Titania nanotubes self-assembled by electrochemical anodization: Semiconducting and electrochemical properties

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ABSTRACT

Titania nanotubes (TNT), thanks to their semiconducting properties, have received wide attention for application in many fields such as photoelectrolysis, dye sensitized solar cells, photocatalysis, and sensors. In this work, highly ordered TNT were grown by controlled electrochemical anodization of titanium sheets. Scanning electron microscope equipped with a field emission gun and electrochemical DC/AC techniques was used to characterize the TNT. Semiconducting properties were investigated through linear sweep voltammetry and electrochemical impedance spectroscopy. Donor concentration (N_{ed}) was obtained by recording Mott–Schottky plots. The high N_{ed} of TNT (around 10^{26} m^{-3}) allows an optimal electron transfer when used as photoelectrode. Frequency dispersion of flat band potential from Mott–Schottky plots ($-0.38 \div +0.40$ V vs. saturated calomel electrode, SCE) was used as an indicator of the amorphous semiconductor behaviour. The dispersion of flat band in heat treated samples was extremely reduced (0.48–0.51 V vs. SCE) because of the conversion to crystalline semiconductor. The depth of space charge was comparable to the TNT wall thickness, meaning that the entire TiO$_2$ nanotube walls formed the space charge layer. Considering the high charge carrier concentration, we can hypothesise a high density of electronic defects (e.g., surface states) that enhances the electron transport by percolation inside a porous photoelectrode. The transition from amorphous to crystalline structure of TNT was detected from the change of semiconducting properties and confirmed by Raman spectroscopy.

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1. Introduction

Considerable efforts have been devoted during the last years to elaborate nanostructured layers which combine the interesting semiconducting and photo/electrochemical properties of titanium oxide with a huge internal surface area and improved charge transport properties [1–4]. Nanostructured TiO$_2$, due to its electrochemical and semiconducting properties, has been attracting attention from both fundamental and applied perspectives, thanks to its unique activity in a broad range of applications: photocatalysis of hazardous chemicals [5], photochromism [6], self-cleaning surfaces [7], solar energy conversion [8], gas sensors [9] and hydrogen storage [10].

Among the nanosized TiO$_2$ films, titania nanotubes (TNT) have raised considerable interest, especially those made by anodization of titanium in fluoride-based baths [11–13]. The dimensions of the tube can be precisely controlled, the diameter being determined by the anodization voltage, and their length by the polarization duration [14]. Whatever the morphology of the nanostructured layer (tubes, wires, columns, grains, etc.), the performances of the TNT are strongly limited by the rate of charge transport through the layer, and consequently by

efficiency of charge separation/recombination. Films made of oriented one-dimensional nanostructures, aligned perpendicular to the substrate, have shown improved charge-collection efficiency by promoting faster charge transport and slower recombination [15–16].

Different authors [17–19] have shown in the past that the electron occupancy of some conduction band states and/or sub-band gap states is a key parameter controlling the charge recombination kinetics, since these states are active in mediating electron transfer processes. Electron occupancy of the states may be induced by optically driven electron injection or by the application of an external potential. Such energy states have been assigned to Ti^{3+} sites in the TiO$_2$ layers. Moreover a high density of these states is often associated with the high surface area/volume ratio of the nanostructured films.

The relevant properties of TiO$_2$ (such as surface area and defect concentration) are directly related to its semiconducting behaviour, which can be affected by the growing method. Usually the difference among the performances of photocatalysts/electrocatalysts is wrongly attributed only to the difference in the surface area and does not take into account the difference in the semiconducting properties [5–7]. Thus, the semiconducting properties of the mesoporous and nanotubular electrochemically grown structures need to be better understood and correlated to their microstructure. The impedance behaviour is a promising characterization method capable of providing the necessary insight [18–20].

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The anodic growth of compact oxides on titanium surfaces and the formation of tubes are in the simplest approach, governed by a competition between anodic oxide formation and chemical dissolution of the oxide as soluble fluoride complexes [21]. The oxide formation is a consequence of the metal oxidation and water dissociation at metal/electrolyte interface:

$$Ti \rightarrow Ti^{4+} + 4e^- \tag{1}$$

$$H_2O \rightarrow 2H^+ + O^{2-}. \tag{2}$$
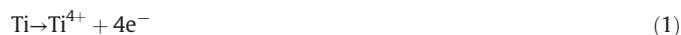
TiO_2 can be formed due to the ion migration in the solid:

$$Ti^{4+} + 2O^{2-} \rightarrow TiO_2 \tag{3}$$

$$Ti^{4+} + 2H_2O \rightarrow 4H^+ + TiO_2. \tag{4}$$

Oxidized metal ions react with O^{2-} ions (from water hydrolysis) to form an oxide layer. Further oxide growth is controlled by high field-aided ion transport (O^{2-} and Ti^{4+} ions) through the growing oxide. As the system is under a constant applied voltage, the field within the oxide is progressively reduced by the increasing oxide thickness (self-limiting process). These reactions are followed by etching of the oxide by fluoride ions present in the electrolyte:

$$TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O. \tag{5}$$
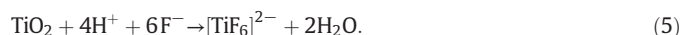
It is possible also a direct complexation of high-field transported cations at the oxide electrolyte interface:

