



# Three-dimensionally Hierarchical Porous Carbon Creating High-performance Electrochemical Capacitors



Yan Han<sup>a</sup>, Shuangxi Liu<sup>b,\*</sup>, Dejun Li<sup>a,\*</sup>, Xifei Li<sup>a</sup>

<sup>a</sup> Energy & Materials Engineering Centre, College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China

<sup>b</sup> Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071, China

## ARTICLE INFO

### Article history:

Received 9 April 2014

Received in revised form 6 June 2014

Accepted 19 June 2014

Available online 25 June 2014

### Keywords:

Hierarchical porous carbon

Hydrothermal treatment

Carbon hollow-spheres

Electrochemical capacitors

## ABSTRACT

Three-dimensionally (3D) hierarchical porous carbon has been prepared through a simple and efficient hydrothermal treatment on colloidal silica as template. Nitrogen adsorption-desorption isotherms and transmission electron microscope images reveal that the porous carbon has a unique 3D interconnected micro-, meso- and macroporous network. The observed 3D interconnected meso/macroporous network originates from the cores of carbon hollow-spheres and the aggregation of crosslinked carbon hollow-spheres, and the micropores exist from the 3D interconnected network inside the shells of carbon hollow-spheres. The electrochemical capacitive tests indicate that the porous carbons exhibit large specific capacitance of about 300 F g<sup>-1</sup> at 1 A g<sup>-1</sup> in 6 M KOH aqueous electrolyte as well as high capacitance retention of 71% when the current density increased by 10 times.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Supercapacitors have sparked enormous interest in the field of electrical energy storage devices due to their excellent performances, such as high power density, long cycle life, wide operating temperature range, and short charging period [1–3]. Activated carbon with large surface is the most widely adopted electrode material [4–7]. Theoretically the higher surface area of electrode material, the higher value of electrical double-layer capacitance is expected. However, the proportionality between the capacitance and specific surface area of activated carbons is not observed in most cases. Because micropores developed in the high surface area carbons cannot be easily accessible by electrolyte ions and thus will not contribute to the total capacitance of the materials. Therefore, it is critical to design and tune the rational porous structure of carbons in meso and macroporous ranges to optimize capacitance performance of the carbon electrode materials.

Recently, hierarchical porous carbon (HPC) materials have been successfully synthesized and shown to exhibit great potential for the high performance supercapacitor applications [8–13]. The hierarchical pores can combine the advantages of each kind of pore with a synergistic effect during the electrochemical

charge-discharge process. The macropores serve as ion-buffering reservoirs, giving a decreased diffusion distance; the mesopores provide the ion-transport pathways with a minimized resistance; and the micropores enhance the surface of electrical double layer. As a consequence, considerable progress has been made to design and construct such HPCs and characterize their promising electrochemical capacitive properties. In this work, three-dimensionally hierarchical porous carbon has been prepared through a simple and efficient hydrothermal treatment using colloidal silica as template. The as-prepared porous carbon has a unique 3D interconnected micro-, meso- and macroporous network, which facilitates the transport of electrolyte ions and offers a good environment for charge accumulation so as to give rise to excellent performances as an electrode material for supercapacitors.

## 2. Experimental

### 2.1. Materials synthesis

All chemicals were of analytical grade and used without further purification. The HPC was synthesized through a simple hydrothermal method using colloidal silica as template. The typical preparation procedure is illustrated in Fig. 1. In the first step, the colloidal silica was prepared by Stöber method and surface modified by 3-amino-propyltrimethoxysilane (APMS) as reported previously [14,15]. Then, phenol (0.20 g) was melted in a flask at 40 °C before the above silica colloid (20 ml) was added slowly

\* Corresponding authors. Tel./Fax.: +86 22 23509005 (S. Liu); +86 22 23766519 (D. Li).

E-mail addresses: [sxliu@nankai.edu.cn](mailto:sxliu@nankai.edu.cn) (S. Liu), [dejunli@mail.tjnu.edu.cn](mailto:dejunli@mail.tjnu.edu.cn) (D. Li).

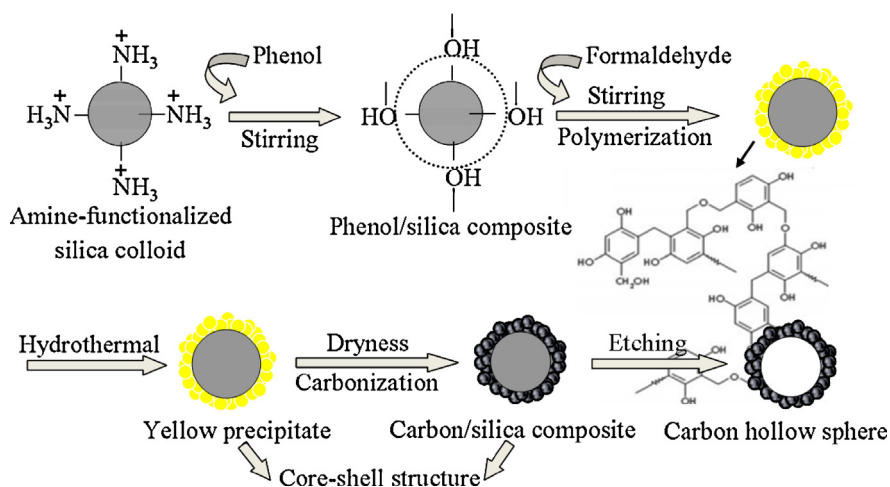


Fig. 1. Schematic illustration of the preparation process of the HPC.

