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*Review*

# Gas Sensors Based on Electrodeposited Polymers

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**Abstract:** Electrochemically deposited polymers, also called "synthetic metals", have emerged as potential candidates for chemical sensing due to their interesting and tunable chemical, electrical, and structural properties. In particular, most of these polymers (including polypyrrole, polyaniline, polythiophene) and their derivatives can be used as the sensitive layer of conductimetric gas sensors because of their conducting properties. An important advantage of polymer-based gas sensors is their efficiency at room temperature. This characteristic is interesting since most of the commercially-available sensors, usually based on metal oxides, work at high temperatures (300–400 °C). Consequently, polymer-based gas sensors are playing a growing role in the improvement of public health and environment control because they can lead to gas sensors operating with rapid detection, high sensitivity, small size, and specificity in atmospheric conditions. In this review, the recent advances in electrodeposited polymer-based gas sensors are summarized and discussed. It is shown that the sensing characteristics of electrodeposited polymers can be improved by chemical functionalization, nanostructuration, or mixing with other functional materials to form composites or hybrid materials.

**Keywords:** pi-conjugated materials; conducting polymers; functional materials; gas sensors; hybrid materials

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## 1. Introduction

Conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh), and their derivatives, have been used as the active layer of gas sensors since the early 1980s [1]. Conducting polymers have many interesting characteristics for sensing including their high sensitivity and short response time; especially, these features are ensured at room temperature. Conducting polymers are easy to synthesize through chemical or electrochemical processes. Chemical oxidation is the easiest synthesis technique since it consists of the mixing of a monomer with an oxidant in solution. However, the electrochemical synthesis is more interesting than the chemical one in the sense that it offers control of the polymerization and doping level, and could be produced over a number of substrates in order to fabricate devices directly. The three-electrode system (working, counter, and reference electrodes) is frequently employed in electrochemical procedures. When using electrochemical methods, these polymers can be synthesized by anodic oxidation of the corresponding monomers in suitable electrolytes (aqueous or non-aqueous) at constant potential, at constant current, or by cycling the potential. In addition, the nature and the size of the counter-ions used have a great effect on the physical properties of the polymer coatings (morphology, porosity, mechanical properties, and thermal stability). To extend the functions or to improve their performances, electrodeposited polymers are frequently mixed with other functional materials such as organic compounds [2], metal nanoparticles [3], metal oxide nanoparticles [4], or carbon nanotubes [5] to form composites with improved sensing properties. Their molecular chain structure can also be modified conveniently by copolymerization or structural derivations.

Amongst many analytical techniques available, the development of chemical sensors has made significant strides in the last two decades. The rapidly growing applications of chemical sensors reflect the extent to which analytical chemists require such sensors for cheap, accurate, convenient, and quick analysis of various analytes. Usually an analyte recognition process takes place followed by the conversion of chemical information into an electrical signal. For incorporation into these chemical sensors, an advantage of polymers is that sensory devices can easily be fabricated from these materials on electrodes by electrochemical polymerization from an electrolyte solution. The electrode configuration of the sensor varies according to the sensing mechanism. Potentiometry and amperometry are used for detection of analytes in liquids, in particular to develop polymer-based pH sensors [6–10] and polymer-based biosensors [11–15]. Alternatively, conductimetry is the most generally used technique for gas detection.

For this latter application, electrodeposited polymers constitute a promising class of materials. Indeed polymer-based gas sensors are interesting for environmental pollution monitoring because, upon exposure to vapor, the polymers show rapid conductivity changes, which are generally reversible, at room or atmospheric temperature. These characteristics are interesting since most of the commercially-available sensors, usually based on metal oxides, work at high temperatures

(300–400 °C) [16–18]. However it is sometimes necessary to modify the structure of electrodeposited polymers to improve their characteristics for gas sensing. This can be done by organic functionalization of the monomer, by nanostructuration or by mixing with other kinds of materials.

Consequently, in this review the emerging trends in electrodeposited polymer-based gas sensors are presented. The successive parts of this review are dedicated to gas sensors based on: (i) electrodeposited polymers, (ii) electrodeposited polymer nanowires, (iii) electro-oxidized functionalized monomers, (iv) electrodeposited films mixing a polymer and an organic material, (v) electrodeposited films mixing a polymer and metal nanoparticles. For each type of sensing material, the characteristics of the sensor's responses are presented as well as the response mechanism of the gas sensors. Furthermore, rather than giving a long list of references, it was decided to focus on some original and interesting examples for each type of sensing material in order to highlight the most promising strategies used to improve the sensing properties.

