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Conducting Polymers in Sensor Design

Jadwiga Sołoducho and Joanna Cabaj

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Abstract

Conducting polymers (CPs) as well as conducting polymer nanoparticles seem to be very applicable for the development of various analyte-recognizing elements of sensors and biosensors. This chapter reviews mainly fabrication methods as well as application of conducting polymers in sensors. Conducting polymers (CPs) have been applied in the design of catalytic and affinity biosensors as immobilization matrixes, signal transduction systems, and even analyte-recognizing components. Various types of conducting and electrochemically generated polymer-based electrochemical sensors were developed including amperometric catalytic and potentiodynamic affinity sensors. A very specific interaction of analyte with immobilized biological element results in the formation of reaction products.

Keywords: conducting polymers, conducting polymer nanoparticles, fabrication of conducting polymer nanomaterials, sensors, biosensors

1. Introduction

A high number of nanostructured materials including conducting polymers (CPs) become extremely essential in sensor and biosensor design. Conducting polymers as artificial convenient materials seem to be very applicable for the development of different analyte-recognizing parts of sensors and biosensors.

Conducting polymers (CPs) have been applied in the design of catalytic and affinity biosensors as immobilization matrixes, signal transduction systems, and even analyte recognizing components. Different types of conducting and electrochemically generated polymer-based electrochemical sensors were developed including amperometric catalytic and potentiodynamic affinity sensors. A very specific interaction of analyte with immobilized biological element results in the formation of reaction products.

Sensors based on conducting polymer materials present a series of effective features depending on the conducting materials as well as on the conducting polymer fabrication/modification methods. Differences of CPs were broadly utilized in the generation of proper polymers. There are clear signs that the capability of conducting polymers to transfer electrical carrier will be exploited in the fabrication of molecular tools.

Due to the sensor implementations, the most important features of CPs are presented as: (i) CPs are readily synthesized by electrochemical and chemical processes; (ii) CPs are strongly sensitive to a wide range of analytes at ambient conditions (i.e. temperature); (iii) a response is expected from their inherent transport properties (i.e. electrical conductivity, rate of energy transfer); (iv) the polymer structure can be modified to display selective responses toward specific analyte; (v) the sensitivity is readily tunable by adjusting the synthetic variables such as incorporated counter ions or polymerization temperature; and (vi) sensor array may be formed through electrochemical deposition, which permits for miniaturization and mass production of sensor tools [1].

Conducting polymer materials of nanosizes have emerged as significant elements of high-performance transducer applications. They possess unique properties associated with high surface area, small dimensions, and bulky counterparts [2]. Conducting polymer nanomaterials have been employed to detect diverse analytes such as toxic gases, volatile organic compounds, as well as biological species. Well known from literature are sensors based on conducting polymer nanomaterial, consisting of polypyrrole (PPy), polyaniline (PANI), poly-(3,4-ethylenodioxythiophene) (PEDOT) [1].

This contribution is reviewing principally fabrication methods of conducting polymer nanomaterials for biosensorics. Major types of biosensors based on conducting polymer nanoparticles including catalytic biosensors and molecularly imprinted polymer-based affinity sensors are presented.

2. Fabrication of conducting polymer nanomaterials

Conducting polymer nanomaterials are potentially useful for the fabrication of miniaturized sensors that enable small sample volumes, portability, and high-density arrays. Nanostructured CPs are favorable for electron transfer and biomolecule stabilization due to their increased surface area and high surface-free-energy. Nanostructured CPs, such as polypyrrole, polyaniline, and polythiophene (PTh), offer excellent prospects for both interfacing biological recognition species and transducing electronic signals to design novel bioelectronic devices [3].

Recently, many procedures for their fabrication with controlled shape and size have been developed. These ranged from lithographic techniques to chemical methods [4]. Moreover, the utilization of nanosize particles with narrow size distribution meets the demands for transparent and flexible sensor platforms.

There are a variety of interesting and useful characteristics associated with chemical approach, for example, template synthesis. Probably the most useful feature of template synthesis is that

it is a general procedure with respect to the types of materials that can be prepared as well as templates that can be involved. Depending on the properties of monomers to be polymerized, the chemistry of the template, and their mutual interactions, that is, whether the monomer interacts electrostatically or whether it is chemically bound to the template, different micro- and nanostructures can be formed. The use of porous membranes with uniform pores yields monodisperse nanocylinders or nanorods, whose dimensions are carefully controlled by the pore size. These tubular or fibrillar structures can remain within the template or they can be extracted from the membrane. Porous materials in which polymer structures are grown can be considered as "encapsulating" materials aimed at the isolation of the functional, conducting micro- or nanostructure from the surrounding.

The synthetic strategies for conducting polymer nanomaterials can be classified into hard-template synthesis, soft-template synthesis, and template-free synthesis [5].

Hard-template synthesis is favorable in tailoring the dimensions of nanomaterials. It is often used in the production of nanosize materials such as nanotubes, nanorods, and nanocapsules. This method has been used to prepare conducting polymer nanomaterials as colloidal nanoparticles, nanofibers, and porous membranes [6]. An easy route to polypyrrole (PPy) nanotubes has been developed with an alumina membrane template. These nanotubes were produced by vapor deposition polymerization coupled with template synthesis. Significantly, the wall thickness of the structures was controlled within the range of a few nanometers [7]. This accurate control on the wall thickness of nanotube indicated that the template-mediated procedure was a precise and effective route for producing polymer nanotubes.

