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A Brief Study on Electrochemical Properties of Polypyrrole/Nano-SiO_2

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Abstract

An attempt has been made to investigate the effect of SiO_2 nanoparticles on the conductivity of polypyrrole conducting polymeric films prepared by an electrochemical method. The obtained nanocomposites were characterized by FTIR, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The results indicate that the conductivity of the nanocomposite was significantly increased in comparison to pure polypyrrole. Fitting the impedance results to an equivalent circuit reveals that addition of SiO_2 nanoparticles reduces the ohmic resistance due to the better conductivity.

Keywords: Electrochemical properties; Polypyrrole nanocomposite; SiO2 nanoparticles

1. Introduction

Electrically conducting polymers (CPs) have been extensively studied over the past two decades [1-3]. Of all known CPs, polypyrrole (PPY) is the most frequently used in commercial applications. Besides the fairly good environmental stability and the possibility of forming homopolymers or composites with optimal chemical and physical properties [4], CPs also show interesting physicochemical properties that is potentially useful to supercapacitors [5], batteries [6], sensors [7], microwave shielding and corrosion protection [8].

As shown in the literature [9-11], some efforts had been made on enhancing the conductivity of PPY for its practical application. Meanwhile, in order to achieve a new function of PPY, one of the most efficient means is to prepare PPY-based composite films where new chemical components, such as nanoparticles of Fe_2O_3 [12] and Pd [13] or nanostructured clays [14], are introduced. To the best of our knowledge, the effects of SiO_2 nanoparticles on the preparation of Polypyrrole have not been investigated so far. The aim of this work is to prepare a PPY/SiO_2 nanocomposite electrochemically and study of its characteristics such as conductivity and morphology.

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2. Experimental

All analytical grade chemicals and solvents were purchased commercially and used without further purification. Cyclic voltammetery (CV) is carried out using a Potentiostat/ Galvanostat EG&G Model 263 A; USA with M 270 software. Electrochemical impedance spectroscopy (EIS) is performed with a Frequency Response Detector EG&G Model 1025; USA with a PC and electrochemical set up that is controlled with M398 software. Electrochemical cell was assembled with a conventional three electrode system: A Pt wire as counter-electrode, An Ag/AgCl-KCl(sat) as reference electrode and a glassy carbon electrode as a working electrode. The FT-IR transmission spectrum of polypyrrole coated is recorded in horizontally attenuated total reflectance mode in the spectral range 3500–500 cm-1 using a Bruker spectrometer. SEM micrographs on films were obtained with a Philips field emission gun Scanning Electron Microscope operated at 25 kV. In a typical procedure, 2 g.dm-3 insulating 50 nm SiO_2 powders were added in deionized water and sonicated for 1 h. Subsequently, 0.1 M H_2SO_4 and 0.1 M pyrrole which was doubly distilled under a reduced pressure were dissolved with vigorous magnetic stirring in this emulsion solution for 30 min. During this step, the solution was deoxygenated with highly pure nitrogen. Then SiO_2-modified PPY was electrochemically polymerized at 0.85 V versus Ag/AgCl in the SiO_2-containing aqueous solution with slow magnetic stirring. For comparison, pure PPY was also polymerized under the same preparation conditions as mentioned above, but with no SiO_2 powders in the monomer solution.

3. Results and Discussion

The FT-IR spectrum of pure PPY is shown in Fig. 1a. A broad and weak band centered at ~3300 cm-1 is due to the characteristic N-H stretching vibration and the C=N and C=C stretching modes of quinoid and benzoid rings occurred at ~1530 and 1410 cm-1, respectively. Fig. 1b show the FT-IR spectrum of PPY nanocomposite. A broad band observed at ~1125 cm-1 corresponds to the characteristic Si–O stretching vibration which shows the presence of SiO_2 nanoparticles in the PPY nanocomposite.

Fig. 2a shows a typical cyclic voltammogram of PPY nanocomposite and pure PPY deposited on the surface of GC electrode after twenty potential cyclings, respectively. It is obvious that the anodic and cathodic currents of PPY nanocomposite are much greater than the cases of pure PPY that can be attributed to the increase in the effective surface of the electrode as the result of SiO_2 nanoparticles in the polymer matrix. Moreover, the background current of PPY nanocomposite is apparently larger than that of PPY, which indicates the PPY nanocomposite modified GCE has larger effective surface area [16].

Impedance spectra of the conducting polymer matrix were employed here to study the characteristics of the nanocomposite conductivity. Fig. 2b illustrates the EIS for PPY nanocomposite and pure PPY film in 0.5 M H_2SO_4 solution under open circuit potential. In Fig. 2b, it can be seen that both the films display similar characteristics, i.e., a depressed semicircle over the high frequency region and a straight line in the low frequency region. As shown in the literatures, the diameter of the semicircle corresponds to the interfacial charge transfer resistance (Rct), and is often called the faraday resistance [17]. Table 1 shows the values of the impedance parameters for PPY and PPY nanocomposite. In spite of the similar shape of the impedance spectra, there is an obvious difference between the diameters of the two semicircles. That is, according to table 1 the Rct (49.688 Ω/Cm2) for PPY nanocomposite is smaller than that of PPY which is 67.25 Ω/Cm2.

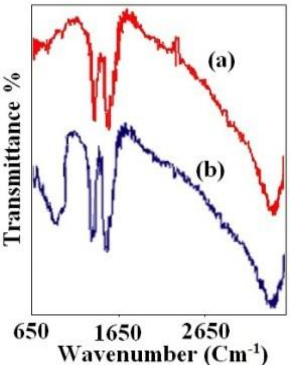

Fig. 1. FT-IR spectra of the (a) pure PPY and (b) PPY/SiO_2 nanoparticles.

