



N-doped mesoporous carbon by a hard-template strategy associated with chemical activation and its enhanced supercapacitance performance



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ABSTRACT

Well-controlled mesoporosity is of importance for porous carbons as electrochemical electrode materials. However, the ordered mesoporous carbons prepared from the template approaches face the fact of relative low specific surface area in comparison to activated carbons. Herein, we employed a hard-template route associated with the chemical activation to prepare N-doped mesoporous carbon by co-casting of carbon and nitrogen precursors into the pore channels of mesoporous silica. The obtained activated N-doped mesoporous carbon (ANMC) material preserved the morphology and mesoporous structure of template, and meanwhile a secondary mesoporosity was introduced by the KOH activation. It was demonstrated that the dominant porosity in ANMC sample was from mesopore, and it possessed a high mesopore surface area ($2505.6 \text{ m}^2 \text{ g}^{-1}$) and mesopore volume ($1.74 \text{ cm}^3 \text{ g}^{-1}$). The N dopant was determined to be pyridinic-N, pyrrolic-N, quaternary-N and pyridine-N-oxide, which did not only contribute the pseudocapacitance but also facilitated the electron transfer in the carbon skeleton. The developed mesoporosity and N doping made this material exhibit superior electrochemical performance that was much higher than those of ordered mesoporous carbon, N-doped ordered mesoporous carbon and activated N-doped carbon samples. Also, the specific capacitance 336.9 F g^{-1} (0.5 A g^{-1}) and the rate capability were higher than those of other reported mesoporous carbons. In addition, the assembled symmetrical supercapacitor simultaneously showed the high energy density and power density, as well as presented the superb cycling ability ($\sim 98.5\%$ capacitance retaining after 5000 runs).

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1. Introduction

As one of the electrical energy storage devices, supercapacitors possess much faster charging rate and higher power density, as well as longer cycle life than those of traditional batteries, and consequently have a broad application in portable electronics, electrical vehicles and so on [1–7]. Based on the mechanism of energy storage, supercapacitors are mainly divided into two categories, electrical double-layer capacitors (EDLCs) and Faraday pseudocapacitors [8]. In spite of large specific capacitance ($> 1000 \text{ F g}^{-1}$) achieved in some pseudocapacitive active materials, such as NiO [9], NiCo_2O_4 [10] and NiCo_2S_4 [11], the energy density of the devices based on these oxides or sulfides is not as high as

their specific capacitance because of the small potential window. Moreover, the poor electron conductivity of oxides and sulfides results in an unsatisfying rate capability that is of great importance for supercapacitors to be used as the energy storage devices with high power density. In addition, pseudocapacitors have a short lifetime compared with EDLCs [12].

The generally used active materials in EDLCs are porous carbons, which have high accessible surface area to form electrical double-layer, suitable pore channel to favor the diffusion of electrolyte ions and good conductivity for electron rapid transport [13,14]. So far, numerous strategies have been employed to prepare porous carbonaceous materials, for instance chemical or physical activation [15,16], sol-gel route [17,18], template method [19,20] and chemical blowing [21,22]. It has been demonstrated that the electrochemical behavior of porous carbons is dependent on the pore structure, including the available surface area, pore diameter and length [23]. EDLCs store electrical energy by forming an electrical double-layer on the interface between electrode and

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electrolyte solution. Therefore, the capacitance of EDLCs is directly proportional to the surface area of electrode that can adsorb electrolyte ions. Activated carbons (ACs), one of the most used porous carbons, have extremely high surface areas, which whereas are inconsistent with their electrochemical performance [24,25]. This may be ascribed to the unavailability of a portion of surface area in ACs because electrolyte ions cannot transport in the micropores with smaller pore dimension than the size of electrolyte ions. As a high power device, supercapacitor should be charged and discharged under a large current. This needs supercapacitor has a superior rate capability besides the specific capacitance. Though microporosity of ACs contributes large specific capacitance, the diffusion of electrolyte ions is restricted. To achieve an excellent rate capability on supercapacitors, introduction of mesoporosity or macroporosity in active materials is urgent [26].

Significant efforts have been devoted on the development of mesoporous carbons by employing the template approach [27–30], for example using surfactants or block copolymers as the soft template and employing ordered mesoporous solids or nanoparticles as the hard-template. Since the first preparation of M41 series of materials by the scientists in Mobil company in 1992 [31], ordered mesoporous materials have attracted tremendous research interests in catalysis, separation, electrochemistry, sensors and so on [32,33]. Ordered mesoporous carbons (OMC) possess highly regular mesoporosity with high surface area, large pore volume and uniform pore size distribution, and exhibit potential applications in a variety of fields [34–39]. The 2–8 nm mesoporosity in OMC has been proved to be suitable for the rapid transfer of electrolyte ions [40]. Kang et al. used an anodized aluminum oxide template to fabricate OMC, which enhanced charge-transfer and electron-transfer rates and increased the number of usable charge storage sites [41]. Zhao et al. employed F127 as the soft-template and used RF resin as carbon precursor to form OMC, and achieved a specific capacitance of $\sim 170 \text{ F g}^{-1}$ in 6 M KOH electrolytes at 100 mV s^{-1} [42]. Wei et al. reported a controllable one-pot method to synthesize N-doped OMC, which had a specific capacitance of 262 F g^{-1} in 1 M H_2SO_4 at a current density of 0.2 A g^{-1} [43].

