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Tertiary structure of cactus-like WO_3 spheres self-assembled on Cu foil for supercapacitive electrode materials

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ABSTRACT

WO_3 microspheres film with a tertiary, textured and porous structure assembled of WO_3 hierarchical nanorods has been directly prepared on Cu foil using a one-step hydrothermal method. The field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) spectrum, X-Ray Diffraction (XRD), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) are used to reveal the surface microtopography, crystal structure, elementary composition, valence state and formation mechanism of WO_3 tertiary structure. Moreover, the electrochemical properties and supercapacitive performances of WO_3 microspheres film are also intensively investigated. The WO_3 microspheres film has high specific capacitances of 485, 426, 372, 319 and 260 F g^{-1} at unit currents of 0.5, 1, 2, 5 and 10 A g^{-1} and exhibits good cycle stability (93% after 5000 cycles) and reversibility (98.5%), a lower charge transfer resistance (0.5 Ω) and high energy densities ranging from 21 to 17 W h kg^{-1} corresponded to high power densities varied from 150 to 3000 W kg^{-1}.

1. Introduction

With the increasing problems of environment and sustainable development, the concepts of low-carbon, energy conservation, environmental protection and new energy have already gone deep into the public [1]. Energy issue is a hotspot research field all over the world, and energy storage is one of the key techniques [2]. Supercapacitor has many advantages such as fast charging [3], long cycle life [4], supernal energy invert efficiency [5], high power density [6] and security coefficient [7], which is widely used in electric vehicles [8], mobile devices [9] and power systems [10]. Generally, supercapacitors could be classified into two categories [11]: the first is electric double-layer capacitor which charge and discharge by adsorption and desorption of ions at the electrode electrolyte interface. And the second is pseudocapacitor which store charges through oxidation reduction reaction in the active material.

Direct deposition of active material on the current collector could take advantage of the two kinds of supercapacitors. The most widely used supercapacitor materials are carbon materials [12], transition metal compounds [13] and conducting polymers [14]. Transition metal compounds, such as RuO_2 [15], NiO [16], Co_3O_4 [17], WO_3 [18], MoS_2 [19] and V_2O_5 [20], are a category of pseudocapacitive materials, due to the presence of diverse valences [21]. Among the numerous transition metal compounds, WO_3 is believed to be one of the most important candidates owing to its multivalence (W^{2+} - W^{6+}), high cycle stability, reversibility and environmental affinity [22]. Preparation of WO_3 with specific structure and morphology will help to improve the supercapacitive properties. It is known that hexagonal WO_3 has multiple voids, such as hexagonal window, trigonal cavity and four-coordinated square window, which could increase the storage capacity [23]. Zhu [24] et al. synthesized h-WO_3 nanopillars as pseudocapacitive electrode. The electrode exhibited high specific capacitances of 421 F g^{-1} at current density of 0.5 A g^{-1}. While Qiu [25] et al. prepared a tetragonal

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nanoflower-like WO_3 pseudocapacitive electrode on Ti foil which had a gravimetric specific capacitance of 196 F g^{-1}. To further improve each index and parameter of pseudocapacitive performances, hierarchical nanostructure WO_3 electrode was synthesized to enhance the surface area, surface/body ratio and permeability. Chen [26] et al. synthesized spherical particles self-assembled by closely packed nanorods. And this electrode showed almost no capacitance degradation after 50000 cycles. Then Huang [27] et al. obtained WO_3 spheres with nest-like morphology, which had a high volumetric capacitance of 10.4 F cm^{-3}. And hierarchical urchin-like WO_3 was prepared and adopted as the anode for lithium-ion hybrid supercapacitor by Xu [28] et al. The electrode boasted a large energy density of 159.97 W h kg^{-1} at a power density of 173.6 W kg^{-1}. According to these literature, hexagonal WO_3 hierarchical nanostructure could be a good candidate for pseudocapacitive electrode material. However, although a lot of WO_3 hierarchical nanostructures have been successfully prepared, such as WO_3 spheres comprised of nanorods, needle bundles and nanoplates. Most of them are secondary structures. To the best of our knowledge, tertiary structure of WO_3 nanoscale material has not been reported till now.

In this paper, we have synthesized cactus-like WO_3 microspheres composed of hierarchical nanorods via a one-step hydrothermal method. The tertiary, textured and porous structure of WO_3 microspheres film is characterized by FESEM, EDX, XRD, TEM and XPS. Through growth process observation and research, the growth mechanism of WO_3 tertiary structure is speculated reasonably. In addition, the electrochemical and supercapacitive properties of WO_3 microspheres are systematically studied.

2. Experimental sections

2.1. Materials

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, ≥99.5%), sodium sulfate anhydrous (Na_2SO_4, ≥99.0%) and concentrate hydrochloric acid (HCl, 36–38%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Rubidium sulfate (Rb_2SO_4, ≥99.9%) and oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$, ≥99.5%) were obtained from Aladdin Industrial Corporation, China. Copper foil (Cu, 3.2 × 2 cm^2, thickness of 35 μm) was supplied by Hefei Kejing Materials Technology Co., Ltd, China. All the solutions were prepared by deionized water.

