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Design, preparation and performance of novel three-dimensional hierarchically porous carbon for supercapacitors

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ABSTRACT

A novel nitrogen-doped three-dimensional hierarchically porous carbon (N-3DHPC) has been designed and prepared by the carbonization of polyaniline (PANI) covered on the three-dimensional macroporous carbon (3DMC), followed by KOH activation to generate micropores and mesopores on the wall of macropores. The pore structure, morphology and surface physicochemical properties of the carbon samples are characterized by nitrogen adsorption/desorption isotherm, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and elemental analysis. The N-3DHPC inherits the morphology of the pristine 3DMC and processes a hierarchically porous structure with a high specific area of 1084.0 $m^2 g^{-1}$ and some nitrogen-doped species on the surface. The electrochemical behaviors of the N-3DHPC are characterized by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) test, electrochemical impedance spectroscopy (EIS) and cycle life measurement. The results show that the N-3DHPC obtains high specific capacitance of 308.4 $F g^{-1}$ at a current density of 1 $A g^{-1}$. Moreover, the N-3DHPC supercapacitor exhibits excellent rate performance, low resistance, high energy density of 10.7 $Wh kg^{-1}$ at the power density of 500 $W kg^{-1}$ and excellent cyclic stability with the specific capacitance retention of 96 % even after 10000 cycles, thus the N-3DHPC will be a promising electrode material for supercapacitors.

1. Introduction

Electrochemical capacitors, also called supercapacitors, have received increasingly growing attention as the alternative energy storage system, due to their greater power density and longer cycle life than batteries and higher energy density than conventional capacitors [1–2,3]. According to the charge storage mechanism, supercapacitors can be divided into two categories: electrical double layer capacitors (EDLCs) and pseudocapacitors [4]. Generally, the capacitance of EDLCs comes from the charge accumulation at the electrode/electrolyte interface [5], while the pseudocapacitance is generated from the reversible faradic redox reactions of electro-active species of the electrode materials [6]. The electrode materials for EDLCs are usually the carbon-based active materials, such as the activated, templated and carbide-derived carbons, carbon fabrics, fibres, nanotubes, onions, nano-horns, and so on [1].

Nowadays activated porous carbons become the most widely-used electrode materials, because of their easy accessibility, good conductivity, high specific surface area, excellent chemical stability and low cost [7,8]. However, the slow ion transport in small micropores of activated porous carbons limits their further effective utilization [9]. Recently, the macroporous carbons with three-dimensional interconnected structure have been recommended as promising electrode materials for supercapacitors owing to their distinctive structural features and good physicochemical properties, which can promote the electrolyte ion transport [10]. Nevertheless, the low specific capacitance still restricts their further applications owing to the limited available specific surface area. In addition, it is well known that suitable micropores and mesopores can provide a highly effective surface area for the charge storage, resulting in high double layer capacitance. Thus, the three-dimensional hierarchically porous carbons possessing well-defined macropores and interconnected micro- and/or meso-pores are very attractive as electrode materials of EDLCs, due to the combination of the excellent performance of mass transport from macropores and the

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advantages of high specific surface areas from micro/mesopores [11].

As well known, the introduction of heteroatoms into the carbon materials can greatly enhance their specific capacitance by inducing the pseudocapacitance and improving the wettability of carbon materials [12,13]. Nitrogen-doping has been regarded as the most feasible way to increase the specific capacitance of carbon materials while keeping their excellent cyclic stability [14]. PANI as a nitrogen-containing conducting polymer is often used to yield nitrogen-doped carbons after carbonization, due to its facile synthesis, good environmental stability and simple acid doping chemistry [15–18]. Another advantage of using PANI as the nitrogen-doped carbon precursor is that the morphology of the pristine carbon materials can be inherited [19].

In this work, the nitrogen-doped three-dimensional hierarchically porous carbon has been prepared through the carbonization of PANI covered on the surface of the three-dimensional macroporous carbon to inherit the morphology of the pristine 3DMC, followed by KOH activation to generate micropores and mesopores on the wall of macropores. Furthermore, the physicochemical properties and electrochemical performance of the obtained nitrogen-doped three-dimensional hierarchically porous carbon for supercapacitors are studied in detail.

2. Experimental

2.1. Preparation of 3DMC, 3DHPC, N-3DMC and N-3DHPC

The 3DMC was prepared by a self-assembly method. Firstly, the polymethylmethacrylate (PMMA) latex with the PMMA particle size of about 280 nm was similarly synthesized according to a modified method [20]. Then 20 g of PMMA latex was mixed with 0.5 g sucrose under stirring for 15 min, followed by the addition of 0.5 mL of 1 mol L^{-1} H_2SO_4. After further stirring for 15 min, the mixture was poured on glass and dried at 60 °C to get the PMMA/sucrose composite. Finally, the composite was placed in a tube furnace under Ar flowing, kept at 150 °C for 6 h and carbonized at 700 °C for 3 h. The heating rate is 0.5 °C min^{-1} below 450 °C and 5 °C min^{-1} above 450 °C. The PMMA was removed in the heating process to leave behind the 3DMC.

