Research paper

Hierarchical porous carbon materials derived from petroleum pitch for high-performance supercapacitors

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A B S T R A C T

In this work, a honeycomb-like carbon material derived from petroleum pitch was synthesized by a simple one-step carbonization/activation method using silica nanospheres as the hard templates. The obtained hierarchical porous carbon materials (HPCs) with a large specific surface area and uniform macropore distribution provide abundant active sites and sufficient ion migration channels. When used as an electrode material for supercapacitors, the HPCs exhibit a high specific capacitance of 341.0 F g^{-1} at 1 A g^{-1}, excellent rate capability with a capacitance retention of 55.6% at 50 A g^{-1} (189.5 F g^{-1}), and outstanding cycling performance in the three-electrode system.

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1. Introduction

Porous carbon materials are the most widely used electrode materials in supercapacitors due to their large surface area, wide pore size distribution, stable physical and chemical properties, and high conductivity. As a by-product of coking and a low-cost carbon sources, petroleum pitch has a high carbon content. Many kinds of carbon materials can be prepared from pitch, such as hollow carbon spheres [1], carbon fibers [2], carbon foam [3], graphene [4], activated carbon [5], and carbon/carbon composites [6].

As electrode materials for supercapacitors, the specific surface area and pore size distribution of carbons play crucial roles in the electrochemical performances. Large specific surface area provides more ion storage sites for the formation of electrochemical double layer (EDL). Therefore, many researchers focused on how to obtain carbon materials with the larger specific surface area and pore structure. For example, Wang [7] prepared activated carbons with different specific surface area by using KOH (1851 m^2 g^{-1}) and ZnCl$_2$ (1471 m^2 g^{-1}) as activators. The former with a larger specific surface area had twice the specific capacitance of the latter. Moreover, even micro-pores smaller than 1 nm can also provide EDL. Chmiola et al. [8] made a conclusion that, when the pore size is less than 1 nm, the hydrated cations are squeezed, and the twisted hydrated cations gradually enter the interior of the pore to form EDL. Huang et al. [9] used the DFT method to construct the theoretical model of EDL with pore less than 2 nm. Due

to the smaller pore size, the hydrated cations can only be aligned in a straight line, and this double layer was called the linear double layer. Therefore, the influence of the pore size and specific surface area on the capacitance value is very important.

In order to regulate the pore structure of carbon materials, researchers have tried many methods. Bhattacharjya [10] have synthesized activated carbon from cow dung by using KOH as activating agent. The results showed that the specific surface area of activated carbon could reach 1984 m^2 g^{-1} and V$_{micro}$ was 0.62 cm^3 g^{-1}, however, the specific capacitance was only 125 F g^{-1} at 0.3 A g^{-1}, which indicated that the porosity utilization rate is low. You [11] used commercial sponge as a supporter and graphene oxide-dispersed pristine CNTs as raw material to prepare porous 3D carbon foam. The specific surface area was up to 1284 m^2 g^{-1}, and the pore size range was less than 5 nm. Although the capacitance was large under small current, the capacitance decreased sharply at large current, and the specific capacitance was only 111 F g^{-1} at a high current density of 20 A g^{-1}. Zhang [12] used MgO as a template and coal tar pitch as precursor to prepare the porous carbon with a specific surface area of 864 m^2 g^{-1}, and its rate performance was only 100 F g^{-1} at 30 A g^{-1}. The poor rate performance is possibly related to the low conductivity, and the pore structure can't be maintained for a long time [13]. Considering the increasing demand for energy and the importance of environmental protection, developing new technologies to effectively use asphalt as a carbon source is one of the most widely concerned topic.

Herein, hierarchical porous carbon materials (HPCs) with a honeycomb-like network structure was synthesized via a simple

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template-assisted method by using pitch and SiO_2 and followed a one-step carbonization/activation treatment by using KOH as an activator. The HPCs show a hierarchical pore structure with high specific surface area (1952.6 $m^2 g^{-1}$), hierarchical pore distribution, and the capacity maintained 289.0 F g^{-1} after 10,000 cycles at 10 A g^{-1}. These merits endow the HPCs with high energy storage capability, excellent rate performance, and good cycle performance as the electrode materials for supercapacitors.