The soft-template approach has occurred as an alternative route to fabricate polymer nano-materials with a good result. Soft template concerns surfactants, polyelectrolytes, liquid crystals, block copolymers, as well as biomolecules [8]. One of the examples of using this method for obtaining polymer nanomaterials was the formation of cylindrical micelles of bis(2-ethylhexyl)sulfosuccinate, through a co-interaction with iron cations in a solvent of low polarity [9].

Template-free synthesis is very accessible without using some specific templates. But this procedure is restricted to individual precursor material. For example, the template-free synthesis of polyaniline (PANI) nanofibers is systematically reported since the first report of Huang et al. [10]. A dispersion polymerization for the mass production of polyaniline nanorods was also presented by Jang's group [1].

Other templating method depends on the use of self-assembled monolayers (SAMs). These layers provide an opportunity to define their chemical functionality and applications with molecular precision and become increasingly valuable tools in the design of surface-confined synthetic routes to complex structures. The use of self-assembled monolayers with suitable functional groups protruding toward the monomer-containing solution can lead—via the suitable synthetic method—to covalent or electrostatic attachment of monomers to these functionalities. Consecutive polymerization results in one-dimensional (1D) or two-dimen-sional (2D) polymeric structures (brushes, "wires", surfaces), depending on the polymeriza-tion method [11, 12].

2.1. Electrochemical template method—polymeric native films

Here we present some applications of monomolecular setups for templated growth of polymeric materials. The thicker films on the electrode can also be used to govern the polymer growth. One of benefits of this procedure is that the thicker layers (i.e. insulating polymers) may block more effectively than monomolecular layers the access of the monomers to the electrode surface. In this situation, the polymer can be grown within defects. There are several works on deposition of conducting polymers onto thicker coating layers, but this results in the formation of composite structures where the coating layer acts as a support rather than a template [13, 14].

An interesting strategy of using polymeric coatings to prepare polypyrrole nanosize structures was reported by Jerome et al. [15–18]. This approach requires the use of an insulating polyethyl acrylate layer deposited on the glassy carbon (GC) electrode onto which pyrrole is electro-chemically oxidized. When a suitable solvent for polyethyl acrylate is utilized, the insulating matrix is swollen and incorporates monomer molecules. The oxidized form of monomer creates within the coating some amount of nuclei that in the next step grow to create channels in the layer. These channels permit the PPy to occur from the polyethyl acrylate film in the form of nanowires. Despite the fact that different insulating layers might be used to template nanowire creation (ca. 350-4000 nm in diameter and hundreds of micrometers in length), films of polyethyl acrylate appear to give the best results [4].

The critical condition for nanowire preparation is the use of solvents with high donor numbers which are known to impart limited conductivity to PPy [19]. As a consequence, the monomer oxidation does not appear at the PPy nanowire, but simply between the electrode surface and foot of the growing polypyrrole wire, due to which the already created nanostructure is pushed away from the electrode.

In solvents with low donicity, PPy nanowires are not created due to the high conductivity of the resulting polymer that grows in cauliflower-like shape as an alternative [4]. Wang et al. [20] have proposed a little different route for fabrication of polypyrrole nanowires. The nanowires were fabricated by voltammetric or potentiostatic oxidation of pyrrole on GC electrode coated with a thin film of paraffin. It was investigated clearly that the nucleation process of PPy is of a 2D type, while the growth of the structure is a 1D process.

The 2D polymeric surfaces modified biosensor electrodes were also close to our earlier experiences [21, 22]. There were published sensing tools, where platinum electrode was modified with polymers obtained in the process of electrochemical polymerization. An example is thin film (550 nm) built of 3-methylthiophene/3-thiopheneacetic acid/2,7-bis[2-(3,4-ethylenedioxythiophene)]-N-nonylacridone [21]. The electropolymerized layer exists in the conducting oxidized state. The overall charge of the polymer was neutral due to the doping anions which are incorporated into the polymeric matrix during the electropolymerization. The optimal current density for copolymer deposition was observed as 12 mA/cm^2, and the polymerization time 1 min [21]. CPs porous film was used as suitable matrix for enzyme immobilization. The immobilization of laccase was performed in a one-step process. It was carried out for 10 min under galvanostatic conditions applying a current density of 3 mA/cm^2.

The optimal conditions presented in the experimental part were obtained considering a high signal-to-noise ratio, and stability of biosensor response [21].

Another CP (poly(*N*-hexyl-2,7-bis(thiophene) acridone)) was exploited by us in ceramic optical biosensor designed for the permanent monitoring of water solutions, **Figure 1** [22].
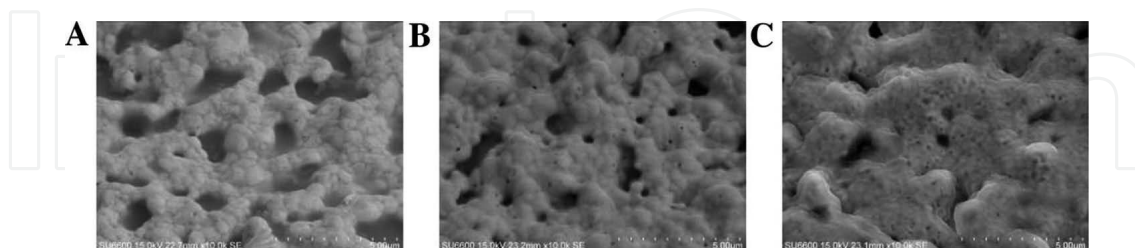
Figure 1. SEM images of: A—platinum bare electrode, B—electrode modified with polymer, C—electrode modified with polymer and laccase. Adapted with permission from Jędrychowska et al. [22].

