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Synthesis and electrochemical properties of CeO_2 nanoparticle modified TiO_2 nanotube arrays

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ABSTRACT

In this paper, a cerium dioxide (CeO_2) modified titanium dioxide (TiO_2) nanotube array film was fabricated by electrodeposition of CeO_2 nanoparticles onto an anodized TiO_2 nanotube array. The structural investigation by X-ray diffraction, scanning electron microscopy and transmission electron microscopy indicated that the CeO_2 nanoparticles grew uniformly on the walls of the TiO_2 nanotubes. The composite was composed of cubic-phase CeO_2 crystallites and anatase-phase TiO_2 after annealing at 450 °C. The cyclic voltammetry and chronoamperometric charge/discharge measurement results indicated that the CeO_2 modification obviously increased the charge storage capacity of the TiO_2 nanotubes. The charge transfer process at the surface, that is, the pseudocapacitance, was the dominate mechanism of the charge storage in CeO_2-modified TiO_2 nanotubes. The greater number of surface active sites resulting from uniform application of the CeO_2 nanoparticles to the well-aligned TiO_2 nanotubes contributed to the enhancement of the charge storage density.

1. Introduction

Ordered nanostructures, such as semiconductor metal-oxide nanowire arrays and nanotube arrays have been extensively studied in recent years because of their advantageous electrical, optical, and magnetic properties. In particular, anodized titanium oxide nanotube arrays (ATO-NTs) are one of the most popular 1D nanomaterials because of their easy synthesis, low cost and wide applications in solar cells [1,2], photocatalysts [3], gas sensors [4], and electrochromic display devices [5–7], etc. The oriented-open structure of ATO-NTs provides not only a large effective surface area but also the electron transfer or ion diffusion channels along the tube wall. Furthermore, the tailorable nanotube length, diameter, and wall thickness of ATO-NTs make it possible to adjust the parameters to obtain optimized device performance [8].

CeO_2 is an attractive material for applications in catalysts [9], solid oxide fuel cells [10], and sensors [11]. CeO_2 has also been reported to be a good counter electrode material in electrochromic devices [12–14] benefiting from its high ion-storage capacity, optical passiveness, good electrochemical reversibility, and stability. Because of its multiple redox states, CeO_2 is also a feasible charge storage material. Efforts have been made to optimize the intercalation kinetics of CeO_2 because bulk CeO_2 does not have a layered or open tunnel structure. One approach is to dope CeO_2 with a wide-bandgap semiconductor metal oxide, such as TiO_2 [14], ZrO_2 [15], or SnO_2 [16], to create a CeO_2 composite with an open distorted microstructure so that the Li ion intercalation process can occur. It has been reported that the use of TiO_2–CeO_2 composites with a Ce/TiO_2 molar ratio of 25–50% can increase the effectiveness of Li ion intercalation by 100 times over pure CeO_2 [17]. Another approach is to fabricate nanostructured CeO_2 [18]. Many researchers have investigated the influence of nanostructure on the electrochemical performance of CeO_2 by fabricating nanostructured CeO_2 using templates [19], controllable electrochemical methods [20], sol–gels [21], chemical vapor deposition [11] or hydrothermal methods [22]. The high surface area of nanostructured CeO_2 prominently enhances the surface redox reaction rate and the electrochemical kinetics, thus leading to an increased charge storage capacity [23]. However, in spite of the intense work on ATO-NTs and nanostructured CeO_2, there has been no report on the electrochemical properties of one-dimensional TiO_2–CeO_2 nanostructures.

In this work, an ATO-NT film modified using nanosized-CeO_2 particles was fabricated using an electrochemical approach. An enhanced charge storage capacity was observed after CeO_2 coupling in comparison with the ATO-NTs and the pure CeO_2 film.

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2. Experimental

ATO-NTs were prepared by an electrochemical anodization process. In brief, after pretreatment by 1 h of electropolishing followed by ultrasonic washing, the Ti plate (Alfa Aesar, 99.6%, annealed, 127 μm in thickness) was put into a 0.15 M NH_4F–glycerin solution (containing 2 vol% water) for anodization. A typical three-electrode system with a platinum wire counter electrode and an Ag/AgCl (1 M KCl) reference electrode was used, and the working area of Ti plate was 0.4 cm^2. The anodization process was performed at 45 V at 25 °C for 6 h. Then, the anodized TiO_2 samples were rinsed with water and ethanol successively and were dried at 50 °C for subsequent use.

CeO_2 nanoparticles were deposited on ATO-NTs using an electrodeposition process. $CeCl_3 \cdot 7H_2O$ (0.1 M) in ethanol was used as the plating solution. Prior to electrodeposition, the ATO-NTs were immersed in the deposition solution for 1 h so that the plating solution could diffuse into the ATO-NTs. The electrodeposition was performed at −10 V (*vs.* Ag/AgCl) for 40–60 s (until the total charge was numerically equal to 60 mC/cm^2). For comparison, a pure CeO_2 film was also prepared by electrodeposition on ITO glass by maintaining the total deposited charge at 200 mC/cm^2. All of the samples (pure CeO_2 film, ATO-NTs and CeO_2/ATO-NTs) were treated at 450 °C for 30 min in a rapid thermal annealing (RTA) furnace before structure and electrochemical analysis.

The morphology of the samples was investigated using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). X-ray diffraction (XRD) (Siemens, D500) was used to confirm the crystal phase of the samples. A high-resolution transmission electron microscope (HRTEM, JEOL JEM2010) equipped with an energy-dispersive spectrometer was used to analyze the microstructure and composition. The voltammetric and chronoamperometric measurements were performed using an electrochemical station (CH Instruments 660C). For electrochemical property characterization, a 0.1 M solution of $LiClO_4$ in propylene carbonate was used as the electrolyte. All electrochemical processes were conducted at room temperature (25 °C).

