DOI: 10.22607/IJACS.2017.S02002

Available online at
www.ijacskros.com

Indian
Journal of Advances in
Chemical Science

Indian Journal of Advances in Chemical Science S2 (2017) 6-9

Conductive Polymers and their Nanohybrid Transducers for Electrochemical Biosensors Applications: A Brief Review

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Received: 12th June 2017; Revised 30th July 2017; Accepted 04th August 2017

ABSTRACT

In the present article, we briefly review the characteristics, synthetic strategies, and notable applications of conducting polymers and their nanohybrids as transducers in electrochemical biosensors. The conducting polymers show unusual electrochemical properties, and they can be directly electrodeposited on the electrode substrate in the form of a thin polymer film which can later be modified with biomolecules. On the other hand, the nanostructured hybrid materials have beneficial advantages such as high surface area and small dimensions. The enlarged surface area enhances the interactions between the electrode materials and analytes, which facilitate adsorption/desorption kinetics for analytes in the materials, which allows a rapid response time and high signal reproducibility. The conducting polymer-based nanohybrids have several synergistic properties between the polymer and the nanomaterials, making them promising candidates for application in sensors as transducers.

Key words: *Conducting polymers, Nanohybrids, Transducers.*

1. INTRODUCTION

Conducting polymers show unusual electrochemical properties such as high electrical conductivity, low ionization potential, high electronic affinities, and optical properties. These properties are only because of their conjugated p-electron backbones. The intrinsic electronic conductivity of conducting polymers ranges from about 10^{-14} to 10^{2} S cm^{-1} [1,2]. Conducting polymers are also known for their ability to be compatible with biological molecules in neutral aqueous solutions, and often, they can be modified to bind biomolecules onto them. Another advantage of conducting polymers is that the electrochemical synthesis allows direct deposition of a polymer film on the electrode substrate which can be followed by biomolecule immobilization [3]. These unique properties of conducting polymers have been exploited in the fabrication of electrochemical sensors and biosensors [3].

A biosensor is a device having a biological sensing element either intimately connected to or integrated within a transducer. The aim is to produce a digital electronic signal which is proportional to the concentration of the analyte. The biological sensing element or receptor (like DNA or enzyme or antibody, etc.) can interact or react with the analyte to produce a biochemical signal. A transducer converts the biochemical signal to a recognizable electronic signal. The transducer of an electrical device responds in a way that a signal can be electronically amplified, stored, and displayed [4].

Conducting polymers themselves are very sensitive to their surrounding environments, which makes them suitable for various sensor transducers. Polymers have traditionally held advantages over metal or inorganic materials, such as easy synthesis and processing, chemical and structural diversity, low weight, and flexibility. Conducting polymers may be the best candidate for fabricating functional organic/inorganic hybrids [5]. The nanostructured materials show unique properties depending on the size and shape. In terms of sensor applications, they have beneficial advantages such as high surface area and small dimensions. The enlarged surface area enhances the interactions between the materials and analytes, which leads to high sensitivity and the small dimensions, facilitate adsorption/desorption kinetics for analytes in the materials, which allows a rapid response time and high signal reproducibility. On the other hand, conducting polymer-based hybrids are expected to have several synergistic properties between the polymer and the inorganic components, making them promising candidates for application in

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sensors as transducers [4,5]. In the present article, we briefly review the characteristics, synthetic strategies, and notable applications of conducting polymers and their nanohybrids as transducers in biosensors.

2. INTRINSIC CONDUCTING POLYMERS AND THEIR ELECTRICAL CHARACTERISTICS

The intrinsic conducting polymers which are extensively employed in electrochemical applications are polyacetylene (PA), poly(thiophene)s (PTh), polyaniline (PANI), polypyrrole (PPy), poly(3, 4-ethylenedioxythiophene) (PEDOT), and poly(phenylene vinylene)s (PPV). The energy band gap and electrical conductivities of these conducting polymers are shown in Table 1.

PA is an organic polymer with the repeating unit $(C_2H_2)n$. The doping of PA enhances the electrical conductivity and yields a broad range of electrical properties, from insulator to metal. The mobility of polarons along the PA chain can be high, and the charge is carried along the chain. However, PA is too unstable to be of any practical value, and its structure comprises the heart of all conjugated conducting polymers [6].