2.2. Nanoparticle monolayers

A smart method of preparation of well-ordered honeycomb polymeric structures was reported by Han et al. [23]. They used monolayers of polystyrene nanoparticles supported on gold to template PANI growth into interstitial voids of the colloid. After dissolution of the template, the products form a negative pattern reflecting the ordered geometry of the particle monolayer (**Figure 2**). The colloidal assembly of polystyrene particles (diameter 600 nm) was prepared by sandwiching a gold substrate between two Teflon elements and adding dispersed polystyrene particles into the solution well of the top block.
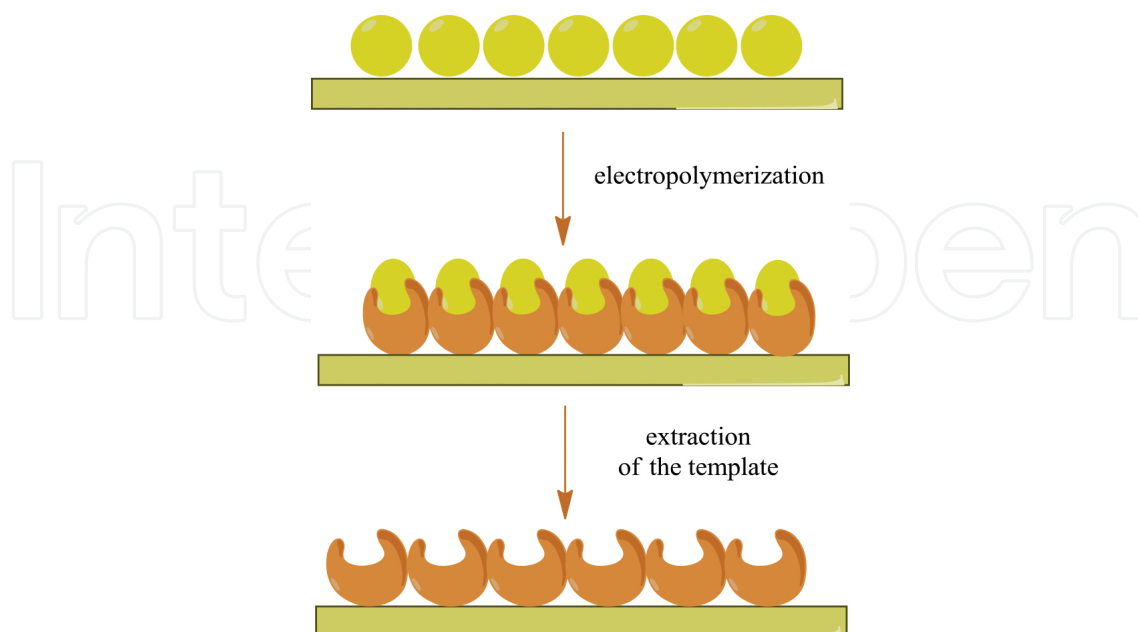
Figure 2. Procedure of formation honeycomb structures with nanoparticle monolayer as template.

The polymerization was performed by potential cycling of the electrode in the acidic solution of aniline. After the process of polymerization the deposits were placed in toluene to dissolve the polystyrene template. The above procedure yields a well-ordered 2D polyaniline honeycomb structure on the gold surface. It was found that the rigidity of polyaniline structure and long-distance order is greatly improved when polystyrene nanoparticles are pre-coated with polyelectrolyte multilayers (polydiallyldimethyl-ammonium chloride and polysodium-4-styrene-sulfonate).

Polyelectrolyte assemblies may also be used to create polymeric models. Briseno et al. also reported [24] truncated eggshell structures of the polyelectrolyte to template the PANI growth. The method involves assembling a film of polystyrene particles covered with a few polyelectrolyte layers onto a gold area. Extraction of the polystyrene templates results in the rupture of the apexes of the spherical polyelectrolyte shells and an expansion of the shells along the surface. The resulting structure consists of truncated eggshell features and retains the hexagonal arrangement of the original polystyrene particles. The polyelectrolyte shells are prepared by alternate assembling of cationic and anionic layers. The outermost layer is anionic and therefore it can assemble cationic anilinium cations from the solution. It was found that aniline is adsorbed onto eggshell structures and infiltrates into the void spaces within the polyelectrolyte multilayers. After immobilization the monomers can be polymerized by electrochemical oxidation in acidic water solution yielding composite polyaniline-polyelectrolyte truncated eggshell assembly.

2.3. Nanoparticle 3D orders

Another approach yielding 3D conducting polymer assemblies was reported by Sumida et al. [25]. This pathway is essentially the same as presented earlier for nanoparticle monolayers. The main dissimilarity is that the particles create 3D lattice rather than a monomolecular layer, consequently the resulting polymer is 3D. The synthetic pathway engages the use of colloidal particles generating "crystalline" lattice organized on the electrode surface. The required polymeric structure is settled onto the template which yields 3D network of the polymer. The main duty of the particles is to mechanically reduce the growth of the polymer to interstitial voids. The polymer creates interconnected macropores linked to each other via a symmetrical network of smaller pores. After the polymeric structure is generated the template may be removed by dissolution (**Figure 3**). The particle array template is usually fabricated of silica or polystyrene monodispersed colloids. The diameter of particles used is found as ca. 200 nm– 1 μm. The colloid crystal phase was prepared by sedimentation of particles onto the electrode [25] or by vertical lifting from the colloidal suspension [26].

Due to an increase in mechanical stability of silica templates, the samples are sintered, which results in necking between neighboring particles [25]. The particle lattice is generated on the electrode, followed in the next step by electro-polymerization of the required monomer. The polymer is grown (electrochemical synthesis) by the template from conductive metal electrode surface onto which the template is organized.

