Review

Applications of conducting polymer composites to electrochemical sensors: A review

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A R T I C L E   I N F O

Article history:
Received 7 August 2017
Received in revised form 30 August 2017
Accepted 1 September 2017

This publication is dedicated to Prof. Joseph Wang on the occasion of his 70th birthday.

Keywords:
Conducting polymer
Composite
Electrode material
Electrocatalyst
Electrochemical sensor

A B S T R A C T

Conducting polymers (CPs) constitute an important class of organic functional materials. Their unique physical and electrical properties and being inexpensive, easy to synthesize, and suitable matrices for biomolecule immobilization have enabled them to find a wide range of use, including playing roles in supercapacitors, batteries, electrochromic devices, solar cells, sensors, and biomedical applications. To enhance the performance of the CPs, various composite materials have been synthesized with carbon-based materials, metals or metal oxides, etc. This review comprehensively discusses CPs and their composites, followed by their applications. The purpose of this review is to summarize the electrochemical sensors that are based on CPs and their composites and to address future aspects of electrochemical sensing materials.

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1. Introduction

Organic π-conjugated polymers have been receiving much attention since the first electrochemical preparation and characterization of polyaniline, formed by the oxidation of aniline on a platinum electrode in dilute sulfuric acid, was reported by Letheby in 1862 [1]. These polymers are electrically conductive, and they are thus called conducting polymers (CPs) despite having been considered insulators before the major breakthrough of creating electrically conductive polymers on polystyrene by treatment with oxidizing or reducing agents [2–4]. CPs are a new class of functional materials [5], and they have received a great deal of attention in various fields due to their light weight, workability, resistance to corrosion, low cost, and excellent electrical, mechanical, optical, and conducting properties [6,7]. The conductivity of CPs
Aniline anodic oxidation

\[ \text{C}_{6}	ext{H}_{5}	ext{NH}_2 \xrightarrow{\text{doping}} \text{C}_{6}	ext{H}_{4}	ext{N}^+ \text{H}^{-} \]

Coupling of radicals

\[ \text{C}_{6}	ext{H}_{4}	ext{N}^+ \text{H}^{-} + \cdot \text{C}_{6}	ext{H}_{5}	ext{NH}_2 \rightarrow \text{C}_{6}	ext{H}_{6}\text{N}^+ \text{H}^+ \text{N}^{-}\text{H}_2 \]

Polynilene propagation

\[ \text{C}_{6}	ext{H}_{4}	ext{N}^+ \text{H}^{-} \xrightarrow{\text{oxidation} \text{and doping}} \text{C}_{6}	ext{H}_{4}\text{N}^+ \text{H}^+ \text{N}^{-}\text{H}_2 \]

Polynilene oxidation and doping

\[ \left[ \text{C}_{6}	ext{H}_{4}\text{N}^- \right]_n \xrightarrow{\text{oxidation} \text{and doping}} \left[ \text{C}_{6}	ext{H}_{4}\text{N}^+ \right]_n \]

**Fig. 1.** Electrochemical polymerization mechanism of polyaniline.

was first observed in polyacetylene, whose conductivity increased 10 orders of magnitude when it was oxidized by iodine vapor [2,8,9]. The instability of polyacetylene in air has led to the discovery of various new types of CPs [10], including polyaniline (PANI), polypyrrole (PPy), polyazulene, polyfluorene, polythiophene, polyterthiophene, and polyaniminonaphthalenes, for use in both fundamental research and industrial applications [11,12]. Since Heeger, MacDiarmid, and Shirakawa were jointly awarded with the Nobel Prize in Chemistry in 2000 for their pioneering work on CPs, CPs have received much attention from both academic and industrial communities. CPs generally exhibit semi-conductivity in their pristine state but can be made more conductive by doping. The term “doping” means that the oxidation and reduction of a \( \pi \)-conjugated system generates \( p \)- and \( n \)-doped CPs, respectively, and doping can be controlled by chemical and electrochemical methods. The oxidized or reduced states of CPs can exist as cation radical, dication, anion radical, or dianion species [6,9]. CPs are semiconductive in nature and have low conductivity. Thus, it is important to increase their conductivity, especially for use in electrochemical applications. To overcome this drawback of CPs, composites of CPs have been intensively studied so that they can be applied in various fields.

2. Electrochemical properties of conducting polymers

Unlike conventional organic polymers, CPs have a high electron affinity and redox activity. The general physical properties of CPs depend on the size and length of the CPs, and they are also described in terms of molecular weight [13]. The chemical properties of polymers mainly depend on the polymer chains, and they are insoluble in aqueous solution. CPs are usually prepared by oxidizing the monomer using oxidizing agents or applying potential or current via electrodes [6,12,14,15]. The original mechanism of PPy formation, first suggested by Diaz et al. in 1981 [16], propagated the polymerization by continuously growing chains via side-to-side coupling of monomeric radical cations into oligomer radicals. As an example shown in Fig. 1, electrochemical growth of PANI involves an initial formation of oligomers, followed by nucleation and polymer chain growth [14]. The doping of CPs can be done electrochemically, which means that the oxidation of CPs generates a \( p \)-doped state and reduction of CPs generates an \( n \)-doped state. The conductivity of the CPs can also be controlled by these redox reactions. Electrochemical preparation methods can control the properties, morphology, conductivity, and thickness of the polymers [2,12,17]. The structures of the different CPs are presented in Fig. 2. In the early stages of this field, the electrochemistry of CPs was intensively studied by Park's and Shim's groups, who investigated the autocatalytic growth mechanism of PANI and its growth kinetics on the electrode surface [14,15,18–21]. In addition, the degradation mechanisms of electrochemically prepared PANI, PPy, and polythiophene were also investigated [22,23]. During the past decades, a number of reports have described applications of CPs. Both monomers and CPs can be functionalized with different materials to tailor their properties. The addition of substrates not only improves functions but also improves the chemical and physical properties of the main polymer chain, including increasing its electrical and mechanical properties. To improve the properties of CPs, CP composites may be prepared from highly conductive nanomaterials and catalysts.
2.1. Composite materials

