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Short communication

Enhancing the capacitance of TiO_2 nanotube arrays by a facile cathodic reduction process

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HIGHLIGHTS

- TiO_2 nanotube arrays were modified by a facile cathodic reduction process.
- Oxygen vacancies were formed and hydroxyls were introduced on the surface of TiO_2.
- The electrochemical activity and conductivity of modified sample were improved.
- The modified sample showed much enhanced capacitance over the pristine one.

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ABSTRACT

TiO_2 nanotube arrays are modified by a facile cathodic reduction process treatment and the results are discussed in terms of their electrochemical activity and conductivity. The instrumental characterizations such as X-ray photoelectron spectroscopy and Raman spectroscopy indicate that the formation of oxygen vacancies in the lattice and introduction of hydroxyl groups on the surface of TiO_2 take place. The capacitance of the modified sample is found to be 13 times larger than the pristine TiO_2 nanotube arrays. This work reveals a feasible and simple method to improve electrochemical activity and conductivity of TiO_2 for supercapacitors application.

1. Introduction

Highly ordered TiO_2 nanotube arrays, have attracted much attention, owing to their high regulation, large surface area, excellent controllability and stability [1–3]. In recent years, the focus was made on using TiO_2 nanotube arrays as an active material for potential charge storage device [4–8]. The findings revealed that unlike carbon materials and other metal oxides [9–11], titania capacitors exhibited the behavior of conventional electric double layer capacitors (EDLC) act by a non-faradic mechanism with a very low specific capacitance. The poor capacitive behavior of TiO_2 was found to be mainly due to its low electrochemical activity and high resistance, originated from its semiconductor characteristic. Since the properties of TiO_2 are very sensitive to oxygen content in the lattice [12,13], controlled introduction of oxygen vacancies (Ti^{3+} sites) into the TiO_2 nanotube arrays has been proved to be an effective method to improve its electrochemical activity and conductive behavior of for supercapacitor application [14,15]. However these approaches are always involved in rigorous heat treatment procedure in hydrogen or argon atmosphere, which is not cost-effective considering the extra requirement of instruments and resources.

In this study, a facile cathodic reduction process to introduce oxygen vacancies into the TiO_2 nanotube arrays is investigated and documented. The cathodic reduction process could be carried out for several minutes employing an electrochemical instrument, following the preparation of TiO_2 nanotube arrays by electrochemical anodization. Consequently, compared to the heat treatment routes, the cathodic reduction process is expected to have enhancement on the capacitance along with its user friendly preparation conditions. When the TiO_2 nanotube arrays were treated with the cathodic reduction process, oxygen vacancies were formed and hydroxyl groups were introduced on the surface of TiO_2, leading to highly improved electrochemical activity and conductivity. The reduced TiO_2 nanotube arrays (denoted as R-TNTs) prepared by the simple cathodic process showed enhanced

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capacitance over the pristine TiO_2 nanotube arrays (denoted as TNTs).

2. Experimental

2.1. Preparation of TNTs and R-TNTs

The TNTs were prepared by an electrochemical anodization process as per the procedure mentioned in earlier report [16]. The R-TNTs were obtained by electrochemical reduction of the TNTs for 20 min in a two-electrode system at room temperature, employing the TNTs and Pt mesh as cathode and anode respectively. 0.1 M Na_2SO_4 solution was used as supporting electrolyte, and the distance between electrodes was exactly fixed as 4 cm. The applied potential of the cathodic process was maintained in the ranges of +2 to +8 V, and the optimum potential was found to be +4 V.

2.2. Characterization of TNTs and R-TNTs

To investigate the microstructure and composition of the samples, field emission scanning electron microscopy (FE-SEM, NANOSEM 450, FEI), X-ray photoelectron spectroscopy (XPS, XSAM800, KRATOS) with Mg K_α X-ray ($h\nu = 1253.6$ eV) at 12 kV and Raman spectroscopy (HORIBA Jobin Yvon LabRAM) with Ar^+ laser of 514.4 nm excitation were employed.

The electrochemical properties of the samples were investigated with electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge–discharge tests by an electrochemical workstation (CS350, CorrTest, China). Experiments were carried out in an undivided compartment with three-electrode system using the TNTs or R-TNTs, saturated calomel electrode (SCE) and Pt mesh as the working, reference, and counter electrodes, respectively. EIS measurements were performed between 100 kHz and 0.01 Hz under a constant potential of −0.1 V (vs. SCE) with a 5 mV rms sinusoidal modulation. The stability of the R-TNTs was investigated by galvanostatic charge–discharge measurement up to 1000 cycles at a current density of 100 $\mu A\ cm^{-2}$. All the electrochemical measurements were performed in a 0.5 M Na_2SO_4 solution at room temperature.