## 2. The Different Configurations of Polymer-Based Gas Sensors

The most widely used sensors based on conducting polymers are chemiresistors and many commercialized devices are based on such sensors since the technologies used for their fabrication are now mature. A chemiresistor is a resistor, whose electrical resistance is sensitive to the chemical environment. Measuring a resistance rather than a current or potential is interesting since the resistance of a material is a bulk transport property and as a result is more sensitive than potentiometric and amperometric methods that are dependent on local electronic structure. The collective system is responsible for carrier transport in conducting polymers and any molecular level perturbations in the film provoke the bulk mobility, thus giving rise to high sensitivity. Chemiresistor consists of one or several pairs of electrodes and a layer of conducting polymer in contact with the electrodes. Such sensors have the advantage that high-precision electrical resistance change of the sensing material can readily be made with inexpensive electronics. To improve the performance of the chemiresistors, a very frequently used geometry to design gas sensors consists of two interdigitated microelectrode arrays [19–24]. Indeed, such interdigitated microelectrodes can be inexpensive enough to be disposable and have minimal external hardware requirements [25]. Furthermore, all of the necessary electronics for high-precision measurements can be placed on a single chip, which enables sensor arrays. Thanks to this geometry, it is possible to use two conducting interdigitated microelectrodes deposited on an insulating substrate to measure conductivity changes between the two combs. In addition, the electrical signal delivered by the gas sensor is generally improved thanks to this geometry. To allow electrodeposition of the polymer both on the combs and in the gap between the two arrays, it is necessary to fabricate microelectrode arrays separated by a small gap (typically a few μm) so that the polymer can be electrodeposited in this gap and can inter-connect the two arrays (Figure 1). Such gas sensors are microfabricated using silicon technology. More precisely, they are usually prepared through a lift-off process that consists of photolithography followed by sputtering leading to the deposition of metallic patterns on oxidized silicon wafers [26]. To make the desired pattern, a Cr/Glass mask for lithography is previously designed using a CAO software and fabricated using a mask generator. Such microsystems are also the most common type of sensors because this process is convenient and cheap. However, such chemiresistors have some limits including the influence of ambient factors and the contribution of the contact resistance of the electrodes to the resistance measured by the sensor. Moreover, the selectivity is not easy to obtain with such sensors since resistance is the only information that can be deduced from the measurements.

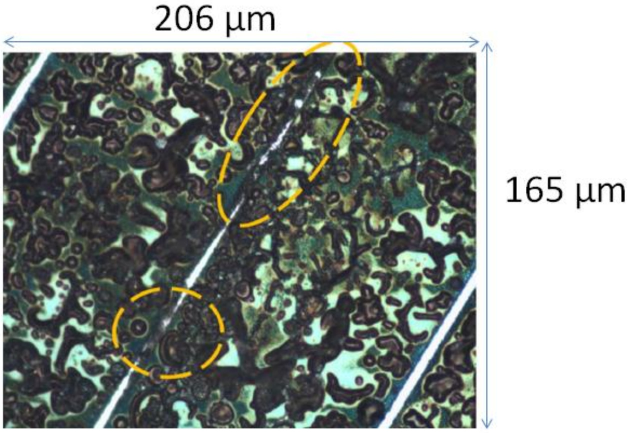

**Figure 1.** Optical microscopy picture of a polypyrrole film electrodeposited on platinum microelectrode arrays (gap between the arrays: 5 µm).

## 3. Gas Sensors Based on Conducting Electrodeposited Polymers and Their Derivatives

### *3.1. Gas Sensors Based on Electrodeposited Polymer Films*

Nearly all widely used conducting polymers such as polypyrrole or polyaniline have already been used as active material in gas sensors. The main parameter used to adjust the efficiency of these sensing materials is the nature of the dopant. Most of these works have been dedicated to the development of gas sensors based on polypyrrole or polyaniline films for the detection of ammonia or volatile organic compounds (VOCs) even if some other gases have been studied such as $CO_2$ for example [27] (Table 1).

