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A poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)/titanium oxide nanocomposite film synthesized by sol–gel assisted electropolymerization for electrochromic application

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ABSTRACT

In this article, we report the facile synthesis of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)/titanium dioxide (PEDOT:PSS/TiO_2) nanocomposite film by sol–gel assisted electropolymerization. The structure, morphology and composition of the films were investigated by different techniques, such as Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, atomic force microscope and X-ray photoelectron spectroscopy. The PEDOT:PSS/TiO_2 nanocomposite film was applied for electrochromic application. The results indicate that the PEDOT:PSS/TiO_2 nanocomposite film exhibits a higher optical contrast and a much better stability as compared to PEDOT:PSS film. The significant performance enhancement can be attributed to the nanoscale particle size and uniform size distribution of PEDOT:PSS/TiO_2 and the synergistic effect between the inorganic nano-TiO_2 and organic PEDOT:PSS material.

1. Introduction

Electrochromism is a reversible change in optical properties due to electrochemically induced redox reactions. Many applications have been envisaged for systems based on electrochromic devices, e.g., light and overheating protection windows, mirrors, optical filters and display panels [1–6].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly promising conducting polymer owing to its extraordinary electrical properties and transparency to visible-light at its doping state [7,8]. The low solubility of pure PEDOT can be circumvented by using a water soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS) as a charge-balancing dopant during polymerization in water to yield a PEDOT:PSS aqueous composite. PEDOT:PSS shows a promising potential for application in electrochromic devices due to its moderately high conductivity and high visible-light transmission [9,10]. For example, Sindhu et al. [11] investigated the electrochromic performance of PEDOT deposited on transparent conducting oxide coated glass and polymer substrates. Nah et al. [12] prepared polyelectrolyte multilayer films composed of PEDOT:PSS and poly(allylamine hydrochloride) by a spin self-assembly method. Fabretto et al. [13] studied the role of water in the synthesis and performance of vapor phase polymerized PEDOT electrochromic devices. Although PEDOT:PSS displays some advantages for application in electrochemical devices, the long-term stability of PEDOT:PSS under harsh electrochemical conditions still needs to be further enhanced. In addition, the conventional procedure to fabricate an electrochromic electrode is quite complicated and time-consuming.

Electropolymerization is a versatile method for producing electrically conducting polymers because of its simplicity and reproducibility. Moreover, the thickness of the polymer film is highly controllable [14,15]. Poverenov et al. [16] studied the major effect of electropolymerization solvent on the morphology and electrochromic properties of PEDOT films. Wagner et al. [17] synthesized PEDOT using ionic liquids as both the growth medium and electrolyte. Du and Wang [18] studied the effects of electropolymerization potential on the properties of PEDOT films. Piron et al. [19] fabricated a three-dimensional π-conjugated system based on 3,4-ethylenedioxythiophene (EDOT) by electropolymerization. So far, many works have been done for preparing PEDOT films by electropolymerization, but it is quite difficult to synthesize organic and inorganic nanocomposite materials by the conventional electropolymerization process. From the fundamental and practical points of view, the organic and inorganic nanocomposite materials are very interesting and may possess significantly different physical and chemical properties [20,21]. In our previous work [22], we prepared a kind of multilayer film composed of PEDOT:PSS and tungsten trioxide through electrochemical deposition using a square-wave galvanostatic method from a one-pot solution. The multilayer film possesses a higher optical contrast and a better stability than PEDOT:PSS. In this article, an

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organic and inorganic composite material, PEDOT:PSS/TiO_2 thin film, was synthesized by sol–gel assisted electropolymerization. The structure, morphology, composition and electrochromic properties of PEDOT:PSS/TiO_2 were characterized through different techniques. The corresponding mechanism for the enhanced electrochromic properties was discussed in detail.

2. Experimental details

2.1. Preparation of precursor solutions and electropolymerization

All chemicals used in this work were purchased from Sigma-Aldrich and used as received. Unless specified, all experiments were conducted under ambient conditions and all solutions were prepared using deionized (DI) water.

Firstly, the titanium(IV) butoxide (TiBO, Mw = 340.32) with a weight of 0.008 g was dissolved in 45 mL ethanol. The ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, Mw = 372.24) with a weight of 0.009 g was dissolved in 5 mL DI water. Sequentially, the EDTA-2Na water solution was dropwise added into the as-prepared TiBO ethanol solution with vigorously stirring for 2 h. The above mixed solution was denoted as solution I. The 18 wt.% PSS (Mw ~ 75,000) water solution with a weight of 0.818 g was dissolved in 50 mL DI water, followed by adding 0.071 g EDOT (Mw = 142.18) with vigorously stirring until the solution becomes transparent. This mixed solution was denoted as solution II, which was dropwise added into the solution I with vigorously stirring. The as-prepared mixture was used for the precursor solution to synthesize the PEDOT:PSS/TiO_2 thin film. The as-designed molar ratio of EDOT:PSS:TiO_2:EDTA-2Na is 20:32:1:1. Solution II was added into another 50 mL DI water and the as-obtained solution was used to synthesize the PEDOT:PSS film.

All electrochemical experiments were performed using a three-electrode system. Indium tin oxide (ITO) coated glass with a sheet resistance R_s = 5–15 Ω and dimensions of 7 × 50 × 0.7 mm (Delta Technologies) was used as the working electrode. Before any deposition, the ITO glass was cleaned by ultrasonication in a series of solvents including acetone, ethanol and DI water for 30 min at each step, and then blow-dried with nitrogen gas. A platinum (Pt) sheet with a dimension of 1 × 2 cm was used as the counter electrode. A saturated calomel electrode (SCE, 0.241 V versus SHE) with a salt bridge was used as the reference electrode. The electropolymerization experiments were carried out with a potentiostatic method under a constant voltage of 1.4 V. The electrodeposition time was controlled at 300 s to prepare the films with a thickness of ~1 μm. The obtained samples were dried at 80 °C for 2 h in a vacuum oven.

