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Full Length Article

# Synthesis of nitrogen-doped mesoporous carbon from polyaniline with an F127 template for high-performance supercapacitors

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ABSTRACT

N-doped mesoporous carbons (N-MCs) were synthesized via the oxypolymerization of aniline with a Pluronic F127 template, sintering at 850 °C in $N_2$ atmosphere, and activation in a KOH solution. The contrast experiments were carried out without the addition of F127 and the obtained sample was defined as N-Cs. The Brunaner-Emmett-Teller measurement, pore size distribution measurements, transmission electron microscopy, and X-ray photoelectron spectroscopy of N-MCs and N-Cs were performed. The specific areas of the N-MCs and N-Cs reached 721 and 394 $m^2\,g^{-1}$, respectively. The specific capacitances of the N-MCs and N-Cs were as high as 318 and 106 $F\,g^{-1}$ at 0.2 $A\,g^{-1}$. The cycle life of N-MCs at different current densities was above 96% after 5000 cycles of charging and discharging, indicating that the N-MCs had excellent cycle stability.

## 1. Introduction

Supercapacitors, prepared with large power density compared with that of traditional batteries and high energy density compared with that of electrostatic capacitors, have been paid much attention in the past decades [1]. Research studies about supercapacitors mainly focus on the electrode materials [2]. As a supercapacitor electrode material, carbon material displays considerable advantages, such as excellent conductivity, low cost, high theoretical specific surface area, and long cycle life [3–5]. However, the drawback of carbon material is the low capacitance value thereof. The synthesis of carbon-based composites and the introduction of heteroatoms into carbon frameworks are both the strategies to increase the capacitance. Carbon-based composites, including carbon-conducting polymer composites (for instance, carbon-polyaniline [6,7], carbon-polypyrrole [8,9]) and carbon-transition metal oxide composites (such as carbon-$NiO_x$ [10], carbon-$Co_3O_4$ [11], carbon-$MnO_2$ [12,13]), have poorer cycle life as opposed to pristine carbon materials. The introduction of heteroatoms not only enhances capacitance [14,15], but also maintains a long cycle life [16].

As a type of heteroatoms, nitrogen atoms have been introduced into carbon frameworks by different methods. For example, the post-treatment method is employed, by which carbon materials are treated with N-containing reagents (e.g. melamine, urea [17]) or atmosphere (e.g. ammonia gas [18]). Another method to introduce nitrogen atoms is the direct N-doping from N-containing precursors. Li et al. reported a doped activated carbon which was prepared from the carbonization of $H_2SO_4$-doped polyaniline at high temperature using a template-free method [19]. Conversely, a template method is promising in order to obtain a high specific area and tune the pore structure. Graphitic N-doped mesoporous carbon was fabricated by Vinu et al. through KIT-6 mesporous silica as a hard template [20]. Wang et al. [21] reported N-enriched mesoporous carbons by the self-assembly of phenolic resins and F127 through a soft-template method at an ammonia atmosphere.

In our study, N-doped mesoporous carbons (N-MCs) were synthesized by the oxypolymerization of aniline with F127 as a template, then sintering and activation on the $N_2$ atmosphere. The schematic of the synthesis procedure for N-MCs is shown in Fig. 1. Micelle structures are formed by the F127 molecules in solution due to their amphiphilic character [22]. The hydrophobic cavities of the F127 micelles are the source for mesopores. The self assembly occurs between the hydrophilic domain of the F127 micelles and the aniline monomers. Then the polyaniline/F127 composites were synthesized via the oxidation polymerization of the aniline

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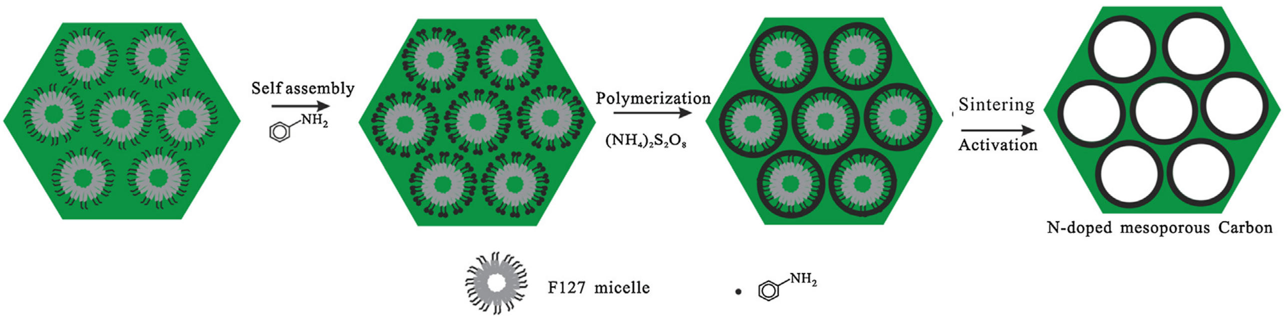

