



Constructing hierarchical porous carbon via tin punching for efficient electrochemical energy storage

Peng Wang^{a, b, c}, Jijian Xu^b, Feng Xu^b, Wei Zhao^b, Peng Sun^b, Zhichao Zhang^d, Meng Qian^b, Fuqiang Huang^{b, e, *}

^a School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, PR China

^b State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

^c University of Chinese Academy of Sciences, Beijing 100049, PR China

^d Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA19104, USA

^e Beijing National Laboratory for Molecular Sciences and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:

Received 24 January 2018

Received in revised form

4 April 2018

Accepted 6 April 2018

Available online 9 April 2018

ABSTRACT

To achieve large-scale preparation of high-performance carbon materials for electrochemical energy storage with a simple and cost-effective method remains a challenge. Here, we report a novel approach to synthesize hierarchical porous carbon with a low melting point metal tin (Sn) as pore forming agent. An aqueous processed tin chloride-polyethylene glycol (SnCl₂-PEG) gel is used as precursor to form Sn/Carbon (Sn/C) composites with homogeneously distributed ultrafine Sn particles (<2 nm) by pyrolysis. After etching Sn nanoparticles, hierarchical porous carbon with high specific surface area (SSA: 846 m² g⁻¹) and abundant pore structure (coexistence of mesopore and micropore) was obtained. The SSA, pore size distribution and pore volume were successfully tuned by controlling the size of the Sn nanoparticle. The capacitive performance of the as-prepared hierarchical porous carbon was evaluated in 1 M H₂SO₄, which exhibits excellent specific capacitance of 240 F g⁻¹. In order to further increase the electrochemical performance, N-doped porous carbon was fabricated by thermal nitridation in ammonia, which shows favorable features for electrochemical energy storage such as high specific surface area (1175 m² g⁻¹), uniform micropore volume (0.46 cm³ g⁻¹) and rich nitrogen-doping (4.45 wt%). This N-doped sample exhibits outstanding specific capacitances of 360 F g⁻¹ and excellent cycling stability in aqueous electrolytes. The above achievements indicate that combining low melting point metal as pore forming agent with a sol-gel protocol can be a unique and reliable method for preparation of high performance supercapacitor electrode materials.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

With increasing consumption of energy, considerable attention is paid to new sustainable energy technologies, such as Li-ion batteries, fuel cells, solar cells and supercapacitors. Supercapacitors have fast charge/discharge rate, high power density, good operational safety, and long lifetime [1–5]. Supercapacitors have been regarded as most promising power sources for portable

systems and automotive applications. A great deal of research effort has focused on the design and construction of compact electrode materials for supercapacitors, such as graphene [6,7], carbon nanotubes [8], carbon onions [9–11], carbon nanosheets [12,13], hierarchical porous carbons [14,15], etc. It is well known that the surface area and porosity are the key concerns in supercapacitor performance [16]. Due to their high surface area, higher electrical conductivity and hierarchical porous channels, hierarchical porous carbon is considered as the promising candidate for supercapacitors. For example, hierarchical porous carbon had been prepared by carbonizing the ion exchange resin containing cations (Fe, Ni, Mn, Zn etc.) [16–19], however, hydrogen must be needed to reduce metal ions during carbonization, this process was very

* Corresponding author. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China.

E-mail address: huangfq@mail.sic.ac.cn (F. Huang).

dangerous and costly. Furthermore, hierarchical porous carbon can also be obtained through pyrolysis various organic sol-gel, which by using inorganic templates, such as mesoporous SiO_2 or SiO_2 particles [20], etc. and organic templates [21] (surfactant, or triblock copolymers, etc.). However, these methods were complicated and time-consuming. Therefore, it is essential to find a unique method for preparation hierarchical porous carbon.

It is found that tin compound may be used as activator to prepare hierarchical porous carbon electrode materials for supercapacitors. Sn/C nanocomposites with small Sn particles (especially within 10 nm) distributed in various carbon materials have been prepared [21,23]. These works prove that Sn nanoparticles are ideal sacrificing pore former to prepare mesoporous carbons. However, the synthesis of Sn/C nanocomposites by a tandem plasma reaction method [22] or by carbonizing divalent Sn complex, Sn(Salen) [23] is difficult for large-scale preparation. So, a more flexible and simple method for Sn/C nanocomposites remains to be found.

Here, we propose a simple method for preparing Sn/C nanocomposites with homogeneously distributed Sn nanoparticles based on sol-gel. PEG and SnCl_2 can form gel easily, and by a simple heat treatment of the gel, Sn/C nanocomposites with homogeneously distributed ultrafine Sn particles (within 2 nm) can be obtained. In as prepared Sn/C nanocomposites, Sn particles have smaller size than reported. This is a unique advantage of our method, for smaller pores mean greater surface area. After etching Sn particles, micropores obtained within carbon materials, which exhibits very promising electrochemical performance. After annealed at ammonia atmosphere, the obtained N-doped porous carbons with high specific surface area, uniform micropore volume and rich N-doping. This N-doped sample exhibits outstanding specific capacitances of 360 F g^{-1} and excellent cycling stability in aqueous electrolytes.