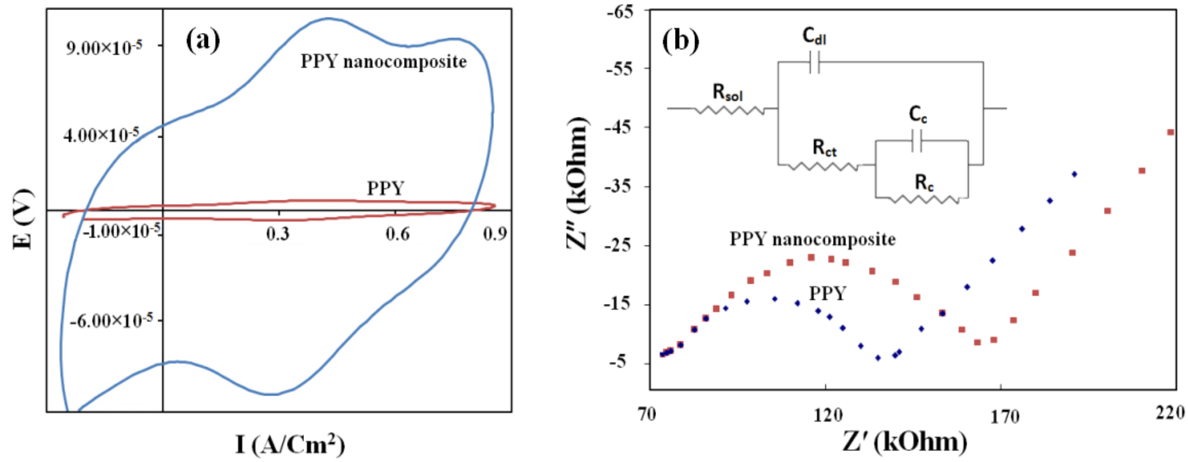

Fig. 2. Cyclic voltammograms of the films in 0.1M H_2SO_4 at $50mVs^{-1}$ (a) and EIS of the films in 0.5M H_2SO_4 solution on the GCE under open circuit potential (b).

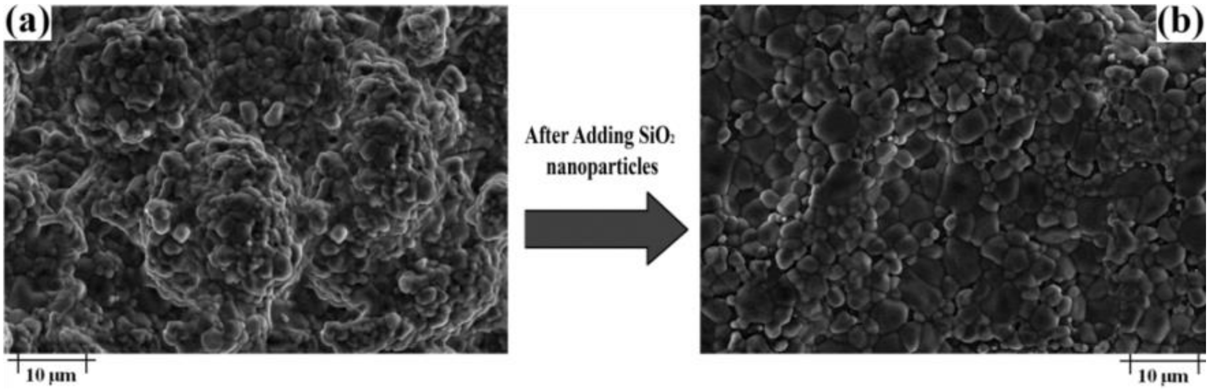

Fig. 3. SEM images of PPY/SiO_2 nanocomposite film (a) and PPY film (b) on glassy carbon electrode surface.

Table 1. Impedance parameters values extracted from the fit to the equivalent circuit for the impedance spectra recorded.

Type	Rct (Ω/Cm^2)	Rc (Ω/Cm^2)	Rsol (Ω/Cm^2)
PPY	67.25	275.10	68.34
PPY nanocomposite	49.68	179.41	64.92

In other words, the PPY nanocomposite film presents a much lower electrochemical charge transfer resistance than the pure PPY film, suggesting its more active sites for faradic reactions and easier charge-transfer at the interface owing to the presence of the SiO_2 nanoparticles.

The SEM images of the PPY nanocomposite film and pure PPY film on GCE surface were shown in Fig. 3. To the best of our knowledge, it is the first report of PPY/SiO_2 nanocomposite obtained through one step electrodeposition. Fig. 3a shows the typically granular raspberry morphology of pure PPY [18]. Comparing Fig. 3a and 3b, it is found that the PPY nanocomposite film exhibits particularly denser and more compact morphology. As shown in the literature [19], denser and more compact morphology would reflect on the enhancement in conductivity. This is consistent with our experimental data.

4. Conclusions

A PPY/SiO_2 nanocomposite film was successfully electropolymerized at a surface of GCE in nano silica containing aqueous solution and it was characterized by IR, CV, EIS and SEM. FT-IR spectra confirm the presence of SiO_2 nanoparticles in the PPY nanocomposite. The incorporation of a little amount of SiO_2 nanoparticles changed the electrochemical properties and morphology of the PPY film greatly. According to CV and EIS experiments, the PPY nanocomposite film exhibit better conductivity than the pure PPY film. The surface morphology of the resulting composite is denser and more compact, which is responsible for the enhancing conductivity, raising one order as compared with that of pure PPY. Owing to the good characteristics of the PPY nanocomposite film, it has an obvious improved effect and makes the nanocomposite have more active sites for faradaic reaction, and larger specific capacitance than pure PPY film.

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