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Nitrogen-doped hierarchical porous carbon materials prepared from meta-aminophenol formaldehyde resin for supercapacitor with high rate performance

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ABSTRACT

In this work, nitrogen-doped hierarchical porous carbon materials (NHPCs) are prepared by a two-step method combined of a hard template process and KOH-activation treatment. Low cost and large-scale commercial nano-SiO_2 are used as a hard template. The hierarchical porosity, structure and nitrogen-doped surface chemical properties are proved by a varies of means, such as scanning electron microscopy, transition electron microscopy, N_2 sorption, Raman spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. When the prepared NHPCs materials are used as the electrode materials for supercapacitors in KOH electrolyte, they exhibit very high specific capacitance, good power capability and excellent cyclic stability. NHPC-800 carbon shows a high capacitance of 114.0 F g^{-1} at the current density of 40 A g^{-1}, responding to a high energy and power densities of 4.0 Wh kg^{-1} and 10 000 W kg^{-1}, and a very short drain time of 1.4 s. The excellent capacitive performance may be due to the synergistic effect of the hierarchical porosity, high effective surface area and heteroatom doping, resulting in both electrochemical double layer and Faradaic capacitance contributions.

1. Introduction

As a novel type of energy storage devices, supercapacitor has lots of distinctive merits like high power density, good reversibility, high power density, and broad energy storage application prospects. Thus, this device has attracted tremendous interests and attentions [1–3]. Two types of supercapacitor could be defined based on the mechanism of energy storage. One is called electrochemical double layer capacitors (EDLCs) in which the energies are stored by the electrostatic charge uptake at the electrolyte/electrode interfacial regions; the other is pseudocapacitor which stores charges via fast reversible redox reactions of the electro-active species. EDLCs require electrode materials with tailored porosity adapted to the size of electrolyte ions, high effective specific surface area and suitable surface polarity, represented by multitudinous porous carbon materials. Pseudocapacitors could give high specific capacitance, but its electrode materials, mainly metal oxides (e.g. RuO_2 and NiO) [4–6], metal hydroxide (e.g. $Ni(OH)_2$ and $Co(OH)_2$) [7,8] and conductive polymers (e.g. polyaniline and polypyrrole) [9–12], is always of high cost, low conductivity, or poor cycle life. To date, porous carbon holds great promise as electrode material owing to their low price, excellent conductivity, tailored porosity, and quite stable physicochemical properties [13–18].

It is a well-known fact that the capacitive behavior of supercapacitors depends intimately on the physical and chemical properties of their electrode materials, so a great deal of efforts have been put into developing desired electrode materials for supercapacitors. Previous reports also showed using porous carbon as electrodes still suffered from several regrettable drawbacks, such as low power density and poor specific capacitance. Recently, hierarchical porous carbon materials have been proved to possess distinctive potential for high performance supercapacitor because the well-defined hierarchical porosity could effectively concert each pore level during the charge/discharge process [19–25]. That is the mesopores or macropore channels with larger pore size could serve as micro reservoirs of electrolyte and the expressway for ion-transport, resulting in a decreased diffusion distance and high power performance; and the micropores within the wall of the meso/macro pores supply high effective specific surface area

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for double layer capacitance to obtain high specific capacitance. Generally, some templates with a special nanostructure (e.g. porous silica oxide or metal oxide) [23,26–28] or molecular structure (e.g. triblock copolymer F127) [22,29] are used to construct hierarchical porosity. The preparation of these templates is complicated and time-consuming, and some have not been put into mass production. These deficiencies strongly restrict their commercial application potentials. Considering the large-scale commercial application of supercapcitor, the synthesis of hierarchical porous carbon materials using a mass-producible template with low cost is very attractive. On the other hand, suitable heteroatom-doping in carbon framework has been proved to improve the capacitive performance of the carbon electrode materials. The doped heteroatom groups could not only induce additional pseudo-capacitance via reversible redox reaction, but also improve the wettability between the electrodes and electrolytes (usually hydrophilic electrolytes), consequently improving the whole capacitive performance of the supercapacitor [11,18,30,31].

Nano silica (nano-SiO_2) has been mass produced, and is low cost and easy to obtain. It has been broadly applied in ceramic, textiles, catalysis, rubber modification, and so on. In this paper, the commercial nano-SiO_2 are used to assist in a synthesis of N-doped hierarchical porous carbon materials (NHPCs) as a template. As shown in Scheme 1, the NHPCs materials are prepared by a template/activation combination method. Firstly, the mesoporosity is fabricated via a template method by using a large-scale produced nano-SiO_2 as hard template. Afterward, micropores are created within the pore wall of mesopores by using a KOH-activation process. As a result, a typical hierarchical porosity is built of mesopores and micropores created by nano-SiO_2 and KOH respectively. Meanwhile, N-doping was achieved by using *m*-aminophenol as raw materials. The prepared NHPCs samples are applied as electrodes of supercapacitor, and show excellent capacitive performance with a very high specific capacitance up to 260.5 F g^{-1}, impressive rate capability of 44% ranged from 0.2 to 40 A g^{-1}, and good recycling charge/discharge performance.

