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Soft-template hydrothermal systhesis of nanostructured Copper(II) Tungstate cubes for Electrochemical Charge Storage Application

Chao Wei, Ying Huang*, Xin Zhang, Xuefang Chen, Jing Yan

Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710072, PR China

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ABSTRACT

In this work, the soft-template hydrothermal method is firstly applied to synthesize nanocrystal $CuWO_4$ cubes for the electrode materials in in electrochemical charge storage application. The structures and morphologies of as-obtained materials are characterized via X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The effects of the soft-template (P123) and surfactant (Hexamethylenetetramine) also are verified by the electrochemistry test including CV, GCD, EIS. As a result, the $CuWO_4$-PH (synthesis with the assistance of P123 and Hexamethylenetetramine) shows a excellent specific capacitance (C_{sp}) of 302.40 mAh g^{-1} at the current density of 1 A g^{-1} and a good rate capability (60.7% retension rate of original Csp even at 10 A g^{-1}), as well as cycle life (82.1% retention rate of original C_{sp} after 2000 cycles). These results reveal that our obtained $CuWO_4$-PH could be a promissing electrode material.

1. Introduction

In recent years, the imminent depletion of non-renewable energy and the seriousness of global warming issues have forced researchers to trigger tremendous efforts for energy storage devices such as batteries, fuel cells and supercapacitors [1–3]. Supercapacitors (SCs), also named as electrochemical capacitors (ECs), are of great interest and have attracted considerable attention due to high capacitance and rate capability, as well as high power density and energy density [4]. It should be noted that the performance of SCs is mainly determined by the electrode materials. In general, although tranditional carbonaceous materials have long cycle stability and high power density, their low energy density greatly limits their applications. On the other hand, pseudo-capacitor materials such as RuO_2, MnO_2 and TiS_2 possess sufficient capacitance yet instability during charge-discharge process [5–9]. Therefore, many recent researches have forced on non-noble transition metal oxides and hydroxides due to higher capacity undergoing faradaic reactions, which are similar to those used in batteris. However, some of these materials are defined as "pseudocapacitive" materials and applied into the field of supercapacitor despite the fact that pseudocapacitance materials should have all the similar electrochemical signatures of the capacitive-type materials such as the characteristics of mirror-like charge-discharge responses and rectangular cyclic voltammograms. So when taking account into the fundamental definition of pseudo-capacitance, transition metal oxides and hydroxides should be described more as high charge storge battery-type materials than pseudo-capacitance ones [10–16].

It is generally known that metal oxide materials can be divided into three categries: (i) single metal oxides such as NiO, MnO_2, Co_3O_4, RuO_2, etc, (ii) binary metal oxides such as $NiMoO_4$, $NiCo_2O_4$, $CoWO_4$, etc, (iii) hybrid metal oxide materials such as $NiCo_2O_4$/GO, $NiWO_4/Co_3O_4$, $MnMoO_4$/NiO, etc [17]. In recent years, binary metal oxides and hybrid oxide materials have been investigated thoroughly and reported to show excellent C_{sp} than single metal oxides materials due to various oxidation states and high electrical conductivity [18,19]. Among binary metal oxides, tungstate has drawn wide attention for its excellent catalytic and electrochemical characteristics. As reported in some literatures, the binary metal oxides of tungstate deliver good conductivity with a range from 10^{-7} to 10^{-3} S cm^{-1} because the W atoms greatly enhance the conductivity and then made contributions to the better electrochemical performance [20,21].

As a member of tungstate, Copper tungstate ($CuWO_4$), as a renowned n-type semiconductor with a bandgap of ca. 2.25-2.45 eV, have been used in various fields such as photoanodes,

* Corresponding author.
E-mail address: yingh@nwpu.edu.cn (Y. Huang).

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laser host, sensors, photoelectrolysis electrodes, etc [22–24]. However, there are few reports on the application of electrode materials of SCs due to its irregular morphologies and low specific surface area. In addition, the preparation methods such as microwave, spray pyrolysis, sol-gel, etal, are important to synthesize the suitable structred $CuWO_4$ for better electrochemical performance [25]. To date, R. Dhilip Kumar etal have perparaed successfully the uniform morphology of $CuWO_4$ by microwave assisted method with electrochemical characteristic of the maximum specific capacitance of 77 F g^{-1} [26]. S. Karuppuchamy etal have investigated $CuWO_4/WO_3$ nanopowders via simple microwave irradiation methodn with C_{sp} of 15.08 F g^{-1} at 0.25 A g^{-1} [27]. Nevertheless, the metioned methods above synthesizing $CuWO_4$ materials suffer from the problems of irregular morphologies, easy aggregation and poor stability.

We believe that the limited capacitance of above reported $CuWO_4$ materials might be ascribed to inappropriate material size effect and irregular morphology. So the key of investgating this kind of $CuWO_4$ is identifying a synthsis method to obtain nano-size distribution $CuWO_4$ with the merit of higher specific surface areas and more sufficient edges. We herein firstly report a novel approach for successfully synthesizing $CuWO_4$ using Pluronic P123 (PEO20-PPO70-PEO20) as soft-template and Hexamethylenetetramine (HMT) as surfactant by hydrothermal method. P123 is chosen as the soft-template due to its environment friendliness and commercial availability. It is assumed that P123 molecules can limit the material size and promote the formation of regular morphology, which is benefical for finally improving the performance of electrodes.