2. Experimental

2.1. Chemicals

All the reagents were purchased from Sigma-Aldrich and were analytical grade. They were used without further purification.

2.2. Synthesis of hierarchical porous carbon

Hierarchical porous carbon (HPC) was prepared by pyrolysis. Typically, 4 g of polyethylene glycol (PEG-10000) and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (from 0.3 mmol to 2 mmol) were dissolved in 40 mL of ethanol under vigorous stirring, followed by heating at 60°C for 30 min to form a clear solution. The obtained solution was transferred into a dish to evaporate ethanol at 60°C for 8–10 h, resulting in a gel. The prepared products were named P-HPC-0.3 (0.3 mmol of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), P-HPC-0.5 (0.5 of mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), P-HPC-1.0 (1.0 of mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), P-HPC-2.0 (2.0 of mmol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$),

respectively. Calcination was performed in an Ar flow (300 sccm) at 900°C for 2 h with a heating rate of $10^\circ\text{C min}^{-1}$. After cooling down to room temperature, the samples were soaked in 20 mL of HCl solution (2 M) for 12 h, then washed by de-ionized water for three times, followed by drying overnight. The as obtained products were named HPC-0.3, HPC-0.5, HPC-1.0 and HPC-2.0, respectively. To improve electrochemical performance further, nitrogen doping was promoted by providing a NH_3 flow (50 sccm) at 850°C for HPC-1.0 sample. We obtained nitrogen-doped porous carbon, and termed as NPC-1.0. The preparing process of HPC-1.0 was presented in Fig. 1.

2.3. Structure characterization

Scanning electron microscopy (SEM) images were obtained by Hitachi-S4800. Transmission electron microscopy (TEM) images were achieved on a JEOL-2100F TEM operated at an acceleration voltage of 200 kV. Nitrogen adsorption/desorption isotherms were measured at 77 K on a Micromeritics ASAP 2460 analyzer. Samples were degassed at 200°C for 24 h prior to the measurement. The SSA of the samples was calculated using the Brunauer–Emmett–Teller (BET) method with the adsorption data at the relative pressure (P/P_0) range of 0.05–0.2. The total pore volumes were estimated at $P/P_0 = 0.99$. The pore size distribution (PSD) curves were calculated from the adsorption branch using the nonlocal density functional theory (NLDFT) model assuming the slit pore geometry. Raman spectroscopy was performed with a laser micro-Raman spectrometer (Renishaw in Via, Renishaw, 532 nm excitation wavelength). X-ray diffraction (XRD) measurement was performed with Lab XRD-6000 using Cu-K α radiation over the range of $2\theta = 10\text{--}80^\circ$ using an operation voltage and current of 40 kV and 40 mA, respectively. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with Thermo Scientific, ESCALAB 250Xi. The measuring spot size was 500 μm and the binding energies were calibrated by referencing the C 1s peak (284.8 eV).

2.4. Electrochemical characterization

All the electrochemical experiments were carried out using a computer controlled electrochemical workstation (CHI760E). The electrochemical impedance spectroscopy measurements were performed over a frequency range from 10^5 to 10^{-2} Hz at an amplitude of 5 mV. The cycle life tests were conducted by CV measurements with a constant scan rate of 0.01 V s^{-1} for 5000 cycles. The SC tests were performed in a three-electrode system in 1 M H_2SO_4 with Pt wire as counter electrode and Ag/AgCl electrode as reference electrode. The work electrode was fabricated by mixing 30 mg of HPCs and 3 ml of polyvinylidenedifluoride (PVDF, 5 mg ml^{-1}) with NMP as solvent. And then 100 μl of mixture was dipped onto a highly compressive 3D graphene network (area: $1 \times 1 \text{ cm}^2$, thickness: 1.2 mm, mass: approx. 1.0 mg) coated on a graphite plate. So 1 mg of HPC was onto a highly compressive 3D

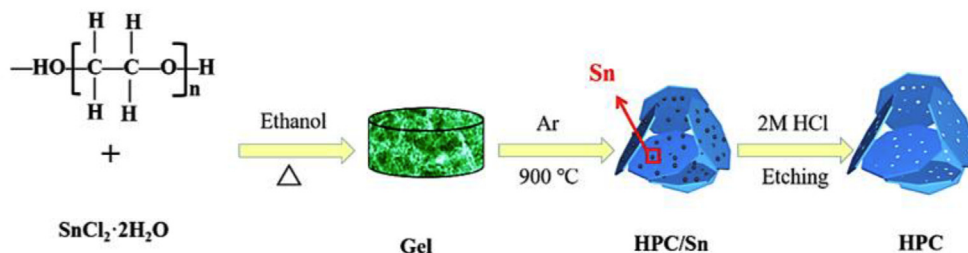


Fig. 1. Schematic illustration of the synthetic process for hierarchical porous carbon using PEG (PEG-10000) as carbon source and metal Sn as pore-forming agent. (A colour version of this figure can be viewed online.)

Download English Version:

<https://daneshyari.com/en/article/7847919>

Download Persian Version:

<https://daneshyari.com/article/7847919>

[Daneshyari.com](https://daneshyari.com)