Carbon-based materials, such as carbon nanotubes (CNTs), graphene, carbon dots, and porous carbon are considered to be promising materials in several applications [24–27]. The rapid development of carbon materials occurred because of their excellent conductivity, high chemical stability, mechanical strength, and large surface area [28,29]. All of these properties can be utilized to develop new types of electrochemical sensors. Using carbon materials alone has a significant drawback, especially when used in sensor devices: they lack selectivity for target molecules. Formation of carbon composites and functionalization is therefore vital for use in specific applications. Their use in electrochemical sensors specifically requires selectivity, and making composites with CPs is a most promising way to improve their performance. Carbon materials are used in composites because they can be treated as inorganic or organic reagents, depending on their inherent carbon structure. Otherwise, metal or metal oxide nanoparticles (NPs), such as Au, Pt, Pd, Ni, Cu, TiO$_2$, MnO$_2$, ZnO, and Fe$_3$O$_4$, are another class of materials [30] that exhibit unique properties compared to their bulk counterparts. NPs have been exploited in many fields, including their use in biomedical research, optoelectronics, catalysis, sustainable energy, and electrochemical devices. In particular, use of metal/metal oxide NPs as electrode materials results in high performance relative to bulk metal electrodes [31,32]. For example, AuNPs display excellent activity and have been a base material for electrochemical sensing electrodes [33–35]. A number of approaches have been used to synthesize NPs, including wet chemical synthesis, monolayer formation, dendrimer-mediated assembly, electrochemical deposition and many more [30,36]. Metal NPs possess high activity and high biocompatible surface area and can be functionalized with secondary materials, including carbon materials, enzymes, and CPs. The preparation of composites of CPs and metal NPs has been reported [37]. Compositing CPs and metal NPs can prevent agglomeration and restacking of metal NPs by steric hindrance and electrostatic interactions. Moreover, in electrochemical devices, these composites can increase the electron transport rates between the electrolyte and current collectors or electrode materials. In the field of bioanalytical chemistry, biologically active materials, mainly enzymes, DNA, proteins, antibodies, and antigens, have played important roles. Wang's group reviewed that many enzymatic reactions are involved in a large number of biosensor devices [38]. For these biomolecules to be applied, they must be attached to or functionalized with a matrix that is chemically inert and does not change the properties of biomolecules. Use of a polymer matrix as the host material for the incorporation of biomolecules is a promising pathway.
2.2. Conducting polymer composites

The unique properties originating in CP-carbon composites make them promising candidates, particularly in electrochemical devices [39–41]. Several methods to synthesize new CP composite materials have been reported and involve using template-oriented synthesis, vapor polymerization, chemical functionalization, in situ generation of CP composites, etc. Beside these methods, electrochemical techniques provide a convenient approach to fabricate CP composites, and they can easily control the morphology, thickness, chemical state, and conductivity of the composites. Different types of materials and composites are presented in Fig. 2. Composites of CPs utilize CPs as a primary component and at least one secondary component, which may be an organic, inorganic or biological species. These materials include metal ions, NPs, nanostructures of metal and metal oxides, carbon materials, molecular species, i.e., metallophthalocyanines, and biologically active components such as enzymes, proteins, antibodies, and antigens. The goal of preparing a new composite material is to observe new distinct properties that are not observed in its individual components [42–45]. Thus, using a synergetic strategy to generate composite materials is vital. CP nanocomposites demonstrate interfacial adhesion between CPs and the secondary component, and the composition ratio will affect the properties of the nanocomposites. Composites of CPs displayed enhanced properties compared to the mere CPs [46]. These composites exhibit outstanding performance in energy storage [47], as catalysts [48], in fuel cells, and in biomedical [49–53] and many more applications [54]. During the past few decades, CP composites have been used in the fabrication of biosensors [52,55–58]. CPs are a promising base material that is suitable for the incorporation and functionalization of biomolecules [59].

The most common immobilization methods are electrochemical entrapment and physical adsorption within the CPs and attachment to the CPs by affinity reactions or covalent bonds. Physical adsorption involves electrostatic interactions between the CPs and biomolecules because the CPs and biomolecules have distinct surface charge properties based on their functional groups. However, other interactions, such as hydrophobic and van der Waals forces, are also involved in the physical adsorption process, especially in the adsorption of antibodies and proteins [60]. The adsorption process was studied in biosensors by using glucose oxidase on PPy [61]. The main advantage of the adsorption technique is that it does not require functionalized monomers. However, because of relatively weak forces involved in the adsorption of biomolecules, the biomolecules may leak out from the interface of the electrode during long experiments [62]. The entrapment of enzymes by electrochemical techniques was later proposed to increase the binding efficiency of the biomolecules; an example, glucose oxidase was entrapped in PPy films via an electropolymerization process to obtain a matrix of glucose oxidase and PPy [63,64]. This method, compared to the physical adsorption process, resulted in a direct and prolonged immobilization. However, the enzymes or biomolecules were partially exposed and buried within the polymer films, which may have resulted in less efficient target accessibility. The main drawback of this process is that it is more suitable for only water-soluble monomers and is not useful for monomers that are soluble in non-aqueous solvents. Thus, strongly attaching enzymes on CPs via covalent bonding were proposed. This approach commonly uses N-hydroxysuccinimide/1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide (NHS/EDC) chemistry to couple carboxylic acids (–COOH) to amine (–NH2) groups. Most importantly, the coupling reaction can be performed in aqueous solutions, which can preserve biomolecules [65]. These types of sensors displayed excellent stability during long measurements due to the covalent attachment of the enzymes or proteins on the stable electrode surface [66–68]. During the past few decades, CPs and their composites have been used in the fabrication of biosensors [52,56,58,69]. In addition, covalent functionalization of CPs with biomolecules has been used to study drug delivery and bioimaging applications [70–74].

