensors enable the highly sensitive and selective detection of target compounds in biological samples, as well as precise drug release, cell position monitoring, and the development of artificial organs. Therefore, they provide a substantial contribution to the development of clinical medicine and biomedical science.

6.1 DNA biosensors

These days, PNCs are frequently seen in DNA biosensors. The field of medicobiology is expanding rapidly. A basic DNA sensor operates on fundamental principles. The application of a DNA probe to a surface causes the transplanted DNA chain to hybridize with the appropriate pair. This hybridization, sometimes referred to as transduction, can be detected by optical or electrochemical means. The use of electrochemical indicators to identify transducers led to the development of DNA biosensors, which are now widely used. Current advances in research are summarized and discussed in the following section. The most popular DNA biosensor to identify the BCR / ABL fusion gene in chronic myelogenous leukemia is shown in Figure 7. The PANI-AuNP-Cts-GS combo, which has a functional capture probe, is necessary for this. Both 3 ft biotin and 5 ft SH were used to label the hairpin-shaped capture probe. The biotin electrode probe was used to detect the streptavidin-alkaline phosphatase (AP) enzyme. The electrochemical signal generated by the catalytic reduction of 1-naphthyl phosphate to 1-naphthol is detected with diffuse pulse voltage, which is detected in the range of 10 to 1000 pM (Wang et al., 2014). Ag⁺ was detected with a DNA biosensor employing PANI-AuNP PNC. The combination of Ag⁺ that can be reused is formed when the electrochemical biosensor reforms cysteine, which is released with Ag+ from cytosine. The biosensor developed in this work exhibited high selectivity and a satisfactory detection limit for silver ions. A PNC called PANI-nf-AuNP was obtained through the encapsulation of AuNPs in polyaniline nanofibers (PANI-nf) that was used in the development of an alternative DNA electrochemical biosensor. An electrode of gold was used in the PANI-nf-AuNP sensor for the detection of Staphylococcus aureus DNA. The maximum level of measurement varied between 150×10^{-12} and 1×10^{-6} mol/L. A DNA biosensor was created using PANI-Fe₃O₄-CNT PNC to identify Neisseria gonorrhoeae using a DNA probe. Diffuse pulse voltammetry studies showed that the biosensor could detect in the 1×10^{-19} -1 $\times 10^{-6}$ -M range. MicroRNA-16 was detected with a detection limit of 0.1 nM using a relatively recent DNA biosensor that used PANI-AuNP PNC and a streptavidin-AP conjugate to transduce biotinylated target sequences. The polypyrrole-polyaniline-gold (PPy-PANI-Au) PNC-based DNA biosensor has a detection limit of $1 \times 10^{-6} - 1 \times 10^{-13}$ M and can identify target DNA by transmission, non-complementary and single- and double-base mismatched chains. An Ag nanoparticle functionalized polypyrrole and poly (3,4-ethylenedioxythiophene) (PPy-PEDOT) nanotube DNA biosensor was used to detect DNA transduction using EIS. The improved sensor detected DNA chains that were thiol capped (Radhakrishnan et al., 2013).

6.2 Cholesterol

A crucial structural element of nerve cells and the plasma membrane is cholesterol. Based on variables such as body weight, age, and sex, the normal blood cholesterol level might range from 5.2 to 6.2 mM. Hypercholesterolemia, defined as levels greater than 6.21 mM, considerably increases the possibility of cardiovascular disease, cardiac arrest due to coronary artery disease, and elevated blood pressure. On the contrary, liver disease and anemia may be due to low cholesterol. As a result, assessing clinical disorders caused by aberrant cholesterol levels requires precise cholesterol determination (Gudzune et al., 2014; Tuteja & Rader, 2014; US Preventive Services Task Force et al., 2016; Youheng et al., 2024). Conventional cholesterol testing technique uses an electrolytic sterol transducer based on the activity of cholesterol oxidase (ChOx). The selectivity of this sensor can be considerably increased by adding an enzyme electrode. Alagappan employed AuNPs-f-MWCNTs-PPy-ChOx/GCEAuNPs-f-MWCNTs-PPy-ChOx/GCE to create a cholesterol biosensor. Two phases were involved in the development of the biosensor: A wet chemical method was used to synthesize AuNPs-f-MWCNT, which was then electrically polymerized with pyrrol. Au-f-MWCNT increases conductivity, while PPy acts as a support matrix and immobilizes ChOx. The PPy-based biosensor showed a linear response in the concentration range of 2 to 8 mM, with detection thresholds of 0.1 mM and 10.12 μ A*mM-1*cm-2, respectively. Li et al. designed and constructed a CPH-based biosensor platform (Li et al., 2015). Phytotic acid can be used as a dopant and cross-linker in an all-solution procedure to create the biosensor. The use of the bifunctional chemical glutaraldehyde to cross-link cholesterol esterase/cholesterol oxidase (ChEt/ChOx) in the PANI hydrogel matrix allowed for high density and dependable enzyme deposition onto the three-dimensional PANI nanostructure. The PANI hydrogel film is made in about 3 min. With a wide linear range (0.3-9 mM), significant sensitivity, reduced detection limit, and fast reaction time (approximately 3 s), this biosensor shows outstanding sensing capability due to the particular properties of CPHs, such as being extremely permeable to biological substrates and rapid electron transfer. Because CPs are easy to scale, the proposed CPs-based biosensor platform has great potential as a low-cost sensor for diagnostic purposes, medical surveillance, and biomedical devices. By coating a screen printed electrode with taurine modified PEDOT, a cholesterol biosensor can be made without the use of enzymes (Thivya et al., 2020). The sulfonic acid in taurine improves the electrochemical performance of the sensor by establishing electrostatic bonds with the polymerization main chain, which leads to excellent stability, dispersion, and a large area of cholesterol adsorption through the induction matrix. The low detection limit of the sensor of $0.95 \,\mu$ M (S/N = 3) allows a quick identification of low cholesterol levels in a variety of body fluids.



