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Fabrication and properties of electrode material composed of ordered titania nanotubes and pEDOT:PSS

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ABSTRACT

We report on the two-stage preparation method of electrode material composed of titania nanotubes and poly(3,4-ethylenedioxythiopene):poly(2-styrenesulphonate) conductive polymer (pEDOT:PSS). Initially, titania nanotube arrays were produced by the anodization process of Ti substrate. Next, the polymer was potentiostatically deposited onto the thermally annealed nanotube arrays from the electrolyte containing monomer and counter ion. The obtained material was characterized by means of Raman spectroscopy, SEM and photoluminescence spectroscopy. On the basis of electrochemical studies, a radical decrease in the electrode material resistance after conductive polymer deposition was detected. The enhancement in registered current under UV–vis irradiation was almost 4 times higher for a composite with the highest amount of deposited pEDOT:PSS in comparison to pristine titania nanotube array film.

1. Introduction

Combined materials consisting of inorganic and organic components have been attracting much interest in recent years. The combination of metal oxide (inorganic element) with a conductive polymer (organic component) creates opportunities to construct high-quality organic/inorganic interface with expected synergistic effects in electronic and ionic properties between the composite counterparts [1–3]. The latest research trends involve the investigation of such heterojunctions composed of metal oxides, i.e. ZnO [4], MnO_2 [5] and electroactive polymer, e.g. polyaniline [6], polypyrrole [7] or poly(3-methylothiopene) [8], and their application in gas sensors, photovoltaic cells and supercapacitors.

Poly(3,4-ethylenedioxythiophene) doped with poly(2-styrenesulphonate) (pEDOT:PSS) macromolecular counter ions is among the most frequently investigated electroactive polymers because of its chemical stability and commercial availability of both the polymeric and monomer ethylenedioxythiopene forms [9]. On the other hand, among low dimensional systems and architectures, titania nanotubes (TiO_2 NTs) continue to be rigorously researched due to their promising application in various fields such as, photocatalysis, photoelectrochemical water-splitting, biomedical implants and dye-sensitized solar cells [10,11]. The highly ordered titania nanotube array can be applied as a substrate material of electrodes owing to its high surface area and chemical/electrochemical stability. Therefore the combination of these two materials, namely, TiO_2 NTs and pEDOT:PSS having different but complementary properties, may result in a synergistic effect, i.e. exhibit superior properties in comparison to their pure counterparts. To our knowledge, there are only few reports on the preparation and characterization of TiO_2 nanotube infiltrated by pEDOT polymer. These studies are focused on the deposition process of pEDOT driven by the potentiodynamic [12] or potentiostatic procedure [13], and driven by the current in the pulse protocol applied to the electrode [14]. However, only Janaky et al. [12] demonstrated photoactivity of TiO_2–pEDOT nanocomposite, whereas Kowalski et al. described changes in impedance spectra after polymer deposition. Furthermore, according to Kowalski et al., titania support can be removed by etching using diluted hydrofluoric acid, and the remaining conductive polymer has a unique porous nanostructure.

Concerning the preparation method, efficient infiltration from solution of a high molecular weight polymer into the nanotube support can be challenging, although both dip-coating and spin-coating have been utilized for this purpose. However, the intrinsic electroactivity of a monomer precursor molecule can also be exploited to electrochemically infiltrate the polymer in situ into titanium oxide NT framework. In this work, we elaborate this approach and propose potentiostatic deposition of pEDOT:PSS inside and on the top of titania nanotube array network. The performed characterization of obtained composite material is focused on its structure, morphology and electrochemical activity. It is shown that the novel organic–inorganic material exhibits higher currents registered under illumination than its pure counterparts, i.e. TiO_2 nanotubes and pEDOT:PSS.

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2. Experimental

The synthesis of organic–inorganic composite material was carried out in two steps: a) anodic growth of titania nanotube arrays, and b) electrochemical synthesis of pEDOT:PSS onto titania surface. Before nanotube formation, titanium foil (Aldrich, 99.7%, thickness = 0.25 mm, s = 0.7 cm^2) was ultrasonically cleaned in acetone, ethanol and water. Anodization took place in the two-electrode arrangement where Pt gauze served as a cathode and titanium substrate as an anode. Electrodes were immersed in ethylene glycol solution containing 2% v/v of water and 0.3 wt.% NH_4F. Samples were anodized at the electrode potential established at 60 V for 1 h at 20 °C and under continuous electrolyte stirring. After anodization, samples were immersed in deionized water and dried on the hot plate at 80 °C. Finally, the samples of titania nanotubes were annealed at 450 °C for 1 h using the heating rate of 2 °C/min in a tube furnace under oxygen atmosphere (in order to remove organic residues from electrolyte) and allowed to cool gradually back to ambient temperature.

The second stage of composite material preparation was based on potentiostatic deposition of pEDOT:PSS from aqueous solution containing the monomer (EDOT, c = 0.015 M) and supporting electrolyte (NaPSS, M = 70,000, c = 0.1 M taking into account SO_3^{2-} group concentration). The previously prepared TiO_2 nanotubes served as a working electrode and Ag/AgCl/0.1 M KCl as a reference electrode. Polymer films were deposited at 1.2 V vs. Ag/AgCl/0.1 M KCl consuming charge of 100, 200 and 300 mC cm^{-2}. According to the charge consumed during electrochemical polymerization, the composite samples were ascribed as TiO_2/PP-100, TiO_2/PP-200 and TiO_2/PP-300. In order to verify the location of polymer after the deposition step, titania nanotubes were selectively dissolved in diluted hydrofluoric acid (0.5%) for 10 min.

