



Sn@SnO₂ attached on carbon spheres as additive-free electrode for high-performance pseudocapacitor



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ARTICLE INFO

Article history:

Received 1 March 2016

Received in revised form 20 April 2016

Accepted 15 May 2016

Available online 16 May 2016

Keywords:

Sn@SnO₂ attached on carbon spheres

In-situ formation

Conductive reagent-free electrode

Electrochemical stability

Pseudocapacitor

ABSTRACT

Utilization of metal oxide/supports interface structures could generate high-performance electrochemical materials for clean energy storage and conversion. However, designing the metal oxide/supports interfaces with highly enhanced conductivity and cycle durability remains a significant challenge. Here, we demonstrate an in-situ growth technique to synthesize a Sn/SnO₂@C composite with nano-Sn species attached on surface of carbon spheres (denoted as Sn/SnO₂@C) during the carbonization of a sol-gel precursors of tin (IV) tetrachloride pentahydrate (SnCl₄·5H₂O) and Resorcinol-Formaldehyde (Sn⁴⁺-RF) in N₂. We investigate the nucleation and crystal growth of Sn/SnO₂ from Sn⁴⁺-RF precursor to Sn/SnO₂@C composite with the variation of the concentration of acid value and heat-treatment temperature. Sn/SnO₂@C-(1.0, 800) composite as supercapacitor electrode achieves a maximum specific capacitance of 906.8 F g⁻¹ at a scan rate of 1 mV s⁻¹ in 6 M KOH solution, and an excellent cycle durability of 2000 cycles at 5 A g⁻¹. The electrochemical performances demonstrate that charge storage occurs in Sn/SnO₂@C mainly due to redox reactions between the binary oxidation states: Sn↔Sn(OH)₆²⁻(IV) in basic electrolyte, hierarchical porosity and Sn/SnO₂@C distinct structure, which is formed in situ. The work provides new insights into the rational design of Sn@C composites electrode materials for pseudocapacitor and other electrochemical devices.

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1. Introduction

Supercapacitors have attracted extensive attentions because of their excellent properties such as high power density, long cycling stability, and improved safety in the modern electronics [1]. One of the critical factors determining electrochemical performances of supercapacitors is the properties of active electrode material [2]. In general, the performance of a supercapacitor mainly depends on electrodes, electrolytes, and device configuration. Hence, majority of the current research on supercapacitors is focused on obtaining high-performance electrodes materials, such as transition metal oxides, carbon, graphene-based [3,4].

The most widely known pseudocapacitors are RuO₂ [5,6], MnO₂ [7–9], Co₃O₄ [10–13], V₂O₅ [14,15], SnO₂ [16–18]. Moreover, the metal oxides and carbon composites have been developed which

combines the merits of both components. The advantages of the carbon-metal oxide composite as electrode materials are [19,20]: (i) the carbon structure not only serves as the physical support of metal oxides but also provides the channels for charge transport. (ii) The high electronic conductivity of carbon structure benefits to the rate capability and power density at a large charge/discharge current. (iii) The electro-activities of metal oxides contribute to high specific capacitance and high energy density of the carbon-metal oxide composite electrodes. The compositional constituent, microstructure and physical properties (porosity, electronic conductivity, pore size distribution, specific surface area) of metal oxide-carbon composites could be expected to have a synergistic effect on the performance of the supercapacitor electrodes.

SnO₂ has been found to show potential application as a supercapacitor electrode due to its high theoretical capacity [16–18,21,22]. A large amount of work has been focused on the synthesis of SnO₂ core shell hierarchical architectures by various controllable synthetic strategies to promote their application properties [23]. From the precursor (Sn⁴⁺-RF composite

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microspheres), we have fabricated nanocrystalline SnO₂ hollow spheres by high temperature treatment of Sn⁴⁺-RF spheres in air. The specific capacitance of nanocrystalline SnO₂ is up to 178.86 F g⁻¹ at a scan rate of 1 mV s⁻¹ in 1 M KOH solutions [18]. However, during the charge/discharge process, the hollow metal oxides show volume change, which leads to pulverization of hollow spheres and a loss of contact with the current collector, resulting in a rapid capacity decay [24]. Therefore, it is highly valuable to enhance cycle stability without changing the characteristic features of SnO₂ by rationally designing the key structural feature and taking into account all of the above considerations [25].

Designing Sn-C interfacial structures for enhanced stability and mass transport, we treated the precursors in N₂ and obtained carbon attached Sn composite, in which Sn grew thermally-driven and reduction reaction occurred on the surface of carbon spheres during heat treatment [26]. The unique structural feature and good mechanical stability were preliminarily investigated by us. Enriching our previously work [26], we prepared a series of Sn/SnO₂@C composites at present and determined that the structure constructed by binary oxidation states Sn/SnO₂ finely attached on carbon which provided a large surface area of 488.7 m² g⁻¹ for surface redox reactions, the rapid diffusion of the ion electrolyte, a high specific capacitance and the excellent charge/discharge stability.