Several polymers were electrochemically deposited onto colloid lattice templates including polypyrrole, polyaniline, polythiophene, polybithiophene, and so on and various electro-
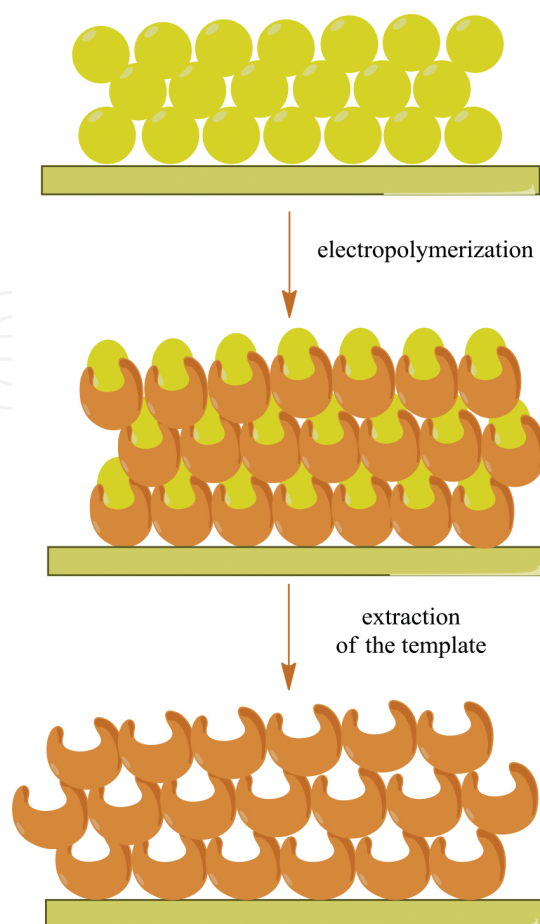
Figure 3. Procedure of formation polymeric inverted opals using 3D colloid crystals.

chemical techniques were employed to polymerize monomers on the template [11]. The most general is potentiostatic deposition, which permits credible monitoring over the structure of the growing polymer. The chronoamperometric transients expose at the start rather low current densities adequate to growth of polymer within the empty spaces of the template. In the next step, there is a rapid growth of current due to an increase in electrochemical process area when the new material reached the membrane/bulk solution interface. Polymerization above this transition point results in the subsequent growth of a cauliflower-like structure on the membrane surface; thus, effective preparation of replicas of colloidal particles requires avoiding deposition times that last too long [25].

Similar transient points are observed on potential-time dependence in galvanostatic deposition. After filling the template with polymer, a quick change in the potential is found when the growth front extends above the template/bulk solution interface [26]. The polymerization can also be processed by potentiodynamic methods, that is, cyclic voltammetry. Supposing the regulation over the thickness of the coating layer is more difficult, the inversed polymeric opals are characterized by improved quality originating from well-controlled polymerization process. This appears to fil efficiently the interstices in the colloid crystal and to generate a compact and defect-free structure [27].

3. Sensor based on transduction

3.1. Amperometric sensor

In case of amperometric sensors, signal is proportional to the concentration of an analyzed species. Specific target species are electroactive ones, that are able to be oxidized or reduced, when the oxidation or reduction potential is zero. The best known to this moment ampero-metric sensor is the Clark Oxygen Cell (developed in 1956). In this type of biosensors, concentration of a biocatalyst substrate is detected by the O_2 consumption by oxidase catalyzed process, or by the generation of H_2O_2. Electrochemical biosensors (**Figure 4**) are based on mediated or unmediated electrochemistry for electron transfer [27].
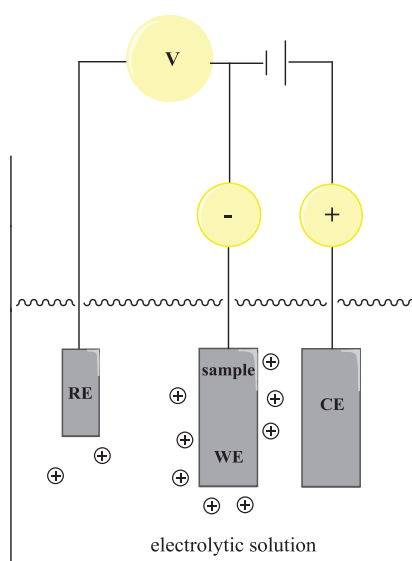
Figure 4. Scheme of amperometric sensor.

Direct electrical communication between redox enzyme and electrode was presented earlier by us [21]. However, usually this contact is prohibited because of a donor-acceptor separation distance - a major factor controlled the electron transfer rates. The most redox proteins (diameter 80–150 Å, laccase 50 Å) have the redox centers deeply embedded and therefore electrically insulated. That is, redox enzymes that form a donor-acceptor pair with an electrode support lack electrical contact with this support. In these systems, the biofunctions of the biocatalysts are electrochemically stimulated by electron transfer [21]. The electrical contact may be improved significantly by the application of CPs.

3.2. Piezoelectric sensor

An operating of this type of sensors is based on an acoustic wave expanded by an applied alternating current between two electrodes or interdigitated electrode fingers deposited on a piezoelectric solid that is, quartz. The types of piezoelectric transducers are based on the way of acoustic wave propagated between the electrodes. These tools are mainly used for gas phase

monitoring, where H_2S, CO_2, O_2, NO_2, Hg, toluene as well as acetone sensors have been created [27, 28].

