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Promising porous carbons derived from lotus seedpods with outstanding supercapacitance performance

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ABSTRACT

Biomass-derived porous carbons are widely regarded as one of the most promising electrode materials for supercapacitors owing to their natural abundance and low-cost. Herein, we present a facile approach to synthesize promising porous carbons via a two-step fabrication process using lotus seedpods (LS) as the biomass precursor. Firstly, the LS is hydrothermally treated in a KOH aqueous solution. After filtration and drying, the hydrothermal product is directly subjected to simultaneous pyrolysis and activation, giving LS-derived porous carbon materials. The morphology, structure and textural properties of the carbon materials are investigated by scanning electron microscopy, transmission electron microscopy, and N_2 sorption isotherms. The porous carbon prepared under optimal conditions exhibits a relatively high BET surface area of 1813 $m^2 g^{-1}$ and an average pore size of 3.30 nm. Such porous carbon shows outstanding capacitive performance (402 $F g^{-1}$ at 0.5 $A g^{-1}$), good rate capability and excellent cycling stability (95.4% of capacitance retention after 10,000 cycles) in 6 M KOH electrolyte. More importantly, the as-assembled symmetric supercapacitor delivers a high energy density of 12.5 $Wh kg^{-1}$ at power density of 260 $W kg^{-1}$.

1. Introduction

The development of sustainable and renewable power sources is of great importance to world development because of the rapidly escalating energy crisis and the worsening environmental pollution. Supercapacitors are currently being considered internationally as one of the most promising green energy storage devices due to their high power density, ultra-fast charge and discharge rate, long cycling life and safe operation, which are expected to play a dominant role in future energy solutions [1,2]. Based on the electrode design, supercapacitors can be grouped into two main categories including electric double-layer capacitors (EDLCs) with carbon electrodes and pseudocapacitors with metal oxide or conducting polymer electrodes [3–6]. In principle, EDLCs rely on charge separation at electrode/electrolyte interfaces to store energy, while capacitance generation in pseudocapacitors is based on the Faradaic charge transfer reactions between the electrolyte and electroactive species on the electrode surface [7,8]. Although pseudocapacitors possess a relatively high specific capacitance (200–1200 $F g^{-1}$), the outstanding cycle stability of EDLCs makes them used in nearly 100% of commercial supercapacitors [9]. In this regard, EDLCs show great promise from the price point of view as compared to pseudocapacitors due to their stability as well as the low-cost of carbon materials [10–12].

Activated carbons (ACs) are the most widely used electrode materials for EDLCs because of their high specific surface area, relatively good electrical conductivity, and high chemical stability [13,14]. In general, ACs for EDLC electrodes are prepared by a two-step process, in which carbon precursors are pyrolyzed at temperature in the range 600–900 °C in an inert atmosphere, followed by physical and/or chemical activation at elevated temperature [15]. Although ACs possess large specific surface area (>1000 $m^2 g^{-1}$) and pore volume (> 0.5 $cm^3 g^{-1}$), only about 10–20% of the "theoretical" capacitance was observed due to the presence of electrochemically inaccessible micropores [16–18]. On the other hand, very large pores also reduce the capacitance as often noticed in carbon activation studies [19]. That is to say, the capacitive performance is only slightly

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correlated with the specific surface area of ACs [20], being also influenced by other factors such as the pore size, electrical conductivity, and surface functionalities [21,22]. Among them, a suitable pore size of the ACs is critical to ease the mass transfer of electrolytes within the pores. It is reported that a pore size distribution of 2–5 nm, which is larger than the size of two solvated ions, has been considered as an effective way to improve energy density and power capability [23]. In addition, a relatively narrow pore size distribution is favored since it can reduce ion scattering and consequently enhance the electrode kinetics. Recently, tremendous research efforts have been devoted to the synthesis of ACs with tailored pore size and distribution, electrical conductivity, and surface functionalities [22].

Considering the potential scale of EDLCs applications, the production of ACs starting from renewable biomass materials is of significant importance in lowering the fabrication costs of EDLCs. Up to now, however, only a small portion of biomass materials such as bamboo [24], soybeans [25], coconut shell [9], auricularia [26], celtuce leaf [27], and eulaliopsis binata [28], etc. are used as carbon precursors for the production of ACs for EDLC electrodes. Therefore, the search for new precursors those are cheap, accessible and with potential to create significant economic valorisation, as in the case of using plant biomass materials, is still needed. With this in mind, we herein employ the lotus seedpods (LS) as the carbon precursor to develop a simple and facile method for the large-scale production of ACs. It is well known that lotus (*Nelumbo nucifera* Gaertn) is a perennial aquatic plant and is widespread in China. Lotus root and seed are regarded as a popular health food. However, LS is usually discarded except when sometimes used as a traditional medicine with hemostatic function [29–31]. The vast majority of LS becomes wastes of markets and factories, thereby resulting in great resources waste and environmental pollution. On the other hand, LS has a high fiber and oxygen contents [32], therefore, the LS should be a promising carbon precursor for the production of ACs due to its cheap and abundant as well as a sustainable biological resource.