under stirring. Because the electrostatic interaction between phenolic hydroxyl groups and ammonium groups on the surface of the colloidal silica sphere, the phenol can be absorbed and coated on the surface of the colloidal silica spheres. After stirring for 1 h, formaldehyde solution (37 wt.%, 0.3 mL) was added to the reaction mixture and stirred for 24 h at 40 °C. Subsequently, the obtained homogeneous solution was transferred and sealed in an 25 mL Teflon-lined autoclave, and maintained at 100 °C for 24 h. The light yellow solid product was obtained by centrifugation, washed and dried at 100 °C for 24 h. Finally, the above-prepared composite was carbonized at 800 °C for 2 h under N<sub>2</sub> flowing and etched by hydrofluoric acid (HF, 40 wt.%) to remove silica template.

## 2.2. Materials characterization

The morphology of the as-prepared HPC was characterized by scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, Philips Tecnai G<sup>2</sup> F20). Thermogravimetric analysis (TGA) was carried out on an NETZSCH TG 209 apparatus with a heating rate of 10 °C min<sup>-1</sup> under air. Raman scattering was determined using a Renishaw inVia Raman spectrometer ( $\lambda=514.5$  nm). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD with a Al K $\alpha$  X-ray source. And nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020 analyzer at 77 K. The specific surface area ( $S_{\text{BET}}$ ) was calculated from nitrogen adsorption isotherms using the Brunauer-Emmett-Teller (BET) method, whereas the total pore volume was determined by the single point method at  $P/P_0=0.97$ . The pore size distribution (PSD) was analyzed using the density functional theory (DFT) method from the adsorption branch.

## 2.3. Electrochemical measurement

All electrochemical experiments were carried out using a three-electrode system at room temperature. For making a working electrode, as-prepared HPC, acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 90:5:5 were pressed between two pieces of 1 × 1 cm<sup>2</sup> nickel foam. The mass of porous carbon contained in each working electrode was between 3 and 5 mg. Before electrochemical tests, the electrodes were vacuum soaked with 6 M KOH aqueous solution. Electrochemical measurements were carried out with 6 M KOH aqueous solution as the electrolyte, Ni foil and Hg/HgO electrode as the counter and reference electrodes, respectively.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on CHI 660D electrochemical

analyzer. The galvanostatic charge-discharge tests were studied using LAND CT2001A instrument.

## 3. Results and discussion

The SEM and TEM micrographs of the hierarchical porous carbon are shown in Fig. 2. From the SEM images at different magnification (Fig. 2a and 2b), it can be observed that the sample is composed of microspheres with size of 80–100 nm. These spheres stack up each other into grape-like aggregates and then these aggregates interconnect in different directions into a three-dimensional network, leading to the formation of interconnected meso- and macropores. Meanwhile, the cracked spheres with apparent cavities and partial cave-in on the surface of some spheres indicate the hollow nature of the as-prepared carbon spheres. Further details of the microstructure of the HPC can be seen in the TEM images (Fig. 2c and 2d). As shown, the strong contrast between the dark edge and pale center confirms the hollow structure of the carbon microspheres. The core sizes of the carbon spheres is about 60–80 nm, agreed well with the sizes of colloidal SiO<sub>2</sub> particles used, and the thickness of the shell is about 10–30 nm. In addition, the high resolution TEM image (the inset in Fig. 2d) reveals that the shells of carbon spheres consist of localized graphitic structures, which lead to a large number of defects such as edges and pores.

Moreover, the graphitic structure of the HPC is further studied by Raman spectroscopy (Fig. 3a). Two characteristic peaks around 1343 and 1595 cm<sup>-1</sup> could be observed. The peak at 1595 cm<sup>-1</sup>, known as the G band, corresponds to the stretching mode of C–C bonds of typical graphite. The band at 1343 cm<sup>-1</sup>, known as the D band, is assigned to the defects and disorders in carbonaceous solid. The intensity ratio ( $I_{\text{D}}/I_{\text{G}}$ ) of the two bands is about 0.90, verifying the low degree of graphitization of the as-obtained HPC [16–18]. Thermogravimetric analysis (TGA) can provide information about the carbon content as well as the quality of the HPC because the oxidation temperature reflects the material defect degree (Fig. 3b). The HPC starts to oxidize at 400 °C, which is much lower than that of ideal graphite (600 °C) [18]. With the temperature increasing, the HPC begins to decompose at 500 °C in air and is exhausted at 650 °C. The ash content of the HPC after combustion at 900 °C is 0% w/w. These results indicate that the carbonization is carried out enough despite a high defect degree of the HPC, and the obtained HPC has high purity without SiO<sub>2</sub> residue.

X-ray photoelectron spectrum (XPS) was used to study the surface compositions of the HPC. The survey scan spectrum shows the presence of carbon and oxygen (Fig. 4a). No signal related with silicon is observed, suggesting the silica is completely removed.

Download English Version:

<https://daneshyari.com/en/article/6613229>

Download Persian Version:

<https://daneshyari.com/article/6613229>

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