Concerning VOCs detection, an interesting micro-gas-sensor composed of PPy-sensing film, Pt micro-heater and Au electrodes on a stress free $SiN_x/SiO_2/SiN_x$ diaphragm was fabricated [19]. Three different polypyrrole thin films were electrodeposited as chemiresistors to test the effect of anions, thickness, and surface roughness of the PPy films on the response to ethanol vapors. The experimental results showed a typical sensitivity to ethanol of 5 µV ppm$^{-1}$ at 30 °C. The best results were obtained for the PPy film having the lowest thickness and the highest roughness (butanesulfonate-doped PPy). Similarly, gas sensors were built from $SiO_2$ substrates with two interdigitated gold electrodes (the gap width between these electrodes was 8 µm) prepared by standard photolithography [20]. Originally, the sensing layers of polyaniline were prepared *in situ* by electrochemical polymerization from a drop of an aqueous aniline solution in sulfuric acid placed in the gap between two gold electrodes. These PANI films were successfully used for ethanol and acetone sensing. In this study, an interesting correlation was established between the doping level of PANI film, which can be changed by varying the acid concentration, and the sensing properties of the polymer material. Indeed, more sensitive signals were obtained in the presence of gas when PANI films were more highly doped. Polyaniline thin films can also be doped with Keggin type

12-tungstophosphoric acid [28]. In this case, the sensor behavior of the films on exposure to acetone vapor indicated the physical adsorption of acetone on the polymer matrix with a fast recovery of the film on re-exposure to air. A better sensitivity to acetone vapor was observed with the films containing this dopant than with more classical ones. Rather than trying to obtain the ideal polymer layer, Barisci *et al.* fabricated an array of sensors based on eight polypyrrole films doped with eight different dopants deposited on the same chip [29]. They used these eight simultaneous signals to successfully identify and quantify benzene, toluene, ethyl benzene, and xylene compounds. The dopants used were mostly sulfonated anions and were chosen because they were highly soluble in water, able to easily form electrodeposited polypyrrole, and were composed of various chemical structures which could lead to various chemical interactions. As expected by the authors, these sensors showed different sensitivities to the various gas compounds. This strategy, which is inspired from the concept of the electronic nose, is a very promising one and has led to sensitive and reproducible responses to various VOCs. The same concept was used by Hamilton *et al.* [30] who used a seven sensors array forming an electronic nose. The seven sensors were coated by polypyrrole films containing various counter-anions (containing perchlorate, hexafluorophosphate, and sulfonate anions) at different concentrations. Resulting materials were used for the sensing of five different VOCs: methanol, ethanol, acetone, butanone, and pentanone vapors. This sensor array performed well for discriminating the different vapors tested and was able to separate the compounds according to their physical properties and chemical structure.

As shown for the detection of VOCs, the main way to modify the properties and sensitivity of conducting polymers consists of changing the nature of the counter-anion. For ammonia detection, the problematic still remains the same and so most of the studies use polymers with various dopants. One of the first examples of polypyrrole film deposited on a microelectrode array for ammonia sensing was developed by Yadong *et al.* [22] who reported that submicrometer polypyrrole film exhibited a useful sensitivity to $NH_3$. The $NH_3$ sensitivity was detected by the change in resistance of the polypyrrole film which was attributed to the formation of a positively charged electrical barrier of $NH_4^+$ ions in the film. The electrons of the $NH_3$ gas acted as the donor to the p-type semiconductor polypyrrole, with the consequence of reducing the number of holes in the polypyrrole and increasing the resistivity of the film. A more recent work was done by Patois *et al.* who studied four different electrodeposition potentials, five counter-anions, and three salt concentrations to assess the effects of these parameters on the ammonia sensing properties of polypyrrole films [23]. Amongst the so-obtained PPy films, the most sensitive one was prepared using an electrodeposition potential of +2.0 V/SCE, a pyrrole concentration of 0.1 M, and $ClO_4^-$ as dopant. These conditions led to a gas sensor (Figure 2) operating at room temperature with high detection efficiency, good reproducibility, fast response, and low detection limit (around 3 ppm) that is below the ammonia toxicity values, since the long-term allowed concentration in which people may work is 20 ppm [31]. Other studies from Carquigny *et al.* [24] and Brie *et al.* [32] presented ammonia sensors using electrosynthesized PPy film doped with either lithium perchlorate or toluenesulfonic acid but the detection limit of these sensors was higher (around 10 ppm). The sensitivity of the sensors was greatly improved for polypyrrole doped with perchlorate anions. The response of the sensor was stable in time over two months and it was shown that the less conductive polymer films exhibited the most sensitive responses to ammonia, thus demonstrating the influence of the initial conductivity of the film. Finally, Bai *et al.*

electrochemically deposited polypyrrole from a solution of sulfonated polyaniline, which was used as a dopant, on an ITO substrate to obtain an ammonia sensor. This original dopant led to a sensing material which appeared sensitive to ammonia for concentrations higher than 20 ppm [33].