3. Application to electrochemical sensors

3.1. Electrochemical sensors

Electrochemical sensors convert chemical reactions of the target species on electrodes into electrical signals that exhibit changes in current, potential, and conductivity [75]. These sensors can be divided into voltammetric/amperometric, potentiometric, and impedimetric sensors as illustrated by Wang, who has greatly contributed to the field of electrochemical sensors and biosensors [76,77]. Electrochemical methods offer very low detection limits, high selectivity, and require only a very small volume of sample to obtain the signals. Measurements of turbid samples of whole blood, fat globules, red blood cells, and hemoglobin are possible using electrochemical techniques, whereas spectrophotometric measurements of these systems usually present interference effects [78,79]. Electrochemical devices consist of a system of either two or three electrodes. A typical three-electrode cell consists of a working electrode that is made of platinum, gold, and/or carbon; a reference electrode that is usually a silver–silver chloride electrode (Ag/AgCl); and a platinum wire or foil is used as a counter/auxiliary electrode. The working principle of a voltammetric sensor is to measure the current while applying a potential to the working electrode relative to a reference electrode. The response current is the result of the electrochemical reaction that occurs at the electrode surface and the electrode/electrolyte interface layer. The electrochemical reaction is limited by the rate of mass transport of the species to the electrode [80]. Voltammetric methods include linear sweep voltammetry, cyclic voltammetry, hydrodynamic voltammetry, differential pulse voltammetry, square-wave voltammetry, polarography, and stripping voltammetry. These techniques have a wide range of applications, a broad dynamic range and a low detection limit. In amperometry, a constant potential is applied to the working electrode and the resulting current is measured with respect to time. The difference between amperometry and voltammetry is that amperometry lacks a potential sweep, instead using a potential step. The resulting current at a given potential is proportional to the concentration of the electroactive species in the sample, and the current is given by Cottrell’s equation. Amperometric sensors have more sensitive and selectivity because the oxidation or reduction potential used for detection is characteristic of the analyte species [81,82]. Potentiometric sensors measure the potential difference between the working electrode and the reference electrode when no significant current is flowing [80]. The measured potential is mainly used to determine ion activity in an electrochemical cell. In potentiometric measurements, the potential difference can be calculated by using the Nernst equation, where \( E_{cell} \) signifies the observed cell potential at zero current. This value is also referred to as the electromotive force, or EMF. The lowest detection limits of potentiometric devices are currently often realized with ion-selective electrodes (ISE) [77,83]. The impedance of a generic electrical component is calculated by dividing the AC potential by the AC current in electrochemical impedance spectroscopy, i.e., dividing an incremental change in voltage by the resulting change in current. The experimental approach is to perturb the cell with a small-magnitude alternating potential and to observe the way in which the system reacts to the perturbation in the steady state. Impedance sensors can be divided into two types, depending on the presence or absence of specific recognition elements. The function of the first type of this sensor is based on an...
impedance change caused by the binding of targets to receptors (antibodies and nucleic acids) that have been immobilized onto the electrode; the other type of sensor's response is based on surface changes caused by adsorption and desorption of target species as a result of growth [78]. The discussion on the construction of electrochemical sensors in this review will be limited to CPs and CP composites.

3.2. Polyaniline and composite sensors

PANI has emerged as one of the most promising CP materials in many applications. Composites of the polymer were used in the fabrication of many devices for different applications including batteries, biofuel cells, and thermoelectric and energy storage devices [84–89]. In addition, a chemical sensor for the detection of dissolved oxygen was reported based on the PANI-modified electrode [90]. The most promising application of these composites, however, was found in electrochemical applications. In particular, the fabrication of electrochemical sensors based on PANI and PANI composites has become a popular approach in many electroanalytical studies and offers high sensitivity and selectivity to detect target molecules. The detection of glucose was reported using composites of PANI and NiCo2O4 NPs. This non-enzymatic glucose sensor exhibited high electrocatalytic performance in glucose analysis. The catalytic active sites in NiCo2O4 with conductive PANI played a synergetic role in the oxidation of glucose and exhibited good sensitivity and a lower detection limit [91]. A selective dopamine sensor was developed by the electrochemical deposition of poly(3,4-ethylenedioxythiophene)-graphene oxide (PEDOT-GO) nanocomposite followed by electrochemical reduction of nanocomposite [92]. As shown in Fig. 3a, a dual polymer system of catalytic molecularly imprinted polymers on a PANI layer was used as a recognition layer for the electrochemical detection of catechol [93]. Despite the unique properties of PANI composites, there are some limitations to their use in biosensors under physiological conditions. For example, PANI is inactive at neutral pH. Composites of PANI with metal NPs and carbon materials were developed that showed remarkable electrochemical activity in many applications. For example, recently, highly sensitive glucose sensor was developed based on a composite PtNP/PANI hydrogel electrode. The nanostructured PtNPs and the PANI aerogel on which they sit have a synergetic effect between them that results in the immobilization of a high density of GOx, which aids efficient oxidation of glucose. This sensor probe showed high sensi-

Fig. 3. (a) Schematic of the MIP-conducting polymer hybrid electrode imprinted with catechol. Adapted with permission from Ref. [90]. Copyright 2009 American Chemical Society. (b) Schematic of the PtNPs and enzymes-loaded 3D porous PANI hydrogel hydride electrode. Adapted with permission from Ref. [91]. Copyright 2013 American Chemical Society.
tivity and a very fast amperometric response for glucose detection [94]. As shown in Fig. 3b, a similar PtNP/PANI hydrogel-based electrode was used to detect human metabolites, and the performance of the sensor probe was excellent [95]. Recently, an impedimetric immunosensor based on a AuNP-functionalized PANI and multiwalled carbon nanotube (MWCNT) composite electrode for 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide detection was developed [96]. The sensor probe was prepared by electropolymerization of aniline and 3-aminobenzoic acid in the presence of AuNPs onto a MWCNT-coated screen-printed electrode. An antibody was covalently attached to the sensor probe to improve the sensitivity of antigen detection. The developed impedimetric sensor showed a wide linearity range, high stability, and a detection limit of 0.3 ppb 2,4-D. Molybdenum disulfide (MoS2) is a layered transition metal dichalcogenide in which the metal Mo layers are sandwiched between two sulfur layers and stacked together by weak van der Waals interactions. MoS2 constitutes a graphene-like nanomaterial; however, the limitation of MoS2 is its low electronic conductivity. MoS2 was combined with PANI via the facile oxidation of aniline monomers on the MoS2 matrix. This composite material served as an excellent conductive skeleton with a high electrocatalytic surface area, and it also supported a direct path for electron transfer. The hybrid PANI-MoS2 material exhibited a superior electrochemical performance to pure PANI and MoS2; hence, this material was used for the electrochemical detection of DNA molecules [97]. Metal electrodes are very stable and can be used in many electrochemical applications; however, in biological applications, the metallic surfaces may cause undesirable poisoning effects as well as nonspecific catalysis. In the fabrication of biosensors, one of the major issues faced by researchers is the fouling of electrode surfaces. To overcome this obstacle, polyethylene glycol (PEG) was grafted onto PANI nanofibers [98]. This composite material was conductive and possessed a large surface area, while showing excellent antifouling activity in single protein solutions and complex human serum samples. The antifouling effect was attained by making the surface hydrophilic, thereby avoiding interactions with nonspecific proteins in the complex biological samples. The researchers used this composite to fabricate an electrochemical biosensor to detect the breast cancer susceptibility gene BRCA1. Furthermore, gene sensing is a very powerful tool for the diagnosis of a wide variety of diseases, from common viral infections to cardiovascular diseases and cancer. For the purpose of detecting nucleic acids in biological samples, many CP composites were prepared in lieu of metal or metal-oxide electrode materials. For instance, a new method was developed for the sensitive detection of nucleic acids using a surface with PANI deposited upon it [99]. In this case, the polymer was deposited by enzyme-catalyzed formation and template-guided deposition in which a reporter enzyme catalyzed the deposition of PANI onto the analyzed nucleic acid molecules by forming an intramolecular complex. The optical and electrical properties of the polymers thus formed are altered after the interaction with the nucleic acids and can be quantitatively measured. One of the more recent projects on this topic involves the use of graphene-based PANI arrays for the electrochemical detection of DNA, which focuses on improving the sensitivity of detection by controlling the texture of the substrate [100].

