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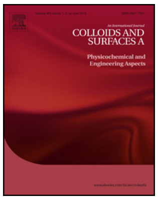


Hollow SnO_2 microspheres and their carbon-coated composites for supercapacitors

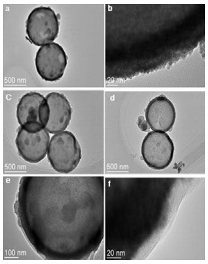
Suzhen Ren*, Ying Yang, Meiling Xu, Hongmin Cai, Ce Hao, Xuzhen Wang

College of Chemistry, Dalian University of Technology, Dalian 116024, Liaoning Province, PR China

HIGHLIGHTS

- Fine controlled core shell structure of sPS@SnO_2 particles.
- Hollow SnO_2 microspheres are prepared via template assisted method in hydrothermal environment and high-temperature calcination treatment for removal of sPS.
- SnO_2@C composite hollow spheres were fabricated.
- SnO_2@C composite leads to an improved electrochemical performance in supercapacitors due to a suitable carbon coating.

GRAPHICAL ABSTRACT



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ABSTRACT

In the presence of sulfonated polystyrene (sPS) template, sPS@SnO_2 core shell particles formed via the interaction between the functional group of -SO_3H on the template surface and ions of Sn^{2+} from the precursor of $SnSO_4$ which were in ethanol-aqueous medium. After high-temperature calcination treatment for removal of sPS, the sPS@SnO_2 changed into SnO_2 hollow spheres. With the further carbonization of the sPS@SnO_2@glucose composite microspheres, SnO_2@C composite hollow spheres were fabricated. Using SEM, TEM, and N_2 adsorption - desorption technology, the structure, specific surface area, and the core-shell structure formation mechanism were determined. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) properties of SnO_2 hollow spheres and SnO_2@C composites were investigated, respectively, in the foam nickel electrode under alkaline condition. The specific capacitance of SnO_2@C composite hollow spheres could reach 25.8 F g^{-1} in 1 mol L^{-1} KOH aqueous solution and showed excellent charge-discharge behavior.

1. Introduction

Electrical double layer capacitors (EDLCs) or supercapacitors have drawn more and more attention in recent years due to their fast charge and discharge rate, high power density (one to two orders of magnitude higher than batteries), long cycle lifetime (two to three orders of magnitude longer than batteries), and high reliability [1–3]. Basically, supercapacitors have two energy storage mechanisms; one is the electrical double layer capacitance and another pseudocapacitance. The most crucial factor determining the electrochemical property lies in the structure and composition of electrode materials. Research has thus been focused on increasing energy density without sacrificing cycle life or high power density.

As we all known, ruthenium oxide is rare and very expensive, leading to limit of practical application in supercapacitor. Therefore, the development of new electrode materials with low

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* Corresponding author at: Dalian University of Technology, Chemistry, 2 Linggong Road, Dalian, PR China. Tel.: +86 411 84986073.
E-mail address: rensz@dlut.edu.cn (S. Ren).

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cost for supercapacitor is still a challenge. Among the oxide nanomaterial, SnO_2 has gained prominent interest because of its potential applications in various fields [4]. It is well known that the physical and chemical properties of the materials depend greatly on the size, shape, and composition of the particular material. Therefore, researchers are actively engaged in developing tin oxide nanostructures with different sizes and shapes such as core-shell and hollow microspheres, for a wide range of applications [5–11]. Graphitic carbon is the most commonly used anode materials in lithium ion batteries (LIBs) and supercapacitors. Pristine SnO_2 is a typical semiconductor with low electronic conductivity (bandgap is 3.6 eV). In order to improve the electronic conductivity of SnO_2, carbon is often used as a conducting phase to form a composite [12–26]. Carbon coated SnO_2 for LIBs leaded to longer cycle lifetime and stability. SnO_2@C nanostructures showed unusual reversible Li storage capacities [18–24]. Hence, combining SnO_2 and porous carbon to take advantage of the virtues of the two materials may be a viable alternative. However, SnO_2@C nanocomposite structure for supercapacitor electrode is still a challenge for stability and specific capacitance.

Although great efforts have been dedicated to template-free routes for the preparation of hollow particles, coating against colloidal template particles is still the most effective and general method for the preparation of hollow particles with a narrow size distribution and well-defined shape [27–30] . It requires the controlled construction of desirable functional structure. The common difficulties in template-based synthesis are from creating uniform coatings of desired materials (or their precursors) on the surface of templates and maintaining their structural integrity after removing templates. Moreover, controllable preparation of hollow particles with complex architectures, such as multi-shell structure, via a simple coating process still remains difficult.