**Table 1.** Electrodeposited polymers and polymer derivatives used for gas sensing.

| Polymer | Dopant (D) or Side Chain (S) | Analyte | Reference |
|---|---|---|---|
| Polypyrrole | D: tetrafluoroborate | Carbon dioxide | [27] |
| Polypyrrole | D: decane sulfonate, butane sulfonate, methylphosphonic acid | Ethanol | [19] |
| Polypyrrole | D: 12 different dopants mostly including sulfonated anions | Benzene, toluene, ethyl benzene, xylene | [29] |
| Polypyrrole | D: 7 different dopants with perchlorate, phosphate and sulfonate anions | Ethanol, methanol, acetone, butanone, pentanone | [30] |
| Polypyrrole | D: perchlorate | Ammonia | [22] |
| Polypyrrole | D: 5 dopants perchlorate, phosphate, borate and sulfonate anions | Ammonia | [23] |
| Polypyrrole | D: perchlorate | Ammonia | [24] |
| Polypyrrole | D: lithium perchlorate and toluenesulfonic acid | Ammonia | [32] |
| Polypyrrole | D: sulfonated polyaniline | Ammonia | [33] |
| Polypyrrole (nanowires) | D: sodium dodecyl sulfate | Ammonia | [34] |
| Polyaniline | D: sulfuric acid | Ethanol, acetone | [20] |
| Polyaniline | D: Keggin type 12-tungstophosphoric acid | Acetone | [28] |
| Polyaniline (nanowires) | D: sulfuric acid | Ammonia | [35] |
| Polypyrrole derivative | S: hydroxyalkyl and carboxyalkyl | Alcohols, hexane, triethylamine, toluene, acetonitrile | [36,37] |
| Polypyrrole derivative | S: alkoxy | HCl, ammonia, NO, oxygen | [38] |
| Polypyrrole derivative | S: alkyl, sulfonic acid, ammonium, esters alkoxy | Ethanol, acetonitrile | [39] |
| PEDOT derivative | S: ether | Ethanol, acetonitrile | [40] |

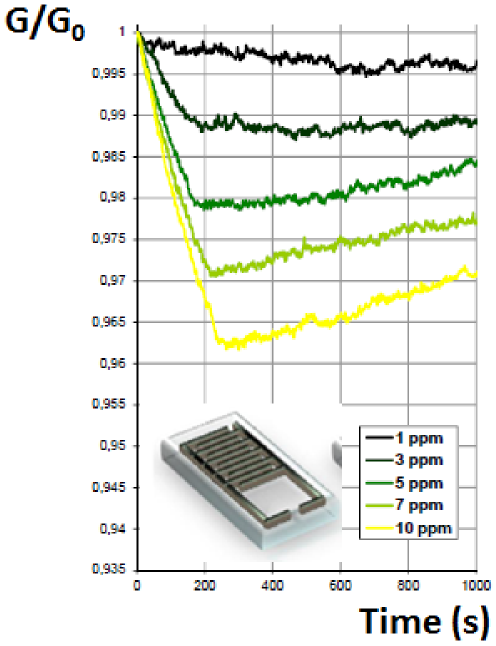

**Figure 2.** Conductimetric response to ammonia changes of a polypyrrole film deposited at +1 V/SCE from an aqueous electrolyte containing 0.1 M $LiClO_4$.

In conclusion, polypyrrole has been extensively used as material for the sensing of VOCs or ammonia. It has been shown that the sensing properties of polypyrrole can be very different depending on the nature and concentration of the dopant. Consequently, the dopant appears as the key factor for such sensing material. This is due to the changes in conductivity and morphology caused by the change in the dopant structure. From the literature, it could be believed that polypyrrole films having a low initial conductivity are the most efficient. The main drawback of gas sensors based on electrodeposited polymers is their lack of selectivity. One solution to partially solve this problem is the use of arrays containing many different polymers as sensing materials as shown by Barisci *et al.* [29] and Hamilton *et al.* [30]. From our point of view, such devices are the only ones in the future that can lead to selective gas sensing.