Herein, we presented a facile approach to synthesize porous carbons with high specific surface area *via* a two-step fabrication process using LS as the biomass precursor. Firstly, the LS was hydrothermally treated in 1.5 M KOH aqueous solution at 120 °C for 2 h. After filtration and drying, the mixture was directly subjected to pyrolysis in a N_2 atmosphere, giving porous carbons after residual alkaline being removed. The main advantage of this method lies in that pyrolysis and chemical activation can be accomplished simultaneously. Another advantage is that the KOH retained in hydrothermal product can act as activating agent in activation process, therefore only small amount of KOH were used in our method (*i.e.*, the mass ratio of KOH and LS is around 1/17.5). Moreover, hydrothermal treatment in the presence of KOH can introduce oxygen-containing groups, which may then be efficiently transformed into micropores in the following pyrolysis process [26,28,33]. The as-prepared porous carbon shows a very high specific surface area of 1813 $m^2 g^{-1}$, a high oxygen content of 31.06 wt%, an excellent capacitive performance (402 $F g^{-1}$ at 0.5 $A g^{-1}$), and a high energy density (12.5 $Wh kg^{-1}$ at 260 $W kg^{-1}$). Such low-cost and high-performance electrode material is potentially useful for high-power supercapacitors.

2. Experimental

2.1. Materials

LS (without seeds) was collected from a local plantation in China and was prior washed, cut into pieces and dried. All of the other chemicals were analytical grade and were purchased from Aladdin Reagent (Shanghai) Co., Ltd. without further treatment.

2.2. Preparation of LS-derived porous carbons

Firstly, 10 g LS was added into 200 mL of 1.5 M KOH aqueous solution. After stirring at room temperature for 30 min, the mixture was sealed into a Teflon-lined stainless steel autoclave (250 mL) followed by hydrothermal treatment at 120 °C for 2 h. The hydrothermal product was collected by filtration (without washing) and dried at 120 °C for 12 h (in 58% yield). The obtained product was then pyrolyzed in a tubular furnace (GSL-1700X, Hefei Kejing Materials Technology Co., Ltd., China) under N_2 flow for 2 h. The final temperature and heating rate of the furnace were 700–900 °C and 4 °C min^{-1}, respectively. Finally, the resulting samples were washed with diluted HCl solution and water until neutral pH was reached. The products were denoted as LSC-*x*, standing for carbon prepared from LS, where *x* (*x* = 700, 800, or 900) stands for the pyrolysis temperature (for LSC-800, yield: 10%). For comparison, an inactivated carbon named as DC-800 was prepared by direct pyrolysis of LS at 800 °C in N_2 for 2 h.

2.3. Structural characterization

The morphologies of the obtained porous carbons were characterized by scanning electron microscopy (SEM, JEOL JSM-6610LV). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 microscope operating at 200 kV. The crystallographic information of the carbons was investigated by powder X-ray diffraction (XRD, Rigaku D/Max 2500PC). Raman spectra were collected on a Renishaw inVia Raman spectrometer. The textural properties were characterized by N_2 sorption measurements at 77.3 K (Micromeritics TriStar II 3020). The specific surface area (SSA) was obtained by Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) was calculated from the adsorption branches of the isotherms using the density function theory (DFT) model. The total pore volume (V_{total}) was estimated from the adsorbed amount at a relative pressure p/p° of 0.99. Micropore volume (V_{mic}) was calculated using the t-plot method.

2.4. Electrode preparation and electrochemical measurements

The working electrodes were typically fabricated by mixing the porous carbon as the active material (80 wt%), carbon black (10 wt %), and polytetrafluoroethylene (PTFE, 10 wt%) in ethanol and then coated onto the nickel foam current collectors (1 cm × 1 cm) with a spatula. The premade electrodes were pressed under a pressure of 10 MPa for 5 min and finally dried at 100 °C for 12 h in an oven. The density and thickness of the loading composite on each electrode was controlled to be 1.71 $g cm^{-3}$, and 17.2 μm, respectively, and the nickel foam and active material are 90 mg and 3.0 mg. The two symmetrical electrodes were separated using a polypropene membrane separator soaked with electrolytes (6 M KOH) in a CR2032 stainless steel coin cell. The capacitive performance of single electrode was studied on a CHI760D electrochemical workstation (CH Instruments Inc., Shanghai, China) using a standard three-electrode system with platinum wire and Hg/HgO electrode as counter and reference electrodes, respectively, in 6 M KOH electrolyte at 25 °C. Cyclic voltammetry (CV), galvanostatic charge-discharge (GC) technique and alternating potential impedance were employed in the electrochemical investigations. CV tests of individual electrode were carried out between −1.0 and 0 V (*vs.* Hg/HgO). GC tests were performed at different current density varying from 0.5 to 20 $A g^{-1}$ in the same potential range as the CV test. The specific capacitance based on GC was calculated using the equation [27,34]: $C_g = I/(mdV/dt)$, where *I* is the constant current and *m* the mass of active materials, and *dV/dt* is calculated from the slope obtained by fitting a straight line to the discharge