$$Ti^{4+} + 6F^- \rightarrow [TiF_6]^{2-}. \tag{6}$$

The complexation reactions lead to pore formation and the individual pores begin to interfere with each other, and start competing for the available current. This leads under optimized conditions to a situation where the pores equally share the available current, and self-ordering under steady state conditions is established. During anodization, continual growth of oxide takes place at the inner interface, and chemical dissolution of the oxide layer occurs simultaneously. Steady state is established when the pore growth rate at the metal oxide interface is equal to the dissolution rate of oxide film at the outer interface. The reason for separation into tubes, as opposed to a nanoporous structure, may be ascribed to the accumulation of fluoride species at the tube bottom and thus to the establishment of an anion containing weaker (and more soluble) TiO_2 structure between neighbouring pores/tubes.

In our work, nanotubular/mesoporous TiO_2 were grown via anodization of titanium sheets through potentiostatic polarization. The anodization was performed in order to grow high aspect ratio, crystalline TiO_2 nanotubes on the Ti metal surface. Impedance and Mott–Schottky experiments were conducted under different conditions in order to analyse the semiconducting properties of the oxide layer.

2. Experimental details

2.1. Anodization of titanium

Anodization of Ti was carried out with titanium sheets (99.2% purity, Alfa Aesar), 0.5 mm thick, after cleaning by ultrasonic bath in acetone (30 min) and ethanol (20 min). The electrochemical polarization was performed at room temperature in an electrolyte composed of 400 mL ethylene glycol + 1.43 g NH_4F + 7 mL H_2O. A graphite disc was used as counter electrode.

Nanotubular TiO_2 were generated by anodization at a constant cell potential of 28 V for 18 h, using a Sorensen's Suppliers mod.DCR150-12B system power supply and a Hewlett-Packard digital multimeter mod.3457 for current acquisition, using a software compiled in LabVIEW. The as prepared samples were subsequently thermally air treated at 450 °C for 2 h (up/down ramp 1 °C/min), to obtain the anatase phase, as reported elsewhere [22].

The surface morphology of the formed TNT, pore size and distribution were characterized by using a LEO mod.1530 scanning electron microscope equipped with a field emission gun (FEG-SEM), operating in the range 5–20 kV.

Raman spectra were collected with a Renishaw inVia confocal Raman microscope using an excitation line of 532 nm (2.33 eV) with a $50\times$ objective lens, and an incident power of 1 mW on the samples.

2.2. Electrochemical characterization

For the electrochemical characterizations, a cell with a platinum counter electrode and a saturated calomel electrode (SCE) as reference was used. All the electrochemical measurements were conducted in 1 M Na_2SO_4 (pH = 6.5) solution at room temperature, using a PARSTAT mod.2273 (Princeton Applied Research) potentiostat/galvanostat/FRA. To study the electrochemical properties of Ti/TNT, a set of linear sweep voltammetry measurements was carried out with a scanning rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was used to evaluate the properties of the different Ti/TNT under AC polarization. EIS experiments were conducted in the frequency range from 1 MHz to 50 mHz with an amplitude of 10 mV and a DC potential in the range from −0.5 to +0.5 V vs. SCE. Bode plots were derived and the data evaluated and fitted to a suggested equivalent circuit using the ZSimpWin 3.1 program (EChem Software).

In addition, Mott–Schottky experiments were carried out to evaluate the capacitance behaviour under DC potential polarization with the superposition of an AC signal (V_{ac} = 10 mV) at constant frequency in the range of 20 kHz–1 Hz. The potential was scanned, from −1.0 V to 1.5 V vs. SCE, with a staircase profile (ΔV = 10 mV, delay 10 s).

3. Results and discussion

3.1. Electrode characterization

SEM micrographs of the self-assembled TiO_2 nanotubes are presented in Fig. 1. TNT are composed of elongated and narrow nanotubes (Fig. 1b) with a mean pore size of 58 nm and a length of 10 μm (Fig. 1a). After the heat treatment, the mean pore size (Fig. 1c) had a small increase (up to 64 nm), while the mean wall thickness changed from 18 nm to 20 nm and the length remained at 10 μm.

Raman spectra of as prepared (a) and thermal treated (b) TNT are shown in Fig. 2. After the thermal treatment, the formation of crystalline anatase phase is evident (Fig. 2b).

3.2. Electrochemical characterization

3.2.1. Linear sweep voltammetry

From the I–E curves of Ti/TNT electrodes (Fig. 3) it is clear that they do not exhibit any polarization current when anodic potential is below 1.6 V vs. SCE. This value is more positive than the theoretical potential of O_2 evolution by electrolyzing reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, $E° = 0.987$ V vs. SCE), due to the high overpotential effect of the TiO_2 semiconductor. Instead, in the cathodic region, the current sharply increases at potential below −0.5 V vs. SCE. These results demonstrate a typical characteristic of n-type semiconductor [18,22].

Diode-like I–E-characteristics at semiconductor TiO_2/electrolyte interface (i.e., current-blocking characteristics in the anodic direction and current-passing behaviour in the cathodic direction) are dominated by majority carrier transfer, i.e., the exchange of electrons via the conduction band.