In our recently work, attention has been directed to SnO_2 hollow spheres with fine- controlled core-shell structures. The SnO_2 hollow spheres were obtained by calcination of sPS@SnO_2 composites where sPS is a sacrificial core [30]. In this paper, carbon-coated SnO_2 (SnO_2@C) hollow composite spheres can further be easily obtained by calcination the sPS@SnO_2 particles which covered glucose as the carbon precursor [23,31,32]. They are well controlled shape and size and with a high specific surface area. The products were examined for their application as supercapacitor electrode materials.

2. Experimental section

2.1. Synthesis of PS spheres

PS particles with different sizes were prepared by microemulsion polymerization. Typically, 35 ml of DI water and 6.3 ml of styrene were added into a three necked round-bottom flask and the solution was stirred at 1200 rpm for the formation of the emulsion. The emulsion was then bubbled with nitrogen gas to remove oxygen and maintained at an inert atmosphere. The reaction was carried out at 70 °C. When the reaction temperature was attained, 5 ml of 0.02 mol L^{-1} potassium peroxydisulfate (KPS) solution was added. After a couple of min 5 ml of 0.005 mol L^{-1} CTAB was added and then 5 ml of 0.0042 mol L^{-1} SDS solution in DI water was added 5 min later. N_2 purge was continued for a period of 15 min after the addition of all the reactants. The polymerization process was then initiated and stirring was continued for a period of 9 h. The end point was determined by the formation of a thick white liquid which was then thoroughly washed with ethanol and DI water and stored in ethanol for further use as seed material.

2.2. Preparation of SnO_2 hollow spheres

Firstly, PS seed particles were immersed in large quantity of concentrated sulfuric acid and stirred at 40 °C and for the appropriate time, thereby controlling the thickness of the sPS shell [33]. Then, in a typical synthesis, 50 mg of prepared sPS spheres were dispersed in 10.0 ml of ethanol by ultrasonication. After added a small amount polyvinylpyrrolidone (PVP) dissolved in water as surfactant to the sPS ethanol solution, freshly prepared 0.05 mol L^{-1} $SnSO_4$ (10 ml) solution was added drop by drop and the solution was stirred for 8 h to form sPS@SnO_2 particles as shown in Fig. 1. Finally, these dried sPS@SnO_2 particles were transferred to furnace and calcinated (heating rate, 5 °C min^{-1}) at 550 °C under air for 2 h. Hollow SnO_2 particles were then obtained.

2.3. Synthesis of SnO_2@Carbon hollow spheres

sPS@SnO_2 core-shell spheres was coated with carbon through hydrothermal calcination reaction [23,31,32]. In a typical synthesis, 30 mg of sPS@SnO_2 spheres were dispersed in 4 ml of H_2O, 10 ml of ethanol, and 0.4 g of glucose. Then the mixture was transferred to the autoclave. The reaction temperature was 180 °C, and time was set to 15 h. After this reaction, sPS@SnO_2@C was obtained. In the last step, sPS@SnO_2@C was put into tube furnace and treated under N_2 for 4 h at 700 °C. The hollow SnO_2@C composite spheres were obtained.

2.4. Characterization

Scanning electron microscopy (SEM) images were taken using a QUANTA 450 (FEI, America). Transmission electron microscopy (TEM) was conducted together with energy dispersive X-ray spectrometer as its mode has been utilized to examine the dimensions, structural details, and chemical composition of the samples (Tecnai F30 with a field emission gun operating at 200 kV). N_2 adsorption/desorption measurements were used to investigate the porosity structural properties of spheres. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method via a micromeritics ASAP 2010 M instrument. The pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method [34–36].

2.5. Electrochemical measurements

The electrochemical experiments were carried out using a conventional three-electrode cell. The working electrode was prepared as followed: SnO_2 microspheres, carbon blacks, and binder (60% of polytetrafluorethylene aqueous suspension) at a mass ratio of 80:10:10 were added and mixed well in *N*-methyl-2-pyrrolidone (NMP) until it formed the slurry with proper viscosity, and then the slurry was uniformly coated on a disk-like nickel foam (with the active area of 1 cm^2) by dipping, dried at 80 °C for 12 h in a vacuum drying oven, then pressed at 4 MPa for 30 s in order to assure a good electronic contact. Thus, the working electrode obtained. The mass of SnO_2 microspheres material was 0.0278 g for SnO_2 hollow spheres and 0.0194 g for SnO_2@C composite. CV and GCD measurement were carried out in a system, in which platinum foil and Ag/AgCl (saturated KCl) electrodes served as counter and reference electrodes, respectively, and using 1 mol L^{-1} KOH aqueous solution as the electrolyte. The CV experiment was performed within -1 V to 0 vs. reference electrode and in scan rates range of 10–50 mV s^{-1}. The charge/discharge curves were measured at different current densities from 0.1 to 1 A g^{-1} within a potential window (-1.0 to 0 V). The measurements were carried out by means of electrochemical analyzer systems, in CHI 660C (CH Instruments, USA).