3.3. Poly(diaminonaphthalene) and composite sensors

One of the earliest preparations of poly(2,3-diaminonaphthalene) (DAN) and poly(1,8-DAN) through electrooxidative polymerization was reported in 1989 [101]. The polymer films were formed by potential-sweep electrolysis in electrolytic solutions. Following that, the preparation of 1-amminonaphthalene polymer from its monomers by using a chemical oxidative polymerization was reported in 1993 [102]. They synthesized the polymers in high yields using H2O2 in the presence of a Fe catalyst. One of the early reports of the use of aminonaphthalene polymers for the electroreduction of oxygen was published in 1991 [103]. The authors formed a film of poly(2,3-DAN) on the electrode surface and used it for electrochemical catalysis. In 2002, a copper complex of poly(1,5-DAN) was formed and, in combination with poly(terthiophene carboxylic acid), this complex was used for the electrochemical reduction of oxygen [104]. Similar to this result, poly(1,8-DAN) and a cobalt complex on poly(1,8-DAN)-coated electrodes were also used for the electrochemical reduction of oxygen [105]. In 2000, a humidity sensor was developed by using poly(1,5-DAN) [106]. Since polymers such as PANI and PPV have relatively high conductivities in air, it is difficult to detect a change in humidity by measuring conductivity changes. Poly(1,5-DAN), on the other hand, exhibits electrical resistance that is proportional to the amount of absorbed water; it was therefore used in combination with doped carbon in the fabrication of a humidity sensor. The doped carbon contributed better sensing ability and higher stability to the polymer film. Apart from being used as a sensing material, poly(1,5-DAN) has also been used in many different applications. Selenium (Se) is an important antioxidant that is found in trace amounts in the human body; however, higher concentrations are toxic to humans as well as other organisms, and its detection is thus important. A strategy to detect Se(IV) ions by using poly(1,8-DAN)-modified gold electrodes was developed [107]. Se(IV) specifically interacts with aromatic o-diamines to form derivatives of piaselenole. Dopamine is one of the most important neurotransmitters; being electrochemically active opens opportunities for its easy detection and thereby the diagnosis of many related diseases. In this regard, aminonaphthalene composites have been used as electrode materials to enhance the electrode’s detection ability. In 2009, poly(1,5-DAN) was combined with Cibacron blue to form a composite film that acts as electrode material for the selective detection of dopamine [108]. The sulfonate groups in the composite film help repel negatively charged interfering species, thus facilitating the specific detection of dopamine. Shim et al. entrapped reactive blue 4 dye in poly(1,5-DAN) to form a composite film layer on an electrode surface for the simultaneous detection of dopamine and acetaminophen [109]. To further this methodology, in 2015, Mir et al. combined poly(1,5-DAN) with GO to form a composite layer on AuNPs that had been electrochemically deposited on a carbon electrode surface. This electrode surface attained a high signal enhancement and showed the lowest detection limit for dopamine (5 nM) [110]. In addition to neurotransmitters, the DAN polymer has also been used as an electrode material in the detection of glucose, H2O2, and other environmentally and biologically important molecules. For example, in 2010, HRP was immobilized on poly(1,8-DAN) on a gold NP-modified electrode to detect H2O2 [111]. To simultaneously detect glucose, ascorbic acid, and dopamine, poly(1,5-DAN) with incorporated nickel NPs was prepared [112]. The polymer matrix showed a strong electronic interaction with the metallic NPs, which resulted in enhanced conductive properties in the polymer film. To enhance the sensitivity of the sensing surface, Tamburri et al. grew a polymer film of poly(1,8-DAN) on platinum plates in the presence of single-walled nanotubes to form a composite layer [113]. A series of films were prepared by using untreated and KOH-, HNO3-, and HNO3/H2SO4–treated nanotubes. The charge transport in the composite films was strongly enhanced by the insertion of nanotubes. The current density was enhanced as much as 140 times greater than that of the pure poly(1,8-DAN) films, indicating a possibility for significant signal amplification. To further this improvement, in 2012, poly(1,5-DAN) was functionalized with MWCNTs and then used to form a composite film on an electrode surface [114]. The composite film, in comparison with the polymer surface, showed an enhanced signal and analyte peaks that were
more clearly separated in the voltammetric response. This material was then used for the simultaneous detection of ascorbic acid and uric acid, as well as the electrochemical detection of \( \text{H}_2\text{O}_2 \) when horseradish peroxidase was immobilized.