2. Experimental

2.1. Material preparation

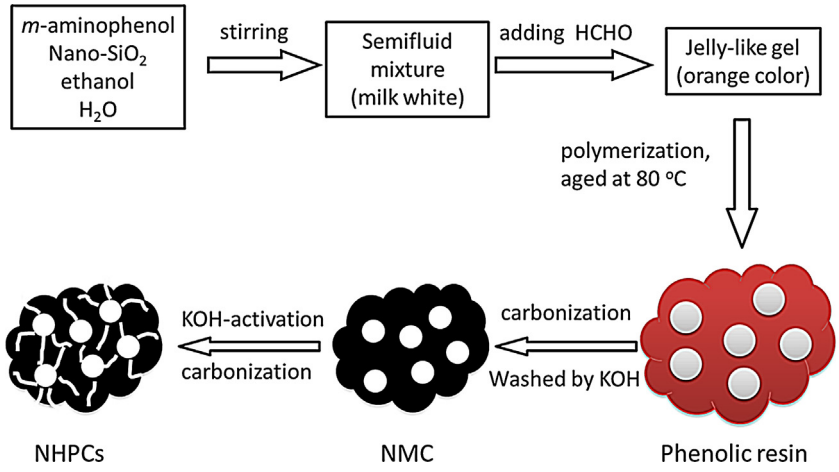
Nano-SiO_2 with a diameter averaged in 20 nm was purchased from Nanjing Tansail Advanced Materials Co., Ltd. All other chemicals were purchased from Shanghai Chemical Reagents Company and used directly without further purification. In a typical procedure, 1.8 g of *m*-aminophenol and 0.2 mL of concentrated HCl solution (37%) were dissolved into 12 mL 1:1 ethanol/H_2O mixture under magnetic strirring at room temperature. Afterward, 3 g of nano-SiO_2 are added into the above solution and violently stirred to form a semifluid mixture with a milk white color. Then, 2.4 g of formalin (37%) was dropped into the semifluid mixture under violent stir. The mixture quickly turned red and solidified within 5 min to give a jelly-like hydrogel with dark red color. The obtained resin hydrogels were further aged for 4 h at 80 °C, dried in air, and was pre-carbonized at 600 °C for 1 h under N_2 atmosphere. The N-doped mesoporous carbon materials (NMC) are liberated from the obtained residue by washing with KOH solution and water in sequence. The NMC materials were then mixed with the same weight of KOH, and were further activated in a tubular resistance furnace for 2 h under N_2 atmosphere to give the N-doped hierarchical porous carbon materials. For convenience, the final products are denoted as NHPC-600, NHPC-700, NHPC-800 and NHPC-900, where the number stands for the activation temperature.

2.2. Materials characterizations

The microscopic morphology of the prepared carbon materials were observed with a scanning electron microscope (SEM, Sirion 200 FEI Netherlands) and a transmission electron microscope (JEM2100, JEOL, Japan). The surface chemical properties were determined by X-ray photoelectron spectroscopy (XPS, Escalab 250, USA). X-ray diffraction (XRD) patterns were conducted by using a Brucker D8 Advance diffractionwith Cu Karadiation. Raman spectra were given by a LabRAM HR800 from JY Horiba. The specific surface area and pore size distributions (PSDs) of the hierarchical carbon materials were measured by Nitrogen sorption test using a ASAP 2020 equipment (Micrometitics USA). Brunaner-Emmett-Teller (BET) surface area (S_{BET}) was calculated using the N_2 adsorption isotherm data within the relative pressure of 0.05-0.25. Total pore volume (V_T) was obtained at $p/p^0 = 0.995$. Microspore volume (V_{micro}) was determined by t-plot method. Mesopore volume (V_{meso}) was calculated by subtracting the micropore volume from the total pore volume. PSDs were determined by applying the nonlocal density functional theory (NLDFT) model on the adsorption isotherms and assuming a slit-shape pore.

2.3. Electrochemical measurement

The working electrodes are prepared by mixing the investigated carbon materials with 5 wt.% of polytetrafluoroethylene (PTFE)



Scheme 1. Illustration of the preparation of N-doped hierarchical porous carbon materials.