### *3.2. Gas Sensors Based on Conducting Polymer Nanowires*

A possibility to improve the sensitivity of polymer-based gas sensors consists of the nanostructuration of polymers, and particularly in the preparation of polymer nanowires. For example Tuan *et al.* developed a facile and effective electrochemical route for directly growing polyaniline nanowires on platinum interdigitated microelectrodes [35]. The gas sensing properties of the so-prepared nanowires, whose diameters varied from 50 to 200 nm, and lengths up to hundreds of micrometers, were explored and the results obtained demonstrated that PANI nanowires have good potential as novel ammonia sensors. However, they were tested in the range concentration going from 25 to 500 ppm, and so it is not possible to know if the limit of detection is improved by this nanostructuration. On the contrary, Kim *et al.* prepared polypyrrole nanowires leading to a great improvement in the limit of detection of ammonia sensors [34]. This was done using a new self-patterning method of conducting polymers consisting of magnetic alignment, electropolymerization and a selective etching process. More precisely, Ni nanowires were grown into an anodic aluminium oxide template by electrodeposition, magnetically aligned on Au electrodes as a sacrificial seed layer to grow the PPy nanowires. Then, PPy nanowires were obtained by selectively etching the Ni nanowires in acidic solution. This nanostructuration led to a strong increase in the sensitivity of the PPy-based ammonia sensor and also to a strong improvement in the limit of detection since it was possible to obtain a signal for a concentration in ammonia of 0.2 ppm thanks to the large contact area between metal electrodes and PPy which significantly reduced the contact resistance. Similarly, hydrogen gas sensors have been fabricated based on polypyrrole nanowires synthesized through template-free electro-oxidation of pyrrole [36]. Resulting conductometric sensors were investigated for their sensitivities toward five concentrations of hydrogen gas at room temperature. Compared to previously reported sensors, the developed sensors therein featured fast and reversible responses due to the high porosity of the PPy nanowires-based sensitive films.

In conclusion the nanostructuration of conducting polymers is an emerging and promising strategy in the field of gas sensors. In particular a marked improvement of the sensitivity and detection limit of polymer-based sensors is clearly possible thanks to the nanostructuration. On the contrary, this strategy does not solve the problem of the gas selectivity of the polymer-based active layers.

### *3.3. Gas Sensors Based on Electrodeposited Polymer Derivative Films*

Another strategy that can be considered to improve the characteristics of polymer-based gas sensors consists of the modification of conducting polymers by organic chemistry. Using this approach it is possible to incorporate reactive chemical groups in polymer backbones to facilitate the interactions between functionalized polymer materials and gas analytes. This could result in an improvement of the sensitivity, stability, or selectivity of the gas response. For most of the classical electrodeposited polymers, such modification of the polymer chain structure is easy and that is why many studies have been dedicated to this topic. Sometimes, the introduction of chemical groups to the polymer backbone has another positive effect that is the increase of the polymer solubility in water or in another solvent.

One of the most exhaustive works using this approach was done by Deng *et al.* [37,38] who electrodeposited eight different conducting polymer films formed from pyrrole and N-substituted pyrrole derivatives: polypyrrole, poly(*N*-methylpyrrole), poly(*N*-butylpyrrole), poly[*N*-(2-cyanoethyl)pyrrole], poly[*N*-(2-carboxyethyl)pyrrole], poly(*N*-phenylpyrrole), poly[*N*-(6-hydroxyhexyl)pyrrole], and poly[*N*-(6-tetrahydropyranylhexyl)pyrrole]. These N-substituted pyrrole derivatives were tested as sensitive materials for gas sensing and the results demonstrated that they may be employed as coating for many different organic vapor sensing (alcohols, triethylamine, hexane, toluene, and acetonitrile). The influence of the pendant side chain and the influence of the side-chain length were proved. In addition the differences of sensing behavior observed from one polymer to the other were also attributed to the polarity of the films and to their hydrogen bonding ability. Another work from Krondak *et al.* investigated the chemosensitive properties of polypyrrole derivatives obtained by anodic oxidation of 4,4′-dimethoxy-2,2′-bipyrrole and 4,4′-dibuthoxy-2,2′-bipyrrole on interdigitated electrodes. The obtained polymers demonstrated high sensitivity to HCl gas and also some response towards $NH_3$, NO, and oxygen, but with much lower sensitivity than towards HCl [39]. The influence of the doping level of the conducting polymer derivatives on the sensing of several VOCs was studied by Vercelli *et al.* [41]. In particular, polypyrrole derivatives modified by alkyl groups, alkoxy groups, ammoniums, sulfonic acids and esters, and poly(3,4-ethylenedioxythiophene) modified by ether groups were used to detect VOCs such as ethanol or acetonitrile (Table 1). It was found that heavily doped polymers were not sensitive to gas vapors. On the contrary, appreciable and selective responses (depending on the substitution pattern) were obtained with low-doped polymers. These results make clear that such conducting polymers are good candidates for VOC sensors when used in a low-doped state. Amongst the various substituents low-doped alkyl-substituted polypyrroles appeared as the best candidates for this application.

