



One-pot synthesis of interconnected porous carbon derived from coal tar pitch and cellulose for high-performance supercapacitors

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ABSTRACT

Interconnected porous carbons were successfully synthesized via a facile one-step method from abundant and low-cost coal tar pitch (CTP) and microcrystalline cellulose (MCC) for high-performance supercapacitors. The as-prepared IPCs possess unique interconnected porous networks and large surface area (up to $3305 \text{ m}^2 \text{ g}^{-1}$), which could mainly be ascribed to the combined effects of template effect from MCC and adequate KOH activation during pyrolysis. MCC can be converted into crumbed graphene sheets and embedded into the derived carbon block during activation, thereby improving the electron transfer pathway. IPC_{2-0.2-8} with exceptionally large surface area, well-developed porosity and 3D interconnected networks exhibits high capacitance of 308 F g^{-1} at a current density of 1 A g^{-1} , good capacitance retention of 75% even at a high current density of 20 A g^{-1} , and excellent cycling stability in 6 M KOH electrolyte. The symmetric supercapacitor can deliver an energy density of 21.9 Wh kg^{-1} at a high power density of 461.6 W kg^{-1} in 1 M Na_2SO_4 electrolyte. Easy synthesis, low cost, and excellent electrochemical performance make IPCs hold great promise for potential applications in energy-related technological fields.

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1. Introduction

Supercapacitors, one of the most promising energy storage devices, have been highly valued due to their fast charge–discharge rate, high power density, and ultra-long cycling life in recent years [1,2]. Electrode materials, as a key factor affecting its performance, have been widely studied [3,4]. Among various electrode materials, porous activated carbons (ACs) with large specific surface area (SSA), tunable pore size, and high chemical stability are highly desired as advanced electrode materials for supercapacitors [5,6]. A high-performance supercapacitor electrode should have a reasonable pore structure and high SSA to accommodate a large number of electrolyte ions at the electrode/electrolyte interface and thus promote the formation of electrical double layer [7,8]. In general, macro/mesopores facilitate rapid ion transport by serving as ion-buffering reservoirs and ion transport pathways, and micropores enhance the formation of an electrical double layer [9]. However, not all of the BET surface area (S_{BET}) is electrochemically accessible. Micropores smaller than 0.5 nm are typically considered

inaccessible to electrolyte ions [8]. Most ACs produced commercially are micropores (<2 nm) [10,11] and suffer from kinetic limitations as electrodes. In addition, poor rate performance is usually observed because of high ion-transport resistance, poor electronic conductivity, and insufficient ionic diffusion within the tortuous micropores [7,9]. The capacitance of ACs typically decreases significantly at a high current density, particularly in cases wherein micropores dominate [12]. For most porous carbons, dead pores constitute a large proportion in the overall porosity, which is highly disadvantageous for ion transport or diffusion [13,14]. Therefore, increasing the ion accessible area of ACs while maintaining the charge transport and ion diffusion pathway are crucial to achieve high capacitance at ultrafast charging rates.

Template carbonization is an effective method for precisely controlling the structure of porous carbon at the nanometer level [15,16]. However, most templates are expensive and their post-synthesis removal to produce a carbon replica requires additional processing steps that are usually time consuming and harmful for the environment, particularly with the use of hydrofluoric acid [12,17]. These factors severely hinder the practical utilization of templates despite their usefulness in fundamental research [18]. Hence, a facile and economical method must be developed to obtain porous carbon with high SSA and an appropriate structure

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for practical application of porous carbons in the energy storage field.

Coal tar pitch (CTP), a by-product of the coking process of the coal industry (more than 55 wt%), and contains mainly carbonaceous polycyclic aromatic hydrocarbons. It is cheap, abundant, thermoplastic and has a high carbon yield [19,20]. Therefore, CTP is a promising precursor for fabricating low-cost porous carbon materials. Natural materials with meticulous design and ingenious hierarchical porous structure have been widely employed in newly developed energy storage materials. Biomasses with different natural structures have been used as biotemplates or precursors for design of materials for energy conversion, storage, and capture of carbon dioxide [21,22]. Cellulose is the most abundant renewable polymer worldwide and is well-known as the main component of plants which supplies nutrients, including water, ions, and small molecules [23,24].

Here we have designed three-dimensional interconnected porous carbons (IPCs) via a facile one-step method. CTP and KOH were employed as carbon source and activating agent, respectively. Cellulose was used as template to develop macropores. These well-developed macropores provide a large number of active sites/alleyways for the activation agent during the subsequent KOH activation step, cause a more homogeneous diffusion of KOH and produce more effective micro- and mesopores. The obtained IPC_{2-0.2-8} has a large S_{BET} of 3305 m² g⁻¹ and excellent electrochemical properties, such as high specific capacity (308 F g⁻¹ at current density of 1 A g⁻¹) and extraordinary cycling stability (101.7% capacitance retention over 20000 cycles). Given the cheap and abundant raw materials, excellent electrochemical performance and high yield (29.8 wt%) of IPC_{2-0.2-8}, this novel electrode material is extremely promising for the development of advanced energy storage devices.

