



Short communication

Oxygen-rich and hierarchical porous carbons prepared from coal based humic acid for supercapacitor electrodes



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ABSTRACT

Hierarchical porous carbons (HPCs) were prepared from coal-derived humic acid (HA) through a facile KOH activation method and used as electrode materials for supercapacitors. The obtained HPCs possess hierarchical porous structure consisting of micropores less than 1.8 nm, mesopores mainly falling in the narrow range of 3.5–4.5 nm and macropores, together with high oxygen content (>24.0 wt.%). And the HPC based electrodes deliver high volumetric capacitances with a maximum value of 201 F cm⁻³ at a current density of 5 A g⁻¹, as well as high rate capabilities and excellent cycling stabilities.

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1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, have attracted significant attention due to their excellent properties [1]. Porous carbons (PCs) are regarded as the most promising supercapacitor electrode materials, because of their high surface area, electrical conductivity, chemical stability and low cost [2,3]. It is well known that the actual energy storage occurs predominately in the smaller micropores of the PCs, and narrow pore size distribution (PSD) can lead to an increase in capacitance and stored energy density [2]. The mesopores can decrease ion-transport resistance, and the macropores shorten the ion diffusion distance [4,5]. Moreover, introducing of oxygen functional groups to the PC surface is an effective strategy to improve the wettability of electrode to aqueous electrolyte, which can also induce additional pseudocapacitance to the overall capacitance [1,3]. Considering the facts described above, as electrode materials for supercapacitors, it is of great significance to design and produce PCs with a combination of hierarchical porosity, centralized PSD and high oxygen content.

Up to now, template techniques have been widely employed to synthesize PCs with well-defined pore characteristics. However, these procedures are complicated, time-consuming and high cost, which restrict their application to mass-production [6,7]. Furthermore, the incorporation of oxygen groups into the carbon matrix is often achieved through oxidative modifications, most of which are unstable and may lead to

poor electrochemical performance [8]. In addition, the volumetric capacitance is also a crucial technology parameter in supercapacitor applications, which is calculated by multiplying the gravimetric capacitance with the corresponding packing density. However, the well-developed porosity often results in low mass density, and how to balance the porosity and mass density of porous carbons still remains challenging [9,10].

The present work developed a simple and low cost method to prepare hierarchical porous carbons (HPCs) from coal-derived humic acid (HA) through mild KOH activation. The as-obtained HPCs possess moderate surface area, centralized pore size distribution and high oxygen content, delivering high volumetric capacitance, excellent rate capability and cycling performance as supercapacitor electrodes.

2. Experiment

Coal based HA (Xinjiang Shuanglong Co., Ltd) was treated with a mixture of hydrochloric acid and hydrofluoric acid to reduce the ash content to below 1 wt.%. Other deashing methods that are based on cationic surfactant or NH₄OH can also be conducted, which avoid the use of hydrofluoric acid. The elemental analysis of the resultant pure HA was listed in Table 1. Potassium hydroxide and pure HA were mixed with low KOH/HA mass ratios (0.50, 0.75 and 1), followed by adding some deionized water and stirring overnight. The compounds were activated in a tube furnace under a N₂ atmosphere at 700 °C for 1 h with a heating rate of 5 °C min⁻¹. After cooling naturally to room temperature, the activated materials were washed with diluted hydrochloric acid, rinsed with deionized water until pH = 7, and dried at 110 °C for 2 h. The obtained materials were referred as HPC1, HPC2

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Table 1
Elemental analysis of the pure HA.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	O ^a (wt.%)
HA	66.3	3.3	1.4	29.0

^a Oxygen determined by difference.

and HPC3 correspondingly. For comparison, PC₀ was also prepared following the same procedure but without the addition of KOH. It should be noted that the KOH/HA mass ratios are lower compared to those (2–5) in conventional preparation methods for porous carbons as supercapacitor electrodes, resulting in lower consumption of diluted hydrochloric acid for washing the activated materials correspondingly.

N₂ adsorption/desorption isotherms were measured using a Quantachrome Autosorb-iQ-MP analyzer at 77 K. The specific surface areas were calculated by a Brunauer–Emmett–Teller (BET) method. The total pore volumes were estimated from the single point adsorption ($P/P_0 = 0.99$) and pore size distributions (PSD) were derived from density functional theory (DFT). The morphology of the sample was observed by a scanning electron microscope (SEM, JSM-6390LV, JEOL) and transmission electron microscopy (TEM, JEM-2100, JEOL). X-ray photoelectron spectroscopy (XPS, Axis Ultra) was used to investigate the surface chemical composition.

The supercapacitor electrodes were made with 85 wt.% HPCs, 5 wt.% polytetrafluoroethylene and 10 wt.% acetylene black. A two-electrode cell was used for electrochemical tests with a 3 M KOH solution as the electrolyte. Galvanostatic charge/discharge (GC) and cyclic voltammetry

(CV) were carried out by an electrochemical analyzer system (SCTS, Arbin). The gravimetric capacitances ($F\ g^{-1}$) were calculated from the charge–discharge curves according to $C_g = I\Delta t/m\Delta V$, where I , Δt , m and ΔV are the discharge current (A), discharge time (s), the mass (g) of the active materials in the signal electrode and the voltage drop upon discharge, respectively. Then, the gravimetric capacitance was converted to volumetric capacitance ($F\ cm^{-3}$) by $C_v = \rho C_g$, where ρ is the packing density of single electrode.

