



Supercapacitance of bamboo-type anodic titania nanotube arrays

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ABSTRACT

Highly oriented titania nanotube arrays are formed by self-organizing anodization of Ti foil in organic electrolytes in the presence of fluoride ions. The effects of tube length and the tube wall stratified layer on the electrochemical capacitance of these bamboo-type nanotubes are investigated. Field emission scanning electron microscopy (FESEM) is used to characterize the surface morphology, while cyclic voltammetry is used to investigate the pseudocapacitive properties of these nanostructured electrodes. The bamboo-type titania nanotube array with a higher aspect ratio shows a higher specific capacitance value of $52 \mu\text{F cm}^{-2}$ in 1 M Na_2SO_4 with excellent reversibility characteristics. The introduction of surface defects by annealing in NH_3 increased the specific capacitance value to $118 \mu\text{F cm}^{-2}$. This simple and cost-saving binder-free electrode is considered a promising candidate for supercapacitor applications.

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1. Introduction

Supercapacitors have triggered enormous research efforts in recent years due to their excellent properties, such as a high power density and fast charge–discharge, filling the gap left by conventional capacitors and batteries [1]. Their interesting characteristics originate from two unique charge storage mechanisms, electrical double layer capacitance (EDLC) and pseudocapacitance [2]. The former is based on a non-faradic reaction from the accumulation of charges through electrostatic interaction at the electrode–electrolyte interface, and the latter is based on faradic redox reactions on the surface of active materials [3]. In addition, the specific capacitance for both storage mechanisms can be maximized by using a material with a high specific surface area, such as porous carbonaceous materials or nanostructured conducting polymer and metal oxides [1–3]. Hence, knowledge of the surface and interface characteristics is crucial for improving the capacitance performance.

Recently, self-organized titania (TiO_2) nanotubes have been investigated for use as binder-free supercapacitor electrodes [4–6]. This nanostructured surface can be fabricated using the optimized anodization condition for titanium (Ti) foil in fluoride electrolytes. Ideally, Ti foil is used directly as a current collector, which provides direct and uninterrupted charge transport pathways, while TiO_2 nanotubes provide the active area for charge storage activity [5]. The tube structures also form surface electrical fields and reduce recombination by confining the injected electrons to the central zone of the tubes, as observed in dye-sensitized solar cell applications [6,7]. To increase

the surface area, bamboo-type TiO_2 nanotubes with irregular tube walls are prepared from stratified layers. These stratified layers can be synthesized using two methods: voltage pulsing or water-induced oscillation during anodization in organic electrolytes [8]. For the latter method, control of the water content is needed to form a side-wall stratified layer of bamboo-type TiO_2 nanotubes.

However the major drawback of using TiO_2 as supercapacitor electrodes is the wide band gaps of 3.0 eV and 3.2 eV for the rutile and anatase phases, respectively, which results in low electrochemical capacitance. In general, TiO_2 nanotubes serving as an electrical double layer capacitor could only provide a very low specific capacitance of approximately $10\text{--}40 \mu\text{F cm}^{-2}$ [5]. Recently, many research studies have been conducted to improve the electrical conductivity of this material by inducing surface defects through annealing (oxygen vacancies, reduction of Ti^{4+} to Ti^{3+}), changing the crystal structure (anatase, rutile), doping with non-metal materials (nitrogen, carbon) and making nanocomposites with electroactive materials (nickel oxide, polypyrrole). Annealing is a straightforward method to improve electrical conductivity but at higher temperatures (650 °C and above), the tubes will start to collapse [9]. Even at 450 °C cracks can occur in the tube walls and can slow down electron transport [10]. However, annealing at the correct temperature and conditions can also lead to the loss of oxygen from the material and the formation of Ti^{3+} near the surface region, thus improving the electrical conductivity.

This paper reports the effect of anodization time on characteristics of the structure, such as tube length and tube wall irregularities, to improve the electrochemical capacitance. This paper also reports the effect of annealing conditions to produce Ti^{3+} on the surface of TiO_2 nanotubes. Three samples (A, B and C) are prepared with different anodization times and annealing atmospheres. The characterization tools used in this study are field-emission scanning electron

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microscopy (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV).

2. Experimental

2.1. Nanotube preparation

Pieces of titanium foil (0.125 mm thick) were sonicated and degreased in acetone, ethanol and de-ionized (DI) water for 10 min each to remove surface impurities and contamination. Electrochemical anodization was performed in a two electrode cell at 20 V in an electrolyte containing glycerol and DI water in a ratio of 75:25 and ammonium fluoride (0.5 wt.%) at room temperature. Ti foil was used as the anode, and platinum wire was used as the cathode. The anodization time was 1 h for sample A and 5 h for sample B. Both samples were annealed at 500 °C for 2.5 h in an O₂ atmosphere with heating and cooling rates of 10 °C min⁻¹. Sample C was prepared with a 5 hour anodization and was annealed at 500 °C for 2.5 h in an NH₃ atmosphere.