The Raman spectra were recorded by using a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation by means of an argon ion laser emitting at 514 nm.

The SEM images of titania and composite layers were obtained using a scanning electron microscope (EVO-40, Zeiss) equipped with EDX accessory.

The photoluminescence (*PL*) measurements were carried out by using a laboratory setup consisting of 0.3 m Czerny–Turner spectrograph (SR303i, Andor) equipped with an ICCD camera (DH740, Andor). Samples were excited with UV LED (365 nm center wavelength, 9 nm FWHM, 350 mW output power). The excitation radiation, focused by quartz lens, was falling on the sample surface at an angle of 45°. Additionally, the band-pass filter (UG11, Schott) was applied between the excitation source and the sample to block UV LED radiation above 380 nm. The fluorescence signal was collected perpendicular to the sample surface using a microscope objective and focused on the entrance of optical fiber. In the detection path the band-pass filters (GG44, Schott) were used for blocking the excitation radiation.

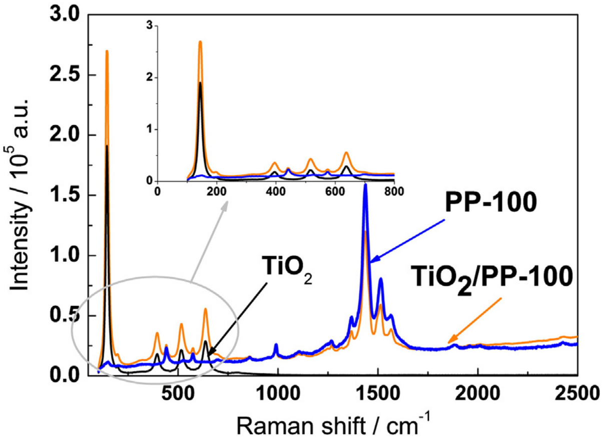

Fig. 1. Raman spectra registered for TiO_2 nanotubes, pure polymer and TiO_2/pEDOT:PSS composite.

The electrochemical measurements were performed using an AutoLab PGStat 302N potentionstat–galvanostat system in the standard three-electrode assembly thermostated at 20 °C. The cell contained 0.5 M Na_2SO_4 with Pt mesh as a counter electrode and Ag/AgCl/0.1 M KCl electrode as a reference electrode. The solution was purged with argon for 50 min and an Ar-cushion was present above the electrolyte during the measurements. Electrochemical impedance spectroscopy (*EIS*) measurements were carried out at open circuit potential in the frequency range from 0.1 Hz to 20 kHz and a 10 mV rms amplitude. The impedance data were analyzed on the basis of an electrical equivalent circuit (*EEQC*) using an EIS Spectrum Analyzer [15]. The modified Powell algorithm [16] with the amplitude weighting r_a was used:

$$r_a(\omega, P_1 \ldots P_M) = r_c^2/(N-M)$$

where N is the number of points, M is the number of parameters, ω is the angular frequency, and $P_1 \ldots P_M$ are the parameters. Parameter r_c is defined as:

$$r_c^2 = \sum_{i=1}^{N} \frac{\left(Z_i' - Z_{i_{calc}}'\right)^2 + \left(Z_i' - Z_{i_{calc}}'\right)^2}{Z_i'^2 + Z_{i_{calc}}'^2}$$

where i corresponds to the measured values of impedance and i_{calc} is attributed to the calculated values; N is the number of points.

The photocurrent measurements were carried out at +0.2 V bias voltage. High-pressure 150 W xenon lamp (Osram XBO 150) equipped with AM1.5 and IR cut-off filters, and the automated light chopper with a period of 20 s was used as a light source. The light intensity was adjusted to 100 mW cm^{-2}.

3. Results and discussion

3.1. Raman spectroscopy

The Raman spectra recorded in ordered titania nanotubes, conductive polymer and composite material deposited onto titania substrate are shown in Fig. 1. A number of bands characteristic for pure anatase crystalline form of TiO_2 were distinguished in the samples of pristine titania and composite material. The bands located at 144, 198, 395, 516 and 637 cm^{-1} are attributable to $E_{g(1)}$, $E_{g(2)}$, B_{1g}, A_{1g}, B_{1g} and $E_{g(3)}$ active anatase modes, respectively [17]. In the case of composite layer, besides the bands characteristic for titania, the signals corresponding to the totally oxidized form of pEDOT were recorded; the latter were similar to the bands observed in the samples of pure polymeric film deposited on the flat titanium metal plate. The positions of bands attributable to polymer [18,19] and their description are presented in Table 1.

3.2. SEM with EDX

Scanning electron microscopy was employed to investigate the surface morphology of titania nanotubes and composite electrodes.

Table 1
Recorded polymeric frequencies for composite material and their description.

Raman shift/cm^{-1}	Absorption band
574	Oxyethylene ring deformation
700	Symmetric C–S–C deformation
991	Oxyethylene ring deformation
1101	C–O–C deformation
1267	C_α–C_α inter-ring stretching, C_β–H bending
1368	C_β–C_β stretching
1433	Symmetric $C_\alpha{=}C_\beta$ (–O) stretching
141 and 1564	Asymmetric $C_\alpha{=}C_\beta$ stretching

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