For the last few years, scientists have explored the possibility of using composite-material sensors by combining both silicon and polymers, examples of which include embedding of silicon sensing elements in polymer skins [29], packaging of silicon-based sensing devices in protective casing of polymer layer [29], and so on. Silicon-based tactile sensors have proven to provide high sensitivity, high spatial resolution, and ease of integration into electronic devices. There was also reported a piezoelectric polymer-based, skin-like tactile sensor which was selectively sensitive to stress and shear forces [29].

3.3. Optical sensor

Optical sensors are developed as tools based on the measurements of light absorbed or emitted as a consequence of a biochemical reaction. These sensors may be used for determination of pH, O_2, CO_2, and so on. [27]. Classically, these tools incorporate a material at the tip or on the side of the cable, which can generate an optical signal related to the concentration of analyte in the sample [28].

4. Sensor based on application mode

Different types of sensors have been fabricated using conducting polymers in various transduction modes. The transduction modes may be classified into five classes based on the operating rules, namely conductometric, potentiometric, amperometric, colorimetric, and gravimetric procedures [30, 31]. The conductometric mode utilizes changes in electrical conductivity as a result of a target species interaction. The conductivity of conducting polymers bridging the gap between two adjacent electrodes is mainly estimated as a function of analyte concentration, and it may also be monitored with a fixed potential in a sample.

4.1. Chemical sensors

There are many chemicals of concern that have to be determined, including toxic gases, volatile organic species, alcohol, and humidity. Different types of conducting polymer nanostructures have been used as elements of various detectors. Chemically synthesized polymer nanoparticles suspended in solvents can be simply deposited on a prefabricated electrode by drop casting to construct a sensor tool. Strongly sensitive chemiresistive sensors based on polypyrrole nanotubes were developed to determine toxic gases as well as volatile organic compounds [32].

PPy nanomaterial was transported onto a polydimethylsiloxane solid by a dry-transfer process and then micro-patterned Au electrodes were deposited onto the nanotubes by thermal evaporation. Different CPs such as PPy nanoparticles, PEDOT nanorods, and PEDOT nanotubes were introduced as well into electrode matrix to cause discriminative reactions toward individual target species in a sample. The lowest measured concentration of the sensors was

ca. 0.01 ppm for ammonia, selectively. Electrochemical polymerization process permits, in a governable manner, deposition of the polymer on an electrode.

Recently, PPy nanowires (grown electrochemically on a microelectrode) were used as conductometric transducers to detect hydrogen gas at room temperature (**Figure 5a**) [33]. It was observed that the polypyrrole nanowires were assembled at high density (**Figure 5b**); moreover, a few of the nanowires bridged the gap between the electrodes (**Figure 5c**). The sensor was exhibited to various amounts of H_2 at room temperature in a limited space, during which the resistance of the polypyrrole nanowire electrode was verified. The resistance of the nanosized wires was supposed to reduce during exposition to H_2 (reducing gas). The sensors were characterized with a linear detection of ca. 600–2500 ppm for the gas. The sensitivities were observed depending on the quantity of the settled nanowires.
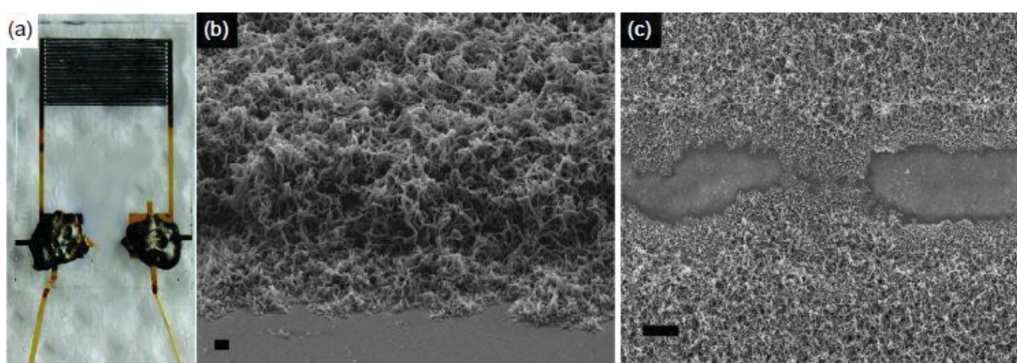
Figure 5. (**a**) Picture of a gas sensor electrode, (**b**) SEM images of polypyrrole nanowires settled on the electrode, and (**c**) top view of PPy nanowires bridging the insulating gap between the gold electrodes. Adapted with permission from Yoon [36].

Moreover, it was observed that PANI is able to interplay with H_2. There was reported immediate interaction of H_2 with doped polyaniline nanofibers to provoke a modification in the conductivity of the nanofibers [34]. The direct mass uptake of H_2 by polyaniline nanofibers was found as well by a quartz crystal microbalance (ca. 3% relative to the nanofiber mass). A reliable program of the H_2/PANI reaction provokes H_2 interacting with doped PANI at the charged amine nitrogen, proceeded after the dissociation of H_2 and the creation of N–H bonds at the amine nitrogen of the polyaniline [34, 35]. Afterward, charge transport between adherent amine nitrogen atoms regains the polyaniline back to its classical doped, emeraldine-salt pattern with a deliverance of H_2.

The nanoparticle-modified sensor for volatile organic compounds (VOCs) detection was reported by Vaddiraju et al. [37, 38]. They used, at first, oxidative chemical vapor deposition (oCVD) method as a comprehensive and substrate-independent technique for the formation of well-adhered conducting polymer layers which may be used as a platform to anchor the Au nanoparticles and ameliorate the robustness of the sensor. The resistive answer of the nanoparticle/polymer layers is used to determine the inherence of VOCs. The metal nanoparticles were grafted onto the surface of the functionalized conducting copolymer films using thiol as the linker molecule [39].

