TiO₂ nanofibrous chemoresistors coated with PEDOT and PANi blends for high performance gas sensors

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Abstract

Hybrid sensors consisting of nanofibrous scaffolds of TiO₂ coated with thin films of self-assembled conductive polymer (CPs) blends have been recently tested in their capability of detecting traces of some gaseous markers of metabolic diseases, treated meat or spoiled food and explosives, and the resulting sensors have been compared in their sensing properties. In the present study, fibresimilar chemoresistors, based on the integration of a nanosized TiO₂ and different blends of organic polymers (PEDOT:PSS and PANi:PS) were designed and set up. The resulting sensors showed an overall enhancement of sensing performances (sensitivity, selectivity, rapid responses, etc.) and greater lifetimes, and decrease in drawbacks of each polymer. Sensing characteristics towards NO₂ and NH₃ were tested at both the equilibrium and within a shorter time upon the rapid sensor responses, and results were discussed. Since the reaction between sensors and analytes was assumed to occur at the interface between CPs and TiO₂, the resulting film structures were also investigated through scanning and transmission electron microscopy.

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1. Introduction

Electrospun nanofibres have been confirmed to be suitable candidates for ultra-sensitive gas sensors since they significantly increase surface area to volume ratios of coatings. Such a feature may both affect sensor
sensitivity and its response time [1,2]: the higher the specific surface area of the sensing material the higher the sensitivity of the resulting sensor. Such a sensing strategy tries to reproduce and mimic most of common natural hair-like sensing structures. Nanostructured layers may improve sensor features with respect to those of compact films, enhancing analyte-sensor interactions and reducing some bulk drawbacks (i.e. long analyte diffusion–release time, analyte entrapment, film poisoning, etc.). The electrospinning technique, patented by Formhals in 1934, is an appealing technology, since it is easy to use and cost-effective, providing fibres with diameters in the range from micron to submicron (<100 nm).

![Fig.1. Schematic representation of the experimental set up used to obtain chemosensors based on Pt-Ti IDEs coated with a thick nanofibrous scaffold of titania (by electrospinning), and an overlying thin layer of CP (by dipping)](image)

The combination of metal oxides and organic polymers in integrated nanostructures improve the sensitivity and selectivity of CPs [3,4]: the resulting sensors can operate at room temperature and the selectivity towards different gas species can be tuned up by adjusting the surface to volume ratio of nanosized metal oxides. In addition, the resulting composites are typified by improved long-term stability and their properties depend not only on the characteristics of their constituents but also on their morphological and interfacial features in combinations. In the present study, the properties of gas chemoresistors based on nanofibrous scaffolds of titania functionalized with selected CPs (PEDOT:PSS or PANi:PS) were tested.

2. Experimental and Results

The nanostructured IDEs, consisted of 40 pairs of electrodes of sputtered Ti and evaporated Pt, respectively (150 nm thick and 20 µm width electrode, 20 µm gap). TiO2 nanofibers were grown up directly on interdigitated electrodes (IDEs) as transducers, through electrospinning, and annealed in order to achieve the titania crystallization [5]. Such a layer improved specific surface area and gas permeability. TiO2 nanofibrous IDEs were dipped into freshly prepared solutions of PEDOT-PSS (EtOH:H2O)sol and PANi:PS (CHCl3)sol, in order to obtain thin films covering the fibres (Fig.1). TEM pictures (Jeol JEM
2010 equipped with LaB6 gun operating at 200 KeV) reported a remarkable shrinkage of TiO$_2$ fibres after annealing at 550 °C in air (Fig. 2a).

The boundary between uncovered and covered fibres with the PEDOT:PSS film after dipping is easily visible in Fig. 2b by the different colour of fibres and background, where the organic polymer also appears homogeneous. After drying of differently coated (PEDOT:PSS and PANi:PS) chemoresistors, their electrical parameters were tested by measuring the current changes under varying voltage (Fig. 3). A linear behaviour similar to that of a flat polymer layer was confirmed (data not shown). Additionally, the linearity of Current-Voltage (I-V) curves suggests a good adhesion of the sensing structure to the metal electrode and the proper functioning of sensors. A doping effect of TiO$_2$ nanostructures on the electrical features of

![Fig. 2. a) TEM micrographs of as-spun (left side) and annealed (right side) fibres of TiO$_2$; b) SEM micrograph of titania fibres partly dipped in PEDOT:PSS solution (darkish portion).](image)

![Fig. 3 Comparison between Current-Voltage curves of PEDOT:PSS/TiO$_2$ (a) and PANi:PS/TiO$_2$ (b) chemoresistors when relative humidity was increased up to 50%.](image)
polymers is also reported in literature, inducing a decrease in the energy gap and the increase in the charge carriers available [3,4]. A strong dependence on water vapour percentage was reported for both sensors (greater than that of flat films - data not shown), regardless the polymer used for coating. However, the behaviour of the two blends at increasing relative humidity conditions diverged, according to their physical properties (i.e. PS-hydrophobic and PSS-hydrophilic, respectively): while the PANi-based sensor increased the current vs. voltage slope at increasing humidity, the PEDOT-based one exhibited a decreased slope. Gas measurements were carried out at ambient humidity (40% RH) and under synthetic air (2% RH). Both high sensitivity and selectivity were reported for PEDOT- and PANi-based sensors to NO\textsubscript{2} and NH\textsubscript{3}, respectively, as reported in Fig.4 (a,b). Faster and higher responses to NO\textsubscript{2} were recorded by PEDOT:PSS/TiO\textsubscript{2} at 40% RH when compared to dry ambient conditions (data not shown). The role of water vapour when gases interact with such nanostructures is currently under investigation, but preliminary results suggested there was an improvement in speed of response and then in the sensing performances when the carrier gas was humidified (data not shown).

![Fig.4](image)

Fig.4. a) Comparison between PEDOT:PSS/TiO\textsubscript{2} and PANi:PS/TiO\textsubscript{2} sensor curves to NO\textsubscript{2} at 40% RH. Response time was limited to 90 s (I: current value after gas exposure, I\textsubscript{0}: current value before measurement under air flow); b) PANi:PS/TiO\textsubscript{2} sensor curve depicting the normalized current changes when increasing concentrations of ammonia within the range 100-500 ppb were flowed through the measurement chamber for 90 s.

References