PTh is a linear polyaromatic compound which is insoluble in organic solvents. PTh is an important conducting polymer used to manufacture the environmentally and thermally stable materials and useful in super capacitor, polymer light-emitting diodes, batteries, solar cells, memory devices, and transistors [5].

PANI is a conducting polymer of the semi-flexible rod polymer family, and it is widely used as electrode material in many electrochemical applications. Polymerization of aniline involves oxidation of aniline monomer to form dimeric species which subsequently form oligomers and eventually yielding PANI [3].

PPy is widely studied conducting polymer due to its ease of preparation, superior redox properties, stabilized oxidized form, capacity to give towering conductivity, water soluble, commercially accessible, and valuable electrical and optical properties. The films of this polymer can be achieved by electrochemical polymerization. The conductivity of these films when cycled electrochemically varies from 100 to 200 S cm^{-1} between a conducting state and an insulating state. PPy can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer [7].

PEDOT is a conducting polymer based on 3, 4-ethylenedioxythiophene monomer. PEDOT has low redox potential, very high stability, reasonable band gap, and high optical transparency in thin-film form. It finds applications in organic light-emitting diode displays, solar cells, capacitors, printing wiring panels, transparent electrodes for thick-film electroluminescence, source gate, and drain in the quickly developing organic semiconductors field [5].

PPV is a diamagnetic substance having a structure which is intermediate between that of PA and PPy and has an extremely low electrical conductivity of the order of 10-13 S cm^{-1}. The electrical conductivity enhances on doping with iodine, ferric chloride, alkali metals, or acids but with low stability. In general, unsubstituted unaligned PPV shows reasonable conductivity with doping ranging from 10^{-3} to 100 S cm^{-1}. The oriented PPV is highly crystalline, mechanically strong, and environmentally stable [6].

3. SYNTHETIC ROUTES TO CONDUCTING POLYMER-BASED NANOHYBRIDS

3.1. Electrochemical Synthesis of Conducting Polymers

Electrochemical synthesis is a simple, cost-effective, and reproducible method to produce the films with required thickness and uniformity. The monomers which possess relatively low anodic oxidation potential and susceptible to electrophilic substitution reaction can give conducting polymers by electrochemical techniques [6]. Electrochemical synthesis is performed by applying suitable current or potential in the three-electrode cell using monomers in electrolyte system. The monomers are first electro-oxidized to a cation radical by oxidative coupling which is followed by coupling to form dications. This process is repeated several times leading to the formation of polymer [2,8]. Electrochemical synthesis is rapidly becoming the preferred general method for preparing electrically conducting polymers because the thickness of the film can be controlled by varying either the potential or current with time. Electrochemical polymerization of conducting polymers is generally employed by (i) Constant current or galvanostatic; (ii) constant potential or potentiostatic; and (iii) potential scanning/ cycling or sweeping methods.

3.2. Preparation of Conducting Polymer Nanohybrids

A variety of methods have been used to prepare conducting polymer-based nanohybrids. The main synthesis strategies can be classified into the following four categories:

3.2.1. Impregnation followed by reduction

Conducting polymers containing either nitrogen or sulfur atoms in their repeating unit are attractive candidates for the preparation of metal/polymer hybrids. The functional groups of these polymers such as −COOH, −CN, $-NH_2$, and −SH can interact with the charge on nanomaterials, namely, metal cations through ion-ion or ion-dipole interactions and get impregnated. For example, PPy and PANI have a nitrogen atom in their heterocyclic ring, and PTh and PEDOT have a sulfur atom in their heterocyclic ring.

Thus, Ag, Au, and Pd nanoparticles could be readily deposited on the surface of PANI, PPy, and PEDOT nanostructures without any dispersing or reducing agents [5].

3.2.2. Concurrent redox reactions

The conducting polymers such as PPy, PANI, and PTh can be synthesized by oxidative polymerization using appropriate oxidizing agents. Normally, metal salts (such as copper chloride, ferric chloride, ferric perchlorate, and ferric nitrate) or metal precursors (containing iron, gold, silver, and platinum) can be used as oxidizing agents to achieve the oxidation polymerization of conducting polymer monomers which allow the simultaneous formation of the metal and conducting polymer. Various conducting polymer nanohybrids such as AgCl/PPy/chitosan nanospheres, gold/PANI hollow nanoparticles, gold/PEDOT nanoparticles, platinum/PEDOT nanoparticles, and silver/PPy nanostructures are synthesized by this approach [5].

