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## In situ study of electrochromic properties of self-assembled TiO<sub>2</sub> nanotubes

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### ABSTRACT

Electrochromical properties of anodic self-assembled nanotubes were investigated. It was found that amorphous titania nanotubes were able to insert H<sup>+</sup> ions in a highly reversible manner. Coloration of the TiO<sub>2</sub> nanotubes occurred at potentials below −0.5 V vs. Ag/AgCl in 1M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aqueous solution. The proton insertion reaction probably leads to the formation of a Ti<sup>3+</sup>/Ti<sup>4+</sup> solid solution in the amorphous titania electrode, as was shown by the analysis of the derivative curve. The nanotubular titania electrode shows reasonable color efficiency when compared with other electrochromic materials and it is a promising candidate for the fabrication of low-cost interdigitated electrochromic devices.

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### 1. Introduction

Electrochromism is the ability of a material to show reversible changes of optical properties, such as color and transparency, as a result of an electrochemical oxidation or reduction process [1,2]. Electrochromism was discovered by studying molybdenum trioxide [3,4] but there are some other inorganic and organic compounds that exhibit electrochromic properties. Most inorganic electrochromic materials are based on transition metal oxides of W [5,6], Ir [7], V [8], Ti [9–11] and Ni [12–18]. Organic electrochromic active materials are in most cases functionalized polymers [19–23] or smaller molecules supported on a functionalized transparent substrate [24–28] such as nanostructured titania [29]. Electrochromic organic and inorganic nanocomposites are also known [30]. In spite of recent progress, the choice of materials remains relatively limited by production costs. It is challenging to find materials that can

change color by an electrochemical process, which can be then externally controlled, and show good reversibility for many coloration-bleaching cycles.

Nevertheless, the continuous increase of energy prices and the on-going economic shift towards renewable energy sources and technologies has led to a renewed interest for advanced and reliable electrochromic materials. Electrochromic windows that can switch between a transparent and colored mode represent an enabling technology for advanced “intelligent building” designs having high energy and environmental impact [6,31]. Using electrochromic windows and advanced insulation materials it is possible to continuously adjust, control and optimize the thermal balance of a modern building thus significantly reducing air conditioning and heating costs.

Besides the relatively limited choice of electrochromic materials, a key issue resides in the inability of most electrochromic materials to switch between a transmissive (bleached) state and light absorbing (light dimming) state without altering the spectrum of the transmitted light. For instance, tungsten trioxide switches from transparent to deep blue [5], while nickel oxide switches from transparent

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to brown. This color filtering may be disturbing for some users. Devices that can reversibly dim the transmitted light throughout the entire visible spectrum without any selectivity of the transmitted wavelengths are preferred.

One proven solution is the use of several electrochromic layers of materials so that the spectrum of the transmitted light is corrected and proportional dimming can be achieved at all wavelengths. In theory, using a principle analogous to subtractive color photography, an electrochromic device consisting of three thin films that can be colored red, green and blue can achieve this task [25,32–35]. When color intensities are balanced properly, such a device can switch between a bleached state and a totally absorbing (black) state. Even more, using three independent layers it should be possible to choose any color wanted in the colored state by simply adjusting the proportions between the three colors. However, in spite of the demonstrated principle of color subtraction such devices have not been commercialized yet, mainly due to the manufacturing difficulties and price of thin-film nanostructured electrodes.

Although the electrochromic properties of titania have been known for a while [9,36], the electrochromic properties of self-organized titania nanotubes fabricated by anodization have only been relatively recently demonstrated with respect to  $H^+$  and  $Li^+$  insertion reactions [37,38]. Self-organized titania nanotubes constitute a versatile, low cost functional material whose dimensions may be tuned in accordance to the electrochemical synthesis parameters. For instance it is possible to grow continuous layers of highly parallel titania nanotubes having diameters between 40–120 nm and lengths between 200 nm and 1000  $\mu\text{m}$ . These nanotubes and some of their composites show good reversibility with respect to  $Li^+$  insertion [39–44] as well as relatively fast electrochemical  $H^+$  insertion [45]. When in their pristine form and for tube lengths below 20  $\mu\text{m}$ , the nanotube layers are fully transparent in the visible spectrum with little light interference effects due to their dimensions that are far from the optical wavelengths. Anodic titania nanotubes have already been used in conjunction with other electrochromic materials, such as nickel oxide [46,47], tungsten oxide [32,48], molybdenum oxide [4,49], cerium oxide [50] and niobium oxide [51] in order to improve the electrochromic properties and charge retention of titania. They seem to be an excellent cost-effective choice for the fabrication of interdigitated electrochromic devices that have been manufactured so far using precise but expensive classical photolithography methods [24]. However, in spite of the high interest in electrochromic devices based on self-assembled titania nanotubes, there are still very few studies available on this topic and many electrochemical and structural aspects remain unclear. Given that titania nanotubes represent the starting material for all these composites, we investigated the electrochromic properties of self-assembled titania nanotubes.

