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Electrochemical impedance spectroscopy characterization of conducting polymer/TiO_2 nanotube array hybrid structures

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ABSTRACT

The model suggested by Deslouis and co-workers [14] for describing the behavior of polypyrrole deposited on a metallic substrate is here used for conducting polymers deposited on a nanostructured 3D semiconducting substrate. Impedance measurements were performed on a titanium oxide nanotubular array in the presence of two types of conducting polymers: polypyrrole and poly(3,4-ethylenedioxythiophene), highlighting the modification of the semiconducting properties of the substrate induced by the polymer deposition. The model is shown to be particularly well adapted for the PEDOT/TiO_2 hybrid structure, providing a valuable tool for characterizing the interaction between the conducting polymer and the semiconducting substrate.

1. Introduction

Electronically Conducting Polymers (ECPs) are materials of increasing interest for application in fields such as supercapacitors, electrochromic devices, biosensors, electrocatalysts [1–10]. ECPs have been widely studied when deposited on usual electrode materials with metallic behaviors (platinum, gold, glassy carbon, etc.) and electrochemical impedance spectroscopy (EIS) has been shown to be a convenient method for investigating the transport properties of these mixed ionic/electronic conductors [2,4,5,11–21]. Several models have been suggested for describing the behavior of ECPs on platinum. A complete model has been first suggested by Vorotyntsev et al. [12] for a metal/ECP film/electrolyte system, taking into account the fluxes of electronic and ionic species at the different interfaces and in the polymeric film. Later on, Deslouis and co-workers [13,14] applied this model on conducting polymer films under different boundary conditions (electrolyte/film/electrolyte, metal/film/metal and metal/film/electrolyte) and determined interfacial and transport parameters in the case of a polypyrrole film on a flat platinum electrode in different electrolytes. At last fine theoretical works were developed by Vorotyntsev et al. [15–17] taking into account both the capacitive charging effects and the mixed electron–ion exchange across the film/solution interface.

Attempts to deposit ECP films on a nanostructured 3D substrate have been recently described [18–30]. For instance, deposition of PPy or PEDOT on titanium oxide nanotube arrays (TiO_2-NTAs) is expected to produce innovative 3D junctions with interesting characteristics and performances for applications in the fields of energy storage, photoelectric devices or solar cells [22,29]. Due to the semiconducting properties of TiO_2, the rate of polymerization of the monomer has been shown to be enhanced by light excitation in the anodic potential range (electrophotopolymerization) [26,28,30,31].

The present paper shows preliminary results with the aim of verifying if the approximate theoretical model proposed in Ref. [14] can be extended to the case of an ECP film deposited on a semiconducting nanostructured substrate. It has been shown [30] that electrochemical or photoelectrochemical deposition of PPy on TiO_2-NTAs provides an electroactive hybrid structure, but that the level of electroactivity depends on the electrolyte used during the deposition step, on the anodic potential and on the illumination conditions. EIS appears to be a convenient method for estimating the electronic and ionic conductivities of the hybrid structure, yet for need of comparison a single model is likely to be used, whatever the conditions of ECP formation. Since the model of Ref. [14] allows taking separately into account the contribution of diffusion-migration of ionic and electronic charge carriers inside the film, and charge transfer across substrate/polymer and

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polymer/electrolyte interfaces, we will focus in this work on the modification of the conducting properties of the substrate in the presence of a PPy and of a PEDOT film. The model will be used to compare the behaviors of hybrid PPy/TiO_2-NTA structures obtained under potential scan in two different electrolytes: sodium dodecylbenzenesulfonate (SDBS) in which PPy film is mainly a cation exchanger and lithium perchlorate in which PPy behaves like an anion exchanger film [32]. A particular emphasis is also placed on the role of UV light illumination during the electrochemical generation of PPy, since it has been shown that photoelectrodeposited films often leads to hybrid structures with higher conductivity [26,28]. Since previous studies [10,18,29] have shown the higher stability of PEDOT in comparison with PPy, the behavior of a PEDOT–TiO_2 structure will also be investigated in $LiClO_4$ to check if the model suggested in [14] for PPy deposit is also valid for a PEDOT film photoelectrodeposited from an acetonitrile solution. The modification of the semiconducting characteristics of TiO_2 NTAs (anatase type) covered with either a PPy or a PEDOT film will be discussed and compared in this work.

2. Experimental part

2.1. Synthesis of TiO_2-NTAs

Prior to anodic oxidation, titanium discs (thickness 2 mm, diameter 15 mm, purity 99.6%, purchased from Goodfellow) were polished with silicon carbide abrasive paper (P1200), and then rinsed first with ethanol, and finally in water in an ultrasonic bath. Thereafter the Ti discs were anodized in a 3 wt% NH_4F solution in ethylene glycol containing 2 vol% deionised water using a large area platinum counter electrode in a two electrode setup. The oxidation was performed at room temperature (21 °C) under a constant potential of 20 V vs. Pt for 45 min.

