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Nitrogen-doped hierarchical porous carbon as an efficient electrode material for supercapacitors

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ABSTRACT

Nitrogen-doped hierarchical porous carbon (NHPC) was prepared by a combination of self-assembly and chemical activation and explored as an electrode materials for supercapacitors. Pore structure analysis showed that the pristine mesopores were basically preserved during activation, while the micropores were generated within the mesopore wall in large quantities. Cyclic voltammetry and galvanostatic charge/discharge measurements showed that the as-prepared NHPC exhibited a high specific capacitance of up to 257.8 F g^{-1}, excellent rate capability and good cycling durability in 6 M KOH electrolyte. The enhanced capacitive performance of NHPC can be attributed to the following three points: (1) the generated micropores play a most important role in the formation of electric double layer capacitance; (2) the hierarchical porous structure favors the fast diffusion of the electrolyte; (3) the nitrogen-containing functionalities generate extra pseudocapacitance and improve the wettability of the materials to the KOH electrolyte.

1. Introduction

Supercapacitors, which combine the advantages of both conventional dielectric capacitors and rechargeable batteries, have been considered to be the most promising approach to meeting the pressing requirements of energy storage due to their high power density, long cycling durability, fast charge/discharge rates, and low manufacturing costs [1–4]. According to the mechanism of energy storage, supercapacitors can be classified into electrical double-layer capacitors (EDLCs) and pseudo-capacitors. EDLCs store energy based on electrostatic attraction to generate charge accumulation in the electric double layer formed at the electrode/electrolyte interface, while pseudo-capacitors store energy by the fast, reversible redox reaction at the surface of the active electrode materials [5–7]. Therefore, the performance of supercapacitors is determined, to a large extent, by the chemical and physical properties of their electrode materials. Among various electrode materials available, carbonaceous materials are mostly investigated due to their advantages such as high surface area, good conductivity, electrochemical stability, and relatively low cost [8–12].

Recently, carbon materials with pseudocapacitive behavior have been reported [13–17]. Incorporating heteroatoms, such as nitrogen, into carbon framework can considerably enhance the specific capacitance, because the nitrogen-containing functional groups can induce the pseudocapacitive effect, improve the wettability of carbon with electrolyte, and increase the conductivity of carbon materials [4,18]. Nitrogen-doped carbon materials are usually prepared by two approaches. One is the post treatment of carbon materials with nitrogen-containing reagent (such as ammonia, amine, or urea) [19,20]. Another method is direct carbonization of nitrogen-containing carbon precursors (such as nitrogen-containing polymers, biomass, and ionic liquids) [21–23]. The latter is a promising approach and can realize a homogeneous incorporation of nitrogen into the carbon materials with a controlled chemistry. Li et al. prepared nitrogen-doped mesoporous carbon spheres (NMCS) by a polymerization-induced colloid aggregation method using melamine-formaldehyde resin as a carbon precursor [24]. The NMCS presented a high specific capacitance of 211 F g^{-1} at a discharge current density of 1 A g^{-1}. Chen et al. prepared spherical nitrogen-doped porous carbon using polyacrylamide as carbon precursor and calcium acetate as template [25]. At a current density of 0.5 A g^{-1}, the resultant specific capacitance is 194.7 F g^{-1}.

As known, an appropriate pore structure can also improve the electrochemical performance of carbon-based materials by providing high accessible pore surface, high pore volume, and proper

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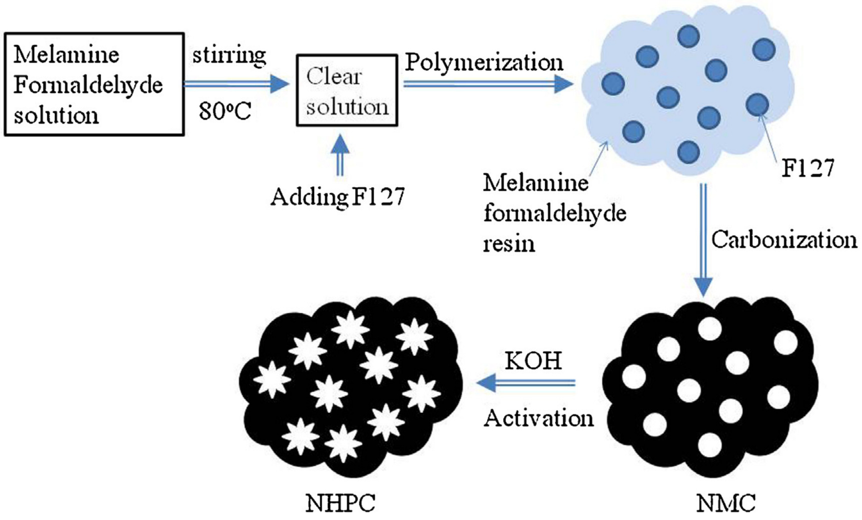

Fig. 1. Schematic illumination for preparing NHPC.