3. Results and discussion

The structure of coal-derived HA is dominated by aromatic moieties containing a wide variety of oxygen-containing functional groups such as carboxylic, phenolic hydroxyl and carbonyl groups [11]. These functional groups are distributed uniformly in the HA, which facilitate the homogeneous KOH activation, and the formation of massive pores with similar diameter. As shown in Fig. 1a, many interconnected macropores with uniform pore size were formed on the surfaces of HPC1. The TEM image (Fig. 1b) reveals that there are lots of mesoporous and microporous texture in HPC1.

Fig. 1c shows N₂ adsorption/desorption isotherms of the HPC samples. All isotherms exhibit combined characteristics of type I/IV curve, steep uptakes below $P/P_0 = 0.01$ suggest that the samples possess some micropores, the obvious hysteresis loops at the P/P_0 from 0.4 to 0.9 indicate the existence of a large percentage of mesopores, and the almost vertical tails at a relative pressure near to 1.0 denote the presence of macroporosity [12,13]. When the HPCs were used as electrode materials for supercapacitors, these macropores serving as

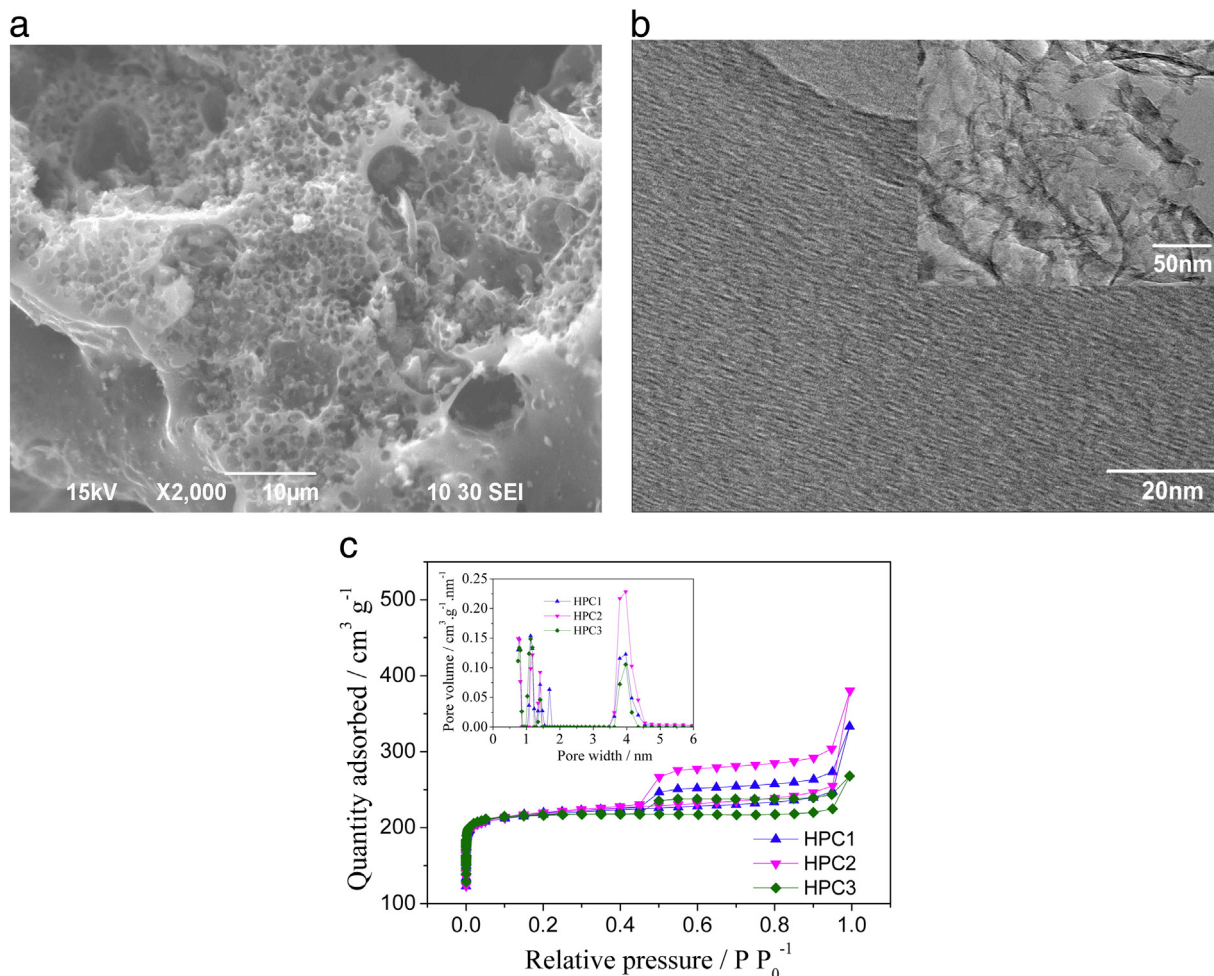


Fig. 1. a. SEM image of HPC1 sample. b. TEM image of HPC1 sample. c. N₂ adsorption–desorption isotherms of HPC samples. The inset is the PSD curves.

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