Consequently, these works showed that polymer derivatives can be successfully used for gas sensing. However, only a few convincing studies have been published and the recent results obtained were not as good as expected. In particular there was no polymer derivative-based sensor which showed an undoubted improvement in sensing characteristics compared to the corresponding non-functionalized conducting polymer.

## 4. Gas Sensors Based on Hybrid Materials

### *4.1. Polymer/Metallophthalocyanine Hybrid Materials*

Metallophthalocyanines have been the most widely used organic materials to prepare hybrid materials by mixing with electrodeposited polymers even if some attempts were carried out using other organic materials such as porphyrins [42] or ferrocenyl derivatives [43] (Table 2). The choice of using metallophthalocyanine comes from the fact that these macrocycles are electron donors which can favor electron transfers with gas analytes. However it is not possible to perform electropolymerization of an aqueous solution containing monomers and insoluble phthalocyanines. That is why it is necessary to render phthalocyanines soluble in water. This approach has been used by Tiwari *et al.* who performed the electrochemical incorporation of a copper phthalocyanine in a polypyrrole matrix in the presence of a cationic surfactant in order to utilize the resulting material for sensing purposes [44]. The sensor films produced by this process were used for the sensing of a nerve gas simulant, dimethyl methyl phosphonate (DMMP), and other vapors like methanol, ethanol, benzene, toluene, and hexane. The sensors were successfully tested and were unaffected by the interfering vapors like ethanol, benzene, toluene, and hexane even at higher concentration, which makes it suitable for DMMP sensing in the presence of them. Instead of using surfactants, N. Guyen Van *et al.* used sulfonated metallophthalocyanines since these compounds are soluble in water due to the presence of sulfone groups in their structure [45]. They incorporated these organic materials during electropolymerization of pyrrole and used the hybrid materials to perform the sensing of $NO_2$ gas. The results obtained with the hybrid materials were better than those obtained with polypyrrole films showing the potential of this combination. Similarly, the *in situ* incorporation of a sulfonated cobalt phthalocyanine into a polypyrrole matrix was achieved by electropolymerization at the surface of platinum interdigitated electrodes leading to a smooth, homogeneous film with a nodular structure [46,47]. This hybrid material was tested as a sensitive layer for ammonia gas sensors and compared with PPy films or cobalt phthalocyanine films. This resulted in a remarkable improvement in the sensing behavior of the so-obtained sensors. Their response to ammonia was fast, reproducible, exhibited a good sensitivity, and had a low detection limit (below 1 ppm). Most of all, the hybrid material responded to ammonia changes whatever the relative humidity value, in contrast to traditional gas sensors based on phthalocyanines.

### *4.2. Polymer/Metal Nanoparticle Hybrid Materials*

Another possibility to prepare hybrid materials is to combine conducting polymers with carbon nanotubes, metal nanoparticles or metal oxide nanoparticles, to improve the characteristics of chemiresistive sensors (Table 2). Indeed, these nanoscale constituents can serve as conduits for charge transport with conjugated polymers behaving as the sensitizing agents or the conducting polymers can be functionalized, introducing specificity for targeted analytes. In some cases the nanoparticles may act as nanoelectrodes that create a matrix of nanoscale polymer sensors to enhance sensitivity and decrease electrical resistance of the device.

