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Hierarchical micro/nanostructured WO_3 with structural water for high-performance pseudocapacitors

Zongming Shao [1], Xiaoming Fan [1], Xiaoyu Liu, Zeheng Yang*, Lei Wang, Zhangxian Chen, Weixin Zhang**

School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Controllable Chemical Reaction & Material Chemical Engineering, Hefei University of Technology, Hefei, Anhui, 230009, PR China

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ABSTRACT

Exploring electrode materials with high energy density is crucial for the application of electrochemical energy storage. Herein, we innovatively synthesized frisbee-shaped architecture of h-$WO_3 \cdot nH_2O$ by a simple hydrothermal method, which is assembled by nanorods of ~80 nm in diameter, with structural water storing in the open hexagonal tunnels via a template-free strategy for supercapacitor application. This electrode material possesses high specific capacitance of 391 F g^{-1} at 0.5 A g^{-1}, superior rate capacity of 298 F g^{-1} at 10 A g^{-1}, and almost 100% capacitance retention after 2000 cycles at 10 A g^{-1}, which can be ascribed to its unique hierarchical micro/nanostructure and water chains within the channels of crystalline h-WO_3. The unique self-assembled frisbee-shaped micro/nanostructure can avoid further aggregation of nanosized building blocks and allow sufficient ions accessible surface, beneficial to increasing deliverable capacity. Notably, the presence of structural water also offers fast hydrated protons transport pathway, resulting in high capacity and good stability at high rate.

1. Introduction

Pseudocapacitors based on the charge storage mechanism of surface-dominated redox (faradaic) reactions are being particularly promising electrochemical energy storage devices due to their key advantages such as high power density, long lifetime and fast charge/discharge rate compared with traditional batteries [1,2]. Of the available redox-active materials, transition metal oxides have been extensively investigated as electrode materials of pseudocapacitors, mainly due to their multiple oxidation states offering high pseudocapacitance, such as ruthenium oxides [3], manganese oxides [4], and tungsten oxides [5]. However, comparatively low pseudocapacitance was usually obtained because of the relatively poor ionic/electrical conductivity and low accessible surface areas for transition metal oxides. Up to now, various approaches have been developed to address these issues to enhance the peseudocapacitance of transition metal oxides, such as developing nanosized or nanostructured materials [6], hybrid materials with conductive matrix [7] and introducing intrinsic defects in electrode materials [8,9].

In cases where ionic mobility and accessible surface areas are limited, during the last decades, many efforts have been focused on developing nanosized or nanostructured transition metal oxides electrode materials to shorten the diffusion length and/or increase the outer surface area in order to improve the electrochemical performances of pseudocapacitors [10,11]. For instance, Li et al. [12] prepared 3D hierarchical Co_3O_4 spheres with an urchin-like structure, which consisted of 1D nanochains composed of nanoparticles with diameter in the range of 5–30 nm. This unique nanostructured electrode material enabled high accessible surface area and short ion transport pathway, thus resulting in high specific capacitance (781 F g^{-1} at 0.5 A g^{-1}) and remarkable rate capacity (611 F g^{-1} at 8 A g^{-1}). Nevertheless, it should be noted that nanosized or nanostructured electrode materials have higher surface energy and therefore may show a larger tendency to aggregate together [13]. Effective strategies to solve these problems need to be explored to achieve high-performance pseudocapacitors. It is highly potential to design and synthesize hierarchical micro/nanostructured transition metal oxides electrode materials, in which the microstructures self-assembled by nanosized building

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* Corresponding author.

** Corresponding author.

E-mail address: zehengyang@hfut.edu.cn (Z. Yang).

[1] These authors contributed equally to this work and should be considered co-first authors.

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blocks not only alleviate further agglomeration of nanoparticles to a large degree, but also shorten the ion diffusion pathway and provide high accessible surface area to deliver high peseudocapacitance simultaneously.

Another strategy for developing high pseudocapacitance for transition metal oxides is to improve their intrinsic ion diffusion in the solid-state structure [14]. Theoretically, tungsten oxides orderly stacked by the WO_6 octahedra have a considerable number of interstitial sites, which are effectively accessible for guest ions diffusion, allowing not only adsorption/desorption of ions at the surface but also insertion/deinsertion of ions into the inner parts of the solid-state structure. Among various tungsten oxides, the hexagonal-phase tungsten trioxide (h-WO_3) is preferred to be employed as electrode material for pseudocapacitors as a result of its larger hexagonal tunnels as well as the typical tetragonal tunnels, benefiting for easy insertion/deinsertion of guest ions into the tunnels in the crystal structure of h-WO_3 [15]. Yao et al. [16] synthesized hexagonal WO_3 nanorods through a facile one-step hydrothermal method for supercapacitors. The results show WO_3 nanorods present high specific capacitance of 319.26 F g^{-1} at current density of 0.7 A g^{-1}. Shinde et al. [17] synthesized nanostructured h-WO_3 films on carbon cloth substrate using simple hydrothermal method. Tungsten trioxide with different morphology is prepared by controlling the deposition temperature. The results show that nanostructured h-WO_3 films present high specific capacitance of 694 F g^{-1} at current density of 0.35 A g^{-1} and superior cycling performance (87% capacitance retention after 2000 cycles). The excellent performance of electrode is owing to its nanostructure morphology forming precise hexagonal tunnels and providing easy access for electrolyte ions.