2. Experimental

2.1. Synthesis of IPCs

A CTP with a softening point of 110 °C was obtained from Hongfeng Coking plant (Changzhi, Shanxi, China) and used as carbon precursor. The proximate and ultimate analyses are shown in Table S1. All chemical were of analytical grade and used without further purification. CTP was firstly pulverized below 100 μm. Then, CTP powders, MCC and KOH were mixed and ground in a mortar for 30 min in the solid state. Subsequently, the homogenized mixture was placed in a tubular furnace and heated to 800 °C under nitrogen atmosphere at a heating rate of 5 °C min⁻¹ for 2 h. The sample was cooled to room temperature, washed with 1 M HCl solution and deionized water thoroughly to remove the ions, and dried at 80 °C for 4 h. The obtained product was denoted as IPC_{x-y-z}, where subscripts x, y, and z represent the masses of CTP, MCC, and KOH, respectively. A series of temperatures (500, 600, 900 °C) were examined to investigate the structural evolution of IPC_{2-0.2-8}. Other ratios (3:1 and 5:1) of KOH to coal tar pitch were also performed. For comparison, CTP was directly activated by KOH, and the derived product was named ACTP. MCC and KOH with a mass ratio of 1:4 were pyrolyzed at 500 °C, 600 °C, and 800 °C, and used to determine the role of MCC during activation; the derived products were termed as AMCC-500, AMCC-600, and AMCC-800, respectively.

2.2. Characterization

The microstructure and morphology of IPCs were analyzed by field-emission scanning electron microscopy (FESEM, JEOL JSM-7001F). Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 F20S-Twin instrument. Nitrogen

adsorption–desorption isotherms were determined by nitrogen physisorption isotherms on a Micromeritics ASAP 2020 analyzer at 77 K. Before measurement, the sample was degassed at 300 °C for 6 h. S_{BET} was calculated from the Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption. The pore size distribution in the micro- and mesopore regions was investigated through DFT method using the adsorption data based on a slit pore model. Total pore volume (V_t) was estimated from the adsorbed amount at a relative pressure $P/P_0 = 0.99$. Micropore volume (V_{mic}) and specific surface area of micropores (S_{mic}) were estimated by t-plot method. The average pore size (D_{ap}) of porous carbon was determined by the equation $D_{\text{ap}} = 4V_t/S_{\text{BET}}$. The crystalline state of the as-prepared IPC_{2-0.2-8} was analyzed using X-ray diffractometer (XRD, DX 2700B) with Cu K α radiation ($\lambda = 0.1514178$ nm). Raman spectra were recorded on Horiba Jobin-Yvon HR800 Raman spectrometer with a laser wavelength of 532 nm. Thermogravimetric (TG) analysis was performed on a thermogravimetric analyzer (Netzsch STA 409C) under flowing (60 ml min⁻¹) nitrogen (99.99%) with a heating rate of 5 °C min⁻¹. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with an Al K α radiation source was used to analyze the chemical bonding state and composition of the samples. Fourier transformation infrared spectroscopy (FTIR) spectra in the region from 400 to 4000 cm⁻¹ were recorded on a BRUKER TENSOR 27 spectrometer by using KBr pellet technique.

The electrical conductivity of IPC_{2-0.2-8} was tested using the previous reported method [25]. Typically, the products were mixed with 2 wt% polytetrafluoroethylene (PTFE) as a binder, dispersed in ethanol and followed by homogenized in an agate mortar until the solvent was almost completely volatilized. Then they were rolled into ~60 μm thickness sheets. After pressed at 10 MPa for 10 s, the obtained sheet was heated at 80 °C for 2 h and cut into 3 cm × 1 cm to obtain resistance. The resistance (R) was measured with a UT30C digital multimeter, and the thickness of activated material was estimated by using an optimal microscope (BK6000, China). The conductivity of the sheet was calculated using the formula $\lambda = L/(R \times W \times d)$, where λ is the electrical conductivity of the sample; and L , W and d is the length, width and thickness of the sheet in cm, respectively.

2.3. Electrochemical measurements

Working electrodes were fabricated by mixing 80 wt% electroactive materials, 10 wt% carbon black, and 10 wt% PTFE in ethanol (the mass loading of the active materials in each working electrode was ~4 mg cm⁻²). The mixture was coated onto a nickel foam current collector and then pressed at 10 MPa for 30 s. Finally the molded electrodes were dried in a vacuum oven at 60 °C for 2 h. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) tests and electrochemical impedance spectroscopy (EIS) were carried out on a CHI 660D electrochemical workstation. The electrochemical performance of the electrodes was first determined in 6 M KOH electrolyte by using a three-electrode system, where platinum foil and Hg/HgO electrode were used as counter and reference electrodes, respectively. CV test of the three-electrode system was conducted between -1 and 0 V. Galvanostatic charge–discharge test was performed in the same potential range at current densities from 0.5 A g⁻¹ to 20 A g⁻¹. EIS measurements were conducted at an amplitude of 5 mV over a frequency range of 10⁻²–10⁻⁵ Hz. The test of cycle life was performed using both CHI 660D electrochemical workstation and a battery test system (LAND CT2001A model, Wuhan LAND Electronics. Ltd.). The symmetric two-electrode supercapacitors were assembled using two single electrodes mentioned above with exactly the same mass, and were conducted in 6 M KOH (0–1 V) and 1 M Na₂SO₄ aqueous electrolytes (0–1.8 V), respectively.

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