Figure 7. Diagrammatic representation of the DNA sensor manufacturing process (Shrivastava et al., 2016).

7. CONCLUSION

Polymer composite material has transformed the area of electrochemical sensors through increased sensitivity, selectivity, and stability. High electrical conductivity, a large surface area, and quick electron transit rates are the particular properties at play. They are usually made up of a mixture of polymers and nanomaterials, such as graphene, carbon nanotubes, and metal nanoparticles. Such material properties help to use this in health care, environmental monitoring, food safety, etc. The use of polymeric composites in sensor technology has opened new avenues in wearable technologies, biosensors, and real-time monitoring systems. However, a lot of development remains to be done, where large-scale production processes, cost, and long-term stability are the constraints. Future research should overcome these constraints along with uncovering more composite material to bring about more performance and user-friendliness of electrochemical sensors. This is an area with great innovation potential and will likely play a huge role in scientific, industrial, and social development.

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Author(s) Biography

Reena Kushwaha

Email: reenakushwaha714@gmail.com

Reena Kushwaha is currently pursuing her Master of Science in Chemistry at Kalinga University, Naya Raipur, Chhattisgarh, India. Her research interests include functional materials, electrochemical sensing technologies, and the application of conducting polymer composites in analytical chemistry. She has recently authored a paper titled "Polymeric Innovations Driving Sensitivity in Electrochemical Analysis: A Review on Conducting Polymer Composites for Electrochemical Sensors." This review explores the synthesis, characterization, and sensing performance of various conducting polymer-based composites, particularly focusing on their sensitivity enhancements in electrochemical applications. The study highlights recent advances and emerging trends that contribute to the development of high-performance

sensors for real-world analytical challenges. As part of her academic engagement, she presented this work at the First International Conference on Biologically Active Molecules 2025 (ICBAM'25), organized by the PG & Research Department of Chemistry, Saraswathi Narayanan College (affiliated to Madurai Kamaraj University), Perungudi, Madurai, on March 7, 2025, in hybrid mode. Her contribution was recognized with a certificate of participation and presentation.

Auwalu Abdullahi Shehu

Email: <u>Auwalgaya65@gmail.com</u>

Auwalu Abdullahi Shehu is currently pursuing his M.Sc in Chemistry at Kalinga University, Naya Raipur, Chhattisgarh, India. He has published a paper titled "Review on Biomolecules Detection Using Nanoparticles" and participated in an International Conference held at Maharana Pratap College of Pharmacy, Kanpur. He also earned a certificate from a one-day online workshop on "Article Publication in Reputable Journals" organized by Maryam Abacha American University of Nigeria. Recently, he authored a review paper titled "Polymeric Innovations Driving Sensitivity in Electrochemical Analysis",

which highlights the role of conducting polymer composites in enhancing electrochemical sensor performance through improved sensitivity, selectivity, and stability.

Dr. Preeti Pandey

Email: preeti.pandey@kalingauniversity.ac.in ORCID: https://orcid.org/0000-0003-3093-2506

Dr. Preeti Pandey is an Assistant Professor in the Department of Chemistry, Faculty of Science, Kalinga University, Naya Raipur, Chhattisgarh, India. She received her Ph.D. in Chemistry from Jiwaji University, Gwalior, in 2015, with research focused on the electrochemical analysis of pharmaceuticals using chemically modified electrodes. She also holds an M.Sc. in Pharmaceutical Chemistry from the same institution. Dr. Pandey has over 11 years of experience in teaching and research. She has participated in five workshops and presented her work at more than 15 national and international conferences. Her academic contributions include over 12 research and review publications in reputed journals and two book chapters in national publications. She served as Co-Convener of the *International Interdisciplinary Conference on Science for Society (IICSS2022)* at

Kalinga University. Her research on the electrocatalytic quantification of the antiviral drug valacyclovir earned her the Best Paper Award at the 2015 *Innovation and Research in Science, Management and Technology* conference in Bilaspur. She was also awarded a Fellowship for Training of Young Scientists (2013–2014) in Chemical Sciences by the M.P. Council of Science and Technology, Bhopal.

ALIGNMENT WITH UNITED NATIONS SUSTAINABLE DEVELOPMENT GOALS (UNSDGS)

This study supports several United Nations Sustainable Development Goals (UNSDGs). It contributes to **Good Health and Well-being (UNSDG 3)** through advancements in biosensors for disease detection and drug monitoring. Applications in water quality assessment align with **Clean Water and Sanitation (UNSDG 6)**, while the development of innovative, high-performance sensing materials promotes **Industry, Innovation and Infrastructure (UNSDG 9)**. The use of cost-effective, reusable composites supports **Responsible Consumption and Production (UNSDG 12)**. Additionally, the sensors' ability to monitor environmental pollutants aids in **Climate Action (UNSDG 13)** and the protection of ecosystems, addressing both **Life Below Water (UNSDG 14)** and **Life on Land (UNSDG 15)**.



