FLEXIBLE COMPOSITE AgNPs-PPy/CELLULOSIC PAPER ELECTRODE FOR ELECTROCHEMICAL DETECTION OF NITRATE

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In this work, we describe a simple strategy for the preparation of a low-cost electrode material based on polypyrrole (PPy) film grown on an insulating cellulosic paper (CP) substrate via *in-situ* oxidative polymerization technique and functionalized by silver nanoparticles (AgNPs) uniformly dispersed on its surface. The properties of the obtained AgNPs-PPy composites were characterized using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. The electrocatalytic activity of the prepared electrode was investigated for the electroreduction of nitrate using cyclic voltammetry in 0.1 M KOH solution. Results demonstrated that the incorporation of AgNPs into the PPy matrix significantly improves the catalytic behaviour of this film. The effect of the amount of incorporated AgNPs on the electrode response was also investigated.

Keywords: composite materials, nitrate, polypyrrole, silver, thin films

INTRODUCTION

Nitrate pollution in groundwater reservoirs and lakes is a common and increasing problem in numerous countries worldwide. Recently, the influence of nitrate on human health has been widely recognized, since it causes serious health risks for human beings.[1] The European Community standards have set the maximum nitrate concentration to 50 ppm in drinking water, *i.e.* 0.8 mM.[2] The nitrate ion itself is not very toxic, but its reduction product, the nitrite ion, constitutes a real danger to health. Thus, the detection and quantification of NO_3^-, as well as its elimination, represent today increasingly demanding work objectives.

Among the different nitrate removal methods, the use of electrochemical techniques has generated significant interest.[3] However, one of these techniques' major challenges was found to be the development of efficient catalysts for nitrate electroreduction. Numerous studies published in the literature are devoted to, for example, the use of bulk metal electrodes, such as Au, Pt, Ag and Cu.[4,5] It was concluded from these studies that this class of electrodes proved to efficiently reduce nitrates. However, such electrodes suffer from several drawbacks, such as expensive substrates, inflexibility, and insensitivity.

Cheap and disposable electrodes require a reliable and sensitive substrate. Paper is an ideal substrate due to its abundance, biodegradability, bendability, light-weight property and recyclability.[6,7] Demonstrations of the utility of paper as a substrate for sensors[8-11] include biodetection[12-14] and heavy metals removal from water.[15] Nowadays, a new generation of electrode materials based on composite films of conductive polymers, incorporating noble metal particles, has been introduced with the aim of enhancing the physical, electrochemical and electrocatalytic properties of the resulting materials.[16-18]

This work aims at investigating the preparation and properties of a simple, low-cost and flexible electrode material, based on silver nanoparticles-polypyrrole (AgNPs-PPy) composite films, synthesized via a simple chemical deposition process on an inert cellulosic paper substrate, for the detection of nitrate in alkaline medium. The electrochemical measurements showed that the enhanced catalytic activity of the prepared electrode was due to the presence of AgNPs in the composite film.

EXPERIMENTAL

Pyrrole (>98% purity, Prolabo product) was used as received in the chemical synthesis of polypyrrole. Iron (III) chloride anhydrous ($FeCl_3$) (Prolabo product) was used as oxidant for the polymerization of polypyrrole. Potassium chloride (KCl), potassium hydroxide (KOH) and silver nitrate ($AgNO_3$) were purchased from Merck. A semi-rigid paper substrate was used, with a surface density of 240-250 $g.m^{-2}$ (ISO536). The geometric surface of the working electrode was equal to 2 cm^2.

Preparation procedure

AgNPs-PPy composites were chemically deposited on a non-conducting cellulosic paper (CP) substrate (1 × 2 cm^2) as follows: first, the substrate was dipped for 15 min in an aqueous solution of 0.1 M pyrrole dissolved in 0.1 M HCl + 0.5 M KCl to apply a layer of the monomer. Then, an appropriate amount of anhydrous ferric chloride ($FeCl_3$), acting as oxidant for the polymerization of pyrrole, was added to the solution. The oxidant to monomer molar ratio was fixed to 2 as described in an earlier work.[19] Upon addition of the oxidant, the monomer pyrrole was continuously oxidized onto the surface of the substrate, which acquired a black color, indicating the formation of the PPy deposit. After depositing PPy, the sample was thoroughly washed with triple-distilled water. The incorporation of AgNPs was conducted by immersing the PPy/CP electrode in an aqueous solution of silver nitrate ($AgNO_3$). Several AgNPs-PPy composites were prepared with different amounts of AgNPs. PPy was also synthesized through a similar procedure and used as reference.