Limited by the relative low surface area compared to ACs, the specific capacitance of OMC has not been significantly improved. There are mainly two kinds of routes to modify OMC therefore to enhance the electrochemical property. One is to introduce pseudocapacitance to OMC, for instance hybridization of oxides [44], sulfides [45] and conducting polymers [46] or doping with heteroatoms [47–51]. Another strategy is to develop second-level porosity in the mesoporous wall therefore to increase surface area and also promote the diffusion rate of electrolyte ions in electrode [52–55]. Lv et al. synthesized a kind of KOH activated micro/mesoporous carbon with the surface area of $\sim 1400 \text{ m}^2 \text{ g}^{-1}$ and specific capacity of 200 F g^{-1} [52]. Ma et al. also reported a micro/mesoporous carbon used NaOH as activation agent, which exhibited a $1600 \text{ m}^2 \text{ g}^{-1}$ surface area and an extremely high specific capacity of 314 F g^{-1} [53]. Li et al. synthesized an ordered mesoporous carbon with a high surface area of $2390 \text{ m}^2 \text{ g}^{-1}$ and a large pore size of 6.7 nm through an organic-inorganic-surfactant tri-constituent co-assembly method with a large capacitance of 112 F g^{-1} in nonaqueous electrolyte at 200 mV s^{-1} [54].

Herein, we reported a strategy to improve the electrochemical performance of OMC by simultaneously employing the doping of nitrogen element and the development of secondary porosity. The N dopant was involved by the co-casting of nitrogen precursor and carbon resource into the pore channel of hard-template, and the secondary porosity was introduced by the KOH chemical activation. The physicochemical properties of the obtained N-doped mesoporous carbon material was systematically characterized via

various techniques, such as electronic microscopy, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy and nitrogen sorption technology. Its electrochemical activity was firstly studied by a three-electrode system using KOH as electrolyte, including cyclic voltammetry, galvanostatic charge/discharge and rate capability. We further investigated its behavior by assembling two-electrode symmetrical supercapacitor. Furthermore, the electrochemical impedance spectroscopy, cycling performance and the relationship of power density and energy density were also explored.

2. Experimental section

2.1. Synthesis

The hard-template, ordered mesoporous silica SBA-15, was hydrothermally prepared using an amphiphilic triblock copolymer of Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as the structure directing agent and tetraethyl orthosilicate (TEOS) as the precursor [27]. Subsequently, ordered mesoporous carbon (OMC) was synthesized using a nano-casting approach by introducing carbon precursor of furfuryl alcohol into the pore channels of SBA-15 followed with the carbonization treatment [30]. The N-doped OMC (NOMC) was obtained with the similar procedure to OMC. Typically, 1.0 g SBA-15 was dispersed into the 20 mL ethanol containing 1.5 mL furfuryl alcohol, and then the mixture was treated at 70°C to polymerize furfuryl alcohol. Next, the polymer/ SiO_2 composite was mixed with 1.0 g melamine (the nitrogen resource) and was heated at 800°C for 2 h under N_2 atmosphere. After removing the hard-template by the twice treatment in a hot NaOH aqueous solution (2.0 M), the NOMC sample was prepared. The activated NOMC sample, denoted as ANMC, was achieved by the thermally treatment of the as-prepared NOMC (1.0 g) with 2.0 g KOH at 800°C for 2 h under N_2 atmosphere.

2.2. Characterizations

The morphology of samples was observed using a scanning electron microscope (SEM, Quanta 250 FEG). The transmission electron microscopy (TEM) images were examined on a transmission electron microscope (FEI Tecnai G2 20). X-ray diffraction (XRD) analysis was performed by a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) as an X-ray source. Raman spectrum was obtained on a RenishawinVia Raman microscope. X-ray photoelectron spectra (XPS) were collected on a VG ESCALAB MK II X-ray photoelectron spectrometer with an excitation source of $\text{Mg K}\alpha$ (1253.6 eV). Nitrogen sorption measurements were carried out at -196°C on a micromeritics ASAP 2020 analyzer. Before adsorption, the samples were outgassed at 200°C for 6 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the total pore volume was calculated according to single point method at relative pressure (P/P_0) = 0.99. The pore size distributions were estimated according to the density functional theory (DFT) method.

2.3. Electrochemical tests

Electrochemical tests were performed on a CHI660E electrochemical workstation (Chenhua, Shanghai, China) at room temperature. In the three-electrode system, platinum sheet electrode, Ag/AgCl electrode and KOH aqueous solution (6 M) was respectively used as the counter electrode, the reference electrode and the electrolyte solution. The working electrode was prepared by coating the slurry, where the mass ratio of active material, acetylene black and polyvinylidene fluoride (PVDF) was 75:10:15, on a piece of Ni foam ($1 \times 1 \text{ cm}$) and then dried at 100°C

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