A system of electrochemical and electrical nanosensor for determination of nitroaromatic explosives vapors (TNT – 2,4,6-trinitrotoluene) was reported by Aguilar et al. [40]. The integrated sensor system consists of two elements with a thin layer coating of liquid crystal 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6): (i) PEDOT nanojunctions for conductometric determination and (ii) electrodes for electrochemical detection (**Figure 3**). Conducting polymers can be integrated with many species to form composites that are sensitive to various chemicals. Polyaniline nanofibers treated with $CuCl_2$ exhibited the capacity to determine hydrogen sulfide with change in resistance by 4 orders of magnitude [41]. Moreover, water-soluble metal salts were to be readily included into polyaniline nanofibers, such as $CuCl_2$, $CuBr_2$, CuF_2, $Cu(O_2CCH_3)_2$, $Cu(NO_3)_2$, $EuCl_2$, $NiCl_2$, $FeCl_3$, and $CoCl_2$ [36]. The salts were sieved to find the best candidates for determination of arsine.

One of the habitual toxic gases is sarin (an organophosphorous derivative). Flexible nerve element sensors based on hydroxylated poly(ethylenedioxythiophene) nanotubes (HPNTs) equipped with unusual surface architectures were also reported [42]. Other gas detecting system was reported by Airoudj et al. as a *multilayer integrated optical sensor* (MIOS) using polyaniline as a sensitive material and demonstrated the detection of ammonia gas [43].

4.2. Biosensors

Biosensor is an analytical tool based on biological recognition element integrated with a signal transduction system. Undoubtedly, biosensors are one of the main issues of nanobiotechnology due to the fact, that commonly biosensing devices consist of various nanostructures meeting also nanosized biomolecules; as well as bio-bio and/or bio-non-bio reactions at nano-level which are consulted during the construction process. Sometimes miniaturization toward nano-dimension permits growth of selectivity as well as sensitivity of tools that are the main benefits of these analytical instruments. According to the recognition principals, biosensors can be classified into two clearly different groups as catalytic biosensors and affinity biosensors [36]. Conducting polymers have been applied in construction of both types of biosensors as immobilization matrixes [28, 44], signal transduction systems, and even analyte recognizing components [36].

In comparison to metals and ceramics, CPs are more compatible to biological structures. Inorganic nanosized materials have been included into biosensor setups by lithography and focused ion beam methods.

Nevertheless, the integration of CP nanomaterials into biosensors has been limited because of their incompatibility with the customary microfabrication procedures. However, the conducting polymers are subjected to chemical instability, weak mechanical properties, and poor biocompatibility, which may negatively affect the performance of the biosensors based on these polymers.

Aiming to solve the above-mentioned problems associated with conducting polymers, composite structures were fabricated by coating conducting polymers on rigid nanomaterials [45]. The composites are expected to maintain the merits and discard the shortcomings of the single component and act as excellent biosensor immobilization scaffolds. For example,

graphene-PANI composite film was successfully synthesized in large scale by a facile electro-deposition method and horseradish peroxidase (HRP) was entrapped onto the film modified electrode to construct a H_2O_2 biosensor [46]. The biosensor exhibited a fast amperometric response after less than 5 s, a good linear range from 1 to 160 μM, and a low detection limit of 0.08 μM.

The incorporation of CNTs into conducting polymers can lead to new composite materials with improved properties due to synergic effects of the two. The π-conjugated structure of the nanotubes allows them to interact with organic aromatic compounds through π-π electronic and hydrophobic interactions [47]. Recently, Lete et al. presented a dopamine sensor based on poly(ethylenedioxythiophene) – PEDOT as well as CNTs. The tyrosinase-based biosensor prepared at low frequency range displayed the lowest limit of detection of 2.4 μM dopamine, the best repeatability of 4.9%, and a recovery of 100.9% for dopamine determination in the presence of catechol [48].

Xu et al. [49] fabricated glucose biosensor based on carbon nanotubes coated with PANI and dendrimer coated Pt nanoparticles. Xian et al. [50] chemically synthesized a composite of PANI nanofibers and Au nanoparticles. Chemical synthesis required several different chemicals, thereby increasing the complexity of the growth process.

Sun et al. have recently reported polypyrrole-Pluronic F127 nanoparticles (PPy-F127 NPs), a novel conducting polymer nanomaterial [51]. These novel nanomaterials were employed in the design of biosensors, which were further used in biochemical assays of L-lactic acid in pig muscle samples. Pluronic F127 was used because it is difficult to obtain PPy nanoparticles with the desired small size and good dispersion. F127 can be used as a template and dispersant for preparing nanoparticles with special shapes [52, 53] as well as according to its good biocompatibility. The reported biosensor had good electrocatalytic activity toward L-lactic acid with a linear range of 15μM–37.5 mM and a low detection limit of 8.8 μM. The L-lactic acid biosensor had also a good anti-interference property toward uric acid, ascorbic acid, glucose, and cysteine [51].

An alternative strategy of using PPy nanoparticles was presented by Yoon et al. [54]. Covalent links between polypyrrole nanotubes and a microelectrode were formed to obtain convenient electrical communication in solution. PPy nanotubes equipped with carboxyl groups were obtained and the carboxyl elements were bonded with the surface amino groups of the modified electrode. A liquid, ion-gated field-effect transistor (FET) sensor was successfully constructed by this procedure. The scheme of the FET sensor is almost the same as the normal metal-oxide-semiconductor FET, except for the gate, which includes the means of transduction from a chemical event to a voltage [55]. Several critical parameters determining the FET sensor response have also been investigated that is, Shirale et al. presented single PPy nanowire-based FET sensors for real-time pH determination. They also examined how the diameter of the nanowire affects the sensor activity [56]. The FET sensors had higher sensitivity with lower diameter and higher length [56].

