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Supercapacitor of TiO_2 nanofibers by electrospinning and KOH treatment

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ABSTRACT

Electrode material of TiO_2 nanofiber was fabricated by electrospinning technique and a post treatment by KOH. Compared with the pristine TiO_2, KOH treated fibers become much more conductive and thus are suitable for supercapacitor. The specific capacitance of treated TiO_2 is dramatically enhanced from 0.04 F g^{-1} to 65.84 F g^{-1} at 1 mV s^{-1} and is about 1500 times higher than that of the pristine. This value is also about several times higher than those of conductive TiO_2 obtained by anodic oxidation or hydrogen annealing. Besides, the treated TiO_2 nanofibers exhibit a good rate characteristics and cycling stability by remaining 78% of the capacitance with increasing the scan rate from 1 mV s^{-1} to 1 V s^{-1} and 90% after 10,000 cycles, respectively.

1. Introduction

Recently, electrical double-layer capacitors (EDLCs), together with faradaic pseudocapacitors capacitor, have received intensive attention for the application as renewable energy devices due to the advantages of high power density, long cycle life and relative high energy density and low cost [1–4]. EDLCs are usually combined with electrochemical cells to provide peak power for vehicles to accelerate or to climb up hills. They can also absorb surge currents or peak energy temporarily produced by wind driven generators, fuel or solar cells. As the counterpart of EDLC, pseudocapacitor is another kind of capacitors based on redox reaction to convert electricity into chemical energy mutually by charging and discharging, such as in RuO_2 and some of other transition metal oxide pseudocapacitors, like MnO_2, V_2O_5, NiO, Fe_3O_4 and Co_2O_3. Theoretically, pseudocapacitor has a large specific capacitance, 1350 F g^{-1} for MnO_2 as an example, and it is around 10–100 times higher than that of EDLC in energy density. However, except for RuO_2, all the other metal oxides or hydroxides are not yet applied in market due to the weakness of worse cyclibility, low energy and power density, which makes it necessary for the further studies on oxide pseudocapacitor.

Nanoscaled TiO_2 has some merits of possessing a high specific surface area, environment-friendly, good physical and chemical stability, low cost, as well as Ti element abundant in the Earth's crust [5]. Recently, a lot of investigations have been conducted on TiO_2 nano-fibers for potential applications as gas and humidity sensors, solar cells, lithium-based batteries and photochemical catalysis [6–9]. However, there are few studies reported on the performance of supercapacitor of TiO_2 since TiO_2 has an extremely high resistivity, much larger than the counterparts of RuO_2 [10–12], MnO_2 [13], NiO [14,15], Co_2O_3 [16], and Fe_3O_4 [17], which are usually considered as promising electrode materials for the high specific capacitance and good cycling stability [18].

Pristine TiO_2 nano-fibers (NFs) are normally used as isolator rather than supercapacitor electrodes for the extraordinary high resistivity. Most recently, doping method was employed to improve the conductivity of TiO_2 NFs to meet the requirement as electrodes [19–22]. For example, Wu and Li reported that TiO_2 nanotubes, fabricated by anodic oxidation, possess a specific capacitance of 5.42 mF cm^{-2} at 0.05 mA cm^{-2} and 8 mF cm^{-2} at 50 mV s^{-1}, respectively [23]. Ramadoss and Kim synthetized TiO_2 nanorods with 85 μF cm^{-2} at 5 mV s^{-1} using the hydrothermal method [24]. Zhou and Zhong prepared hydrogenated TiO_2 network films with 1.07 mF cm^{-2} at 50 mV s^{-1}, in which the conductive TiO_2 NFs were considered as a result of replacing O^{2-} with OH^- by doping hydrogen atoms [25].

In this work, conductive TiO_2 NFs were fabricated using electrospinning method and a post KOH treatment. TiO_2 NFs were dramatically changed from the highly resistive to conductive and accordingly become suitable for supercapacitor electrode material by KOH treatment. The results of cyclic voltammetry (CV), galvanostatic

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charge-discharge (GC) and electrochemical impedance spectroscopy (EIS) demonstrated that the treated TiO_2 NFs have a high specific surface area, much better conductivity, rating and cycling stability for potential applications in supercapacitors.

2. Experimental

2.1. Reagents

Al foil (99.9% in purity, 0.1 mm in thickness), acetone, acetic acid (AA), ethanol, sodium sulfate (Na_2SO_4), titanium tetraisopropanolate (TIT) and polyvinyl pyrrolidone (PVP) were analytical grade (SAEN Chemical Technology Co., Ltd, China) and deionized water was used throughout the whole experiment.

2.2. Preparation of treated TiO_2 nanofibers

PVP was dissolved in a 4 mL mixture of PVP:AA:ethanol in a mass ratio of 1:2:3, noted as precursor A. 1 mL TIT was dissolved in a 3 mL mixture of acetic acid and ethanol, with TIT:AA:ethanol in a volume ratio of 1:1:2, noted as precursor B. After 2 h of stirring, precursor B was slowly added into precursor A for stirring another 4 h to get the final precursor C. Then, precursor C was loaded into a plastic syringe with a volume of 1 mL and a stainless steel needle, which has a blunt end bent at 90° and an inner diameter of 0.25 mm, as shown in Fig. 1. A standard electrospinning operating procedure was carried out under certain conditions with a flow rate of 1 mL h^{-1} for 30 mins, tip-to-collector distance of 15 cm, and a DC voltage of 25 kV between the steel needle and Al collector. The temperature and humidity during electrospinning were respectively controlled at 25 °C and 40%. Subsequently, the electrospun composite fibers with containing TIT and PVP were stabilized at 55 °C for 5 min in air before removed from the Al collector, as shown in the right of Fig. 1. Then the as prepared TIT/PVP polymeric fibers were annealed in a furnace, in which TIT/PVP fibers were slowly heated up to 500 °C at a rate of 1 °C min^{-1}, then hold on at 500 °C for 10 h to decompose PVP completely as while as to prevent the fibers from breaking. Finally, self-standing pure TiO_2 nanofibers were obtained after cooled down the furnace to room temperature.

