



One-pot synthesis of nitrogen-doped ordered mesoporous carbon spheres for high-rate and long-cycle life supercapacitors



Jian-Gan Wang^{a,*}, Hongzhen Liu^a, Huanhuan Sun^a, Wei Hua^a, Huwei Wang^a,
Xingrui Liu^a, Bingqing Wei^{a,b,**}

^a State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shaanxi Joint Lab of Graphene (NPU), Xi'an, 710072, China

^b Department of Mechanical Engineering, University of Delaware, Newark, DE, 19716, USA

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ABSTRACT

Nitrogen-doped ordered mesoporous carbon spheres (N-OMCS) were prepared by a facile one-pot soft-templating and one-step pyrolysis method. The as-obtained N-OMCS possesses an average diameter of around 300 nm, a moderate specific surface area of 439 m² g⁻¹ and uniform mesopore size at around 5.0 nm. Owing to the ordered meso-structure and nitrogen doping, the N-OMCS materials, when used as supercapacitor electrodes, delivers a high specific capacitance of 288 F g⁻¹ at a current density of 0.1 A g⁻¹. More remarkably, the N-OMCS electrode shows excellent rate capability with 66% capacitance retention at an ultrahigh current density of 50 A g⁻¹ and outstanding cycling stability with almost no degradation over 25,000 cycles. The work would open up a new avenue to synthesize carbon spheres with mesoporous structure and nitrogen doping for high-performance supercapacitor applications.

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1. Introduction

The increasing concerns on the global climate change and fossil depletion has aroused worldwide research activities in the development of sustainable energy storage devices. Supercapacitor, also called electrochemical capacitor, has been received significant attention due to the unique characteristics of high power density, fast charge/discharge rate and long cycle life [1]. According to the energy storage mechanism, supercapacitors can be categorized into electrical double layer capacitors (EDLCs) and pseudocapacitors [2,3]. EDLCs store energy through charge accumulation at the surface of the electrode materials, mainly including the porous carbon [4,5]; meanwhile, pseudocapacitors depend on fast and reversible Faradaic reactions of active materials, such as metal oxides/sulfides [6,7] and conducting polymers [8,9].

Although great progress has been made on the high-

performance electrode materials in the past decades, carbon materials still dominate the commercial supercapacitor applications due to their low cost, good electrical conductivity and ultrastable cycle life [4,10,11]. The well-developed carbon materials include activated carbon, carbon nanotube, graphene and carbon aerogel, etc. Nevertheless, the specific capacitance and the rate performance of carbon materials are rather limited despite the specific surface area of carbon can surpass 2000 m² g⁻¹ [12]. This suggests that the electrochemical performance of carbon materials is not totally associated with the surface area because part of the surface sites may not be accessible to the electrolyte ions. It is well-established in the literature that a proper pore size distribution and surface functionality of porous carbon also affect the performance, especially the rate capability [13,14]. In this regard, ordered mesoporous carbon with tunable mesopores is considered as promising electrode materials for high-rate supercapacitors, because the mesopores are favorable for rapid mass transport [15,16]. In addition, incorporation of heteroatoms, such as nitrogen, boron, etc., into carbon structures is useful to improve the electrical and chemical properties of the carbon surface [17–19]. It is of great interest to combining ordered meso-structure and heteroatom-doping into a carbon entity.

The common strategies for the synthesis of ordered mesoporous carbon are hard-templating and soft-templating methods [20].

* Corresponding author.

** Corresponding author. State Key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University and Shaanxi Joint Lab of Graphene (NPU), Xi'an, 710072, China.

E-mail addresses: wangjangan@nwpu.edu.cn (J.-G. Wang), weib@udel.edu (B. Wei).

Hard-templating method usually employs the use of mesoporous silica, which require a tedious and contaminative process such as acid-etching [21,22]. By contrast, soft-templating synthesis shows advantages of easy-processing, cost-effectiveness and eco-friendliness [23]. The organic–organic self-assembly of amphiphilic triblock copolymers (such as F127 and P123) with phenolic resin have been demonstrated to be capable of creating ordered mesopores [18]. Zhao et al. have developed a variety of ordered mesoporous carbon spheres (OMCS) based on the soft-templating method [24,25]. It is noted that the synthesis procedure in their studies needs multiple steps of prepolymerization and hydrothermal solidification. Moreover, the as-obtained meso-carbon materials do not contain nitrogen elements. One feasible way to achieve the nitrogen doping is through chemical activation by NH_3 , which, however, may destruct the meso-structure [26]. Therefore, direct synthesis of OMCSs with nitrogen-doping from organic-organic self-assembly still remains a substantial challenge.

