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Electrodes consisting of PEDOT modified by Prussian Blue analogues deposited onto titania nanotubes – Their highly improved capacitance

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ABSTRACT

In this work we present the outstanding energy storage of prepared inorganic-organic heterojunction where hydrogenated ordered titania nanotubes (H-TiO_2NT) were modified by the hybrid made of poly(3,4-ethylenedioxythiophene) (pEDOT) and iron hexacyanoferrate centres (Fehcf, Prussian Blue). The material TiO_2NT/pEDOT:Fechf was obtained electrochemically by means of: anodization, hydrogenation and finally, electropolymerization of EDOT in the presence of $Fe(CN)_6^{3-/4-}$ ions. Inorganic-organic hybrids were characterized using Raman spectroscopy and secondary ion mass spectrometry (SIMS). The morphology of obtained materials was inspected using scanning electron microscopy (SEM). Electrodes were tested using cyclic voltammetry and galvanostatic charge/discharge cycles in an aqueous electrolyte. The characterization of capacitance was studied by means of multiple (up to 10,000) charge/discharge cycles with the current density of 0.45 mA cm^{-2}. Electrode materials consisting of H-TiO_2, pEDOT and Prussian Blue exhibited the highest capacitance of 26 mF cm^{-2} even after 10,000 cycles. Thus, the capacitance of TiO_2NT/pEDOT:Fehcf was *c.a.* 15 and 8 times higher than the capacitance registered for pure and hydrogenated TiO_2, respectively.

1. Introduction

Electrochemical supercapacitors, as energy storage devices, have attracted growing interest in recent years [1]. Capacitors in general make use of three main classes of materials: porous carbon, transition metal oxides and conducting polymers deposited onto various electrode collectors [2–4]. Porous carbon materials exhibit a relatively low electrochemical double-layer capacitance. Ruthenium oxide is characterized by a very high electrochemical pseudo-faradic capacitance, however its high cost hampers possible commercial application. Conductive polymers are characterized by a high electrical capacitance and cyclability, but unfortunately they exhibit a narrow potential range of electrochemical activity and stability. The extension of potential window and the improvement of specific capacitance can be achieved by fabrication of organic-inorganic heterojunction with TiO_2 [5,6]. Additionally, increase in charge capacity can be achieved by introduction of redox inorganic network, i.e. Prussian Blue analogues into the polymer matrix [7,8].

Highly ordered TiO_2 nanotubes are promising as supercapacitor electrodes, because of the large specific surface area and direct pathway for charge transport in nanotubes as well as facile fabrication directly onto the charge collector substrate. Thus, utilization of TiO_2 nanotubes obtained onto the Ti support as an electrode material might offer an opportunity to improve the capacitance of supercapacitors. However, it should be mentioned that the semiconducting nature of TiO_2 limits the electrical conductivity and hinders specific capacitance in the charge–discharge process and therefore titania requires further modification for further application in energy storage devices [9]. The electrodeposition of polymer films with modified TiO_2 proceeds more efficiently in comparison to pure TiO_2 [6].

Here, studies on the capacitance properties of organic-inorganic heterojunction containing highly ordered titania nanotubes and Prussian Blue embedded into the pEDOT matrix is presented. All investigated electrodes were prepared via electrochemical methods that could be easily scaled up. The presence of each part of heterojunction was confirmed using Raman spectroscopy whereas SIMS technique allows the composition tracking from the material surface down to the base of titania. The obtained heterojunction containing TiO_2, Prussian Blue and pEDOT was characterized using prolonged reversible polarization

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cycles, which allowed to demonstrate enhancement of the capacitance as compared to the pure and hydrogenated TiO_2 nanotubes, as it was reported previously [9–11].

2. Experimental

2.1. Preparation of H-TiO_2 nanotubes

Highly ordered titania nanotubes were prepared via a two-step electrochemical anodization of a Ti plate (Strem, 99.7%) in a fluoride-containing solution. The procedure that leads to the formation of TiO_2 nanotubes was given previously [12]. Anodization process was realized in a two-electrode configuration with a cathode: (Pt grid) and anode (Ti plate) placed 2 cm from each other. Both steps of anodization were performed at temperature (23 °C), electrolyte composition (0.27 M NH_4F in 1%/99% v/v water/ethylene glycol solution) and anodization parameters (40 V, 2 h). Before the second anodization step, the as-formed nanotubes during the first stage were removed by overnight etching in an oxalic acid solution (0.5% wt). To remove surface debris, the titanium plates covered with nanotubes were immersed in 0.05% wt HF for 180 s. The as prepared amorphous TiO_2 nanotubes were transformed to anatase phase by thermal annealing performed at 450 °C for 2 h (heating rate: 2 °C min^{-1}). The electrochemical hydrogenation process, similar to that proposed by Xu et al. [13], was performed in a three-electrode configuration at room temperature, using the crystallized TiO_2 nanotubes as working electrode, Ag/AgCl as reference and platinum mesh as counter electrode. The hydrogenation was performed in 0.5 M K_2SO_4 aqueous solution under the cathodic potential of -1.5 V vs. Ag/AgCl (0.1 M KCl) applied for 20 s, charge consumed equals to 60 mC cm^{-2}. Afterwards, the TiO_2 nanotubes were taken out, washed with deionized water and dried in the air. The hydrogenation process activates the titania surface by lowering of the resistivity and facilitates monomer adsorption and nucleation, resulting in the efficient electropolymerization process [14].

