Performance improvement of macroporous polypyrrole sensor for detection of ammonia by incorporation of magnetite nanoparticles

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ABSTRACT

In this work, polystyrene spheres were employed as templates to prepare polypyrrole inverse opal films on the surface of platinum electrodes. The facilitated access for both outer and inner active sites, as well as the exhibited electrochemical behaviour, turned macroporous PPy into a material more suitable than bulk PPy for electrochemically determining ammonium in samples. However, independently of employing bulk or macroporous polypyrrole, the loss of conductivity suffered by the polymer during the mediating process led to an irreversible increase of the electrical resistance that compromised the sensor's analytical performance. Here, it is shown that the incorporation of magnetite nanoparticles into the walls of the polypyrrole inverse opal films generated a protective effect. This increased the stability of the macroporous mediator due to the preservation of the polaron state, as shown by Raman spectroscopy experiments. Finally, the interaction between polypyrrole and magnetite also positively affected the observed analytical parameters, improving linear range, detection limit and sensitivity of the ammonium sensor.

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1. Introduction

In recent years numerous studies have focused on the development of micro and nanostructured materials to take advantage of their large surface areas in order for them to be applied as sensors. In many cases, these materials exhibit different properties to those observed when they are massively structured. Consequently, it is possible to produce a wide range of smart materials in order to obtain the desired properties for a specific application. In particular, conducting polymers, such as polypyrrole (PPy) with nanodimensions, have attracted great attention in the development of chemical and electrochemical sensors. For this application materials are obtained with a large surface area or volumetric activity which provides more reactivity sites and thus higher intensity signals can be achieved. The mechanical properties, biocompatibility and chemical stability at room temperature of conducting polymers have led to interesting research in different fields of science and technology with specific applications in structural materials and/or

functional electrochemical sensors bioactuators [1–3], biosensors [4,5], solar cells and electronic devices [6].

Among the wide variety of conjugated polymers, polypyrrole (PPy) has been studied in particular detail in recent decades. There are many advantages of PPy which lead to it being considered an excellent candidate to construct functional composite materials, for example: (i) its simplicity and diversity of methods of preparation [7–9]. (ii) Its good electrical conductivity, improved by adding doping agents, which increase the efficiency of charge transfer by overloading the pi bonding orbital along the polymer chain [2,10]. (iii) Its chemical stability and selectivity. (iv) Its excellent mechanical strength. By using different methods, micro and nanostructures (micropores, microlayer, microfibers) have been obtained. These special structures increase the number of electroactive areas [11–15]. With the addition of conductive or redox-active nanoparticles (nanofibers, nanotubes, nanocrystals, etc.) it has been possible to change the load/unload effect of the PPy [1,9,16–18], which improves its performance as an electrical conductor and its sensitivity when it is used as an electrochemical signal transducer [1,12,19].

Due to its convenient properties and low response time, PPy electrodes have been used to measure ammonia as a pollutant in gas emissions [1,12,20] and as an indicator of health disorders

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in aqueous solutions [2,19]. However, the detection processes of ammonia are outside the thermodynamic equilibrium, causing an irreversible increase in the electrical resistance and fast loss of conductivity of the polymer. This makes it necessary to look for new ways to increase the lifetime and sensitivity of the PPy sensors (avoiding fast saturation). Although some methods have already tried to recover the conductivity of polymer conductors [12] these procedures require waiting during the activation time between each measurement, which limits the range and the effective time of detection. In addition, the sensitivity of the sensor decreases after the recovery process application. Previous studies have shown that the performance and the analytical properties of nanostructured electrodes are better than solid electrodes [21,22] since the interactions and reactions occur at the atomic and molecular level generating important changes in the design and applications of the sensors. As result of the nanostructuring materials a higher ratio of surface area/volume is obtained, which provides more active sites available to interact with the analyte [23]. Consequently, the sensitivity of the sensor will be greater than for similar solid or bulk sensors. However, both the bulk and microstructured PPy sensors employed in the determination of ammonia have a low sensitivity range and reduced lifetime [19,20], due to the loss of conductive properties over the detection time. According to our hypothesis, the conductivity loss of PPy sensor for ammonia detection could be solved by adding magnetite nanoparticles to the polymer matrix. It has been shown in previous work that nanoparticles of magnetite increase the conductivity of the PPy and preserve the polymer against fast over-oxidation [9]. This procedure could improve the lifetime of the sensor maintaining its conductivity for a longer period and improving the redox processes [9,24]. In the search for new methodologies to improve the performance of PPy sensors to ammonia detection, some modification of the porous PPy matrix (microstructured PPy) has been proposed by incorporating nanoparticles of Fe_3O_4 into the PPy, as was demonstrated for bulk PPy electrodes in previous work [9].

