



Supercapacitive performance of hierarchical porous carbon microspheres prepared by simple one-pot method



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HIGHLIGHTS

- Hierarchical porous carbon microspheres are synthesized under mild condition by one-pot method.
- Pore structures of HPCMSs can be tailored by adjusting the reactant parameters.
- HPCMSs possess a pore combination of micro-, meso- and macropores with part graphitic layers.
- The energy density of HPCMS supercapacitor is still as high as 6.1 Wh kg^{-1} even at 5000 W kg^{-1} .

ARTICLE INFO

Article history:

Received 3 August 2013

Received in revised form

16 December 2013

Accepted 19 December 2013

Available online 31 December 2013

Keywords:

Supercapacitor

Hierarchical porous carbon microsphere

Simple one-pot method

Furfuryl alcohol

ABSTRACT

The hierarchical porous carbon microspheres (HPCMSs) using furfuryl alcohol as carbon resource have been prepared by a simple one-pot method. The HPCMSs are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption/desorption isotherm at 77 K, cyclic voltammetry (CV), galvanostatic charge/discharge tests, electrochemical impedance spectroscopy (EIS) and cycle life measurements in 6 M KOH. The results show that all the HPCMSs samples, which can be fabricated by adjusting the ratio of furfuryl alcohol/tetraethyl orthosilicate, possess three-dimensionally tailored pore structures with unique micro-, meso- and macroporous systems. Particularly, the HPCMS-2 prepared at the mole ratio of 2/1 (furfuryl alcohol/tetraethyl orthosilicate) shows the largest specific surface area of $709 \text{ m}^2 \text{ g}^{-1}$, and the HPCMS-2 electrode owns specific capacitance as high as 221 F g^{-1} at the current density of 1 A g^{-1} . The supercapacitor using HPCMS-2 as the active material shows high specific capacitance and excellent cycle stability, which exhibits a specific capacitance of 56 F g^{-1} at the charge/discharge current density of 0.5 A g^{-1} . Furthermore, the HPCMS-2 supercapacitor delivers high energy densities of 6.1 Wh kg^{-1} at the power density of 5000 W kg^{-1} , revealing a promising application in supercapacitors.

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1. Introduction

Supercapacitors as novel devices for storing energy, which are divided into electrical double layer capacitors (EDLCs) and pseudocapacitors, have attracted more and more attention for their long cycle life, good reversibility, high power density, etc [1,2]. The activated porous carbon materials as the most widely used supercapacitor materials have the advantages of high conductivity, electrochemical stability, open porosity and low cost [3]. Whereas, the slow ion transportation in small micropores of activated porous

carbon materials restricts their effective utilization <http://www.sciencedirect.com/science/article/pii/S0378775312006738> [4]. Moreover, the porosity of carbon materials plays an important role in the electrochemical capacitive performance of supercapacitors, especially for EDLCs [5]. It is well known that macropores serving as ion-buffering reservoirs are able to minimize the diffusion distances, mesopores can decrease ion-transport resistance, and micropores are capable of increasing the electric-double-layer capacitance [6–10]. As a consequence, hierarchical porous carbons with a pore combination of micro-, meso- and macropores hold great potential for high performance supercapacitor applications [11–13].

Recently, many efforts have been made to prepare hierarchical porous carbons. Xia et al. obtained hierarchical porous carbons of higher capacitance by CO_2 activation, which achieved the

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maximum specific capacitance of 206 F g^{-1} at the scan rate of 5 mV s^{-1} in 6 M KOH [14]. Bhattacharjya et al. synthesized hierarchical hollow core mesoporous shell carbon capsules via a nanocasting technique using the submicrometer sized solid core/mesoporous shell silica microspheres as templates, which exhibited a capacitance of 162 F g^{-1} at 0.3 A g^{-1} in two electrode symmetric system in organic electrolyte [15]. Liu et al. prepared hierarchical porous carbons by CO_2 and KOH activation processes, which delivered a capacitance of 250 F g^{-1} at 0.5 A g^{-1} in 6 M KOH [16]. Ma et al. synthesized Micro- and mesoporous carbon spheres (MMCSs) by templating method and further potassium hydroxide (KOH) activation, which showed a specific capacitance of 314 F g^{-1} at 0.5 A g^{-1} in 6 M KOH [17]. Our group fabricated activated hierarchically porous carbons (HPCs) using nickel oxide and surfactant as the dual template with further activation by HNO_3 [18]. Later, the effects of surfactant template concentration on the supercapacitive behaviors of the activated HPCs were investigated, and the activated HPCs-3 which was prepared at $C_{\text{CTAB}} = 0.27 \text{ mol L}^{-1}$ displayed the maximum specific capacitance of 272 F g^{-1} at the scan rate of 1 mV s^{-1} [19]. However, the above reported methods to obtain hierarchical porous carbons were time-consuming, energy-intensive, or complex due to the extra synthesis of special templates, additional activation and multi-step process. As a result, hierarchically porous carbons with high supercapacitive performance prepared through a simple time-saving and energy-conservative means are urgent to be explored.

To the best of our knowledge, there are few reports about methods of one-pot procedure on preparing hierarchical porous carbon microspheres. Herein, hierarchical porous carbon microspheres are synthesized under mild condition by one-pot method which is different from the previous complex and multi-step routes. Moreover, the physical and electrochemical properties of the as-prepared hierarchically porous carbon microspheres with three-dimensionally tailored pore structures by adjusting the reactant content are studied in detail.