## 2. Experimental

Mirror polished Si wafers (SSP/E-Prime grade quality, Si-Tech Inc.) doped with boron (p-type dopant,  $\rho = 1\text{--}10 \Omega\text{cm}$ ) cut along (100) crystallographic plane were

cleaned with acetone, isopropanol and methanol, in this order, for 15 min in an ultrasonic bath. The native oxide layer was then removed by dipping the Si wafers in 1%wt HF aqueous solution for 30 s followed by rinsing with water and quick drying in a stream of Ar. The cleaned and etched Si substrates were immediately fit into the PVD (Physical Vapour Deposition) chamber which was subsequently pumped down to around  $10^{-6}$  mbar.

A 2  $\mu\text{m}$  thick Ti layer was DC sputtered on the as prepared Si substrate using a laboratory-made PVD device. A 99.9% Ti sputtering target was used and an ultrapure Ar atmosphere was maintained inside the deposition chamber at a pressure of  $8 \times 10^{-4}$  mbar during deposition.

The Ti-sputtered Si wafers were cleaved in smaller rectangular pieces using a diamond tip and then fitted into a laboratory-made special electrochemical cell described elsewhere [45]. The Ti thin-film was anodized in potentiostatic regime by applying a voltage of 60 V for 20 minutes across the two electrode cell using an EG&G Parstat 2273 potentiostat. No reference electrode was used for anodization. The working electrode (Ti thin film) was placed at 3 cm from the counter electrode (a large Pt foil). The anodization bath contained 96.7% glycerol, 1.3%  $\text{NH}_4\text{F}$  and 2%  $\text{H}_2\text{O}$ . The bath was stirred for 24 h before the experiment in a sealed container using a magnetic stirrer in order to ensure perfect homogeneity of the bath.

This procedure leads to the formation of a self-organized array of X-ray amorphous  $\text{TiO}_2$  nanotubes (80–100 nm in diameter, 2.2  $\mu\text{m}$  long, with a wall thickness of 20 nm). The Ti thin film is not completely consumed and a continuous Ti layer, approximately 750 nm thick, is left between the Si wafer and the  $\text{TiO}_2$  nanotubes. Thus, the final configuration from top to bottom is  $\text{TiO}_2/\text{Ti}/\text{Si}$ . It also has to be noted that due to a known volume expansion phenomenon during electrochemical oxidation, it is possible to grow a nanotubular oxide layer up to three times thicker than the corresponding metallic Ti film that was consumed [52].

After anodization the  $\text{TiO}_2$  nanotubes were treated with 0.1% HF for 90 s in order to remove any remainder of the initial compact layer formed during the initial stages of anodization.

The electrochemical properties of  $\text{TiO}_2$  were investigated by cyclic voltammetry and galvanostatic cycling in carefully de-aerated aqueous 1M  $(\text{NH}_4)_2\text{SO}_4$  solutions using a Solartron SI 1287 Electrochemical Interface coupled with a SI 1260 Impedance Analyzer and an EG&G Parstat 2273 potentiostat/galvanostat. A commercial Ag/AgCl reference electrode (Schott, Germany) was used for potential measurements. The microstructure was investigated by Scanning Electron Microscopy (SEM) using a Philips ESEM 130 Scanning Electron Microscope.

In situ diffuse reflectance measurements in the visible range (from 400 to 800 nm) were performed using a Varian 300 spectrophotometer equipped with an integrating sphere DRA-CA-30I. The sample was placed inside the spectrophotometer in a special laboratory-made two electrode electrochemical cell. The working electrode consisted of the  $\text{TiO}_2$  nanotubes while the counter electrode was a Pt wire. After filling with the electrolyte (de-aerated 1M  $(\text{NH}_4)_2\text{SO}_4$  solution) the cell was carefully

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