This work presents the development of an ammonia sensor using a three-dimensionally inverse opal microstructure of polypyrrole with and without nanoparticles of magnetite incorporation with superior sensitivity and durability than those of compact PPy. The effects of the magnetite incorporation into the PPy matrix on the stability and electrical properties of the polymer were analyzed by Raman spectroscopy and cyclic voltammetry. The changes in the sensitivity and detection ranges of the PPy sensors were verified by amperometric detections comprising successive additions of ammonium chloride. The changes in the degree of oxidation of the polymer were also followed by Raman microscopy.

2. Experimental methodology

2.1. Template formation

Sensors of PPy and PPy–Fe_3O_4 were obtained by electropolymerization of pyrrole monomer on a template of polystyrene spheres (PS) deposited on platinum (Pt) as substrate. Prior to the deposition of the suspension of PS on the surface of Pt, the Pt substrate was cleaned in an ultrasonic bath with acetone, ethanol and distilled water and then the surface was activated by immersion in a solution of NaOH 10% (w/w) for 10 min. The PS templates were prepared by dropwise deposition (10 μL) of a suspension of PS on Pt foil. Suspension of PS was prepared as 0.5% (w/w) of PS spheres ($D \approx 460$ nm) in 1×10^{-4} M Triton solution [1]. After deposition the solvent was evaporated in a convection oven at 30 °C and then the PS particles were sintered in a convection oven at 85 °C for 4 h at atmospheric pressure.

2.2. Electrosynthesis of PPy and PPy–Fe_3O_4 films and sensor formation

PPy films were obtained by electropolymerization of previously distilled pyrrole monomer, as described in earlier studies [2,11,12,20]. The electropolymerization of PPy was performed in a conventional cell of three electrodes, using templates of PS on Pt as working electrodes (0.049 cm^{-2} area). A mesh of Pt was used as an auxiliary electrode and an Ag/AgCl as a reference electrode. The electrolyte used was 10 ml of 25 mmol L^{-1} sodium dodecylbenzenesulfonate (DBSA) and 0.05 mol L^{-1} pyrrole. The electropolymerization of pyrrole was carried out by applying an oxidation potential of 0.7 V and 0.7 C.cm^{-2} of electric charge, using an Autolab potentiostat – galvanostat PGSTAT302. Before the polymerization, the open circuit potential (OCP) was allowed to stabilize for about 15 min under an atmosphere of nitrogen. For fabrication of PPy–Fe_3O_4 films the same procedure as pure PPy films described above was followed, but the electrolyte was modified by the addition of 4 mg of Fe_3O_4 nanoparticles ($D \approx 20$ nm). With this procedure homogenous PPy–Fe_3O_4 films have already been obtained [9]. It is important to highlight that same electric charge density (0.7 C cm^{-2}) was applied in all experiments. This guarantees a similar amount of PPy deposited in all the analyses.

2.3. Formation and physical characterization of 3D sensor for ammonium detection

Once the PPy and PPy–Fe_3O_4 films were formed on PS templates, electrodes were immersed in toluene for 24 h with constant stirring to dissolve the PS [14]. Then, the electrodes were submitted to drying at 30 °C for 20 min in a convection oven in order to remove residual solvent that may remain in the pores of the sensors. With this procedure PPy-3D-IO and PPy–Fe_3O_4-3D-IO films were obtained. After that, film morphology was characterized by scanning electron microscopy SEM using JEOL JSM LV 6490 equipment coupled to an Energy Dispersion X-ray microprobe (OXFORD-INNCA Penta FET-x3). The formation of PPy and the structural information of the PPy-3D-IO and PPy–Fe_3O_4-3D-IO sensors were analyzed by Raman spectroscopy using a Micro-Raman (Horiba Jovin Yvon) system at 632.8 nm.

Once PPy-3D-IO and PPy–Fe_3O_4-3D-IO sensors were obtained, they were activated by cyclic voltammetry in 5 ml of 0.1 mol L^{-1} boric acid solution at a scan rate of 50 mV s^{-1}. The performance of the sensors to ammonia detection was assessed by amperometry, applying a constant potential of +0.35 V and successive additions of 10 μl of 0.05 mol L^{-1} NH$_4$Cl in 0.1 mol L^{-1} borate buffer solution, set at pH 10 by addition of NaOH. At this pH, NH$_3$ is the predominant specie (pKa = 9.4). Measurements were performed at room temperature and under an atmosphere of nitrogen using an Autolab PGSTAT30 potentiostat-galvanostat. They were all repeated at least twice.

3. Results and analysis

3.1. Characterization of ammonia sensors

In order to get the three-dimensional formation of the active surface of PPy-3D-IO and PPy–Fe_3O_4-3D-IO sensor it is crucial that the pyrrole monomer reaches all interstitial gaps left by the PS spheres before beginning the PPy electrosynthesis. This guarantees that PPy replicates the three-dimensional morphology of PS templates. A SEM image of the three-dimensional PPy–Fe_3O_4-3D-IO arrangement is shown in Fig. 1a. The homogeneity of such an arrangement is possible due to the alkali activation treatment applied to the Pt substrate, which decreases the surface tension and allows an