### 3.4. Polypyrrole and composite sensors

PPy is one of the most promising CPs and is formed by chemical or electrochemical polymerization of pyrrole. Diaz et al. first proposed the polymerization mechanism of PPy [1]. Then, numerous studies were performed in which polymer-coated electrodes were investigated. PPy and its composites with metal and metal oxide NPs, MWCNTs, graphene, enzymes, and electron-transfer mediators have been studied as electrochemical electrode materials, particularly for electrochemical biosensor applications. Due to the beneficial and unique chemical, physical, and electronic properties of PPy, this polymer has been used in electrochemical sensing materials. Wang et al. reported a new protocol for the electrochemical detection of nucleic acids using PPy coated electrode in flow injection analysis [115]. AuNP-PPy/Prussian blue nanocomposite sensor was reportedly used for the detection of \( \text{H}_2\text{O}_2 \). The composite was prepared by the autopolymerization of pyrrole into PPy and the simultaneous reduction of \( \text{AuCl}^+ \) to elemental Au; at the same time, Prussian blue was produced with the elemental Au and served as a catalyst. This \( \text{H}_2\text{O}_2 \) sensor probe exhibited high sensitivity, fast responses, and a good stability, which resulted from the PPy, and achieved a detection limit of \( 8.3 \times 10^{-10} \text{M} \) [116]. Electrochemical copolymerization of PPy on mesoporous Pt using a boron-doped diamond electrode for the sensitive and selective detection of \( \text{H}_2\text{O}_2 \) was developed. Synergic effects between the MPPt and the PPy copolymers exhibited a selective, and accurate quantitation of \( \text{H}_2\text{O}_2 \). This high sensitivity may have originated from the mesoporous nature of the PtNPs [117]. Another researcher also developed a glucose sensor based on electrochemically deposited AuNPs that were covered by PPy [118]. A DNA sensor was developed using a PPy-AuNP composite electrode in which AuNPs were electrodeposited on a PPy layer to generate nanocomposite films and increase the conductivity of the electrode. The DNA detection was performed by immobilizing the capture DNA strand on the AuNPs, and the hybridization assay was performed by exposing the modified electrode to the target and then the HRP-modified probe strand. A measurable current was obtained from the reduction of benzoquinone, which was observed during the hydroquinone reduction that mediates electron transfer to the HRP-labeled probe strand. This study demonstrated the detection of DNA concentrations at the pM level [119]. The fabrication of electrochemical biosensors based on graphene-PPy composites has become a promising approach in electroanalytical research aiming for various analytical targets and using different strategies. Recently, a combination of graphene and overoxidized PPy composites was reported to simultaneously detect adenine and guanine. The sensor probe was prepared by the electropolymerization of PPy and GO together by using a potential cycling method that was followed by the electrochemical reduction of GO. The obtained PPy-graphene was then oxidized at +1.8 V, resulting in an oxidized surface of a PPy-graphene (PPyoxy-gra) composite layer. The oxidized form of PPy is permeable to cationic species and repels anionic and neutral species, which helps to avoid interference and confers selectivity to the sensor probe. The PPyox-gra sensor probe was used to quantify adenine and guanine and reached low-detection limits of 0.02 and 0.01 \( \mu \text{M} \), respectively [120]. Mao et al. developed a sensor probe that used a PPy-GO composite with poly(ionic liquids) (PILs). PILs/PPy/GO nanosheets containing sensor probes displayed a steady and sensitive detection of dopamine in the presence of ascorbic acid. The presence of PILs on the sensor probe played a key role in separating the oxidation peaks of the DA and AA [121].