Recently, structural water and solvent molecules have been found to play a critical role in enhancing the pseudocapacitive performances of active materials because of the improvement of intercalation of guest ions in hydrous structures [18,19]. Especially, in the case of tungsten oxides, single-file water chains embedded within h-WO_3 nanorods can provide fast proton channels, allowing superior electro kinetics for proton transport in the acid electrolyte to afford the h-$WO_3 \cdot nH_2O$ with high capacitance and fast charge/discharge rate [20]. Although tungsten oxides with a variety of morphologies have been synthesized [21,22], developing a simple yet effective way to fabricate micro/nanostructured tungsten oxides self-assembly with nanosized h-$WO_3 \cdot nH_2O$ building blocks containing structural water has been rarely reported and remains a challenge.

Herein, we report a complex hierarchical frisbee-shaped h-$WO_3 \cdot nH_2O$ by a simple hydrothermal approach. The unique well-aligned micro/nanostructured tungsten oxides show great potential as high-performance electrode materials of pseudocapacitors. As a result, the as-prepared hierarchical frisbee-shaped h-$WO_3 \cdot nH_2O$ self-assembly with nanorods possesses a very high specific capacitance (391 F g^{-1} at 0.5 A g^{-1}) and fast charge/discharge capability (298 F g^{-1} at 10 A g^{-1}). The detailed formation mechanism of frisbee-shaped h-$WO_3 \cdot nH_2O$ was investigated by the time-dependent experiments. We also discussed the combined effects of the hierarchical micro/nanostructures and structural water of frisbee-shaped h-$WO_3 \cdot nH_2O$ on the superior electrochemical performances.

2. Experimental section

2.1. Synthesis of the frisbee-shaped h-$WO_3 \cdot nH_2O$

Sodium tungstate dihydrate (99.5%, AR), acetic acid (99.5%, AR), hydrochloric acid (37.5%, AR) and Sodium chloride (99.5%, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. All of the reagents were used without further purification. All aqueous solutions were prepared with the deionized water.

In a typical synthesis, 0.3 g of $Na_2WO_4 \cdot 2H_2O$ was dissolved in 30 mL of acetic acid (pH = 1.8) under stirring to form a homogenous solution. After stirring for 30 min, white precipitates of tungstic acid were formed and then hydrochloric acid (3M) was added dropwisely to regulate the pH value of solution to 1.8 with continuous stirring. Subsequently, 0.3 g of NaCl was added into the above homogenous solution and continued to stir for 1 h. Finally, the above mixture was transferred into a 50 mL Teflon-lined stainless-steel autoclave and kept at 180 °C for 2 h. The products were collected by centrifugation, washed with deionized water and ethanol and finally dried in a vacuum at 80 °C overnight.

2.2. Physical characterization

The crystallographic characteristics of the as-obtained products were examined by X-ray diffraction (XRD) patterns on a Shimadzu D/max-γB X-ray diffractometer using a Cu Kα radiation source (λ = 0.154178 nm) operated at 40 kV and 80 mA. The morphologies were investigated by field-emission scanning electron microscope (FESEM) (Hitachi SU8020), which was carried out at an acceleration voltage of 5 kV. High-resolution TEM images of the samples were taken on a field-emission transmission electron microscope (JEOL-2010).

Thermogravimetric and differential thermal analysis (TGA/DTA) measurements were conducted on a Mettler Toledo TGA/SDTA 851e Thermal Gravimetric Analyzer with a heating ramp of 10 °C min^{-1} under 30 mL min^{-1} flowing air. The Brunauer–Emmett–Teller (BET) surface area was obtained on a Quantachrome NOVA 2200e surface area and pore-size analyzer at liquid nitrogen temperature. The X-ray photoelectron spectrometer (XPS) data were recorded on a VG ESCALAB 220i-XL spectrometer (UK) equipped with a twin crystal monochromated Al K X-ray source, which emitted a photon energy of 1486.6 eV at 10 kV and 22 mA. Samples were secured onto Al holders and were measured in the analysis chamber at a typical operating pressure of ~7×10^{-9} mbar. Raman spectroscopy with a 523 nm laser and a 10× objective were researched by a micro-Raman spectrometer of HR Evolution (HORIBA Jobin Yvon, France).

2.3. Electrochemical characterization

For preparation of the working electrodes, 70 wt% of the as-synthesized powders were mixed with 20 wt% acetylene black and 10 wt% polytetrafluoroethylene (PTFE) binder in ethanol to form a slurry which was then pressed onto titanium net current collector (mass loading of 9 mg cm^{-2}) dried at 80 °C overnight under vacuum. The electrochemical performances of the working electrode were tested on a CHI660D electrochemical analyzer in an aqueous 1 M H_2SO_4 electrolyte in a three-electrode system with Ag/AgCl and Pt foil as the reference and counter electrode. Electrochemical impedance spectra were carried out at frequencies from 10 mHz to 100 kHz and the amplitude of the potential perturbation was 5 mV.

3. Results and discussion

3.1. Material synthesis and characterization

Hierarchical micro/nanostructured frisbee-shaped h-$WO_3 \cdot nH_2O$ was prepared by a simple hydrothermal method. The crystallinity and phase purity of the as-prepared sample were first investigated through X-ray diffraction measurements. As can be seen in Fig. 1, all of the diffraction peaks can be indexed to be h-WO_3 (JCPDS No. 75-