2. Experimental section

2.1. Materials synthesis

2.1.1. Synthesis of resorcinol-formaldehyde (RF) resin microspheres

The RF resin spheres were synthesized according to our previous literature methods [27]. Briefly, NH₃·H₂O was mixed with resorcinol in a water solution for 5 min at room temperature. After the addition of the formaldehyde solution, the mixed solution was strongly stirred at room temperature for 5 min and subsequently heated at 85 °C for 48 h under static conditions in a Teflon-lined autoclave. The final products were washed with water and ethanol three times, and then dried under vacuum at 80 °C for 12 h.

2.1.2. Synthesis of Sn⁴⁺-RF composite microspheres

The synthesis of the Sn⁴⁺-RF microstructured composite is a simple and environmental friendly procedure consisting of hydrothermal synthesis and assistance of templates, which is composed of the infiltration of a tin precursor into an organic RF gel [17,18,26].

2.1.3. In-situ synthesis of Sn/SnO₂@Carbon composite microspheres

A 0.2 g precursor was heated in a quartz tube at the rate of 5 °C min⁻¹ to 600, 700, 750 and 800 °C, respectively, in a 30 mL min⁻¹ N₂ flow. The heat-treatment was continued for 4 hours before the tube was cool down to room temperature naturally. During the calcination step, the RF gel is carbonized, whereas the inorganic tin precursor is moved from the bulk to the surface and partly reduced to metallic tin with the increase of temperature. The Sn⁴⁺-RF composites finally converted to Sn/SnO₂@C composite, which are constructed by binary oxidation states tin nanospheres highly attached on the carbon support.

Hydrochloric acid as catalyst was investigated for the size of the composite microspheres and the infiltration amount of Sn species. Furthermore, when heat treatment temperature changed, the structure and morphology of tin species on Sn/SnO₂@C surface were also different. The samples prepared at different amount of HCl and calcined temperature are denoted as Sn/SnO₂@C-(*n,m*), where *n* and *m* represent the amount of the HCl solution added to the reaction system and the calcined temperature, respectively.

2.2. Structural characterization

Scanning electron microscopy (SEM) images were taken using a QUANTA 450 (FEI, America), and which was together with Energy Dispersive Spectroscopy (EDS) to observe the chemical composition of samples. Transmission electron microscopy (TEM) graphs were carried out using Tecnai F30 microscope with a field emission gun operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted with two separate systems equipped with monochromatic Al K α sources (ESCALab250, USA) to analyze the chemical composition of the samples. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Thermal Analysis in air or nitrogen flow (40 mL min⁻¹) with a linear heating rate of 10 °C min⁻¹. N₂ adsorption-desorption measurements were used to investigate the porosity structural properties of composite. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method via a micromeritics JWBK 122 W instrument. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. The powder X-ray diffraction (XRD) patterns were recorded from 20° to 80° using a Netherlands' PANalytical X'pert power diffractometer at room temperature employing Cu K α (λ = 0.15408 nm) radiation generated at 40 kV and 40 mA with a scan rate of 16° min⁻¹. All the IR spectra were recorded on a Bruker TENSOR 27 FTIR Spectrophotometer at a resolution of 4 cm⁻¹ for 32 scans (1 s per scan).

2.3. Electrode preparation and measurements

The working electrodes without the conducting additive were prepared. Sn/SnO₂@C composite, Polytetrafluoroethylene (0.6 wt%, PTFE) binder with weight ratio of 9:1 were mixed with a few drops of ethanol. The mixtures were kept ultrasonic for 20 min to form a homogeneous suspension, and then evaporated the solvent. The slurry was uniformly coated on a disk-like nickel foam (with the diameter of 1 cm), and dried at 80 °C for 12 h in a vacuum drying oven, then pressed at 5 MPa for 30 s in order to assure a good electronic contact, finally, the electrode was dried at 80 °C until the mass was unchanged. Thus, the working electrode obtained. The mass of active material was about 1.5 mg in the working electrode. For comparison, we prepared an electrode with conductive additive. The weight ratio is Sn/SnO₂@C composite: conducting additive (acetylene black): PTFE binder = 8:1:1.

Cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS) and Chronopotentiometry (CP) measurement were carried out in a three electrode system, in which platinum filament and Ag/AgCl (saturated KCl) electrodes served as counter and reference electrodes, respectively, and 6 M KOH solution used as electrolyte. The CV experiments performed within the potential range of -0.6 V to 0.6 V vs. Ag/AgCl and the scan rate range was 1 to 100 mV s⁻¹. The charge-discharge curves measured at different current densities from 0.5 to 10 A g⁻¹ and the potential range of -0.6 ~ 0.4 V vs. Ag/AgCl. The CV and charge-discharge measurements were carried out by means of electrochemical analyzer systems in CHI 605E. EIS measurements were performed between 0.01 and 10⁵ Hz. The impedance data were fitted with equivalent circuits by using Z-View software and carried out in Auto lab PGSTAT128N.

3. Result and discussion

3.1. Structural and morphological analysis

To reveal the composition and structure of the prepared samples, XRD and XPS experiments were carried out. Fig. 1a shows the XRD analysis of the samples. It can be seen that pure RF-800 spheres [27] show only one broad peak centered at 25°, which is

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