**Fig. 1.** Schematic of the synthesis procedure for N-MCs.

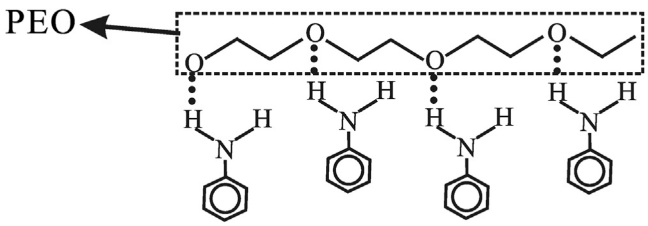

**Fig. 2.** Schematic for hydrogen bonding between oxygen atoms from PEO and hydrogen atoms from aniline monomers.

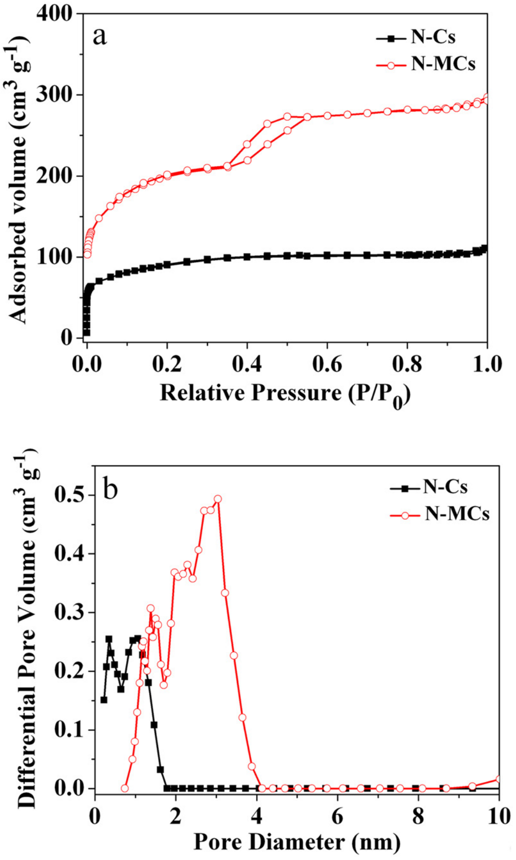

**Fig. 3.** (a) $N_2$ adsorption-desorption isotherms and (b) pore-size distribution curves of N-Cs and N-MCs.

monomers. At last, the sintering and activation were carried out for the removal of F127 and the formation of mesopores. The advantages of this approach are low-cost materials, simple operation and high efficiency. The obtained N-containing carbon materials possess a good application perspective as a supercapacitor electrode material.

## 2. Experimental

### 2.1. Synthesis of N-MCs

Firstly, a solution of 0.3 g of F127 dissolved in 100 mL of distilled water was added to a three-neck flask with continuous and slow stirring. Next, 5.53 mL of aniline monomers was added into the F127 solution slowly. The three-neck flask was placed into an ice bath. Then the polymerization reaction was performed by dripping 50 mL of $(NH_4)_2S_2O_8$ saturated solution into the three-neck flask slowly. Finally, the mixture was slowly stirred for 11.5 h. The generated green precipitates were washed repeatedly using anhydrous ethanol and distilled water, then dried in a vacuum oven at 75 °C for 36 h. Under the $N_2$ atmosphere, the obtained sample including the surfactant F127 was further sintered at 850 °C for 2 h with a ramp rate of 5 °C min$^{-1}$. Then, the obtained carbonized product was dispersed in the KOH solution with a weight ratio of KOH:carbonized product = 4:1, followed by heat at 300 °C for 30 min in a tube furnace. Then the samples were continuously heated to 700 °C for 40 min in the tube furnace under the $N_2$ atmosphere with a heating rate of 3 °C min$^{-1}$. The resulting samples were cooled down, repeatedly washed using 0.5 M HCl and distilled water. The pH value of the filtrate was detected until neutral. And the samples were dried in a vacuum oven at 80 °C for 24 h.

The obtained products were named N-MCs. For comparison purposes, the above process without adding F127 was repeated, by which the obtained samples were named N-Cs.

### 2.2. Characterization methods

The specific surface area and pore-size distributions (PSD) of N-MCs and N-Cs were measured via the Brunaner-Emmett-Teller (BET) method and the density functional theory, respectively, using a Quantachrome NOVA 4200 analyzer. Transmission electron microscopy (TEM, JEM-2010) was performed to observe the microstructure characteristic of the N-Cs and N-MCs. A PHI 5000 Versa Probe apparatus was adopted for the X-ray photoelectron spectroscopy (XPS) study.

### 2.3. Electrochemical measurements

The electrochemical measurements were performed in a three-electrode system. A platinum sheet was used as the auxiliary electrode, and Hg/HgO was used as the reference electrode. A nickel foam with a size of 1 cm × 3 cm, as the working electrode, was coated with a homogeneous slurry containing 95 wt% N-MCs or N-Ms and 5 wt% poly(tetrafluoethylene). Then the nickel foam was pressed under 15 MPa and dried at 80 °C for 6 h in a vacuum. The mass loading of each electrode was ~2 mg. The electroanalytical techniques including the cyclic voltamme-