In this work, we report a facile one-pot soft-templating and one-step pyrolysis method to synthesizing nitrogen-doped ordered mesoporous carbon spheres (N-OMCSs). Nitrogen-containing *o*-aminophenol is purposely employed to initiating the polymerization of nitrogen-doped phenolic resin while crosslinking with the F127 surfactant through self-assembly. The as-prepared N-OMCSs exhibits well-ordered mesopores at around 5.0 nm and a high nitrogen content of 5.31 wt%. When used as supercapacitor electrodes, the N-OMCSs manifest excellent electrochemical properties, such as a high specific capacitance of 288 F g^{-1} together with outstanding rate/cycling performance.

2. Experimental

2.1. Materials preparation

N-OMCS was prepared through an aqueous self-assembly process. In a typical synthesis procedure, 3.0 g of poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer Pluronic F127 ($\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$, $M_w = 12\,600$) was dissolved in 52 ml of deionized water to form a spherical micelle solution (4.5 mM). Subsequently, 1.0 g of *o*-aminophenol, 0.7 g of hexamine and 1.7 g of 28 wt% aqueous ammonia were added to the above solution under magnetic stirring for 1 h (0.50 M). Then the mixture solution was heated to 80°C and keep stirring for 24 h. A solid product was collected by centrifugation followed by washing with water and ethanol and drying at 60°C for 12 h. N-OMCS was finally obtained by carbonization, which was performed at 350°C for 1 h and then 800°C for 3 h under the protection of N_2 flow. For comparison, microporous carbon spheres (CS) were synthesized by the same process but without the addition of F127.

2.2. Materials characterization

The structure and morphology of the products were observed

on scanning electron microscopy (FESEM, NanoSEM 450, FEI) and Transmission Electron Microscopy (TEM, Tecnai F30G, FEI). The phase structure was examined by X-ray powder diffractometer (XRD) and small-angle XRD in $0.5\text{--}4.5^\circ$ range ($\text{Cu K}\alpha$ radiation, X'Pert PRO MPD, Philips). Raman spectra were obtained by Renishaw Invia RM200 (England) at room temperature. The textural characteristics were investigated on Micromeritics ASAP 2020 system at liquid N_2 temperature (77 K). The samples were degassed at 200°C for 12 h in a vessel before measurements. The total pore volume was estimated from the single point adsorption at $P/P_0 = 0.995$. The micropore volume was obtained by t-Plot method. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) method and the pore size distribution was analyzed by density functional theory (DFT). The surface chemistry and elemental analysis of the N-OMCS was carried out on X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific). The elemental composition was measured on a TH-600 carbon/nitrogen/oxygen analyzer and all XPS peaks were calibrated with C1s line at 284.5 eV. The deconvolution was performed on the XPSpeak fitting software and the baseline was obtained using Shirley model.

2.3. Electrochemical measurements

A homogeneous slurry was prepared by mixing active materials (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%). The slurry was then coated onto Ni foam to serve working electrodes. The mass loading of active materials was about 3.0 mg cm^{-2} . The electrochemical measurements were carried out using a three-electrode configuration, which employed 6 M KOH aqueous solution as the electrolyte, platinum foil as the counter-electrode and Hg/HgO electrode as the reference electrode. Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were performed on Solartron electrochemical workstation (1260 + 1287, England). The electrochemical impedance spectra (EIS) measurements were conducted in the frequency ranging from 100 kHz to 50 mHz with a perturbation amplitude of 10 mV versus the open-circuit potential.

3. Result and discussion

Fig. 1 shows the schematic illustration of the fabrication processes of N-OMCS. It is well-known that amphiphilic block copolymer of F127 is generally used as a structure-directing agent to synthesizing OMCS. The formation of ordered meso-structure can be well-controlled by the micelle morphology of F127 through self-assembly with carbon precursors. The common carbon precursor is resol polymerized by phenol and formaldehyde, which, however, does not possess nitrogen-containing species for the subsequent synthesis of N-OMCS. To address this issue, *o*-aminophenol is employed herein as the nitrogen-containing phenol species while formaldehyde is provided by hydrolysis of hexamine. Consequently,

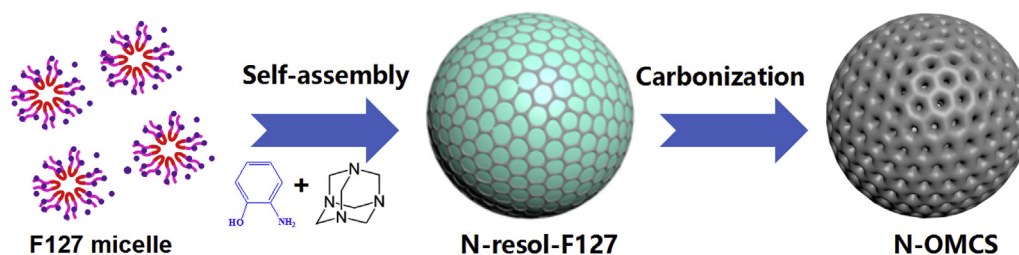


Fig. 1. Schematic illustration of the fabrication processes of N-OMCS. (A colour version of this figure can be viewed online.)

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