



Electrochemical protonation/de-protonation of titania nanotubes decorated with silver phosphate crystals: An enhanced electrochromic color contrast



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ABSTRACT

In the present work, anodically grown self-organized titania nanotubes are decorated with silver phosphate crystals using a layer-by-layer technique from an aqueous solution containing silver and phosphate ion precursors. The TiO₂-Ag₃PO₄ nanostructures are characterized using field enhanced scanning electron microscopy, energy dispersive X-ray analyser, X-ray diffractometry and X-ray photoelectron spectroscopy. The electrochromic behaviours of the TiO₂ nanotube with and without decoration of Ag₃PO₄ crystals are studied by applying a potential pulsed combined with in situ reflectance measurement of the color contrast response. The deposition of Ag₃PO₄ crystals has exhibited an enhanced color contrast of the nanotubes. Among various samples, the amorphous nanotubes decorated uniformly with Ag₃PO₄ crystals without blocking the tube openings has demonstrated the strongest color contrast. The experiments demonstrate that the enhanced color contrast is due to the synergetic contribution from the TiO₂ nanotubes and the Ag₃PO₄ deposits.

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1. Introduction

The phenomenon of reversible color change of some materials associated with the anodic and cathodic bias of an applied voltage or current is termed as electrochromism [1–5]. Such color change phenomenon upon electrochemical bias accompanied with oxidation and reduction reactions can be achieved by applying a very small external bias. As a result, applying the phenomenon of electrochromism, a device with low power consumption and high coloration efficiency can be achieved, and thus this phenomenon has been an important property for the potential applications such as in smart windows, reflective mirrors, and information displays [6–12]. Among various electrochromic materials, metal oxides have been investigated extensively owing to their high electrochemical stability [13,14]. Apart from the intrinsic property of a material, structural morphology of the material in the form of film

in an electrode surface plays a key role in electrochromism, particularly in exhibiting strong color contrast and fast switching between color and bleach states. For example, titania (TiO₂) has been one of the materials which have shown a promising result for application in most of the fields including electrochromism [15–19]. However, it has been demonstrated that as compared to the compact or particulate structured film, vertically oriented tubular structured titanium dioxide film exhibits a better color contrast and fast switching kinetics [20]. The improved electrochromic property of the tubular structured film is attributed to the easy access of the ions to be intercalated or de-intercalated during coloring and de-coloring cycles. Inserting ionic species into TiO₂ structures can change the optical properties by introducing a mid-energy gap, and thus change in absorption and reflectance of light properties of the TiO₂ material under study can be observed [21,22]. The color contrast and the switching kinetics can be further enhanced by in situ doping or loading secondary materials into nanotubes wherein the ion insertion can produce shift of electronic band structure in both the elements [23–26].

In the present study, anodically grown self-organized TiO₂ nanotubes is decorated uniformly with crystalline silver phosphate (Ag₃PO₄) deposits using a layer by layer technique, which has

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enabled us to enhance the electrochromic color contrast of the nanotubes significantly.

2. Experimental details

Self-organized TiO₂ nanotubes were prepared by electrochemical anodization of a titanium sheet (0.3 mm thick) in glycerol (60 vol.%)–water mixture containing 0.27 M NH₄F as described elsewhere [27,28]. For anodization, a two-electrode system electrochemical cell with a platinum counter electrode was used. Anodization was performed by pressing a titanium substrate against a rubber O-ring ($\Phi = 1$ cm) fixed at the bottom wall of a cell using a copper back contact electrode and applying the anodization voltage of 30 V against the platinum cathode for 3 h. However, it should be noted that during anodization the applied voltage is gradually increased with the speed of 0.3 V s⁻¹ from 0 to 30 V and holding this targeted voltage for 3 h. After growing, the nanotube layers were washed and immersed in deionized water for overnight to leach out the trapped electrolyte inside the tubes. The air dried nanotube layers were annealed in air at 450 °C for 3 h to crystallize into anatase crystalline phase. Silver phosphate crystals were deposited onto the as-prepared (amorphous) and the annealed (anatase crystalline) TiO₂ nanotubes using the Successive Ionic Layer Adsorption and Reaction (SILAR) method as described previously [29] with different SILAR cycles. Briefly, each SILAR cycle was consisted of subsequent dipping of the nanotubes in an aqueous solution of 0.25 M AgNO₃ and 0.25 M KH₂PO₄ for 30 min each. After each dip, the nanotube samples were washed in deionized water. Ag₃PO₄ deposited nanotube films were characterized using a field enhanced scanning electron microscope (FE-SEM, S-4800), energy dispersive X-ray analyser (EDX, EMAX Horiba), X-ray diffractometry (XRD, Siemens D-5005), and X-ray photoelectron spectroscopy (XPS, Physical Electronics 5600).