2.2. Electrode characterization

Scanning electron micrographs were taken with a Jeol JSM-840A FESEM with an operating voltage of 5 kV. The phase determination of TiO₂ nanotubes was determined by X-ray diffraction (XRD) Siemens D5000, with a Cu-K α radiation source mounted on a horizontal θ -2 θ goniometer. The X-ray photoelectron spectroscopy (XPS) analysis of TiO₂ nanotubes was performed using an XPS Axis Ultra from Kratos equipped with monochromatic Al K α radiation (BE = 1486.6 eV). The sample was analyzed inside at an analysis chamber pressure of approximately 1×10^{-10} Pa. To correct the possible deviation caused by electrical charging of the samples, the C 1s peak of carbon at 284.5 eV was taken as an internal standard or reference. Cyclic voltammetry was carried out using a Potentiostat/Galvanostat Model PGSTAT-302 N from Autolab, controlled by a USB_IF030 interface card and GPES software installed on a computer. A three-electrode electrochemical cell with Ag/AgCl as the reference electrode and a Pt wire as the counter-electrode was used in the CV experiments with scan rates from 5 mV s⁻¹ to 100 mV s⁻¹ between 0 V and 0.6 V. The electrochemical experiments were performed at room temperature. The as-prepared TiO₂ nanotube film was used as a binder-free working electrode with a 1 cm² nominal surface area. The electrochemical measurements of sample A and sample B were performed in 1 M Na₂SO₄, while sample C was measured in 1 M H₂SO₄.

3. Results and discussion

3.1. Surface morphology

Fig. 1 presents the FESEM micrographs for TiO₂ nanotubes with different anodization times: 1 h (sample A, Fig. 1a) and 5 h (sample B, Fig. 1b). Table 1 presents a summary of the measurements performed on these micrographs. It is apparent that the extended anodization

time increased the nanotube length by 142%, from 413 nm (sample A) to 1000 nm (sample B), while the stratified layer spacing decreased by 30.8%, from 26 nm to 18 nm. This results in an increased aspect ratio, a higher specific surface area, and a higher electrochemical capacitance. It is worth noticing that a ring structure formed in sample B due to stratified layer detachment from the tube opening body. This effect will increase the porosity and produce a larger electro-active surface area of the nanotubes for easy diffusion of the electrolyte [11].

3.2. Phase detection

Fig. 2 shows the XRD patterns of the TiO₂ nanotube arrays annealed in O₂ at 500 °C for 2.5 h (sample B) and the TiO₂ nanotube arrays annealed in an NH₃ atmosphere (sample C) with the same setting as those of sample B. The diffraction peaks can be indexed as the anatase crystalline phase, but the rutile phase was only detected in the O₂ annealed sample (sample B). It is widely reported that annealing at more than 500 °C in O₂ will convert the anatase phase to the rutile phase, while annealing above 650 °C will result in tube collapse [8–12]. Nitridation below 550 °C does not change the TiO₂ crystalline phase, as suggested by Fu et. al. [12]; this explains the absence of the rutile phase in the sample annealed in NH₃. The XPS analysis (Section 3.3) also did not show the presence of any nitrogen peak, which supports the XRD results.

3.3. XPS analysis

To further confirm the identity of the oxide film, an XPS analysis is used to identify the Ti oxidation states of this film. All of the binding energies obtained in the XPS analysis are calibrated using the C 1s peak at binding energy 284.5 eV as the reference. Fig. 3 is the overlaid spectrum of sample B and sample C. The Ti 2p spectra for both samples show the presence of a main doublet composed of two symmetrical peaks with binding energies at 458.48 eV (Ti 2p_{3/2}) and 464.15 eV (Ti 2p_{1/2}), which are attributed to the Ti–O bond [13]. However, the sample annealed in NH₃ (sample C) shows a peak at binding energy 457.7 eV, which suggests that the reduction of Ti⁴⁺ to lower valence Ti³⁺ during NH₃ annealing may have occurred. According to the literature [12,14], this peak is attributed to titanium with oxidation states between +3 and +4, which is correlated with the titanium in a distorted lattice located between the TiO₂ and TiN phases. However, the XPS results did not detect the presence of nitrogen; thus, nitridation did not occur below 500 °C. This phenomenon indicates a synchronous increase in the surface electron density for Ti and O atoms. Considering that the N binding energy represents the same change as those of Ti and O, some authors proposed that the electron-donating effect may originate elsewhere, instead of N, O, and Ti atoms [12,15]. In this work, the electron donating effect must come from the annealing with NH₃, which is also a reducing agent.

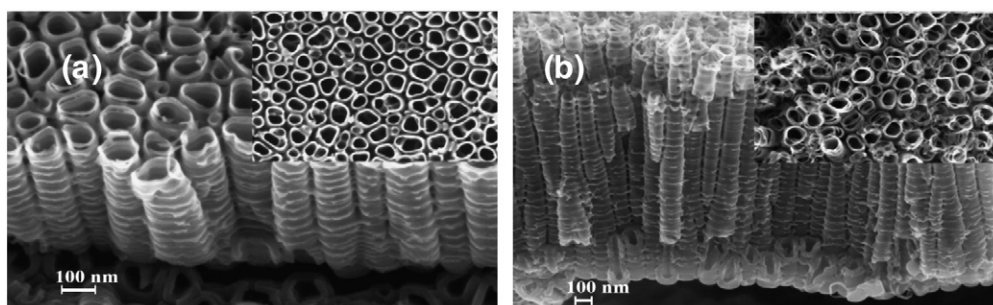


Fig. 1. Side-view FESEM micrographs of anodic titania nanotubes array for different anodization times: (a) sample A (1 h) and (b) sample B (5 h).

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