



Full Length Article

CO₂-activated porous self-templated N-doped carbon aerogel derived from banana for high-performance supercapacitors

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ABSTRACT

N-doped porous carbon materials derived from eco-friendly, renewable and economical biomass resources have attracted interest for applications in supercapacitors due to their porous structures and physicochemical properties. However, controlling the pore structure remains difficult and there is a need to simplify the N-doping process. Herein, we report a porous self-templated N-doped carbon aerogel derived from banana flesh obtained through one-step carbonization followed by CO₂ activation. The specific surface area and pore distribution of the carbon aerogels could be controlled by changing the CO₂ activation time. A specific surface area and total pore volume of 1414.97 m² g⁻¹ and 0.746 cm³ g⁻¹ were achieved. The results show that raw banana flesh provides the necessary N content, which only slightly decreased following activation from 3.25% to 2.25%. On the surface of the carbon aerogel we detected pyrrolic N and pyridinic N groups, which are known to contribute to pseudocapacitance. Furthermore, the specific capacitance of the prepared carbon aerogel reached 178.9 F g⁻¹ at a current density of 1 A g⁻¹. The simple preparation method and excellent electrochemical performance show great potential for application of our porous self-templated N-doped carbon aerogel as an electrode in high performance supercapacitors.

1. Introduction

The global energy crisis has fueled demand for new high-power energy storage technologies [1–3]. Supercapacitors, known as electrochemical capacitors, are efficient energy storage devices due to their high specific capacitance, high-power density, and excellent cycling stability [4–6]. Supercapacitors could be quickly charged and have a long service life even for high current density discharge [7]. Hence, these devices have drawn interest for potential applications in electric vehicles [8], portable electronics [9], wind power [10], and for replacing traditional batteries [11]. The electrode is the core component of supercapacitors [12] and an ideal supercapacitor electrode material requires ion-accessible specific surface area and appropriate porous structure [13]. The ion-accessible surface area is the key parameter to obtain the high gravimetric capacitance. The porous structure consists of micropores, mesopores, and macropores structures. Micropores can provide space, which contributes to a high charge storage capacity and makes full use of the internal carbon surfaces. Mesopores provide a pathway for ion transportation, and macropores provide a large surface area for ion buffering [14]. Therefore, the specific surface area [15] and pore structure [16] are two important parameters which markedly affected the capacitive performance and charge-discharge capacity [17].

Recently, much attention has been paid to the design and control porous structures with suitable pore size distributions. Activation is considered to be an efficient way of increasing the surface area and introducing porosity [18,19]. For example, porous carbon materials have been synthesized with chemical and physical additives as agents for activation [20]. Chemical activation with the use of reagents (porogens) such as KOH and K₂CO₃, has also been applied [21,22]. These alkaline substances corrode the carbon surface and interior when the carbon and alkaline materials are heated together at high temperature, leaving many macropores and mesopores after etching [23,24]. Physical activation approaches include CO₂ activation, which can slowly modify the carbon surface to create micropores. Zu et al. demonstrated that as the CO₂ activation time was prolonged the size and number of micropores increased. Some micropores gradually expanded to become mesopores and macropores [25]. The CO₂ activation step can be performed during the carbonization, which simplifies the process and greatly reduces the cost of the activation process. More importantly, it is facile to control the specific surface area and pore structure of carbon materials by adjusting the activation time.

Previous studies have found that modification of carbon materials by nitrogen doping could introduce active sites and change the electron distribution of the materials [26]. This change could cause a shift of the

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Fermi level towards the valence band in carbon electrodes, thus improving the electron conductivity and capacitive performance [27–29]. Furthermore, this process can also enhance the wettability of the electrolytes to the electrode materials, resulting in the active surface area accessible to electrolytes increased significantly [30,31]. Generally, there are four types of nitrogen configurations are found in N-doped carbon materials, including quaternary N, N-oxide, pyrrolic N, and pyridinic N. Among these, pyrrolic N and pyridinic N are two main configurations that contribute to the pseudo-capacitance, based on Faradaic reactions [32,33]. Many methods for preparing N-doped materials have been developed and these approaches can be divided into two broad categories: direct syntheses and post-treatments. Direct synthesis routes, such as chemical vapor deposition (CVD) [34] and arc-discharge methods [35] and so on, require special apparatus and well-controlled conditions, which has limited their widespread application [36,37]. Post-treatment methods are widely used to obtain N-doped carbon materials including thermal treatments with N-rich compounds [38] or in a N-donor atmosphere [39]. However, these methods usually involve toxic or costly precursors rendering them unsuitable in practice [40]. Thus, fabrication of N-doped materials by self-templated approaches are attractive owing to the simple processes involved and the avoidance of nitrogenous chemicals.

Carbon aerogels, obtained by carbonization of organic aerogels, exhibit both the desirable porosity of an aerogel and its associated high specific surface area [41] together with the excellent electrical conductivity of carbon materials [42,43]. Further, carbon aerogels have high performance in a wide temperature range and exhibit good chemical stability in both strongly acidic and alkali solutions, which makes them promising electrode materials for supercapacitors. Currently, the development of aerogels obtained from sustainable biomass resources has attracted much attention due to the cost-efficient of the precursors and high performance of the products [44–46]. Additionally, the fabrication processes should be environmental friendly and simple. Banana is harvested all year round and is a promising carbon precursor for carbon aerogels owing to its global abundance, fast growth rate and high carbon content [44]. More importantly, banana itself contains a large amount of nitrogen, which could supply the content for N-doping without the need for an additional nitrogen source. Herein, we report a porous self-templated N-doped carbon aerogel based on banana biomass. Our aerogel features many macrospores, mesoporous, microspores, and an N content of 2.25 wt% was achieved by one-step carbonization and CO₂ activation. We found that in this process, the specific surface area and pore distribution of carbon aerogels could be easily controlled by adjusting the CO₂ activation time. Thus, our banana carbon-aerogel uses low-cost raw materials and a simple self-templated method to achieve an N-doped structure. The high specific capacitance of these materials as electrodes shows great promise for applications to high performance supercapacitors with the potential for large-scale production.