A number of studies have focused on the detection of VOCs or other gaseous molecules using hybrid polymer/metal films. The metals used can be precious metals including Au, Ag, Pt, or other metals such as Ni and Cu. One example of gas sensor leading to an improvement in the response has been described by Torsi *et al.* who electrosynthesized polypyrrole doped with copper and palladium inclusions [21]. Gas sensor devices based on these doped organic films showed interesting performances in detecting reducing gases such as $NH_3$, $H_2$, and CO. In particular, the exposure of PPy and Cu-doped PPy sensors to $H_2$ and CO produced an expected enhancement of the film resistance. On the other hand, the electrical response of the Pd-PPy sensor to $H_2$ and CO produced a drastic drop in resistivity, while a resistivity enhancement was produced upon ammonia exposure. This is an interesting result because it shows that the Pd-doped sensor produced a response to $H_2$ and CO which is opposite to that of the other PPy-based sensors. Moreover, the CO and $H_2$ responses of the Pd-PPy sensor were highly reversible and reproducible. Another significant contribution utilizing metallic nanoparticles as the sensitizing agent was demonstrated with an Au/PANI system for $H_2S$ detection by Shirsat *et al.* [48]. In this work, a PANI nanowire network was electropolymerized. Then, this network was electrochemically functionalized with Au nanoparticles of 70–120 nm in diameter. The Au/PANI devices demonstrated superior sensing performance with a very low detection limit for $H_2S$ at room temperature while the unfunctionalized PANI network detection limit was four orders of magnitude higher. In this case, the resulting surface charge of the nanoparticle behaves as a nanogate significantly increasing conduction in the particle localized region and thus leading to a strong improvement in the sensor's sensitivity.

Other types of hybrid materials consist of carbon nanotubes (CNT)/polymer hybrid materials. These active layers are perhaps the most broadly explored hybrid polymer gas sensors. In gas sensors based on CNT/polymer materials, the electrodeposited polymer generally imparts sensitivity, selectivity, and reversibility since CNT has only a low specificity and affinity for gas analytes, these properties confining the role of CNT to transducing elements. Many groups have already tried to use CNT/polymer films for gas sensing, expecting an improvement due to a possible synergetic effect of the CNT transducer and the polymer sensitizing element. Unfortunately, very few convincing results have been obtained. Only the work from Zhang *et al.* led to very interesting results [40]. In this study, electrodeposition was used to functionalize SWNT-COOH networks with chloride-doped PANI for ammonia sensing. The results showed a 60-fold improvement in sensitivity at room temperature over that of unfunctionalized SWNT networks and also led to a very low detection limit.

In conclusion many works consisting of the incorporation of carbon nanoparticles, metal nanoparticles, or carbon nanotubes in electrodeposited polymers have been performed but only a few of them have led to significant improvements of gas sensing characteristics. On the contrary not many works have been dedicated to the preparation of polymer/metallophthalocyanine hybrid materials but the few studies realized have demonstrated the possibility to obtain synergetic effects in the structure and properties of the resulting materials for gas sensing. This strategy is probably one of the most promising since the incorporation of a metallophthalocyanine in the polymer matrix can both improve the sensitivity, the limit of detection, and the selectivity of gas sensors.

**Table 2.** Hybrid materials (combining an electrodeposited polymer and another element) used for gas sensing.

| Polymer | Other Element | Analyte | Reference |
|---|---|---|---|
| Polypyrrole | Copper phthalocyanine | Dimethyl methyl phosphonate | [44] |
| Polypyrrole | Sulfonated metallophthalocyanines | $NO_2$ | [45] |
| Polypyrrole | Cobalt phthalocyanine | $NH_3$ | [46,47] |
| Polypyrrole | Pd, Cu | $NH_3$, $H_2$ and CO | [21] |
| Polyaniline | Au | $H_2S$ | [48] |
| Polyaniline | SWNT-COOH | $NH_3$ | [40] |

## 5. Response Mechanism

The conductivity of electrodeposited polymers strongly depends on their doping levels which can be easily changed by chemical reactions with many analytes at room temperature, thus providing a simple technique to detect gas analytes. Consequently, electron transfers between polymers and gas analytes alter the doping level of polymers and cause the changes in resistance of the sensing material (Table 3). This process occurs for example when PPy or PANI films are exposed to $NH_3$, $NO_2$, or other redox-active gases [23,31–35,49,50]. Electron acceptors, such as $NO_2$, can remove electrons from the aromatic rings of conducting polymers. When this occurs at a p-type conducting polymer, the doping level as well as the electric conductance of the conducting polymer is enhanced. An opposite process occurs when detecting an electro-donating gas. This is the case when ammonia, an electron-donor, reacts with PPy leading to an increase in the electric resistance.

