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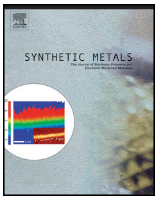

Fabrication and electrochemical capacitance of polyaniline/titanium nitride core–shell nanowire arrays

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ABSTRACT

A novel polyaniline/titanium nitride (PANI/TiN) core–shell nanowire arrays (NWAs) have been fabricated on carbon fibers (CFs) substrate and applied as an electrode material of electrochemical supercapacitor. TiN NWAs were prepared via a seed-assisted hydrothermal process and then ammonia nitridation process. PANI/TiN core–shell NWAs were prepared by electrodepositing PANI onto TiN NWAs. Scanning electron micrographs revealed that TiN NWAs consisted of bundle of small nanowires with a diameter of 10–30 nm and an average length of 1 μm. High-density TiN NWAs offered a high specific surface area for PANI coating layer. Electrochemical measurements showed that a very high specific capacitance of 1064 F g^{-1} at a current density of 1 A g^{-1} (based on the mass of PANI) was obtained for PANI/TiN core–shell NWAs. The specific capacitance of PANI/TiN core–shell NWAs could even achieve 787.5 F g^{-1} at a higher current density of 5 A g^{-1} and still kept 95% capacity retention after 200 cycles. These results indicated that the PANI/TiN core–shell NWAs showed the promising application as supercapacitor electrode materials for energy storage.

1. Introduction

Electrochemical capacitors, also called supercapacitors, store energy by using either ion adsorption or fast surface redox reaction. They can complement batteries in electrical energy storage and harvesting applications when high power delivery or uptake is needed [1,2]. It is well known that the general electrode materials used in supercapacitors are porous carbon materials, transition metal oxides and conducting polymers [3,4]. Nowadays, vertically aligned conducting polymer nanowire arrays (NWAs) have been the focus of intensive research due to their useful and prospective application in different fields ranging from chemical and biological sensing to energy conversion and storage [5–7]. Polyaniline (PANI) is considered as one of the most promising and versatile conducting polymers thanks to its high energy-storage capacity, easy synthesis, low cost and environmental stability [8–11]. Unfortunately, PANI also possesses poor cycling stability derived from the volumetric changes during the doping/dedoping process and poor electrical conductivity in its neutral or alkaline state [12].

Nanocomposite materials have been found to be particularly advantageous for supercapacitor based on PANI, because they combine unique properties of individual nanostructure and have possibly synergistic effects [13]. It has been demonstrated that the use of support materials, such as carbon nanotube and titanium oxide (TiO_2), is an effective method to improve capacitive performance of PANI [14,15]. On the other hand, the well-aligned TiO_2 nanomaterials (e.g., nanotube and nanowire arrays), have attracted more interests due to their wide applications in dye-sensitized solar cells, energy storage and biomedical devices [16–21]. Some previous research work has proven that ordered TiO_2 nanotube arrays, prepared by electrochemical anodization, are an excellent support for PANI materials [22,23]. The high accessible surface area and chemical stability of TiO_2 nanotube arrays are beneficial for the enhancement of the adhesion between PANI and the substrate, and hence improve the cycle life. However, it is not easy to fill PANI into TiO_2 nanotube arrays with a coaxial construction because of the strong surface tension between the nanotube arrays and the air [24]. Moreover, normally prepared TiO_2 nanotube arrays are bundled with titanium substrate, which will limit its application in highly flexible electronic equipment. TiO_2 nanowire or nanorod arrays can be grown on different substrates through hydrothermal or solvothermal processes [25]. Moreover, titanium nitride (TiN) is reported to possess oxidative stability, corrosion resistance, and good electrical conductivity, which makes TiN an excellent

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candidate for electrochemical capacitors in highly corrosive electrolytes [26–28]. Lu and co-workers found that supercapacitors using TiN nanowire/carbon cloth had high power density and excellent cycle stability [29,30].

In this study, we proposed a facile method to fabricate a novel PANI/TiN core–shell NWAs by combining conducting PANI with one-dimensional TiN NWAs. PANI was electrodeposited on TiN NWAs which were grown on CFs. The conductive CFs served as lightweight current collectors and good scaffolds for loading TiN NWAs. It had been found that the PANI/TiN core–shell NWAs exhibited both a superior capacitive behavior and good cyclability. The improved electrochemical properties of the PANI/TiN core–shell NWAs were explored in comparison with the PANI/TiO_2 core–shell NWAs.

2. Experimental

2.1. Preparation of TiO_2 and TiN NWAs

A seed-assisted hydrothermal synthesis and nitridation process were used to prepare free-standing TiN NWAs grown directly on CFs. First, CFs bundle materials (3000 fibers per bunch, 10.0 cm × 0.2 cm) were cleaned with concentrated nitric acid, ethanol and distilled water and then dried at room temperature. The clean CFs was immersed into 0.2 M tetrabutyl titanium ethanol solution for 10 min. The dried CFs was further heated in air at 350 °C for 10 min, forming TiO_2 nanoparticles on the CFs surface. 30 ml of concentrated hydrochloric acid was diluted with 30 ml deionized water, and mixed with 0.9 ml tetrabutyl titanium. 40 ml of this clear solution mixture together with the CFs coated with TiO_2 nanoparticles were transferred to a Teflon-lined stainless steel autoclave. The sealed autoclave was heated at 150 °C for 5 h, and then was cooled down slowly at room temperature. A white TiO_2 NWAs film was uniformly coated on the CFs surface. The as-prepared TiO_2 NWAs were thoroughly washed with ethanol and deionized water and then air dried. The samples were annealed at 550 °C for 1 h under nitrogen atmosphere. Finally, the TiO_2 NWAs were converted to TiN NWAs by annealing in a tubular furnace at 900 °C for 2 h under ammonia atmosphere with a flow rate of 40 ml min^{-1}. A progressive, slow heating ramp was adopted during the nitridation process (room temperature to 300 °C, 5 °C min^{-1}; 300 to 700 °C, 2 °C min^{-1}, 700 to 900 °C, 1 °C min^{-1}).