3. Results and discussion

Typical SEM images of ATO-NTs and CeO_2/ATO-NTs are shown in Fig. 1a and b. The ATO-NTs were highly ordered with average tube diameter of about 100 nm and very thin walls of less than 10 nm in thickness. The length of the nanotube array was about 25 μm, as observed from the cross-section image (see Supplementary Figure S1). Fig. 1b indicates that small particles of CeO_2 homogeneously coated the wall of the ATO-NTs, which resulted in a decrease in the average nanotube diameter to about 50 nm. It is noteworthy that the open top of the CeO_2/ATO-NTs would be very helpful for electrolyte diffusion in electrochemical applications. The XRD patterns of ATO-NTs and CeO_2/ATO-NTs after annealing at 450 °C for 30 min are shown in Fig. 1c(1) and c(2). The XRD peaks at 40.5 ° and 53 ° can be assigned to the titanium substrate. The peaks at 25.5 °, 37.9 °, 48° and 54° are from the (1 1 0), (1 0 3), (2 0 0) and (1 0 5) diffractions, respectively, of anatase-phase TiO_2 (JCPDS No. 21-1272). The typical diffraction peaks of CeO_2 are 28.6°, 33°, 47.5°, and 56.4° from (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively, as shown in Fig. 1c, indicating the crystal phase of the CeO_2 (JCPDS No. 43-1002). Thus, all of the samples that were treated at 450 °C yielded crystalline materials.

The microstructure of the CeO_2/ATO-NTs was further investigated by HRTEM. Fig. 2 shows the TEM images and the diffraction pattern of the corresponding sample. Fig. 5(a) TEM image of CeO_2/ATO-NTs after annealing at 450 °C for 30 min. For comparison, an image of the ATO-NTs before CeO_2 deposition is shown inside on the lower left. In the upper right is an HRTEM image of the nanotubes in (a); (b) is the corresponding electron diffraction pattern.

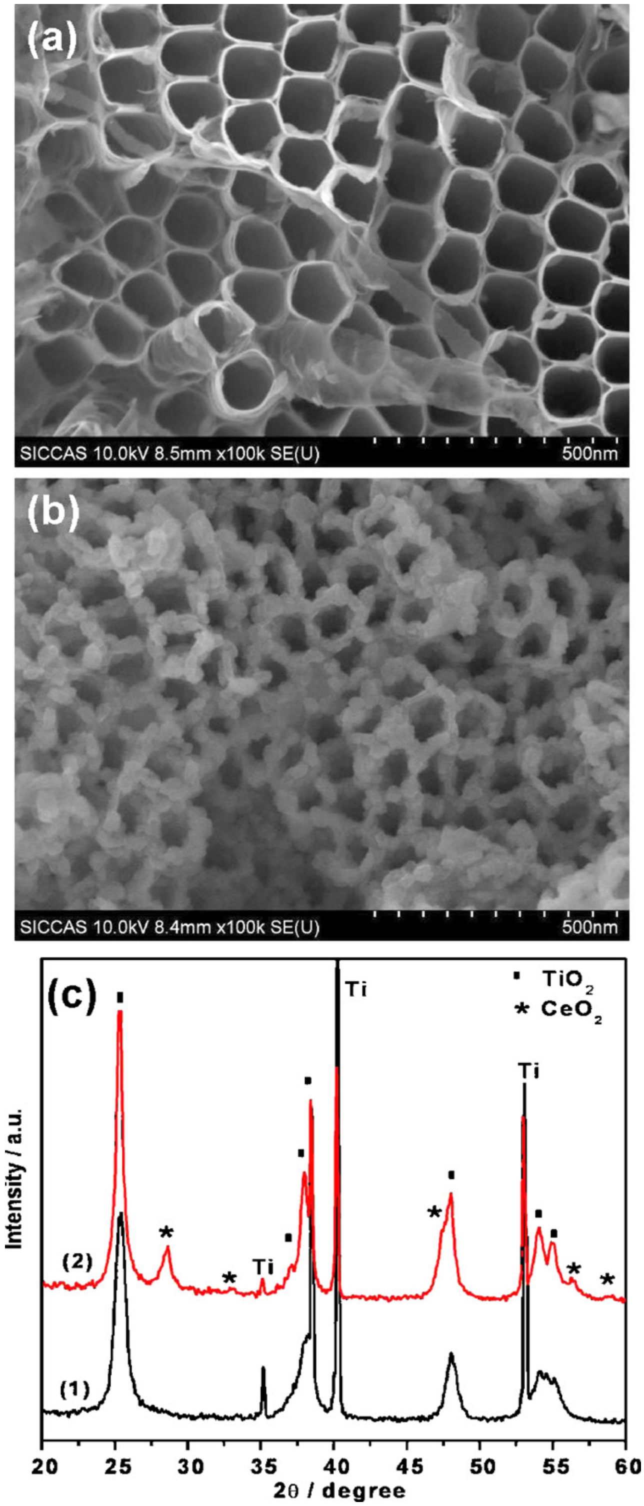

Fig. 1. SEM images of (a) ATO-NTs and (b) ATO-NTs modified by CeO_2 nanoparticles. (c) XRD patterns of the (1) ATO-NTs and (2) CeO_2/ATO-NTs.

Fig. 2(a) presents a bright field TEM image of the CeO_2/ATO-NTs. Compared with the TiO_2 nanotubes without CeO_2 coating (down left inside Fig. 2a), it is obvious that nanoparticles were uniformly deposited deep inside of the TiO_2 nanotubes. The increase in the wall thickness of the nanotubes implies that most of the nanopar-