3. Results and discussion

The top and side views of the SEM images were taken for TNTs and R-TNTs. As shown in Fig. 1a, the structure of the R-TNTs consists of highly ordered tubes with inner diameter of 40–70 nm, wall thickness of 10–15 nm and tube length of 700–800 nm, which are in identical dimension with that of TNTs (not shown). Fig. 1b shows the normalized Ti 2p XPS spectra of the samples, in which two broad peaks centered at about 458.5 and 464.3 eV that correspond to the characteristic of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ peaks of Ti^{4+} are observed for both the samples [12,15]. In comparison to the TNTs, the peaks of the R-TNTs show a negative shift in binding energy. By subtracting the Ti 2p spectra of the R-TNTs with TNTs, there are two extra peaks centered at ca. 458.0 and 459.5 eV (Fig. 1b). These two peaks are consistent with the characteristic Ti $2p_{1/2}$ and Ti $2p_{3/2}$ peaks of Ti^{3+} [15,17], confirming the presence of Ti^{3+} state in the R-TNTs. Fig. 1c compares the O 1s XPS spectra of the samples. Both the samples exhibit peak at 529.9 eV that is a characteristic peak of Ti–O–Ti [12]. Additionally, a shoulder peak centered at 531.5 eV with higher intensity for R-TNTs could clearly be observed, which is attributed to Ti–OH species [12,17]. These XPS characterization findings strongly suggest that formation of oxygen vacancies and

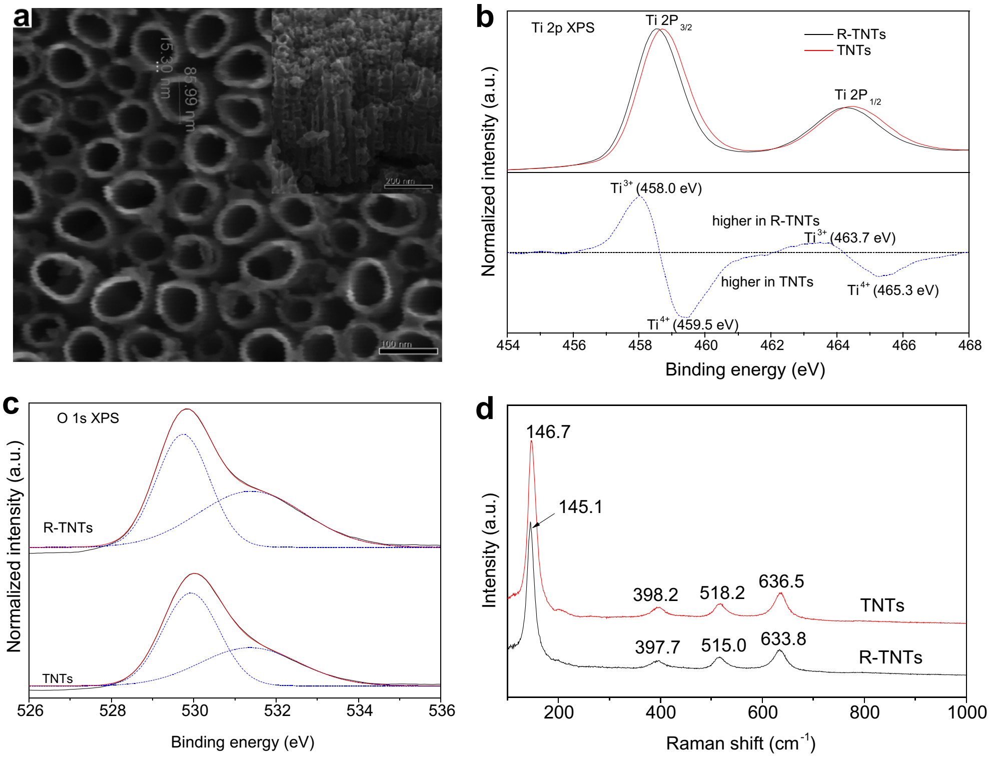

Fig. 1. (a) Typical top view and side view (inset) FE-SEM images of the R-TNTs. (b) Ti 2p XPS spectra of the R-TNTs (black solid line) and TNTs (red solid line), together with their difference spectrum ('R-TNTs' minus 'TNTs', blue dashed line). (c) O 1s XPS spectra of the samples. Black circles are the experimental data, which can be decomposed into a superposition of two peaks shown as blue dashed curves. The red curve is the summation of the two decomposed peaks. (d) Raman spectra of the TNTs and R-TNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)