Tiwari et al. developed a genosensor by using a combination of AuNP, graphene, and PPy materials. At first, GO-AuNP was prepared by a one-pot solution method and coated on an indium tin oxide (ITO) electrode. PPy was then electropolymerized on the GO-AuNP layer. The authors observed that the changes in the PPy morphology increased with the scan rate. This sensor probe used methylene blue (MB) as a redox indicator to monitor the electrochemical signals, and this probe shows a response time of 60 s and high sensitivity (\( 1 \times 10^{-15} \text{M} \)) [122]. In the development of enzymatic biosensors, immobilization of enzymes on polymer films is vital. There are many ways to achieve the immobilization of enzymes: adsorption, entrapment, covalent binding, etc. Among these methods, covalent bonding is the most promising because of the covalent attachment between the polymer film and the enzymes [123]. This method was successfully adopted to develop glucose, aptamer, DNA sensors, and direct electron-transfer process of cytochrome c and other proteins for use in biosensor applications. An enzymatic glucose sensor was prepared using PPy nanowires GOx that was covalently attached to PPyCOOH/PPy composite nanowires. This sensor probe showed not only high sensitivity with a wide linear dynamic range and a low detection limit but also exhibited high stability and a specificity for glucose [124]. Another glucose sensor was built by using a biocompatible chitosan–GOx complex immobilized on a PPy/Nafion/MWCNT nanocomposite electrode. The chitosan-glucose oxidase was encapsulated inside a nanohybrid PPy/Nafion/MWCNT film. The high surface area of the nanohybrid films enhances GOx loading on the electrode surface, which gives the sensor probe high sensitivity and the ability to detect 5 \( \mu \text{M} \) glucose [125]. The authors found that the presence of NaF on the composite enhanced the dispersion of the MWCNTs and increased the stability of the electrode. Another sensor probe, based on a ZnO-PPy composite, was developed for the analysis of xanthine. The xanthine oxidase enzyme, immobilized on a ZnO-PPy composite electrode surface, showed good electrocatalytic activity for the oxidation of xanthine [126]. Shim et al. synthesized a \([2,5-di-(2-thienyl)-1H-pyrrole-1-(p-benzoic acid)](\text{DPB})\) monomer to use in the development of an aptamer sensor for the detection of kanamycin. DPB monomers were self-assembled with AuNPs before electropolymerization on the electrode surface. An aptamer was immobilized on the electrode via covalent bond formation between the –NH\(_2\) groups of the aptamer and the –COOH groups of the poly-DPB. The sensor response exhibited a pair of redox peaks at approximately 0.26 and 0.08 V (vs. Ag/AgCl) when kanamycin was captured by the aptamer-immobilized probe. The sensor showed good selectivity for kanamycin, good long-term stability (up to two months), and a detection limit of \( 9.4 \pm 0.4 \text{nM} \) [127]. Wang et al. developed a neural microelectrode array by using direct electrodeposition of a PPy-gra (PG) nanocomposite and used it to detect dopamine secretion from pheochromocytoma cells. The PG composites that had been deposited on the neural microelectrode array displayed excellent selectivity for dopamine in the presence of ascorbic acid. The authors claim that the electrocatalytic graphene structure, being highly negatively charged, is effective in attracting DA cations to the surface of PG nanocomposites and rejecting AA anions [128]. The amperometric results also suggest that ascorbic acid does not greatly interfere with the detection of dopamine. The sensor probe was used to detect dopamine, which was released from the PC12 by stimulation with K\(^+\) ions. Mndek et al. developed a DNA sensor by using a MWCNT-PPy composite that had been functionalized with a redox PAMAM dendrimer. The nanomaterial has been demonstrated as a molecular transducer in the electrochemical detection of DNA. As shown in Fig. 4, the MWCNT-PPy nanocomposite was formed by electropolymerization of pyrrole on MWCNTs, and the covalent attachment of PAMAM was performed by an electrooxidation method. Ferrocenyl groups were then attached, and an electrochemical signal from ferrocene was
used to detect DNA hybridization. The sensor probe could sense the DNA of the rpoB gene of Mycobacterium tuberculosis in real PCR samples [129]. Another aptasensor using a PPy-PAMAM dendrimer composite was developed to directly detect ochratoxin A (OTA). The aptasensor had a detection limit of 2 ng L⁻¹ OTA, which is below the OTA concentration that is allowed in food by European regulations [130]. In addition, a PPy composite was used to develop an aptasensor to detect prostate cancer biomarkers. The antifouling effect is one of the key characteristics of these types of sensors. Jolly et al. developed a sensor probe that has enhanced antifouling properties by using a PPy-PEG composite electrode. The sensor probe was constructed by attaching PPy-PEG on a gold electrode surface and covalently attaching a N₈,N₈-bis(carboxymethyl)-l-lysine hydrate (ANTA) molecule that was associated with a Cu²⁺ ion complex. The enhanced electrochemical properties of the PPy-PEG-ANTA/Cu²⁺ sensor probe originated from PPy and the redox-active copper complex. Polyhistidine-modified aptamers were immobilized by the Cu²⁺ redox complex onto the PPy-PEG adduct. The variation in the copper redox signal when α-methylacyl-CoA racemase (AMACR; P504S) was detected was monitored by square wave voltammetry (SWV). The sensor probe, composed of hybrid materials, displayed enhanced antifouling properties and detected AMACR at the femtomolar level (0.15 fM) [131]. A biotin-doped PPy dual responsive immune sensor was developed by combined calorimetric recognition and an electrochemical response to effect the ultrasensitive detection of multiple tumor markers. The nanorough surface of the PPy immune sensor, combined with multiple HRP-labeled and antibody-attached NPs, offers great advantages over smooth surface sensor probes. The sensor probe demonstrated a high level of analytical and clinical performance [132].

3.5. Polythiophene and composite sensors

Thiophene-based organic CPs have been known to have commendable conductive properties. Being semiconducting materials themselves, when conjugated with metal NPs, graphene, and carbon materials [133], they show exceptional stability and enhanced conductivity. They can also be modified with specific functional groups that allow them to be chemically attached to transducer molecules in a biosensor, making them a very reliable group of substrate materials [134]. Thiophene-based CP composites have been used in the fabrication of many electrochemical sensors, including those that detect neurotransmitters [139], gases [140], glucose [141, 142], and many other analytes. In the process of attaining high sensitivity and resolution in electrochemical applications, a layer of PPy was sandwiched between two layers of PEDOT, and the surface was coated with AuNPs; the AuNP coating slightly increased the response [143]. This work is one of very few in which different polymer layers have been conjugated together to obtain high sensitivity. To detect analytes in vivo, stability and biocompatibility are as important as sensitivity, and much research has been focused on achieving results in this regard. Fig. 5 shows an example of this approach when a Nafion and PEDOT conjugate was electropolymerized on carbon-fiber microelectrodes [144]. This method resulted in a highly stable and controllable surface for the selective and sensitive detection of dopamine in vivo. A novel human dopamine receptor (hDRD1) was conjugated with a CP nanofiber (NF) to form a multidimensional membrane for
the selective detection of dopamine [145]. To accomplish this feat, multidimensional carboxylated PEDOT (MCPEDOT) NFs with nanorods were used as a transistor in a liquid-ion-gated field-effect transistor-based biosensor. *E. coli* cells that expressed hORD1 were immobilized on MCPEDOT-NFs. The final membrane exhibited a rapid, real-time response within 2 s and a high sensitivity of 100 fM. Polythiophene materials have been proven to be one of the best surfaces for the stable immobilization of antibody molecules in a sensor. Thiophene-based immunosensors are in development for the detection of various diseases. The carboxylic acid–containing CP precursors were self-assembled on the surfaces of AuNPs, and the functional groups on the polymer precursor were used as a platform for the construction of a biocomposite to selectively and detect human, non-small-cell lung cancer [146]. A polymer composite with GO was formed, and the GO was then reduced to form a more conductive surface with a high surface area [147]. During this process, the AuNPs simultaneously formed on the material by NaBH₄ reduction. This process resulted in a highly conducting surface, the polythiophene made the electrode very stable, and functional groups for the immobilization of the antibodies enabled the sensitive detection of carcinoembryonic antigen (CEA). To achieve a more selective sensor surface, hyaluronic acid was doped on to PEDOT [148]. This material has a highly porous structure, is strongly hydrophobic, and has a large number of carboxylic acid functional groups. These functional groups were very useful in immobilizing CEA antibodies to form a highly sensitive, specifically binding sensor surface whose detection limit was 0.3 pg/mL. The commercially available PEDOT:PSS was electrosprun into nanofibers and eventually formed into conducting paper [149]. This conducting paper-based biosensor was demonstrated to sense CEA as an alternative for the conventional indium tin oxide, gold and glassy carbon electrodes.