Wang et al. reported an amperometric glucose biosensor based on a direct-electron-transfer mechanism [57, 58]. They electrochemically entrapped glucose oxidase (GOx) onto the inner

wall of polyaniline nanotube orders fixed from an anodic aluminum oxide (AAO) pattern [59]. A pair of symmetric redox peaks was presented in the cyclic voltammogram, and a seeming constant electron transport rate of 5.8 ± 1.6 s^{-1} was estimated. The biosensor exposed good sensing presentation with a violent response (3 s), a low detection limit (0.3 ± 0.1 μM), a linear range (0.01–5.5 mM), and high sensitivity (97.18 ± 4.62 μA mM^{-1} cm^{-2}). The biosensor exhibited anti-interfering features versus common compounds such as ascorbic acid, uric acid, and 4-acetamidophenol.

Ramanathan et al. reported a single-step electrodeposition technique for the formation of PPy and PANI nanowires to bridge the gap between two electrodes on a silicon wafer [60, 61]. The deposition and growth of the nanowires are based on electrochemical oxidation polymerization.

To further improve the sensitivity and selectivity, a variety of biosensors based on CP composites have been developed, for example, the composites of CPs and carbon nanotubes, metal particles, metal oxide particles, metal salts, chitosan, and biocompatible materials [3].
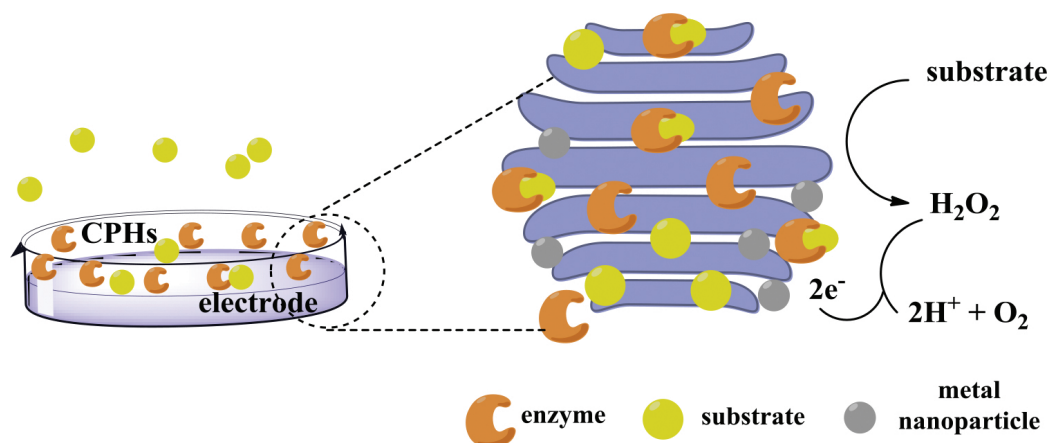
Figure 6. Classic example of electrochemical biosensor based on CPHs.

Recently, the growing attention is addressed to the synthesis of conducting polymer hydrogels (CPHs) and their introduction into functional biosensors. Different synthetic pathways, including templating against a hydrogel matrix [62], cross-linking by multivalence metal ions [63], and self-assembly, have been adapted to generate conducting polymer networks inside the water environment. Among them, there was reported a general CPH synthesis procedure by cross-linking CPs with multi-valence doping-acids [3]. Combining the features of both the CPs and hydrogels, these CPHs present great potential as advanced interface materials to be used in biosensors. Here is presented illustration of a reasonably constructed electrochemical biosensor based on CPHs (**Figure 6**). The CPHs are extremely important in enhancing the sensing properties by (i) spreading the planar electrode to the 3D organic matrix to enhance the efficient interface area, (ii) supplying links between soft and hard materials for sufficient enzyme immobilization, (iii) interfacing the ionic transferring phase and the electron transporting phase to lower the impedance, as well as (iv) ensuring high density loading with catalytic nanoparticles to provoke electron set [63]. Due to these, biosensors based on CPHs

have displayed inviting features such as sensitivity, low detection limit, and quick response time. Until now, the development of CPH-based biosensors has been focused on the reasonable design of both the materials and instruments.

Heller as well as Asberg [64, 65] reported biosensors based on redox hydrogels and metal-ion-cross-linked CPHs, respectively, and suggested that the gels could be brilliant biosensor electrodes because of the benefits: (i) the specific charge transfer properties of CPs allow electron transport [66]; (ii) CPHs with three-dimensional porous nanostructures present a large surface area and short diffusion way; (iii) great biocompatibility [67]. Mano et al. also presented an electron-conducting cross-linked polyaniline-based redox hydrogel. The active film was created in a one-step process (by cross-linking a polymer acid-templated PANI with a water-soluble poly(ethylene glycol) diglycidyl ether (PEGDGE)) [68]. Glucose oxidase was immobilized in the hydrogel by simultaneously co-cross-linking, leading to the electrical wiring of the protein.

Asberg and Inganas investigated a general method to synthesize PEDOT hydrogels using multi-valence metal ions, such as magnesium, iron, and osmium to cross-link the poly(styrenesulfonate) (PSS) groups on PEDOT:PSS into a mesoscopic conducting network of hydrogels [65]. They also developed a biomolecule-enhanced electrode with the electroactive polymer hydrogel PEDOT:PSS in combination with poly(4-vinylpyridine) (P4VPy) cross-linked by osmium [65].