2. Experimental section

2.1. Sample preparation

The schematic for the preparation procedure of the HPCs is illustrated in Fig. 1. A petroleum pitch from Kalamay (Xinjiang, China) was used as the carbon precursor. Silica nanospheres (see Fig. S1 in the Supporting Information) with an average diameter of about 200–230 nm were served as the hard template obtained by a slightly modified Stöber process [14], the initial experimental results show that the optimized mass ratio of petroleum pitch to SiO_2 is 1:2 (for details, see Fig. S2). In a typical synthesis, 1 g of petroleum pitch, 2 g of SiO_2 and 3 g of KOH were added into 30 mL of tetrahydrofuran (THF). The solution was subjected to ultrasonication for 30 min and then a strong magnetic stirring for 6 h. Subsequently, the mixture was dried at 60 °C for 6 h to get rid of the solvent, and then the mixture was transferred to the nickel crucible. The nickel crucible was placed at the constant-temperature zone of the tube furnace, which was heated to 500 °C with a heating rate of 2 °C min^{-1} and then heated to 700 °C for 2 h with a heating rate of 5 °C min^{-1} under constant nitrogen flow rate of 30 sccm. After the reaction, the furnace was cooling down to room temperature before the samples were moved out from the tube furnace. The derived products were immersed in 20% HF solution to remove the SiO_2 template, followed by washing repeatedly with deionized water and ethanol until neutral and drying in oven at 60 °C for overnight to obtain the sample named as $HPC_{1:2:3}$. In addition to the mass ratio of petroleum pitch to SiO_2 and KOH was 1:2:3, the mass ratio of 1:2:1, 1:2:2 and 1:2:4 were investigated using the same procedure and the obtained samples were designated as $HPC_{1:2:1}$, $HPC_{1:2:2}$, $HPC_{1:2:4}$, respectively. The effect of the amount of KOH on the morphology, porosity structure and electrochemical properties of the obtained samples were provided within the Supporting Information (see Fig. S3–5 and Table S1). For comparison, petroleum pitch direct carbonization or activated using KOH (petroleum pitch: KOH = 1:3) was also investigated under the same calcining procedure without adding SiO_2, and the obtained samples were nominated as AC and AC_{KOH}, respectively.

2.2. Sample characterization

The morphology and microstructure of the samples were characterized by X-ray diffraction (XRD, D8, Bruker, Germany) in the 2θ range from 10° to 80°, Raman spectroscopy (SENTERRA, Bruker, Germany), field-emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). The surface areas and pore size distribution of materials were measured using the N_2 adsorption–desorption isotherms (ASAP 2020 Analyzer, Micromeritics, USA). The specific surface area and the pore size distribution were calculated by the BET method and DFT methods, respectively. The macropore structure was investigated using mercury intrusion porosimetry (AutoPore IV 9500 Pore Size Analyzer, Micromeritics, USA).

2.3. Electrochemical measurements

The electrodes were made by mixing active material (80.0 wt%), carbon black (10.0 wt%), polytetrafluoroethylene (PTFE10.0 wt%), and then the slurry was pressed onto the nickel foam current collectors at 8 MPa (see Fig. S6). Finally, the working electrodes drying at 60 °C for 12 h for test. A three-electrode system at a potential window of −1 to 0 V was assembled using the as-prepared samples as working electrode, Pt foil as counter electrode, mercuric oxide electrode as reference electrodes. In a two-electrode system, the capacitor was assembled face-to-face into the holder with a separator, and 6 M KOH solution as electrolyte. The electrochemical performances were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI-660E, Shanghai, Chenhua, China) at room temperature.
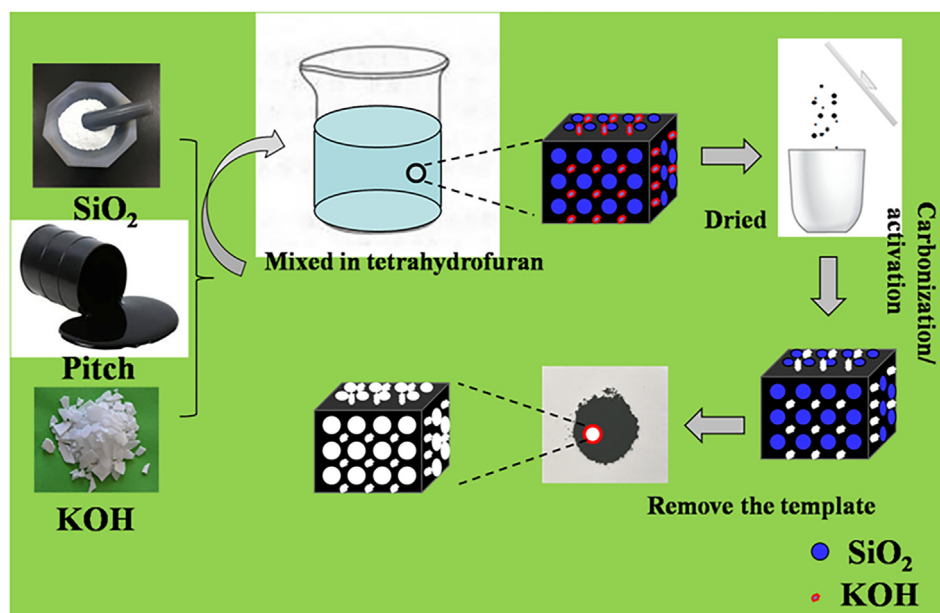

Fig. 1. Sketch for preparation of hierarchical porous carbon materials.