2.2. Characterization

The Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) measurements were carried out with a PerkinElmer Model GX spectrometer. A diamond crystal was used as the ATR plate. X-ray diffraction (XRD) measurements were performed using a Rigaku 2500 D/max diffractometer (40 kV, 100 mA, Cu Ka radiation (λ = 1.54 Å) and Bragg–Bentano θ/2θ geometry). Data were obtained in a continuous scanning mode in the range of 20–80° with a step-width of 0.02° and a scanning speed of 5° min^{-1}. A vertical notch across the film was made using a sharp knife. The notch depth was measured as the film thickness using an Alpha-step 500 profilometer. The average value of the film thickness was obtained from five thickness measurements. Transmission electron microscopy (TEM) images were obtained using a JEOL Model JEM-2010 TEM system and the operating voltage was 200 kV. Atomic force microscope (AFM) measurements were performed in the tapping mode using Digital Instruments Nanoscope DI 3100 and the AFM head was connected to a Nanoscope IV controller. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Analytical AXIS His spectrometer with a monochromatized Al Ka X-ray source (1486.6 eV photons), in a vacuum of 10^{-8} Torr at a constant dwelling time of 100 ms and pass energy of 40 eV. The anode voltage was 15 mV with a current of 10 mA. All the survey scans and the core-level spectra were obtained at a photo-electron take-off angle of 90° (α, with respect to the sample surface). Survey scans were recorded within a range of 0–1100 eV. To compensate for the effects of surface charging, all core-level spectra were referenced to the C1s hydrocarbon peak at 284.6 eV.

The spectro-electrochemical properties of the films were measured using an Autolab PGSTAT30 potentiostat and a UV–vis spectrophotometer (Shimadzu UV 3600) in the 0.1 mol^{-1} lithium perchlorate/propylene carbonate solution as the electrolyte. The UV–vis spectra of the thin films were recorded in the wavelength range of 300 nm to 800 nm at potentials of −1.0, −0.6, 0, +0.6, and +1.0 V. For each thin film, the dynamic optical transmittance was also recorded at the wavelength of interest under a square wave potential oscillating between −1.0 V and 1.0 V at a time step of 20 s.

3. Results and discussion

Fig. 1 is the proposed reaction path for synthesizing PEDOT:PSS/TiO_2 composite film by sol–gel assisted electropolymerization. TiBO is one of the metal alkoxides, which can hydrolyze with water to form a stable TiO_2 gel under a well controlled condition [23]. EDTA-2Na is a polyamino carboxylic acid and chelating agent, which can bind to metal cations through its two amines and four carboxylates. So during the hydrolysis of TiBO, EDTA-2Na could connect with Ti^{4+} through the chelating effect to form a stable complex, denoted as $TiO_x(EDTA)^{4-}$ here. Under a controlled potential, the EDOT, $TiO_x(EDTA)^{4-}$ and PSS will be electropolymerized and co-deposited on the working electrode.

Fig. 2 is the XRD results for the different materials. As can be seen, the PEDOT:PSS, TiO_2 and PEDOT:PSS/TiO_2 do not show evident diffraction peaks, which indicate that all the materials are most likely to be amorphous.

Fig. 3 shows the FTIR results for the different samples synthesized in this work and Table 1 shows the FTIR band assignments extracted from Fig. 3. It can be summarized as follows: for the PEDOT:PSS, C═C asymmetric and symmetric stretching at 1470 and 1402 cm^{-1}, the C–C stretching at 1354 cm^{-1}, C–O stretching at 1087 cm^{-1}, C–S stretching at 983 cm^{-1}, C–S deformation at 830 cm^{-1}, and C–O deformation at 665 and 571 cm^{-1}. The as-synthesized PEDOT:PSS shows the corresponding characteristic FTIR bands and is almost analogous to that of commercial PEDOT:PSS [24]. For the TiO_2, the Ti–O stretching was at 1124 and 1037 cm^{-1}, respectively. The band at 1010 cm^{-1} is from the C–N stretching vibration of EDTA-2Na. The PEDOT:PSS/TiO_2 not only has the bands of PEDOT:PSS but also possesses the bands of TiO_2, but some bands of PEDOT:PSS/TiO_2 show an evident shift or overlap as compared to PEDOT:PSS. For example, the bands of $\nu(C-C)_{ring}$, $\nu(C-O)$, and $\nu(C-S)$ shift from 1354, 1087 and 983 cm^{-1} to 1397, 1128 and 840 cm^{-1} respectively. The bands of $\nu(Ti-O)$ at 1124 and 1037 cm^{-1} in TiO_2 sample overlap at 1127 cm^{-1} in the PEDOT:PSS/TiO_2 film. This is due to the existence of TiO_2 and EDTA-2Na in the composite film

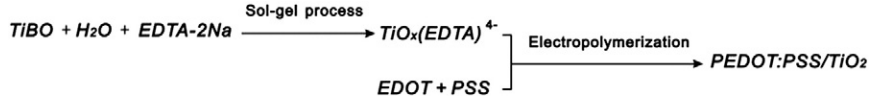

Fig. 1. The proposed reaction path for sol–gel assisted electropolymerization.