Characterisation

Electrochemical measurements were performed using an EC-Lab SP 300 potentiostat-galvanostat with a conventional three electrode cell. The prepared AgNPs-PPy/CP electrode was used as the working electrode; a saturated calomel electrode (SCE) and a platinum wire were used as reference and counter electrode, respectively. The electrocatalytic activity of the electrode for nitrate detection was examined in 0.1 M KOH solution, using cyclic voltammetry.

X-ray diffraction patterns were collected at ambient temperature using a Bruker D8 Advance diffractometer. Surface characterization was carried out using a Carl Zeiss scanning electron microscope, equipped with an energy dispersive X-ray (EDX) system.

RESULTS AND DISCUSSION

Characterization of AgNPs-PPy composite films

Figure 1 (a, b, c and d) show SEM images typical of CP and of the PPy film chemically deposited on the CP substrate, taken before and after deposition of AgNPs on the surface of the PPy/CP electrode, respectively. As shown by the images, PPy exhibits a homogeneous morphology, characterized by a granular microstructure. It is also clear that silver was deposited as nearly-rectangular nanoparticles, homogeneously dispersed on the entire surface of the PPy film, and their mean size is in the range of 60-80 nm.

The EDX spectrum of the AgNPs-PPy (Fig. 1 (e)) confirms the presence of silver particles within the PPy film. Also, it shows the presence of carbon, nitrogen and oxygen. These latter elements were due to the PPy film and the electrolyte.

The X-ray diffractograms of the PPy film before and after deposition of AgNPs confirmed the combination of AgNPs in the PPy matrix, as shown in Figure 1 (f). We can observe several peaks, indicating that the sample is crystallized. The broad peak centered at $2\theta = 22.4°$ is due to the amorphous phase of PPy.[20-22] The peaks located at 2θ values of 37.92°, 44.37°, 64.49° and 81.44° are matched well with the (111), (200), (220) and (222) crystal planes of the face-centered cubic Ag phase, respectively. The mean size of the crystallites, by using Scherrer's formula for the face-centered cubic plane (111), was estimated to be of 3.7 nm. From the XRD patterns, the existence of AgNPs in the PPy matrix was established, which is consistent with the result of the SEM observation.

Electroreduction of nitrate on AgNPs-PPy/CP electrode

The electrochemical behaviour of the AgNPs-PPy/CP toward nitrate reduction was studied by cyclic voltammetry in 0.1 M KOH solution. The potential scan was performed from -0.2 to -1.2 V. The influence of some experimental parameters was investigated and optimized according to the electrode response, and was discussed below.

Influence of electrode material

Figure 2 (a) shows the cyclic voltammetric response of the AgNPs-PPy/CP electrode for nitrate reduction in the 0.1 M KOH solution containing 5 mM $NaNO_3$, compared with those obtained on bare Ag and PPy/CP electrodes. As can be seen, no peak is observed on the PPy/CP electrode, indicating that the pristine PPy film is electrochemically inactive in the potential range between -0.2 and -1.2 V.

In this particular potential window, a well-defined reduction peak current centered at -0.8 V is observed when the AgNPs-PPy/CP electrode is used. In contrast, the bare Ag electrode shows a large overpotential, without any peak, in spite of its high cathodic current density. In addition, in the absence of nitrates in KOH solution, no obvious current is observed on the Ag-PPy/CP electrode over the entire potential range covered.