The protonation of nanotubes was carried out by intercalating protons into the samples from an aqueous solution of 0.1 M perchloric acid (HClO₄) and the degree of intercalation was investigated using cyclic voltammetry and chronoamperometry

applying a potential pulsed combined with reflectance measurement of the color contrast response [24,25,30]. Reflectance measurements were carried out with a fiber optic illuminator (tungsten halogen lamp, Ocean Optics).

3. Results and discussion

Anodization of titanium substrate in a fluoride containing electrolyte provides an effective and facile way to generate self-organized TiO₂ nanotube arrays with high surface area and controllable dimensions, leading to wide range of applications [15]. Fig. 1a shows the top surface and cross-sectional (inset image) SEM views of the TiO₂ nanotubes grown for 3 h of anodization in a fluoride containing glycerol–water mixture electrolyte at 30 V. The nanotubes have an average tube opening diameter of approximately 138 nm and the tube length of approximately 1.4 μ m. When the nanotubes were immersed subsequently in an aqueous solution of silver and phosphate ion precursors as described in the experimental section, Ag₃PO₄ was deposited. The amount of deposit and the uniformity of the deposits are found to be dependent on the number of SILAR cycles (Fig. 1b–d). For example, 5 SILAR cycles deposited very less amount of Ag₃PO₄ deposits (Fig. 1b) while 15 SILAR cycles dumped a large number Ag₃PO₄ masses. So, with the higher number of SILAR cycles, blocking of the nanotube opening with the Ag₃PO₄ mass was observed (Fig. 1d). Thus, after several hit-and-trials, a total of 10 SILAR cycles have been optimized (Fig. 1c). Fig. 1c shows the top and cross sectional (inset image) SEM views of the nanotubes after deposition of Ag₃PO₄ deposits for 10 SILAR cycles. The nanotube samples with and without SILAR deposits were characterized using XRD, EDX, and XPS analysis techniques (Figs. 2–4). The results are in line with our earlier work [29], which suggests the reproducibility of the work and reveals that the deposits are Ag₃PO₄ crystals. The XRD patterns in Fig. 2 reveal that the as-prepared nanotubes are amorphous which when annealed at 450 °C in air are converted into anatase crystalline phase (JCPDS No. 21-1272). Further, the XRD patterns of the nanotubes after SILAR deposition show additional peaks from deposits which correspond to the typical diffraction

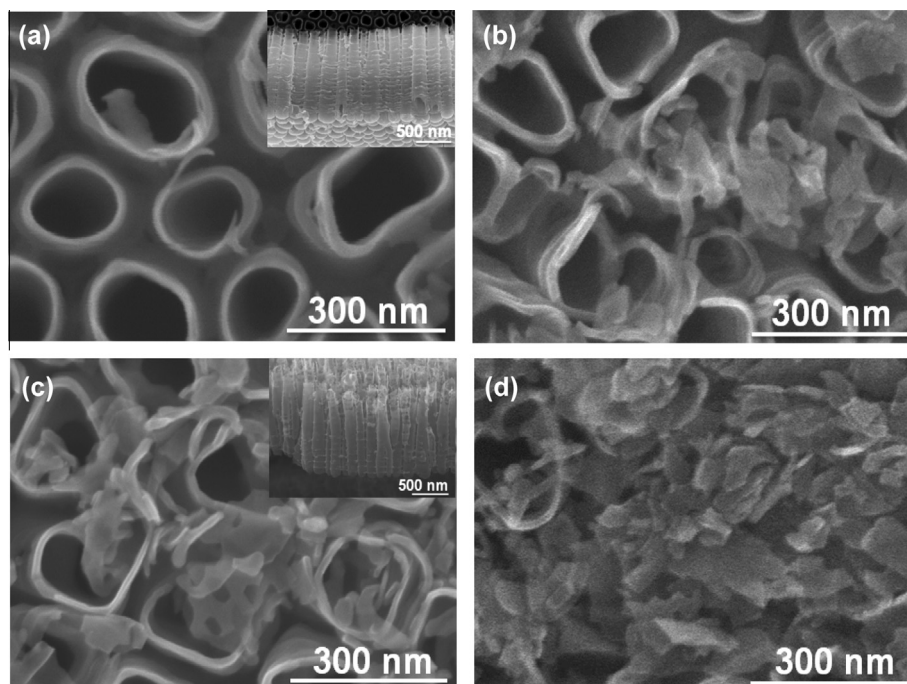


Fig. 1. Top surface SEM views of an anodically grown TiO₂ nanotubular film at 30 V for 3 h in aqueous electrolyte containing 0.27 M NH₄F and 60% (v/v) glycerol, (a) before, and after deposition of Ag₃PO₄ crystals for (b) 5, (c) 10, and (d) 15 SILAR cycles. Insets are the cross sectional views of the corresponding films.

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