3.2.3. Electrochemical deposition

The electrochemical deposition involves a subsequent reduction of metal ions deposited from a solution onto an electrically conductive polymer substrate. When conducting polymers are used as substrate, a variety of inorganic compounds can be introduced into the polymers by electrochemical deposition. Electropolymerization of a conducting polymer on an electrode is generally followed by the electrochemical deposition of an inorganic component [6]. The fabrication of CdS-PPy heterojunction nanowires by electrochemical co-deposition in porous alumina template is reported in the literature. First, CdS was deposited into the cylindrical nanopores of the alumina membrane using CdCl2 and element sulfur as precursors in a dimethyl sulfoxide solution at a current density of 2.5 $mA \bullet cm^{-1}$. Subsequently, PPy was deposited in 0.1 M $LiClO_4$ acetonitrile solution by applying a voltage of 0.85 V (vs. SCE). Similarly, CdS-PANI nanowires and gold-PPy heterojunction nanorods have also been synthesized [2].

3.2.4. Seeding approach

The seeding approach is a widely used to produce micro- and nano-particles. The magnetite nanoparticles are first prepared by a chemical precipitation method and then used as nanoseeds for the polymerization of monomers. For example, magnetite (Fe_3O_4)/PEDOT core-shell nanoparticles can be synthesized through a seeding approach. The magnetite nanoseeds are acid-etched, resulting in iron cations that can initiate the surface-confined oxidation polymerization. During this process, the polymerization kinetics affects highly the morphology of the final product at the nanometer regimen [5].

4. APPLICATIONS AS TRANSDUCERS IN BIOSENSORS

Several biosensor applications of conducting polymers and their hybrids as transducers are reported in literature. Kong *et al*. synthesized PTh/SnO_2 nanocomposites by the *in situ* chemical oxidative polymerization and applied it for NOx detection. Using similar fabrication process, PTh/WO_3 nanohybrids were also designed, and it was observed that the hybrids showed higher thermal stability than pure PTh [5].

PANI has attracted much attention due to various remarkable characteristics such as controllable conductivity, charge transfer capability, and environmental stability. This polymer is described as an interesting material for fabrication of biosensors because it can act as an effective mediator for electron transfer in redox or enzymatic reactions. PANI's transport properties, electrical conductivity, or rate of energy migration provide an enhanced sensitivity. PANI films produced by electrochemical polymerization have shown high electrical conductivity and electro-activity which can serve as electrode materials [6]. The electropolymerized PANI films have been used for the fabrication of glucose biosensors. Athawale *et al*. studied PANI and its substituted derivatives as methanol, ethanol, propanol, butanol, and heptanol sensors. The studies also show that the PANI films are more useful in the detection of CO and hydrogen sulfide sensor [6]. Lactate oxidase and lactate dehydrogenase have been co-immobilized on electrochemically prepared PANI films by physical adsorption technique for the fabrication of a lactate biosensor [3]. A biosensor for hypoxanthine detection was developed by entrapment of xanthine oxidase within a PANI film electropolymerized on a sodium montmorillonite-methyl viologen carbon paste modified electrode [7]. Hypoxanthine was linearly detected in the range from 1×10^{-6} M to 4×10^{-4} M (detection limit of 8×10^{-7} M). An amperometric biosensor for detection of phenolic compounds and based on an *in situ* electropolymerized PANI–polyacrylonitrile composite film was also developed. This biosensor allowed to detect catechol in a linear range comprised between 5×10^{-8} M and 7.5×10^{-5} M [3].

PPy presents a relatively stable electrical conductivity and can be electrosynthesized under biocompatible conditions such as low oxidation potential and neutral pH. Galvanostatic immobilization of nitrate reductase with β-NADH within a conducting PPy film was successfully used to design a potentiometric biosensor for nitrate detection. Nitrate was detected in a linear concentration range between 1×10^{-4} M and 5×10^{-3} M (detection limit of 1.5×10^{-5} M) [7]. A novel amperometric biosensor based on horseradish peroxidase/PPy deposited onto the surface of ferrocene carboxylic acid functionalized sol-gel derived composite carbon electrode for the detection of H_2O_2

Table 1: Energy band gap and conductivities of some important conducting polymers [6].