Many different combinations of materials with the thiophene-based polymers have been examined to be used as glucose biosensors. For instance, immobilized GOx on a polymerized, newly synthesized thiophene conducting monomer to achieve robust covalent binding between the biomolecule and the immobilization platform. The amine groups of the enzyme and the aldehyde groups of the polymer (which had been functionalized on the newly synthesized monomer) bound each other with the help of glutaraldehyde. This conjugation between the polymer-coated graphite electrode and the GOx enzyme resulted in a sensor with a low-detection limit of 2.29 μM for glucose molecules [150]. On the other hand, PEDOT:PSS and poly(vinyl alcohol) were combined to make a conducting matrix and use it as a substrate for the immobilization of FAD-GDH. This conjugated material resulted in high enzymatic activity [151]. Three-dimensional nanoporous PEDOT was electrochemically prepared using a hard-template method [152]. Since the nanostructure possessed a large surface area and is highly stable and conductive, the CuNPs were electrodeposited deeper into the PEDOT nanostructure. The prepared porous CuNP/PEDOT nanocomposite was excellent at electrocatalyzing the oxidation of glucose, owing to its unique structure in which the electrodeposited CuNPs provided many active sites for the oxidation of glucose and the 3D porous structure can facilitate the diffusion of glucose molecules and accelerate electron transfer. *In vivo* examination of glucose has proven to be a more reliable and accurate assessment of diabetes than *in vitro* analysis of patient blood samples. Since CPs are non-toxic organic molecules, many of the polythiophene conjugates are used in the *in vivo* devices. One such approach was taken in 2014: glucose-specific enzymes were immobilized on a PEDOT CP on the microneedle ‘Smart Patch’ sensor platform for painless and continuous intradermal sensing [153]. Apart from being abnormally controlled in diabetes, glucose and its extracellular metabolism can also be indicative of many brain-related disorders, including the formation of tumors in the brain. As shown in Fig. 6, to monitor changes in the extracellular concentration of glucose in the brain, Yang et al. composed PEDOT nanofibers with GOx and electrodeposited them on electrosprun poly(L-lactide) on platinum microelectrodes [154].

### 3.6 Polyterthiophene and composite sensors

Terthiophene polymers are another class of CPs, and their unique properties have allowed them to perform excellently when compared to other CPs. When a terthiophene monomeric unit is functionalized at its 3′-position, rapid polymerization is enabled, made possible by the reduced steric by the lack of a bulky functional group around the polymerization reaction site [155]. An early study of the electrochemical applications of terthiophene polymers was made by Shim et al. In particular, their application was to develop electrochemical biosensors, chemical sensors, and electrocatalytic composite materials [156–160]. For example, Shim et al. developed a portable DNA sensor by electropolymerizing 5,2:5,2-terthiophene-3-carboxylic acid (TTC) monomers on a GC electrode and utilizing it to directly detect DNA hybridization.

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**Fig. 5.** Biocompatible PEDOT:Nafion composite electrode for selective detection of neurotransmitters. Adapted with permission from Ref. [141]. Copyright 2015 American Chemical Society.
Fig. 6. Schematic of fabrication process of GOx-incorporated PEDOT on a microelectrode array: (a) Pt microelectrode array. (b, c) Electrodeposition of GOx-incorporated PEDOT film (PEDOT F-GOx). (c) Electrospinning of PLLA nanofibers on the microelectrode array. (d, f) Electrodeposition of PEDOT around the PLLA nanofibers to form GOx-incorporated PEDOT nanofibers (PEDOT NF-GOx). (g) Schematic of GOx entrapment within the PEDOT structure; corresponding microscope images (h–m). Copyright 2014 Wiley. Used with permission from [151].

Fig. 7. Schematic representation of the immunosensor construction and detection principle.

[161]. A heavy metal ion sensor was fabricated using composites of 3,4-diamino-2,2:5,2-terthiophene (DATT) polymer and EDTA in the presence of a catalyst. Carboxylic acid groups of EDTA were covalently immobilized on the amine-functionalized poly-DATT layer, resulting in a stable and reusable electrode surface that could detect various heavy metal ions simultaneously [162]. They were also tested as biomimetic membranes [163] and to detect superoxide in vivo using a microbiosensor [164]. A sensitive electrochemical assay was developed to detect DNA and proteins by covalently functionalizing hydrazine on the surface of poly-TTCA. The detection signal was amplified by a poly-TTCA/dendrimer assembly that was loaded with AuNPs targeting DNA and proteins linked with hydrazine labels [165]. The direct electron transfer of cytochrome c (Cyt c) was also studied on a poly-TTCA layer electrode. Cyt c that had been covalently bonded to a CP layer was used in bioelectronic devices [166]. The applicability of these cyt c-immobilized membranes as biosensors was tested in the determination of nitric oxide (NO) [167] and NADH [168]. Furthermore, a rapid method to detect heavy metal ions was developed and employed a disposable sensor that had been modified with GO-doped DATT. The metal ions could selectively complex with the nitrogen atoms of the DATT ligand, supported by large amount
of negatively charged GO. Compared with square-wave anodic stripping voltammetry (SWASV) method, chronocoulometry (CC) performed better, having a wider dynamic range and faster analysis time (<1 s). Additionally, the proposed method could be efficiently applied to various water samples in a few seconds [169]. A benzoic acid group bearing 2,2′:5′,5′′-terthiophene-3′-benzoic acid (TTBA) was synthesized and used in various biosensors and chemosensors, including those that detected glucose [170], H2O2 [171,172], phthalate esters [173], and cancer cells [174,175] [Fig. 7]. Recently, Au and Ni, as a bimetallic alloy dendrite, were electrodeposited on the polythiophene CP. As illustrated in Fig. 8, this material exhibited improved long-term stability and an increased electrochemically active area, which was used for the sensitive detection of low concentrations of H2O2 released from living cells, as well as for monitoring the electrochemical oxygen reduction reaction from energy conversion [176]. Above all, a novel nanostuctured AuNP-encapsulated CP was developed for the detection of inducible NO synthase (iNOS). The TTBA monomer and AuNPs were self-assembled and then electropolymerized on the GC surface. Then, iNOS antibody was immobilized on the benzoic acid groups of a nanostructured polymer layer via covalent bonding. This immunosensor exhibited high stability and a good performance compared to other commercial methods [34]. Another group synthesized a new functionalized terthiophene monomer, 3′-((2′:2′:5′:2′′-terthiophene)-3′-yl) acrylic acid (TAA), and used it for the analysis of a DNA assay [177]. Additionally, an acrylic acid and methylhydroxy group-functionalized terthiophene monomer was synthesized from the same group, and it was electropolymerized into CPs to act as a label-free DNA sensor [178]. Additionally, the gene-sensing ability of polyTAA was estimated in its oxidized and reduced states with and without a Fe(CN)64+/3− redox probe. The target-specific oligonucleotide sequence was attached to the porous polyTAA surface via covalent bonding and showed a good sensitivity toward its complementary target in its oxidized state with the redox probe [179]. Among these sensors, terthiophene CPs were successfully used to develop glucose sensors. In general, most of glucose sensors are enzymatic sensors and they used enzymes as catalytic materials for the specific oxidation of glucose, which basically hinders the effectiveness of the sensor in two ways. First, the cost of the sensors is considerably expensive because of the necessity of obtaining the pure form of the enzyme for sensor fabrication. Second, the lifetime and the stability of the electrodes are limited. The proteins are only stable for a short period of time and need to be properly maintained to get optimum results. To avoid these disadvantages, many researchers have formulated non-enzymatic sensor surfaces [38,180,181]. One such approach is the formation of molecularly imprinted polymer (MIP) surfaces; in 2017, Kim et al. fabricated a potentiometric non-enzymatic glucose sensor using glucose-imprinted polythiophene surfaces [182]. These surfaces were formed on AuNPs that had been electrodeposited on SPCE, where an MIP containing acrylamide and aminophenyl boronic acid (as a host molecule to glucose) was immobilized on the carboxylic acid-functionalized polythiophene CP. This sensor system’s detection limit was 1.9 × 10−7 M, with excellent selectivity for glucose over other saccharides in finger-prick human blood samples. The thiophene-based CPs have also been proven to be excellent mediators, increasing the stability of electrode surfaces when they are conjugated with the catalytic materials. Recently, a sensitive and selective NO sensor was fabricated using a zinc-dithiooxamide framework derived from porous ZnO NPs and a polyTBA-rGO composite. The sensor probe displayed an outstanding electrocatalytic performance and was applied to the detection of NO, which is released from normal and cancer cell lines. The porous ZnO was immobilized on the polymer-rGO composite layer, which enhanced the surface area and ion-electron transport rate, resulting in efficient catalytic NO reduction [183].