Once anodized, samples were ultrasonically rinsed in ethanol and deionised water successively. At last, they were annealed at 525 °C for 2 h so as to convert the amorphous TiO_2 structure into a well crystallized anatase structure which has been thoroughly characterized [33]. Anodization of the Ti substrate led to dense and homogeneous TiO_2-NTAs. Raman spectrometry and XRD spectrometry showed that anatase was the only component of the layer. The tubes exhibited smooth walls and were highly-ordered and vertically oriented as it can be seen on the FEG-SEM pictures in inset of Fig. 1. In our case, the flat surface of the samples (working electrode) exposed to the electrolyte, i.e. the geometric surface, S_{geo}, equals 0.78 cm^2. The internal and external radii of the nanotubes, are 21 and 31 nm respectively, the length is about 960 nm and the mean thickness of the walls about 10 nm.

2.2. Electropolymerization of the monomers

Fresh aqueous solutions of 0.1 M distilled pyrrole monomer were prepared in different 0.1 M supporting electrolytes, either sodium dodecylbenzenesulfonate (SDBS) or lithium perchlorate ($LiClO_4$). The resulting polymers are respectively named either PPy(DBS) or PPy(ClO_4). In the case of SDBS, the selected concentration value is much higher than the value of critical micellar concentration (CMC), which has been shown to be about 1.5 mM in aqueous solution [34]. It has to be underlined that PPy deposition performed in similar conditions led to poorly adherent layers on compact titanium oxide samples, whereas the layer on nanostructured oxide layers showed good adherence.

Poly(3,4-ethylenedioxythiophene) (PEDOT) films were obtained from 0.05 M EDOT solutions in as-received acetonitrile solution containing 0.1 M $LiClO_4$. Electropolymerization was carried out on a TiO_2-NTA used as a working electrode by cyclic voltammetry

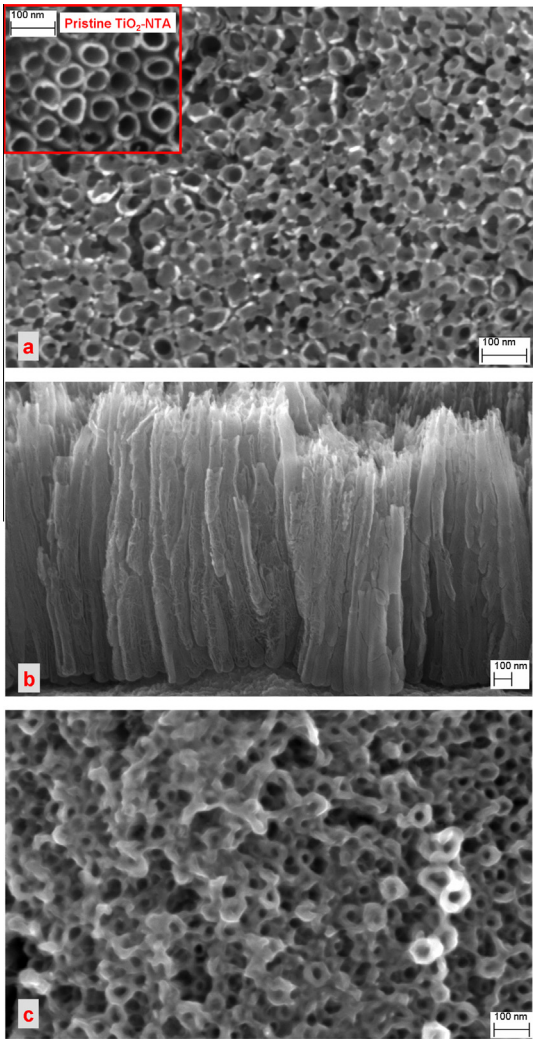

Fig. 1. FEG-SEM images of a TiO_2–polymer junction after 40 scans (a) and (b) TiO_2 nanotubes partially filled by polypyrrole in SDBS, -top view (a) and sideview (b). Inset of Fig. a: FEG-SEM image of a pristine TiO_2-NTA. (c) TiO_2 nanotubes partially filled by PEDOT in $LiClO_4$ and acetonitrile.

between −0.7 and 1.4 V vs. Ag wire, at a scan rate of 100 mV/s, and at room temperature (21 °C). All the polymer layers studied in this work were obtained after 40 consecutive scans. For UV assisted electropolymerization, i.e. photoelectropolymerization experiments the samples were illuminated with a 125 W mercury vapor lamp (HPR 125 W (Philips), wavelength range: 300–400 nm). The UV light source was placed at a distance of 25 cm from the working electrode and the UV beam was perpendicular to the working electrode surface.

2.3. Characterization

The morphology of the resulting hybrid structures was studied by FEG-SEM (Zeiss, Ultra 55) (Fig. 1a–c). A Jobin–Yvon (Labram 010) Raman spectrophotometer equipped with a He–Ne laser (wavelength 632.8 nm) was used to confirm the structure of the polymer films as well as their oxidation state. The thickness of the deposits was difficult to estimate precisely with SEM method but was estimated to be around 1–2 μm in the different cases.

From the deposition charges, the average thickness estimated is also very approximate, since the deposit is not uniform, the coverage rate is uncertain, and the current measured under light exposure is partially due to water oxidation. Nevertheless, a very