Conducting polymer	Band gap (eV)	Conductivity (S cm^{-1})
PA	1.5	$10\text{-}10^3$
Polythiophene	2.1	$10^2\text{-}1.7\times10^5$
PANI	3.2	30-200
PPy	3.1	$10^2\text{-}7.5\times10^3$
PEDOT	1.1	300
PPV	2.5	$3\text{-}5\times10^3$

PA=Polyacetylene, PTh=Poly(thiophene)s, PANI=Polyaniline, PPy=Polypyrrole, PEDOT=Poly(3, 4-ethylenedioxythiophene), PPV=Poly(phenylene vinylene)s

has been reported. Arslan *et al*. have fabricated a polysiloxane/PPy/tyrosinase electrode by entrapment of tyrosinase in conducting matrix by electrochemical copolymerization for determining the phenolic content of green and black tea. PPy was deposited on a platinum-plated nanoporous alumina substrate which enhanced adsorption of the enzyme-glucose oxidase and provided an increased surface area for the sensing reaction [3].

PEDOT has low band gap, high environmental stability, and high optical transparency in the oxidized, conductive state. An amperometric tyrosinase biosensor based on conducting PEDOT has been reported for the estimation of herbicides and phenolic compounds [3,5]. PEDOT is reportedly incorporated to develop the enzymeless creatinine sensor by potentiometry method, which has exhibited a fast response time, low LOD, and good stability [9]. The cholesterol oxidase was entrapped in PEDOP to develop an amperometric biosensor for cholesterol detection. The responses of the enzyme electrode were measured through monitoring the oxidation current of H_2O_2 at +0.7 V versus Ag/AgCl in the absence of any mediator. The detection limit was 4×10^{-4} M, and the response time was 150 s [7].

5. CONCLUSIONS

The review of existing literature on conducting polymers and their nanohybrids show good conductive properties and provide excellent platforms for the immobilization of biological element. They promote rapid electron transfer between the analyte and electrode and enhanced response time, reproducibility, and sensitivity. Therefore, it is concluded that the conducting polymers and their nanohybrids are very promising candidates for application in sensors as transducers.

6. REFERENCES

1. L. Xia, Z. Wei, M. Wan, (2010) Conducting polymer nanostructures and their application in biosensors, ***Journal of Colloid and Interface Science***, **341:** 1-11.
2. T. Ahuja, I. A. Mir, D. Kumara, D. K. Rajesh, (2007) Biomolecular immobilization on conducting polymers for biosensing applications, ***Biomaterials***, **28:** 791-805.
3. M. A. Rahman, P. Kumar, D. Park, Y. Shim, (2008) Electrochemical sensors based on organic conjugated polymers, ***Sensors***, **8:** 118-141.
4. M. Gerard, A. Chaubey, B. D. Malhotra, (2002) Application of conducting polymers to biosensors, ***Biosensors and Bioelectronics***, **17:** 345-359.
5. S. J. Park, O. Kwon, J. E. Lee, J. Jang, H. Yoon, (2014) Conducting polymer-based nanohybrid transducers: A potential route to high sensitivity and selectivity sensors, ***Sensors***, **14:** 3604-3630.
6. R. Kumar, S. Singh, B. C. Yadav, (2015) Conducting polymers: Synthesis, properties and applications, ***International Advanced Research Journal in Science, Engineering and Technology***, **2(11):** 110-124.
7. A. Sassolas, L. J. Blum, B. D. Leca-Bouvier, (2012) Immobilization strategies to develop enzymatic biosensors, ***Biotechnology Advances***, **30:** 489-511.
8. S. Nambiar, J. T. W. Yeow, (2011) Conductive polymer-based sensors for biomedical applications, ***Biosensors and Bioelectronics***, **26:** 1825-1832.
9. S. Prakash, T. Chakrabarty, A. K. Singh, V. K. Shahi, (2013) Polymer thin films embedded with metal nanoparticles for electrochemical biosensors applications, ***Biosensors and Bioelectronics***, **41:** 43-53.