2. Experimental section

2.1. Fabrication of banana carbon aerogel

Banana was peeled and cut into pieces, frozen by liquid nitrogen, and freeze-dried in a freeze-dryer at $-50\text{ }^{\circ}\text{C}$ for 48 h to prepare the banana aerogel (BA). To prepare banana carbon aerogel (BCA), the BA was carbonized under an argon (Ar) atmosphere in a tube furnace, heated from $30\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$, maintained at $300\text{ }^{\circ}\text{C}$ for 1 h. Then, the temperature was increased from 300 to $900\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and hold that temperature for 1 h. The Ar input was then turned off and the system as flushed with CO₂. The furnace was maintained at $900\text{ }^{\circ}\text{C}$ under a CO₂ atmosphere for 0.5, 1, 1.5, and 2 h. After completion of the carbonization and activation, the CO₂ flow was turned off and cooled to $30\text{ }^{\circ}\text{C}$ under Ar atmosphere. The obtained banana carbon aerogel (BCA) products are

denoted as BCA-n, where n indicates the CO₂ activated time (0.5, 1, 1.5, and 2 h). As a control, the BA was carbonized at $900\text{ }^{\circ}\text{C}$ for 2 h without a CO₂-treatment and denoted as BCA.

2.2. Characterization

The morphology of banana carbon aerogel was characterized by scanning electron microscope (SEM; Quanta 200, FEI, The Netherlands). Thermalgravimetric analysis was performed with a thermoanalysis instrument under nitrogen atmosphere in the temperature range of $30\text{--}800\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ (TGA, TA, American). Nitrogen sorption analysis was conducted on a volumetric adsorption analyzer (ASAP2020, Micromeritics, Shanghai, China). The presence of crystal structures was characterized by X-ray diffraction (XRD) from $2\theta = 5\text{--}80^{\circ}$ (Rigaku, D/max 2200). Raman scattering spectra were analyzed with 514 nm excitation (Renishaw System 2000 spectrometer). Elemental analysis was recorded by X-ray photoelectron spectroscopy (PHI5700, Chanhassen, MN, USA).

2.3. Electrochemical measurements

Electrochemical measurements were performed on an electrochemical work station (CHI660E, ChenHua, Shanghai) in a three-electrode and two-electrode systems with 6 mol L^{-1} KOH electrolyte. BCA samples, carbon black and polytetrafluoroethylene (PTFE) binder (8:1:1) were mixed in ethanol, then coated onto nickel-foam current collectors ($1 \times 1\text{ cm}^2$) and dried at $110\text{ }^{\circ}\text{C}$ for 15 h. The active material was 3 mg cm^{-2} on each working electrode. A platinum foil and an Ag/AgCl electrode were served as the counter electrode and reference electrode respectively. The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to characterize the electrochemical properties of the samples. The CV curves were tested by varying the scan rate from 5 to 400 mV s^{-1} (voltage range of -1.0 to 0 V). Galvanostatic charge/discharge measurements were obtained under different current densities (voltage range of -1.0 to 0 V). Electrochemical impedance spectroscopy (EIS) analysis was conducted at the open circuit voltage in the frequency range of $0.01\text{ Hz--}100\text{ kHz}$. In the two electrode system, the specific capacitances (C , F g^{-1}), energy density (E , Wh kg^{-1}), power density (P , W kg^{-1}) could be calculated from the equations: $C = (4I \times \Delta t) / (m \times \Delta V)$; $C = \frac{2}{mv(V_b - V_a)} \int_{V_a}^{V_b} IdV$; $E = \frac{1}{8} C \Delta V^2$; $P = \frac{E}{\Delta t}$, where I (A), ΔV , Δt (s), m (mg), V_a and V_b (V) are the discharge current, scan rate, discharge time, total mass of the active materials and the low and the high potential limit of the CV test, respectively; For the three-electrode system, the specific capacitance (C) was calculated by the following equation: $C = (I \times \Delta t) / (m \times \Delta V)$.

3. Results and discussion

3.1. SEM and TGA observations

The morphology of BA, BCA and BCA-n was observed by SEM imaging. As shown in Fig. 1a and b, the BA sample exhibited pores along the backbone of the crosslinked gel. For BCA we found a 3D honeycomb-shaped pore structure with pore diameters of approximately $50\text{ }\mu\text{m}$ (i.e., macropores) (Fig. 1c and d). These features were attributed to the carbonization process, which decomposed the polymers and oligomers in the banana into small molecules, such as H₂O, CO₂, NH₃ and HCHO, to leave a porous structure [45,46]. The BA sample was further investigated with the use of TGA (Fig. 1m). The rate of mass loss of the BA sample showed four maxima as the temperature was increased. The first peak appeared at low temperature ($< 100\text{ }^{\circ}\text{C}$) and likely corresponded to elimination of residual solvent. The second peak ($170\text{--}320\text{ }^{\circ}\text{C}$) corresponded to a $\sim 25\%$ release of the total volatiles and may represent intrinsic lipid decomposition products, for

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