For the preparation of three-dimensional hierarchically porous carbon (3DHPC), 0.5 g 3DMC was impregnated in 20 mL of 0.1 g mL^{-1} KOH solution, followed by adding 4 ml of 25 % ethanol aqueous solution under stirring for 1 h. The mixture was dried at 60 °C for 12 h to evaporate the solvent and then heated at 800 °C for 1 h at the heating rate of 5 °C min^{-1} under Ar. The activated carbon product was washed with 1 mol L^{-1} HCl and water successively until the pH = 7. Finally, after drying at 60 °C overnight, the 3DHPC was obtained.

For the preparation of nitrogen-doped three-dimensional macroporous carbon (N-3DMC), 0.1 g of 3DMC and 0.2 g of sodium dodecyl sulfate were immersed in 15 mL of 1 mol L^{-1} H_2SO_4 under sonication for 5 min, followed by the addition of 0.2 mL of aniline under intensive stirring at 0 °C for 1 h. Then the above mixture was supplied with 0.46 g of ammonium persulfate solution drop by drop and kept stirring for 6 h. After washing with water and ethanol repeatedly, the resulting 3DMC/PANI was dried at 60 °C overnight and then carbonized at 600 °C for 2 h at the heating rate of 5 °C min^{-1} under Ar to get the N-3DMC.

N-3DHPC was obtained after the KOH activation. The preparation process of N-3DHPC is similar to that of 3DHPC, except replacing the 3DMC with N-3DMC. The preparation strategy is shown in Fig. 1.

2.2. Preparation of the electrodes

To prepare the electrode, the prepared sample, acetylene black and polyvinylidene fluoride binder were mixed at a mass ratio of 8: 1: 1 to get a slurry by adding N-methyl-2-pyrrolidone as a solvent. Then, the slurry was coated on the nickel foam substrate (radius = 0.5 cm) with a spatula, dried at 60 °C, and pressed at 16 MPa to confirm a good electronic contact between the nickel

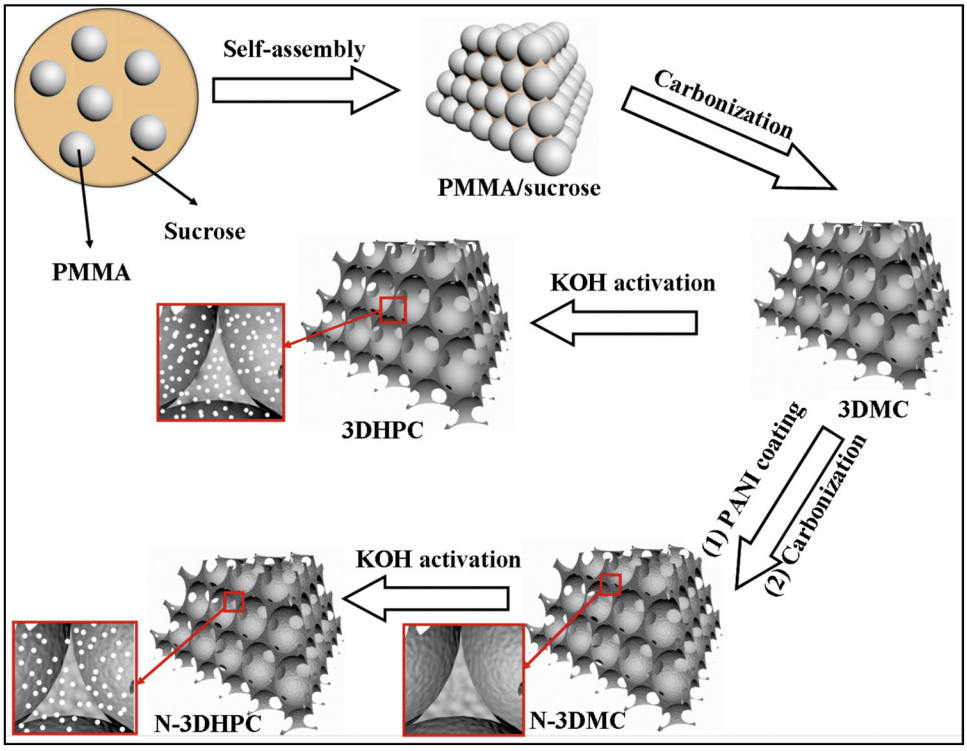

Fig. 1. Schematic illustration of preparation strategy.