The response mechanism of a PANI film is special since its doped state can be controlled by acid/base reactions. This is widely used to detect acidic and basic gases. When exposed to ammonia gas, PANI undergoes de-doping by deprotonation [51–53]. Indeed, the protons on –NH– groups of PANI are transferred to ammonia molecules to form ammonium ions while PANI itself turns into its base form. When the ammonia atmosphere is removed, the ammonium ion is reversibly decomposed to ammonia gas and proton. After reaction with acidic gases (HCl, $H_2S$, and $CO_2$) in the presence of water, PANI is doped [54–57]. Simultaneously, water can transfer protons to PANI, thus leading to a modification of the polymer film conductivity. Such proton transfer is also possible with PPy films. Indeed, a decrease in the resistance of a PPy film was observed when it was exposed to the vapor of weak acids such as $H_2S$ and $CH_3COOH$, indicating a proton transfer from the acidic gas to PPy and an increase of the doping level of the polymer [58,59]. Furthermore, it was proved that ammonia can remove protons from PPy [60,61]. If the formed ammonium was bound close to the counter-anion, the proton transfer process is reversible. However, a nucleophilic attack on the carbon atom of PPy backbones usually occurs, which may cause an irreversible change in PPy [62].

Concerning hybrid materials, phthalocyanines are good π-electron donors, so when a hybrid film of phthalocyanine and conducting polymer is exposed to $NO_2$, electrons transfer from phthalocyanines to $NO_2$, for example, lead to an increase in charge carriers (hole) [45]. In some cases, a catalyst incorporated in the conducting polymer film can help in detecting some inert analytes. This is the case for Pd/PPy and Cu/PPy nanocomposites since it was found that the sensitivity of these sensors was strongly increased due to both interactions between ammonia molecules and metallic inclusions and to the modification of the polymer film caused by the inclusion of conductive metal nanoparticles [21,48]. In the case of hybrid materials made of carbon and polymers, carbon has only the role of transducing element while the polymer imparts sensitivity, selectivity, and reversibility. Consequently, the response mechanism is not changed by the presence of carbon except if the latter has been previously functionalized [40].

**Table 3.** Response mechanism of electrodeposited polymer-based gas sensors.

| Response Mechanism | Gas or Catalyst | Response | Reference |
|---|---|---|---|
| Electron transfer | Electron acceptor ($NO_2$) | Conductivity increase | [31–35,45] |
| | Electron donor ($NH_3$) | Conductivity decrease | [49,50] |
| Proton transfer | Acid (HCl, $H_2S$, $CO_2$, $CH_3COOH$) | Conductivity increase | [54–59] |
| | Base ($NH_3$) | Conductivity decrease | [51–53,60,61] |
| Catalysts (Pd, Cu, C) | DMMP, $NH_3$, $H_2S$ | Enhancement of the response (conductivity increase or decrease) | [21,40,48] |

## 6. Conclusions

An attempt has been made to present an overview on the prospects of electrodeposited polymers in gas sensors, recently reported, and to outline some of their latest advances. Electrodeposited polymers have been proved to be able to provide numerous opportunities for fabricating new gas sensors due to their intrinsic features. In particular, these polymers allow the preparation of gas sensors having good sensitivity and selectivity, at room temperature, due to their electrical conductivity and charge transport properties. As a result electrodeposited polymers are now recognized as very good sensitive materials for the development of highly selective, specific, stable, economic, and handy gas sensing devices. However electrodeposited polymers still have many unexplored possibilities, and so a lot of future research will probably be dedicated to the development of new polymer-based chemical sensors. One of the most promising ways for the future is the nanostructuration of electrodeposited polymers since the electrosynthesis of polymer nanowires has recently led to strong improvements in the sensing properties of conducting polymers. In addition the landscape for hybrid conducting polymer systems is rich in potential with numerous materials, each with their own chemical, electrical, and physical properties, yet to be explored for chemical sensing. From the perspective of electrodeposited conducting chemical structure, little has been undertaken for these hybrid devices. The addition of functional groups opens up an avenue to further tune these devices in addition to variations in the base polymer and higher level structures, even though this approach has not lead to significant advances in past years. One can also envisage more complex hybrids containing polymer blends, multiple nanoparticle materials, and the combination with organic materials such as phthalocyanines for sensor arrays to analyze gas mixtures. As our understanding of the electronic and physical structure of interfaces in these hybrid materials continues to mature, electrodeposited materials and hybridization options may also enable the design of advanced systems including gas specific sensors.

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## Author Contributions

All co-authors contribute to the writing of this review article. In particular, OS contributes to Section 2, TP and SC to Section 3, SL to Section 5, and BL to Sections 1, 4 and 6.

## Conflicts of Interest

The authors declare no conflict of interest.

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