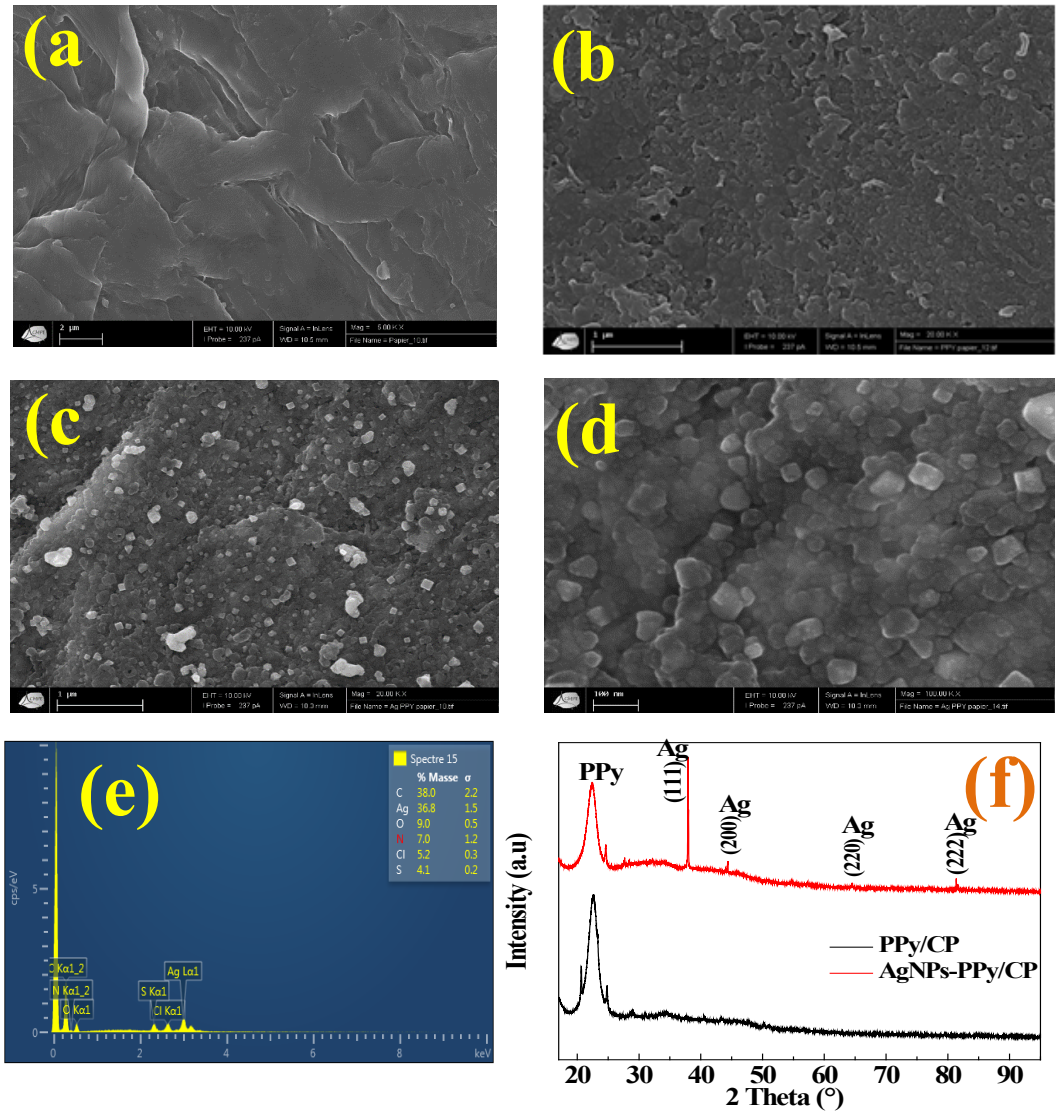

Figure 1: (a), (b) and (c, d) SEM micrographs of the cellulosic paper (CP), PPy and AgNPs-PPy films, respectively; (e) EDX spectrum of the AgNPs-PPy film; (f) XRD patterns of pristine PPy and AgNPs-PPy film

A comparison of these results reveals the electrochemical behaviour of the AgNPs-PPy/CP modified electrode towards nitrate reduction, and also highlights the role of AgNPs in the catalytic activity of the composite film. This may be attributed to the increase of the electrode surface area due to the uniform distribution of nano-sized Ag particles, also to the high electrical conductivity and intrinsic catalytic properties of Ag for the reduction of nitrates.

The same strategy was used to compare the electrochemical behaviours of the AgNPs-PPy/CP electrodes prepared with different amounts of AgNPs. Figure 2 (b) shows cyclic voltammetric curves recorded on three different AgNPs-PPy/CP electrodes prepared at 5, 10 and 15 min deposition durations of AgNPs. It can be observed that the increase of Ag synthesis time leads to an increase of the reduction current of nitrate. In addition, the cathodic peak potential shifts toward more negative potential values. This is probably due to the contribution of the hydrogen evolution reaction (HER). One can see that in the case of high Ag synthesizing durations (15 min), the

nitrate reduction peak potential value (around -1.1 V) is observed in the so-called hydrogen region. Therefore, the peaks obtained with the modified electrodes synthesized at durations of 5 and 10 min reflect the net current densities of the nitrate reduction without the HER (peak potentials centered at -0.71 and -0.83 V, respectively). Thus, the best catalyst in terms of reduction current vs nitrate (without competition of HER) is the electrode modified by Ag deposited for 10 min. Here, higher peak currents for nitrate reduction could be attributed to higher effective surface areas, improved mass transport and higher catalytic effect due to the electronic properties of the AgNPs. Therefore, the electrode synthesized at this deposition time (10 min) will be considered for further analysis in the rest of this study.