2. Experimental

2.1. HPCMSs synthesis

The preparation strategy is shown in Fig. 1. HPCMSs were prepared by self-assembly of cetyltrimethyl ammonium bromide (CTAB), polyacrylic acid (PAA), tetraethyl orthosilicate (TEOS) and furfuryl alcohol (FA). Firstly, the anionic polyelectrolyte PAA and cationic surfactant CTAB micelles co-organized into complex particles by the electrostatic attraction between them. After the addition of TEOS and FA, they penetrated in the interspaces between the complex particles formed by PAA and CTAB micelles,

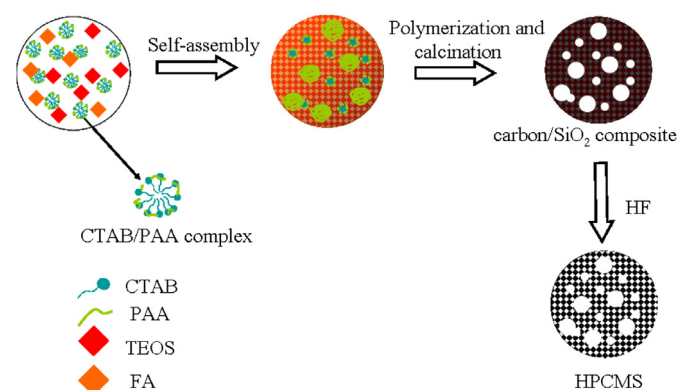


Fig. 1. Schematic illustration of preparation strategy of HPCMSs.

and then TEOS hydrolyzed in situ in alkaline environment. Meanwhile the hydrolyzed negatively charged silica oligomers disturbed the electrostatic attraction between PAA and CTAB, and the co-assembly of the mesomorphous PAA/CTAB complexes was also perturbed. Next, the silica oligomers cross-linked around cationic surfactant CTAB micelles with the FA filling the interspaces, and PAA chains separated from the PAA/CTAB complexes to form PAA chain domains. After the calcination of the mixture, the carbon/ SiO_2 composites were formed. Finally, when the silica was dissolved in 46% HF solution, the HPCMSs were obtained with a combination of micropores (templated by the TEOS-generated silica), mesopores (templated by CTAB micelles), and macropores (templated by phase-separated PAA). In a typical procedure, 0.55 g of CTAB was dissolved in 25.0 mL of deionized water, and 6.0 g of PAA (25 wt% solution) was added under continuous stirring to obtain a clear solution. The solution was supplied with 2.2 mL of ammonia (25%–28%) and became a milky mixture. After additional 20 min of stirring, 2.08 g of TEOS and various amounts of FA were added to the above mixture at a mole ratio of FA/TEOS in the range of 1.0–3.0. After further stirring for 15 min, the mixture was transferred into an autoclave, and then kept at $80 \text{ }^\circ\text{C}$ for 48 h. Subsequently, the mixture was evaporated at $50 \text{ }^\circ\text{C}$ to obtain FA/silica gel film. The FA/silica composite was polymerized at $150 \text{ }^\circ\text{C}$ for 6 h, and calcined at $900 \text{ }^\circ\text{C}$ for 3 h under an Ar flow to prepare carbon/ SiO_2 composite. The heating rate was $2 \text{ }^\circ\text{C min}^{-1}$ below $600 \text{ }^\circ\text{C}$ and $5 \text{ }^\circ\text{C min}^{-1}$ above $600 \text{ }^\circ\text{C}$. The as-prepared carbon/ SiO_2 composite was immersed in an excess amount of 46% aqueous HF solution to dissolve silica, followed by washing with deionized water and drying to obtain hierarchically porous carbon microspheres. The synthesized hierarchically porous carbon microspheres were named as HPCMS- x . “HPCMS- x ” denotes hierarchically porous carbon microsphere samples, wherein x represents the mole ratio of FA/TEOS.

2.2. Characterization

The morphology and microstructure of the synthesized HPCMSs were characterized by scanning electron microscopy (SEM, JSM-6610LV, JEOL) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The microstructure of HPCMSs was evaluated by X-ray diffractometer (XRD, D/MAX-3C, Rigaku) using $\text{Cu K}\alpha$ radiation (30 kV , 30 mA , $\lambda = 1.5418 \text{ \AA}$). The specific surface area and pore structure of the HPCMSs were determined by N_2 adsorption/desorption isotherm at 77 K (JW-BK112) after the prepared samples were degassed at $110 \text{ }^\circ\text{C}$ overnight. The specific surface areas were calculated by the conventional Brunauer–Emmett–Teller (BET) method. Micropore volumes (V_{mic}) of the samples were analyzed by Horvath–Kawazoe (HK) theory. Pore volumes (V_{total}) and the pore size distribution (PSD) plot were derived from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model.

2.3. Electrochemical measurements

To prepare the EDLC electrode, 80 wt% the HPCMS sample, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) binder were well mixed to get a slurry by adding N -methyl-2-pyrrolidone as a solvent. The slurry was filled into the nickel foam substrate using a spatula, dried at $80 \text{ }^\circ\text{C}$ overnight, and then pressed at 16 MPa for 1 min in order to assure a good electronic contact between the nickel foam substrate and the active material. Finally, the as-prepared electrode was dried at $80 \text{ }^\circ\text{C}$ in vacuum for 24 h.

The electrochemical performances of the as-prepared electrode were characterized by cyclic voltammetry (CV), galvanostatic charge/discharge tests and electrochemical impedance spectroscopy (EIS) on

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