The integration of the benefits of organic conducting structures and hydrogels, CPHs present a hopeful interface for biosensor electrodes. The hierarchical structures of CPHs ensure an open porous system, a large surface area, and an organic matrix, which are profitable for enhancing the permeability of bio-species, increasing the interfacial area of electrodes, and immobilizing enzymes evenly and densely [3].

Another important issue in biosensor design concerns the relationship between receptors and transducers and the way they are coupled. Comprehensive receptors containing enzymes, antibodies, nucleic acids, and cells have been inserted into CPs through adsorption, entrapment, or covalent bonding. A well-known example concerns enzyme-based glucose determination for diagnostic of diabetes. Commonly, amperometric glucose determination has been reached with GOx electrodes. The GOx has been immobilized on electrodes by chemical cross-linking, electrodeposition, or electrostatic interactions [69]. The latest developments have suggested variants to the classic biocatalyst electrode [70, 71].

CPs nanomaterials have primarily been adapted as the conductive matrix with redox features. A FET-based sensor was reported by using GOx-attached PPy nanotubes as the conductive channel [72]. The polypyrrole nanotubes were fabricated by the chemical polymerization of pyrrole-3-carboxylic acid inside the cylindrical pores of an alumina membrane. A novel glucose sensor was developed by Wu and Yin, who utilize polyaniline-wrapped boron nitride nanotubes equipped with platinum nanoparticles as the electrode material [73]. Enzyme, according to the procedure, was mixed with the Pt/PANI/boron nitride nanotubes, which resulted in a cotton-like enzyme nano-hybrid. The nano-hybrid electrode has had good acid stability and heat resistance.

Molecularly imprinted polymers (MIPs) are tailor-made biomimetic materials that are capable of selective recognition toward target molecules. The selective recognition property, high stability, easy preparation, and low cost of these MIPs make them extremely attractive as sensing materials in biosensors and chemical sensors [74].

Molecularly imprinted sensors that demand no receptors have also been designed by CPs. For example, a simple procedure for the photoelectrochemical sensing of microcystin-LR (MC-LR) was obtained by utilization of PPy/titania nanotubes with MC-LR recognition places [75]. MC-LR is an agent that can induce structural as well as functional bothers of the liver, and is a potential cancer threat [76]. Due to its omnipresence and high toxicity, MC-LR is an agent of concern in water and environmental monitoring.

Zhou et al. reported an electrochemical sensor based on molecularly imprinted PPy for epinephrine recognition [77]. Pyrrole was electropolymerized with epinephrine on the surface of an electrode coated with silica nanoparticles and CNTs. After the removal of silica nano-particles and epinephrine, a molecularly imprinted PPy/CNTs porous layer could be formed on the electrode. The amperometric answer of the PPy/CNTs electrode was recorded by adding of epinephrine in PBS. Also Li et al. [78] reported molecularly imprinted polymer arrays (3D MIP arrays) as the sensing materials. ZnO nanorods were deposited on indium tin oxide coated polyethylene terephthalate film and used as high-surface 3D scaffolds for 3D MIP arrays deposition. The obtained results indicated that this 3D MIP arrays-based electrochemical sensor exhibits high sensitivity and good selectivity for epinephrine.

Cai et al. prepared polyphenol nanocoating on the tips of CNTs in the presence of a template protein. Then, they relied on measurements of impedance to monitor the recognition. This nanosensor was sensitive and selective; moreover, it was also capable of detecting protein conformational changes [79]. Using TiO_2 NTs as the microreactor, Liu et al. fabricated MIPs onto the internal surface of TiO_2 nanotubes and used them as working electrode for photo-electrocatalytic and photocatalytic degradation of 9-AnCOOH [80]. Similarly, Tran et al. reported a novel photoelectrochemical sensor by surface modification of molecularly imprint-ed polymer on highly ordered and vertically aligned TiO_2 nanotube arrays which could be used for photoelectrochemical determination of perfluorooctane sulfonate [81].

5. Summary and outlook

Conducting polymers are favorable materials for both nanotechnology and biosensorics. The intensity of conducting polymer application in sensors and biosensors design increases permanently. For example, sensors based on conducting polymer-based nanocomposites show several inviting characteristics depend on the composite materials as well as on the CPs' formation procedure. Common utility of CPs is recently broadly utilized in design of suitable polymer-based nanocomposites. There were observed clear appearances that capability of CPs to transport electrical charge will be utilized in the design of different molecular tools. Furthermore, the conducting polymers will be adopted for integration nanosized elements and

probably in the construction of single receptor molecule-based sensors within such molecular tools.

Frequent studies on conjugated polymer nanotubes and nanowires established that improvements in their molecular structure, crystallinity, and an increase in conjugation length are responsible for the increase in the room temperature conductivity when the diameter of such fibrillar structures decreases.

Sensors play a crucial role in environmental diagnostics, medical monitoring, industrial safety checking, as well as security. CP nanomaterials are supposed to possess much unexplored capability for sensor appliances. CP-based biosensors are likely to address the issues of biocompatibility for continuous monitoring of biological metabolites and drug dosages, and the possibility of *in vivo* sensing. Consequently, the forthcoming development into CP nanomaterials-based sensors may proffer large promise for the design of future-generation sensor instruments. Notably, it is envisaged that convenient and flexible high-performance sensors will soon be constructed by utilization of conducting polymer nanomaterials.

Acknowledgements

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