Electrochimica Acta 129 (2014) 211–221

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Photo-assisted electrodeposition of an electrochemically active polypyrrole layer on anatase type titanium dioxide nanotube arrays

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ARTICLE INFO

Article history:
Received 7 November 2013
Received in revised form 17 February 2014
Accepted 17 February 2014
Available online 3 March 2014

Keywords:
TiO_2 nanotube array
Polypyrrole
Impedance
Photoelectropolymerisation

ABSTRACT

Our purpose is here to produce a large area 3D junction between anatase type TiO_2 and polypyrrole (PPy) in a Ti/TiO_2 nanotube array (NTA)/PPy assembly with the help of electrochemical methods only. We report herein the influence of light and background salt on the electrochemical polymerization of pyrrole from aqueous electrolytic solutions on titanium oxide NTAs, a well-known large specific area n-type semiconductor substrate. As titanium dioxide is known to be poorly conducting in the anodic potential range, we confirmed that light is able to initiate a polymerization process of pyrrole, at a moderately high anodic potential. For comparison with results obtained in sodium dodecylbenzenesulfonate (SDBS) at micellar concentration, we used here also lithium perchlorate as background salt at a 0.1 M concentration, and PPy growth was found to be faster in the presence of $LiClO_4$. Moreover in the latter case polypyrrole could be initiated in the dark as well, yet at an enhanced deposition rate under UV light. In the two solutions. the resulting polypyrrole films were found to be electroactive, i.e. able to undergo electrochemically driven doping/undoping processes, yet with a higher electroactivity for the film obtained in $LiClO_4$. SEM-FEG and Raman spectroscopy experiments confirmed respectively that i) the initial steps of the photo-assisted electrodeposition of polypyrrole films occur first at the mouth of the titanium dioxide nanotubes, before leading to the well-known cauliflower-like morphology for PPy and ii) PPy is systematically produced in a doped state.

1. Introduction

The study of semiconductor-electrolyte interfaces is of a great interest in research as a consequence of their numerous applications. The understanding of their behaviour has an impact on numerous technologies such as environment treatment (pollutant degradation), microelectronics, sensors, photocatalysis, photovoltaics, and energy storage for example. Among the most used semiconductors, TiO_2 is well known for its low cost, chemical stability, and photoelectric conversion [1].

A way to improve metal oxide performances is to control their morphology at the nanoscale [2,3]. Precisely, the nanostructuration of TiO_2 produced by anodization of a Ti foil enables to achieve highly ordered and vertically oriented nanotubular morphology. That leads to an increased specific area, direct transport pathways and the formation of a high density of surface states that influence the interfacial electron-transfer process [4].

Covering a nanostructured TiO_2 interface with a conducting polymer film is expected to produce innovative 3D junctions possessing interesting photoelectrochemical characteristics and/or performances [5]. Among conducting polymers, polypyrrole (PPy) electrodeposition has been widely studied on usual electrode materials (platinum, gold, glassy carbon for example), thanks in part to its relatively easy electrosynthesis process and long term chemical and electrochemical stability [6,7]. During electropolymerization process, anions from the electrolyte [8] are incorporated in the polymer film to compensate the cationic charge resulting from the oxidation (i.e. doping) state of the growing conducting polymer film and are responsible for its ion exchange properties. It is well-known that the chemical composition of the electrolytic solution, and in particular, the type and size of the ions of the background salt present in the electrolyte are determining for the ion exchange behaviour of conducting polymers [9] and enable to control their electrochemical properties [10]. For instance, PPy films doped with large anions such as dodecylbenzenesulfonate (DBS) anions are expected to be mainly cation exchangers as a consequence of the irreversible entrapment of DBS^- anions in the polymer matrix, unlike PPy/ClO_4^- that are mainly anion exchanger films.

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http://dx.doi.org/10.1016/j.electacta.2014.02.106
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Attempts to electrodeposit polypyrrole on titanium oxide nanotube arrays have been recently described [5,12–14]. The challenge is to oxidize the pyrrole monomer in a potential range in which titanium dioxide, a n-type semiconductor, is depleted from majority carriers and only photooxidation is able to provide the holes necessary for electropolymerization. Another goal is to generate a doped and electroactive conducting polymer in tubes with a few tens of nanometers diameter. In the work published by Jin *et al.* [5], electropolymerisation was carried out under UV light (at 253.7 nm) and was shown to lead to photoelectrochemically active TiO_2-NTA/PPy junctions resulting from the electrodeposition of PPy on the outer- and inner-walls of the NTs. In spite of these convincing observations, UV light was not always used in several other works published later on and sharing the same goal, i.e. electrodeposition of PPy on TiO_2-NTAs [11,13] which led incidentally or not in both studies to polypyrrole films whose electrochemical activity was not evidenced. On the other hand, localisation of polypyrrole electrodeposition was selected in a convincing and accurate manner by using SDBS at a micellar concentration as well as current pulses shown to favour diffusion of pyrrole into or between the TiO_2 nanotubes depending on the inner diameter of the tubes and the void between them [11]. In some yet more recent contributions, beneficial effect of light on the electrodeposition process of electronically conducting polymers on metal oxide type semiconductors was thoroughly investigated and evidenced in the course of the photoelectrochemical polymerisation of PANI and PPy on nanoporous WO_3, PANI on TiO_2-NTAs [12]. Light was used by Janaky et al. [14] for PPy deposition on TiO_2-NTAs in a SDBS solution at micellar concentration. The authors clearly evidenced that polymerization was photoinitiated and that electropolymerization was likely to contribute to the overall polymerization reaction, once a seed layer of PPy was formed. The important result of their work was to show the higher electroactivity of the hybrid junction in comparison with an uncovered TiO_2-NTA layer.