2.3. Measurements of treated TiO_2 nanofibers

Usually, the conductivity of TiO_2 can be improved by doping with conductive materials, such as molybdenum oxide or carbon. In addition to doping approaches, conductive TiO_2 were also reported by annealing in hydrogen atmosphere or synthesized by anodic oxidization [23–27]. In this work, conductive TiO_2 was obtained by KOH treatment. First, self-standing pure TiO_2 NFs were fabricated by electrospinning and annealing processes mentioned above. Then pure TiO_2 NFs were soaked in 1 mol L^{-1} KOH solution for 1 h at 40 °C. Consequently the KOH treated TiO_2 NFs were obtained after removing KOH solution and rinsed for several times by deionized water till the pH decreases to the neutral value. Finally, a supercapacitor was constructed by using KOH treated TiO_2 NFs as the electrodes, Al foils as the current collector, isolating paper as the separator and 1 mol L^{-1} Na_2SO_4 injected as the electrolyte for cyclic voltammetry (CV) measurement. It can be observed that the color of treated TiO_2 NFs turn rapidly from the original white into grey blue just as starting the CV measuring within (+) 1 to (−) 1 V for 5 min, as shown in lower right of Fig. 2. This phenomenon of color change in our experiment is quite similar to that of TiO_2 nanotubes fabricated by anodic oxidization in Ref. [23]. Such a color change, according to Chen et al. [28], was attributed to the defects introduced into the TiO_2 NFs by chemical doping, resulting in narrowing the band gap from 3 eV to 1 eV and in consequence absorbing most of the visible light for TiO_2. For the electrical properties measuring in this work, cyclic voltammetry (CV) and galvanostatic charge-discharge (GC) measurements were performed on TiO_2 electrodes with an active area of 2 cm^2 and a voltage up to 1 V. electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 1 Hz to 1×10^5 Hz with an amplitude of 10 mV. The cycling stability was tested by continuous CV cycling at a scan rate of 0.2 V s^{-1} for 10,000 times.

3. Results and discussion

3.1. SEM results

The TIT/PVP as-spun composite fiber has a quite smooth surface with an average diameter of about 400 nm, as shown by the image of field emission scanning electron microscopy (FESEM) in Fig. 3(A). According to the spectrum of energy-dispersive X-ray spectroscopy (EDS) in the inset of Fig. 3(A), we can see that these fibers mainly consist of Ti, C and O, and the atomic ratio of O:Ti (21:1) is much higher than the stoichiometric ratio of 2:1 for TiO_2 due to PVP present in the as-spun material. However, after annealed at 500 °C for 10 h, the fibers have a significant reduction on weight from 11.64 mg to 2.51 mg and lose 78% of the original weight owing to TIT and PVP decomposed into CO_2, CO and H_2O [29]. The effect of PVP's decomposition also reflects on the change of fiber size that the fiber's average diameter decreases from 400 nm to around 180 nm as a result of shrinking (as shown in Fig. 3(B)). Meanwhile, the ratio of O:Ti in sequence decreases approximately to the stoichiometric of 2:1 (see the EDS spectrum in the inset

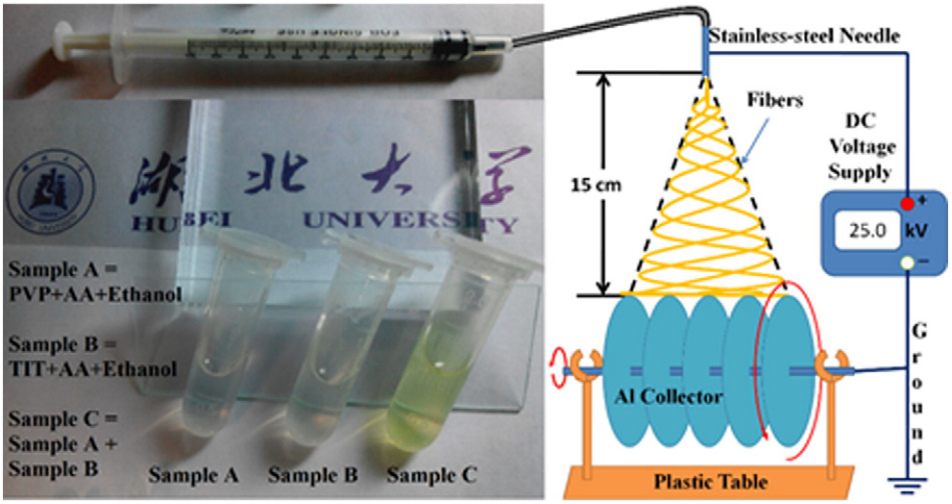

Fig. 1. Schematic diagram of electrospinning method.