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Electrochemical reduction and capacitance of hybrid titanium dioxides—nanotube arrays and “nanograss”

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ABSTRACT

In this paper, we report enhanced electrochemical capacitance of well-aligned TiO_2 nanotube arrays with “nanograss” synthesized by electrochemical anodization. The conductivity of hybrid materials is improved by electrochemical reduction method, exhibiting an outstanding specific capacitance of 14.3 mF cm^{-2}, which is 14 times larger than pristine ones. The specific capacitance further increases up to 20.5 mF cm^{-2}, which is 43.4% higher than reduced ones with selectively retention of “nanograss” by ultrasonic treatment. We expect that the electrochemical-reduction approach and controllable morphology modification offer a potential path for developing high-performance energy storage devices.

1. Introduction

Supercapacitors, as one of promising electric storage device, show tremendous potential applications in portable devices, electric vehicles and household electric storage [1–4]. Compared with conventional batteries, supercapacitors possess competitive advantages of high power density, quick charge, high Coloumbic efficiency and long-life cycle [5], but undeniable disadvantage of lower energy density [6]. In principle, supercapacitors are categorized as electrical double layer capacitors (EDLCs) and pseudo-capacitors based on the mechanism of charge storage [7]. More specifically, the EDLCs store energy by separating charges at electrode/electrolyte interface, while pseudo-capacitors involve fast redox at the electrode and electrolyte [8]. In either types, nanostructured materials with high specific surface area (SSA) do offer large interface area, which is the most effective approach to improve capacitance [9].

Highly ordered TiO_2 nanotube (TNT) arrays fabricated by electrochemical anodization have shown promising potential for supercapacitor electrodes according to their physical/dimensional characteristics: (i) nano-sized tubular structure provides large surface area; (ii) 1D nanotube structure accelerates electrolyte diffusion and quick-charge transporting; (iii) anodic-formed TNTs have good adhesion on Ti substrate with low interfacial impedance [10]. However, low electrical conductivity of n-type TiO_2 semiconductors (rutile and anatase: 3.0 eV and 3.2 eV) [11,12] limits its potential as supercapacitor electrodes. The approaches, such as metal-ion doping (V, Ni, Cr, Mo, Sn, and so on) [13], nonmetal-ion doping (C, N, F, P and S) [14], co-doped or tri-doped with transition metals and nonmetals [15], and reduction [16], have been developed for enhancing conductivity of pristine TiO_2. Compared with other techniques, the reduction technique might offer chemical stabilization, thermal stability, and less facility cost [17].

Since Chen et al. promoted the fabrication of black TiO_2 by high-pressure technique, a variety of methods have been applied to prepare high conductive TNTs for supercapacitor electrodes [18,19]. Lu et al. improved conductivity of TNT arrays by thermal treatment under H_2 atmosphere at temperature range between 300 to 600° C, yielding the specific capacitance of 3.24 mF cm^{-2} at a scan rate of 100 mV s^{-1} [20]. Wu et al. performed low-temperature (320° C) hydrogen plasma treatment on TNT films, exhibiting a capacitance of 6.37 mF cm^{-2} at a current density of 2 mA cm^{-2} [21]. Li et al. synthesized thin film TiO_2 by electrochemical reduction in organic electrolytes, obtaining dramatic improvements on area-specific capacitance of 2.63 mF cm^{-2} at galvanostatic measurement of 50 μA cm^{-2} [22]. Similarly, Zhou et al. and Wu et al. carried electrochemically reduction on TNT arrays, achieving the capacitance of 1.84 mF cm^{-2} and 20.08 mF cm^{-2} [23,24]. Although the capacitance of TNTs are enhanced after reduction treatments, the research have been focused on improving their conductivity, lacking of investigation and discussion on capacitance affected by structural information (i.e. morphology, dimensions and structural parameters).

The TNT arrays anodized by fluoride-based ethylene glycol electrolytes [25] are normally covered by a layer of “nanograss” with a diameter of several tens nano-meter and length up to a few

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tens of micrometers, and the formation is described by bamboo-splitting model [26]. The “nanograss” morphologies may reduce light absorption [27], inhibit electron transfer [28], and hinder the ions transport [29], therefore, which have been assumed to be a detrimental factor in photoelectrochemical applications and have to be cleaned for getting a better performance. However, these “nanograss” on TNTs for supercapacitor applications is desirable since the “nanograss” offers extra specific surface area. Seamless integration of “nano-grass” layer and TNTs might be beneficial to transfer electrons as well.

In present work, we report fabrication and electrochemical characteristics of seamlessly integrated TNT arrays with “nanograss”. The hybrid TiO_2 “nanograss-nanotubes” are electrochemically reduced to enhance their conductivity. Electrochemical measurements demonstrate that capacitance of the hybrid TNTs and “nanograss” are increased dramatically due to additional “nanograss” contribution. This approach provides a simple and low-cost route for developing high-performance supercapacitors.

2. Experimental details

2.1. Materials and Reagents

All materials and reagents were used as received without further purification or treatment. Titanium foils (99.8% purity) were purchased from Baoji Titanium Industry Co. Ltd, China. Ethylene glycol (EG, 99.5%) and ammonium fluoride (NH_4F, 96%) were from VWR International, LLC for the electrolyte preparation. Sodium sulfate decahydrate ($Na_2SO_4 \cdot 10\,H_2O$) was purchased from Sigma-Aldrich Inc. Acetone, isopropanol, absolute ethanol and deionized water were used during the whole experiment.