2. Experimental

2.1. Synthesis of $CuWO_4$-PH nanocubes

All chemicals were purchased from commercial sources and were the highest purity available. They were used without further purification. Deionized water and ion exchanged membranes were used in all the experiments. In a typical experimental method, first 1 g P123 was dissolved into 25 ml of distilled water with stirring for 12 h to get transparent solution, and then 2 mmol $Cu(NO_3)_2$ was added into the above solution under stirring for 1 h to form blue transparent solution called A. Then 2 mmol Na_2WO_4 and 8 mmol HMT were absolutely dissolved into 10 ml of distilled water to get transparent solution called B. Then solution B was added dropwise into solution A under stirring for 2 h and subsequently a cream green solution was obtained. The resultant product was transferred to a 50 ml Teflon lined autoclave and heated at 100 °C for 10 h and then cooled to room temperature naturally. The as-obtained green precipitates were collected by ultracentrifugation and washed with deionized water and ethanol for several times and then dried overnight. Finally, the samples were calcinated at 500 °C (heating rate: 3 °C min^{-1}) for 2 h to remove the soft-template P123. For the purpose of investgating the influence of P123 and HMT, we also prepared the $CuWO_4$-P and $CuWO_4$ under the condition of adding P123 and without adding P123 and HMT, respectively.

2.2. Characterization of the electrodes

The structures of the fabricated samples were examined by X-ray diffraction analysis (XRD) (Rigaku, model D/max-2500 system at 40 kV and 100 mA of Cu Ka). The X-ray photoelectron spectroscopy (XPS) spectra were registered by an ESCALab 250 electron spectrometer (Thermo Scientific Corporation). The infrared spectra was recorded on a Bruker Tensor 27 FT-IR spectrophotometer (Bruker Corporation, Germany) by KBr as the carrier. The surface morphologies of the materials were investigated by scanning electron microscope (SEM, Hitachi, S-4800, JAPAN) and a model field emission transmission electron microscope (FETEM, USA, Tecnai F30 G2 FEI CO.).

2.3. Electrochemical measurements

The working electrode materials were prepared by mixing the obtained sample, acetylene black and Polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10. The hybrid was mixed with little N-methy1-2-pyrrolidone (NMP) for homogeneity and then coated on nickel foam substrates (1cm × 1 cm) as the working electrode and dried at 60 °C for 12 h, the as-prepared electrodes loaded with the hybrid were then pressed at 10 MPa for 60 s. The typical mass loading of the sample in each electrode is in the range of 4–6 mg. Electrochemical measurements were performed on an Electrochemical Workstation of Series G 750 (USA GAMRY) with the three-electrode system, platinum electrode and the standard calomel electrode (SCE) were used as the counter and reference electrodes respectively. 2 M KOH solution was served as the electrolyte at room temperature. Cyclic voltammogram (CV) was recorded between −0.1 and 0.45 V at scan rates ranging from 2 to 50 mV s^{-1}. Galvanostatic charge/discharge testing was conducted at different current densities from 1 to 10 A g^{-1} between 0 and 0.45 V. The test of cycle life for 2000 cycles at 1 A g^{-1} was operated on a LAND battery program-control test system. The electrochemical impedance spectroscopy (EIS) measurements were manipulated in a frequency range from 0.01 Hz to 100 kHz at open circuit potential with an amplitude of 5 mV. All experiments were measured after 180 s delay time. In order to obtain real and accurate the value of capacity, the values of C_{sp} were calculated from the charging-discharging curve by the following equation:

$$Csp = \frac{Q}{m} = {}^{I}\Delta t/_{3600} m \quad (1)$$

where C_{sp} (mAh g^{-1}) is the gravimetric capacity, I (mA) is the current, ΔV (V) is the potential window, m (g) is the mass of the active material and t (s) is the discharging time. A further detailed clarification on this view is mentioned in the supporting information.

3. Results and discussion

The phase purity of the as-synthesized materials were confirmed by representative XRD analysis. As shown in Fig. 1(a, d, g), all the as-preapared powder samples have similar narrow characteristic peaks locating at 15.1°, 19.2°, 23.8°, 24.9°, 29.2°, 31.6°, 36.7° and 43.8°, which match well with the (010), (001), (110), (0-11), (-1-11), (111), (200) and (-121) planes, respectively. All the metioned crystal planes are in good agreement with the standard patterns for triclinic phase $CuWO_4$ (JPCDS: no 80-1918). In addition, no more redundant peaks occured by impurities such as WO_3 are found, indicating the high purity of the as-synthesized samples. The nanostructures and morphologies of samples are examined by SEM characterization. Fig. 1b show the morphology of $CuWO_4$ and it obviously reveals that microstructured $CuWO_4$ rods with a length of about 7 μm and a diameter of about 0.6 μm have a rough surface, which various irregular particles are anchored on the surface of $CuWO_4$. Moreover, without the assistance of P123 and HMT, the $CuWO_4$ microrods agglomerate to form large micelles. Compared to the morphology of $CuWO_4$, the $CuWO_4$-P and $CuWO_4$-PH are composed of relatively ordered cube-like architecture with nano-sized of 200–300 nm and the thickness of 50–140 nm (as shown in Fig. s2). As shown in Fig. 1(e, h) and s1, one can see that cube-like $CuWO_4$-P and $CuWO_4$-PH have a relatively smooth surface. Furthermore, highly densely materials consisted of proper dispersion nanocubes are displayed due to the existence