The present work aims at comparing pyrrole (Py) electropolymerization on a TiO_2 nanotube array in two different solutions. A particular emphasis is placed i) on the role of UV light illumination during the electrochemical generation of PPy and ii) on the influence of the electrolyte anion. The deposition is performed by successive cyclic voltammetric scans. The characterization of the obtained composite structures is carried out by field emission gun-scanning electron microscopy (FEG-SEM) and Raman spectroscopy so as to determine respectively the morphology and the oxidation state of the polymer deposit. Another important part of this contribution focuses on the analysis of electrochemical behaviour of the PPy films electrochemically grown on nanotubular TiO_2 substrates as a function of the PPy electrodeposition parameters (light, background salt) using a potentiodynamic technique (Cyclic Voltammetry, CV) performed in the dark or under UV exposure, and electrochemical impedance spectroscopy (EIS).

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 disc was 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.

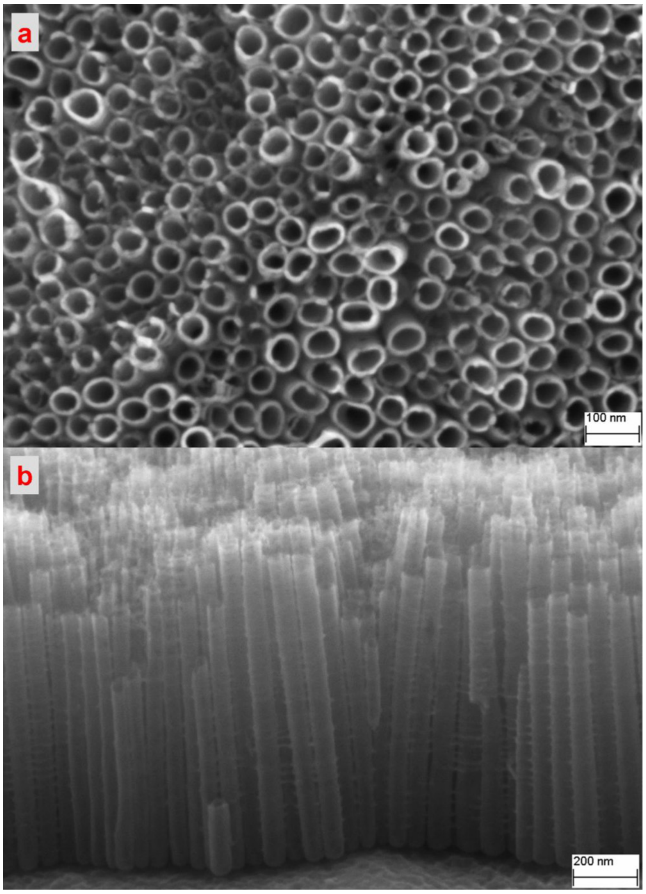

Fig. 1. FEG-SEM images of a pristine TiO_2-NTA: a) top view and b) side view.

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 [4]. Anodization of the Ti substrate led to dense and homogeneous TiO_2 nanotube arrays (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 Fig. 1. According to a geometric model previously used [4,15,16] which considers a regular network of identical and equally spaced nanotubes, the developed surface of the whole nanotube arrays is given by the following equation:

$$S_t = \frac{8\pi h R_2}{\sqrt{3}(4R_2 - 2R_1 + y)^2} \times S_{geo}$$

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. In this equation, R_1 and R_2 are respectively the internal radius and the sum of R_1 and the half thickness of the wall of the nanotubes, whereas y is the thickness of the void between the tubes and h is the average length of these latter. That leads to a developed surface (S_t) of approximately 50 cm^2 for all the nanotube arrays produced and used throughout this work, taking into account the values of 21 nm, 26 nm, 13 nm and 960 nm for R_1, R_2, y and h respectively.

2.2. Electropolymerization of Pyrrole

Fresh aqueous solutions of 0.1 M distilled pyrrole monomer were prepared in different 0.1 M supporting electrolytes, either