3.7. Others

Even though the conventional polymers and their composites have been extensively used, some of the less-known polymers such as polyazulene, polyindole, and polycarbazole, have also been utilized in different electrochemical sensors. In 2008, a label-free DNA hybridization detection was reported using poly(indole-5-carboxylic acid) conducting polymer. The polymer was formed on the glassy carbon electrode and was used for complimentary, non-complementary, and single nucleotide mismatch detection [184]. In 2016, the ZnO functionalized poly(indole-5-carboxylic acid) nanocomposite was also tested for DNA detection [185]. Similarly, poly(indole-6-carboxylic acid) was also used for the detection of DNA hybridization [186]. The poly(indole-6-carboxylic acid) was doped on to the MWNT to form a nanostructure composite for the label-free femtomolar detection of hepatitis B virus related DNA [187]. Apart from the DNA detection, the indole-5-carboxylic acid was also used to fabricate sensors for monitoring pesticides by conjugating it with iron oxide nanoparticles. The polymer/iron oxide was bioconjugated with acetylcholinesterase on the glassy carbon electrode to obtain sensitive detection of pesticides malathion.

Fig. 8. Preparation of the dealloyed-AuNi@pTBA electrode for H2O2 detection.
and chlorpyrifos [188]. The tetracyanoquinodimethane-conjugated poly(indole-6-carboxylic acid) was used for the selective oxidation of dopamine [189]. For the oxidation of formic acid a gold-composited polyindole was synthesized, where Au clusters were embedded in the cages of polymer flakes to form an interfacial Au-polyindole composite [190].

Along with polyindole, polyaniline and its composites were also studied for different applications. At early stage, electrochemical growth and spectroscopic properties of polyaniline were studied using impedance and in situ spectroelectrochemical techniques at platinum electrodes [191]. Recently, azulene and thiophene acetic copolymer was formed on the electrode surface to fabricate a sensor for the detection of H2O2 [192]. In another report, p-type polyaniline was composited with n-type polybenzimidazobenzenophenanthroline-poly(ethylene oxide) (BBL-PeO) to form a donor–acceptor layer. This composite layer was used for the electrochemical and spectrochemical studies [193]. The polyaniline layer was electropolymerized to obtain a hydrophobic solid-state electrode for the selective identification of potassium ions. Polarization of polyaniline solid contact was implemented as a convenient approach to address the issues of irreproducible standard potential of solid-state potassium ion-selective electrodes [194]. Polyaniline and poly(3-[E]-2-azulene-1yl)vinyl[thiophene were prepared by electrochemical methods in various configurations on to the platinum substrate [195]. Both monolayer- and bilayer-modified electrodes with these materials were analyzed for their electrochemical performance as sensing probe materials for the detection of dopamine and 4-nitrophenol using square wave voltammetry. Some of the other polymers, such as poly-o-phenylenediamine, were conjugated on a single-walled carbon nanotube. The polymer was molecularly imprinted to specifically recognize kanamycin molecules and the electrode was used for its electrochemical detection [196]. Similarly, functional dicarbazole conductive polymer was electrochemically polymerized and characterized for different electrochemical applications [197].

4. Conclusions

We have summarized the preparation, functionalization, and recent advancements in the application of conducting polymer conjugates in the fabrication of biosensors. The published works suggest that among the conducting polymers, conjugates of polyaniline, polypyrrole, and polythiophene show promising characteristics for future applications. Furthermore, the polypenthiophene composites have demonstrated a reasonably high stability and electrical conductivity compared to the other polymer composites. Along with the conventional single polymer systems, many researchers are currently combining two or more polymers with a catalytic nanomaterial to form a highly sensitive conjugated material that generates very sensitive signals when used for any type of sensing application. These nanomaterials with multiple functional groups can provide the most suitable platform for the attachment of different recognition elements. These studies open the way for a new class of materials, in which the unique characteristics of various materials can be combined to form a single multifunctional material.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2015R1A2A1A13027762).

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