2.2. Synthesis of WO_3 microspheres film

WO_3 microspheres film were directly synthesized on Cu foil using a one-step hydrothermal method. Tungstic acid precursor solution was prepared as follows: 8.25 g $Na_2WO_4 \cdot 2H_2O$ powder was completely dissolved in 25 mL deionized water to form sodium tungstate solution. The hydrochloric acid solution (HCl, 2 mol L^{-1}), which is obtained by diluting the concentrate hydrochloric acid (HCl, 36–38%), was dropwise added into sodium tungstate solution to adjust the pH value to 2.0. Some white precipitate appeared during this adding process. Then the liquid is stirred by magnetic stirrer and precipitate disappeared. After that, the liquid was diluted to 250 mL and 0.40 g $H_2C_2O_4$ was added. When the final pH value was adjusted to 2.0, the tungstic acid precursor solution was obtained. Before hydrothermal reaction, 0.45 g Rb_2SO_4, a Cu foil with the rough surface facing upwards, and 20 mL precursor solution were added into a 50 mL teflon-lining in sequence. Then the lining was sealed in a stainless steel and kept at 180 °C from 0 to 8 h. After cooling down naturally, the Cu foil coated with WO_3 film was rinsed repeatedly by deionized water and dried at 80 °C for several hours.

2.3. Characterization of WO_3 microspheres film

The micro morphology of WO_3 film was characterized by field emission scanning electron microscopes (FESEM, JEOL, JSM-7500) and transmission electron microscope (TEM, JEOL, JEM-2100F). The crystal structure of WO_3 film was measured using X-Ray Diffraction (XRD, Rigaku Dmax-2550 diffractometer using Cu Kα radiation) and high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F). And the elementary composition and valence state of WO_3 film was studied by X-ray photoelectron spectroscopy (XPS, Thermofisher scientific china., ltd, ESCALAB 250Xi) and energy dispersive X-ray (EDX) spectrum installed on the FESEM.

2.4. Electrochemical and supercapacitive tests of WO_3 microspheres film

The electrochemical tests were performed on an electrochemical workstation (Shanghai Chenhua Instrument, Inc., CHI760E) with a three-electrode test system in 1 mol L^{-1} Na_2SO_4 solution. The working, reference and auxiliary electrodes are Cu foil coated with WO_3 film, Ag/AgCl electrode and Pt foil. Cyclic voltammetry (CV) curves and galvanostatic charge-discharge (GCD) curves were recorded in the range from 0.0 V to 0.6 V. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range from 1 Hz to 1 M Hz.

3. Results and discussion

3.1. Synthesis and structural characterization of WO_3 microspheres

Fig. 1a–d shows the field emission scanning electron microscope (FESEM) images of WO_3 microspheres film synthesized directly on the rough surface of Cu foil by hydrothermal method at 180 °C for 4 h. In general, the distribution and sizes of WO_3 microspheres are uniform in Fig. 1a at low magnification. There exist a large number of pores among microspheres, resulting in a porous structure. At middle magnification shown in Fig. 1b, it can be seen that these microspheres are connected with each other tightly by sharing a part of spherical surface. The diameters of these WO_3 microspheres are estimated to be several micrometers. Interestingly, the single microsphere looks like a cactus (the inset in Fig. 1b). From Fig. 1c at high magnification, the WO_3 microspheres are composed of numerous nanorods with a hierarchical structure. The main rods grow pointing toward the center of WO_3 microspheres whereas the dendritic rods grow along the hexagonal-symmetry axis on the side surfaces of the main rods. And the dendritic rods grow crossing each other to form a textured structure. These crossed nanorods generate voids which result in a porous structure for each WO_3 microsphere. The main rods have a diameter of about 50 nm and that of dendritic rods is below 20 nm. Fig. 1d is a cross-sectional view of WO_3 microspheres film. Since the thickness of Cu foil is 35 μm, the thickness of WO_3 microspheres film can be estimated to be approximate 20 μm. And the WO_3 membrane is closely contacted with Cu foil.

The elemental composition of WO_3 microspheres film is identified by energy dispersive X-ray (EDX) spectrum as shown in Fig. 1e. The membrane is mainly composed of tungsten (W) and oxygen (O) whereas the peaks of platinum (Pt) derive from metal spraying, indicating high purity of WO_3 microspheres film. The crystal structure of WO_3 microspheres film is studied by X-Ray Diffraction (XRD) in Fig. 1f. The diffraction peaks appeared at 13.9°, 23.4°, 28.1°, 36.8° and 49.4° could be indexed to (100), (002), (200), (202) and (220) crystal planes of hexagonal phase of WO_3 (JCPDS: 01-085-2460). No peaks of impurities are detected, which further