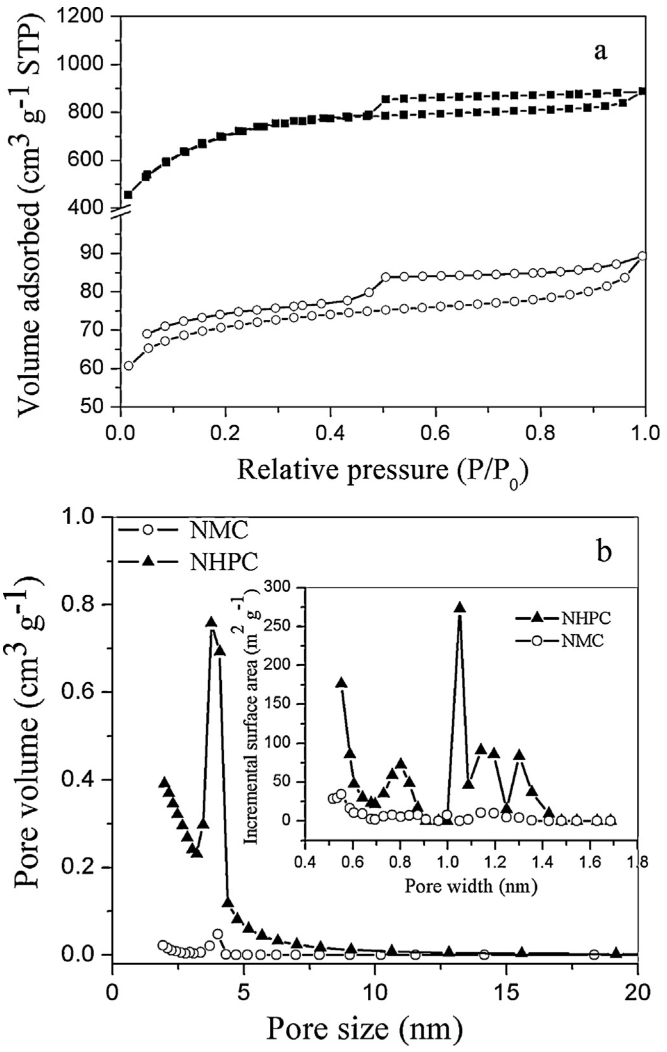

Fig. 2. Nitrogen adsorption-desorption isotherms (a) and pore width distribution curves of NMC and NHPC (the inset in (b) are micropore size distribution based on NLDFT model).

pore size distribution for fast electrolyte diffusion. Mesopores can decrease the diffusion resistance of electrolyte ions and micropores are more capable of increasing the electrical double-layer capacitance. Therefore, a nitrogen-doped carbon with more micropores, large mesopores, and appropriate micropore-mesopore architecture holds great potential for high performance supercapacitor application. In this work, a nitrogen-doped mesoporous carbon (NMC) was prepared by carbonization of the tri-block copolymer F127/melamine-formaldehyde resin composite. NMC was subsequently used as a raw material to prepare nitrogen-doped hierarchical porous carbon (NHPC), in which micropores were developed within the wall of mesopores by post activation. In this architecture, mesopores would provide fast diffusion channel for electrolyte and the diffusion distance from mesopores to micropores would be very short owing to the fact that micropores just locate within the mesopores wall. This unique pore structure plus nitrogen-containing functionalities enable NHPC to exhibit high capacitance, excellent rate capability and cycle durability in supercapacitors.

2. Experimental

2.1. Preparation of NHPC

Fig. 1 The preparation of NHPC is composed of two steps, namely, the preparation of NMC and further activation by KOH. The preparation strategy is shown in Fig. 1. In a typical synthesis, 20 g melamine was added to 40 ml of 37 wt% formaldehyde

Table 1
Surface area and pore-structure parameters of NMC and NHPC

Sample	S_{BET}[a] ($m^2 g^{-1}$)	S_{micro}[b] ($m^2 g^{-1}$)	S_{meso}[c] ($m^2 g^{-1}$)	V_T[d] ($cm^3 g^{-1}$)	V_{meso}[e] ($cm^3 g^{-1}$)
NMC	220.2	139.4	80.8	0.15	0.092
NHPC	2254.8	1668.1	586.7	1.37	0.57

[a] BET surface area;
[b] micropore surface area;
[c] mesopore surface area;
[d] total pore volume;
[e] mesopore volume.