2.2. Fabrication

Ti foils (30 mm × 12 mm × 0.3 mm) were ultrasonically (Finn-Sonic M12) cleaned in acetone, isopropanol and DI water for 15 mins in each solution, as shown in Fig. 1 (a), and then dried with nitrogen at room temperature. One surface of Ti foil was fully covered by Scotch tape to prevent forming TNTs, and partly covered on the other side for a defined rectangle region with area slightly larger than 1 cm^2 for growing TNTs.

The TNTs were fabricated by anodization of Ti foil at room temperature (25° C), using a fluoride-containing electrolyte solution (97 vol% EG, 3 vol% DI water, and 0.5 wt% NH_4F) as electrolyte with magnetic stirring [30,31]. The anodization was performed in a two-electrode configuration apart from the distance of 3.5 cm using Ti foil as anode and thick Ti sheet (1 mm) as cathode. Both electrodes were placed parallel to apply constant voltage of 60 V between the electrodes for 5 hours, as shown in Fig. 1(b). After anodization, as-prepared TNTs were rinsed with absolute ethanol in ultrasonic bath (BRANSOIC 3510E-MTH) to strip “nano grass” debris covered on TNTs, shown in Fig. 1(c). After anodization, the hybrid TiO_2 nanotube arrays and “nanograss” were annealed at 500° C (LENTON WHT6) in air for 3 hours to obtain anatase phase.

2.3. Electrochemical reduction

The exposed metallic Ti substrate of annealed samples were sealed with photoresist (SU-8-2150, Microchem), which was baked

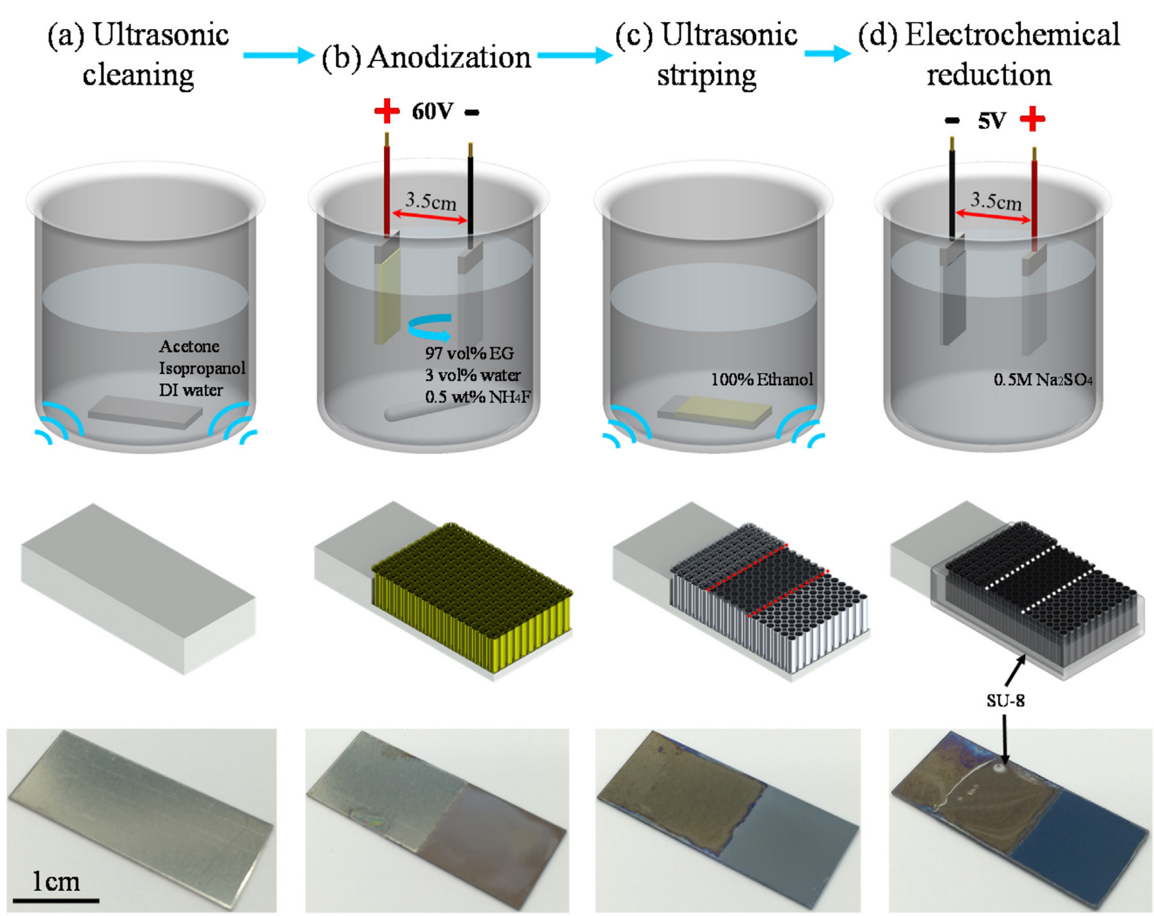

Fig. 1. The synthesis process for supercapacitor electrode via anodization technique and electrochemical reduction (a) ultrasonic cleaning, (b) anodization, (c) ultrasonic stripping, (d) electrochemical reduction.