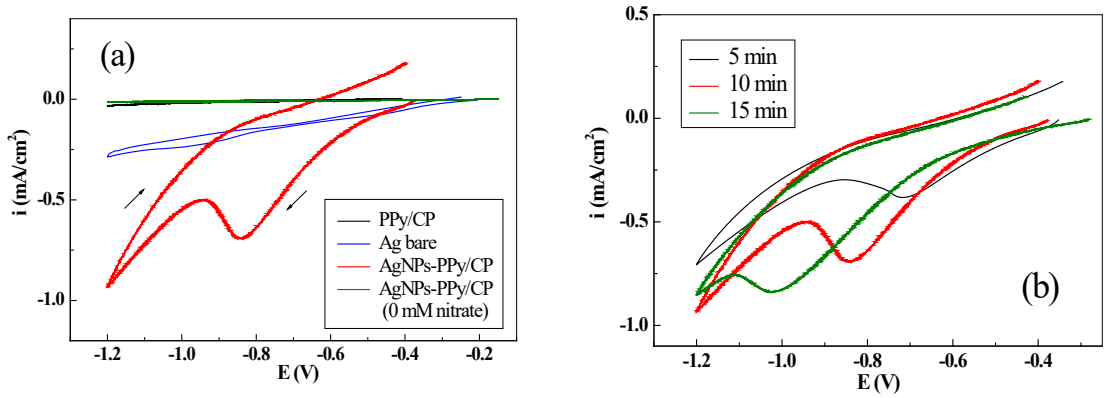

Figure 2: (a) Cyclic voltammograms of PPy/CP, bare Ag electrode and AgNPs-PPy/CP in solution containing 5 mM nitrate and 0.1 KOH; (b) Cyclic voltammograms of 5 mM nitrate for AgNPs-PPy/CP electrodes prepared at different Ag particles deposition times (Scan rate = 50 mV/s)

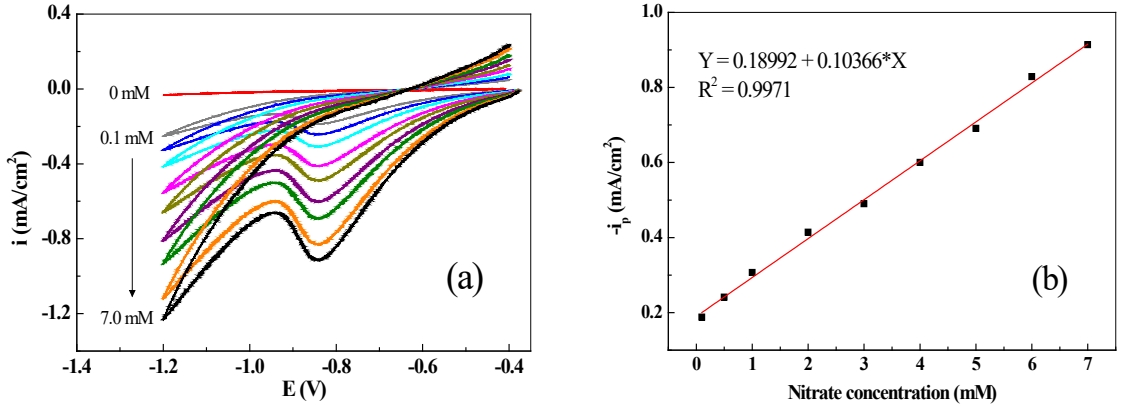

Figure 3: (a) Cyclic voltammograms of AgNPs-PPy/CP electrode in 0.1 M KOH solution with different concentrations of nitrate (Scan rate = 50 mV/s); (b) Linear plot for nitrate concentration *vs* current response

Influence of nitrate concentration

The effect of nitrate ions concentration on the cyclic voltammetric response of the AgNPs-PPy/CP electrode was investigated. Figure 3 (a) displays the electrode response in the presence of different concentrations of nitrate, ranging from 0.1 to 7.0 mM. As can be seen, the reduction peak current increases with increasing nitrate concentration in the solution, which confirms the catalytic behaviour of the electrode.

In addition, the plot of the cathodic peak current as a function of nitrate concentration gives rise to obtaining a straight line (Fig. 3 (b)). These results suggest that the proposed electrode can further be used for the determination of nitrate in the concentration range of 0.1-7.0 mM, with good sensitivity (0.10366 mA/cm^2 mM).

CONCLUSION

An AgNPs-PPy composite has been synthesized on a non-conducting cellulosic paper substrate by the chemical deposition process. The SEM and XRD characterizations established that the AgNPs-PPy composites were successfully formed. The prepared electrodes demonstrated high catalytic activity for nitrate electroreduction

in 0.1 M KOH solution. The amount of AgNPs is a key parameter that has a significant effect on the electrode activity; thus, the latter can be easily controlled by varying the silver deposition time. The highest electrocatalytic response was observed for the electrode synthesized at 10 min deposition time. To conclude, the proposed electrode is relatively inexpensive and may be used for the detection of nitrate.

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