2.2. Fabrication of PANI/TiO2 and PANI/TiN core–shell NWAs electrodes

The TiO_2 NWAs covering CFs (TiO_2 NWAs/CFs) and TiN NWAs covering CFs (TiN NWAs/CFs) were immersed in an aqueous solution containing 0.1 M aniline monomer and 1 M sulfuric acid, respectively. Aniline was distilled under vacuum condition for purification treatment before use. Electrodeposition process was carried out in a standard three-electrode setup using a saturated calomel electrode (SCE) as the reference electrode, Pt plate as the counter electrode and a bunch of TiO_2 NWAs/CFs as the working electrode. Electrochemical polymerization of aniline was carried out using a potentiodynamic method [6]. The electrodeposition of PANI on TiO_2 NWAs/CFs was performed for 20 cycles in the potential range of −0.2–1.0 V at a sweep rate of 25 mV s^{-1}. The electrodeposition of PANI on TiN NWAs/CFs was performed for 30 cycles in the potential range of −0.2–0.9 V at a sweep rate of 25 mV s^{-1}. After electropolymerization reaction, the obtained samples were washed with distilled water and ethanol. The mass of PANI deposited on TiN NWAs and TiO_2 NWAs could be obtained by measuring the weight difference before and after the deposition of PANI utilizing an electronic balance with an accuracy of 0.1 mg. In our study, the lower anode potential was used for PANI electrodeposition on TiN NWAs. The more cycling number was accordingly needed to obtain the same mass loading of PANI. Herein, the loading amount of PANI on PANI/TiO_2 and PANI/TiN core–shell NWAs was both 2.5 mg.

2.3. Structure characterization

The surface morphology and microstructure of TiO_2 NWAs, TiN NWAs, PANI/TiO_2 and PANI/TiN core–shell NWAs were investigated by means of scan electron microscopy (SEM, Hitachi S-3000, Japan). Raman spectroscopy was performed on a Raman spectrometer (Raman, Oceanoptics Benchtop Raman System, USA) using a He–Ne laser that emitted the samples at 785 nm excitation with wave between 0 and 2,000 cm^{-1}. X-ray diffraction patterns were recorded with a Bruker-AXS Microdiffractometer (XRD, D8 ADVANCE, Germany) with the use of Cu-*K*a radiation source.

2.4. Electrochemical measurement

The electrochemical performances of the samples were measured in a three-electrode system by cyclic voltammetry and galvanostatic charge–discharge measurement, using a CHI760C electrochemical workstation (Chenhua, Shanghai). Pt plate and saturated calomel electrode were used as the counter electrode and reference electrode, respectively. Electrochemical impedance spectra were recorded using an electrochemical workstation (EIS, ZAHNER-im6ex, Germany) from 10 mHz to 100 kHz with an alternate potential amplitude of 5 mV. EIS measurements were carried out at an open potential of 0.5 V (vs. SCE) after CV tests. All electrolyte used above was 1 M H_2SO_4 aqueous solution. The specific capacitance (C) is calculated using the following Eq. (1) [17].

$$C = \frac{Q}{\Delta V \times m} = \frac{I \times t}{\Delta V \times m} \qquad (1)$$

where C is the specific capacitance, I is the charge–discharge current, t is the time of discharge, ΔV is the voltage difference between the upper and lower potential limits, and m is the mass of active materials.

3. Results and discussion

3.1. Morphological characterization

The preparation process for PANI/TiO_2 and PANI/TiN core–shell NWAs electrodes was illustrated schematically in Fig. 1a, which mainly involved three steps. First, ordered TiO_2 NWAs were prepared on CFs by a seed-assisted hydrothermal method. Second, the TiO_2 NWAs aligned on the CFs were annealed in ammonia atmosphere to form TiN NWAs. Finally, PANI/TiN core–shell NWAs were formed by fully coated PANI onto the TiN NWAs surface via anodic electrodeposition. In addition, PANI/TiO_2 core–shell NWAs were prepared through direct electrodepositing PANI onto the TiO_2 NWAs for a comparison. In particular, there had some difference on the preparation of TiO_2 and TiN NWAs in our study when compared with the previously reported paper [29]. The titanium precursor for seed solution was tetrabutyl titanium ethanol solution in our experiment, which was titanium chloride aqueous solution in the reported paper [29]. The well separated TiO_2 NWAs were formed and supported on carbon fibers in our study, indicating that the titanium source for seed solution was not restricted to titanium chloride. In addition, the as-prepared TiO_2 NWAs were annealed in nitrogen atmosphere at 550 °C in our experiment. In fact, it was found the structure of CFs would tend to collapse if annealed in air atmosphere containing oxygen gas. So a nitrogen protective gas was needed. Fig. 1b shows optical images of the CFs covered with active