2.2. Fabrication of H-TiO_2/pEDOT:Fehcf

Electrochemical polymerization was carried out to obtain the inorganic-organic heterojunction H-TiO_2NTs/pEDOT:Fehcf. The electrochemical deposition was performed according to the two stage procedure proposed in Ref. [15]. The first stage covers potentiostatic electropolymerization from an aqueous solution containing monomer EDOT in the presence of $Fe(CN)_6^{3-/4-}$ ions. As a working electrode flat titanium plate or hydrogenated titania NTs layer were used. The reference electrode was Ag/AgCl(0.1 M KCl) whereas a platinum mesh was used as a counter electrode. The potentiostatic electropolymerization was realized under the potential of 1.5 V vs. Ag/AgCl(0.1 M KCl) and consuming the charge of 50 mC cm^{-2}. For comparative studies, the H-TiO_2/pEDOT:Cl, H-TiO_2/Fehcf were also produced. Electrochemical depositions were performed in an aqueous solution containing 0.1 M NaCl and 0.001 M EDOT (in order to obtain H-TiO_2/pEDOT:Cl) or $Fe(CN)_6^{3-/4-}$ [16] (in order to obtain H-TiO_2/Fehcf), by potentiostatic polymerization of 1.5 V vs. Ag/AgCl(0.1 M KCl) consuming charge of 50 mC cm^{-2}.

2.3. Apparatus

The surface morphology and cross-section view were examined using the Schottky field emission scanning electron microscopy (FEI Quanta FEG 250) with an ET secondary electron detector. The Raman spectra were recorded by a confocal micro-Raman spectrometer (InVia, Renishaw) with sample excitation, by means of an argon ion laser emitting at 514 nm operating at 5% of its total power (50 mW). The crystal structure of TiO_2 and H:TiO_2 samples was also determined from X-Ray diffraction patterns (XRD), using X-ray diffractometer (Xpert PRO-MPD, Philips) with copper K_α radiation ($\lambda = 1.5404$ Å). The chemical composition of modified titania nanotubes was examined using Time of Flight Secondary Ion Mass Spectrometer (TOF SIMS). The TOF SIMS 5 (ION-TOF GmbH) working in dual beam mode was used to obtain composition versus depth profiles. Bi^+ 30 keV ions and Cs^+ 2 keV ions, both incident at 45° to the surface normal, were used as the analysis and sputter. The Cs^+ sputter beam was rastered over 350 μm·350 μm while the 100 μm·100 μm central region of the sputter crater was analyzed with the Bi^+ ions. Negatively charged secondary ions induced by Bi primary ions were collected using time of flight mass spectrometer. Intensities of characteristics signals versus sputtering time were analyzed using SurfaceLab 6 software (ION-TOF GmbH). To determine variations in vertical composition of the samples the following signals were chosen: C^- ($m/z = 12.00$), $^{18}O^-$ ($m/z = 17.99$), CN^- ($m/z = 26.00$), $^{34}S^-$ ($m/z = 33.97$), Ti^- ($m/z = 47.95$), Fe^- ($m/z = 55.94$) and $^{46}TiO_2^-$ ($m/z = 77.94$).

Electrochemical experiments (cyclic voltammetry – CV, chronopotentiometry – CP, electrochemical impedance spectroscopy – EIS) were performed using the AutoLab PGStat 302N potentiostat-galvanostat system (Methrom, Autolab) in a standard three-electrode assembly, where different working electrodes were tested: TiO_2, H-TiO_2, H-TiO_2/pEDOT:Cl, H-TiO_2/Fehcf and H-TiO_2/pEDOT:Fehcf with the geometric surface area of 0.3 cm^2 but characterized the real surface

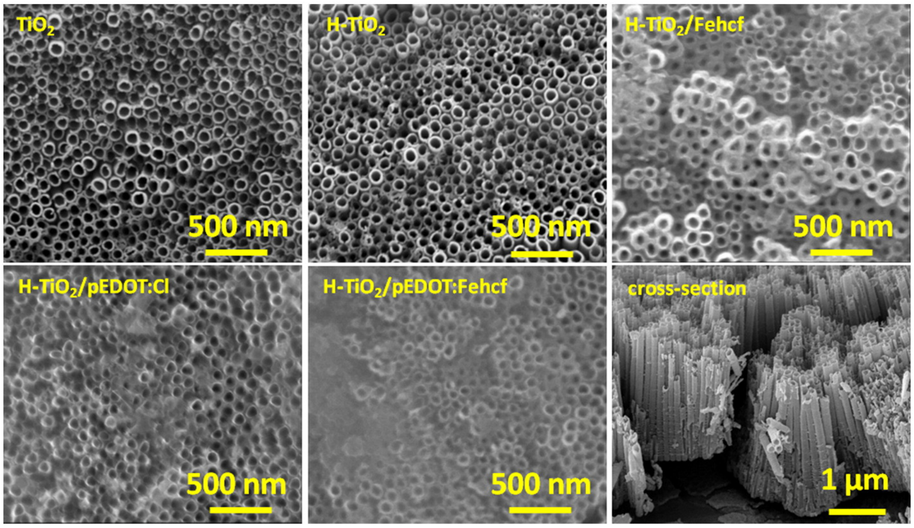

Fig. 1. Surface SEM image of TiO_2, H-TiO_2 and composite materials: H-TiO_2/Fehcf, H-TiO_2/pEDOT:Cl and H-TiO_2/pEDOT:Fehcf and cross-section image of H-TiO_2.

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