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Functional Biomass Carbons with Hierarchical Porous Structure for Supercapacitor Electrode Materials

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ABSTRACT

This paper presents nitrogen and boron co-doped KOH-activated bamboo-derived carbon as a porous biomass carbon with utility as a supercapacitor electrode material. Owing to the high electrochemical activity promoted by the hierarchical porous structure and further endowed by boron and nitrogen co-doping, electrodes based on the as-obtained material exhibit significantly enhanced specific capacitance and energy density relative to those based on most similar materials. An asymmetric supercapacitor based on this novel carbon material demonstrated satisfactory energy density and electrochemical cycling stability.

1. Introduction

High-performance supercapacitors are widely used as highly efficient electrical energy storage devices for vehicles, electric power distribution, railways, telecommunications, and other consumer electronics products [1–3]. Electrode materials are the main contributors to the electrical energy storage capacity of supercapacitors, and have been attracting significant attention in the past decade [1,4–11]. In particular, carbon-based electric double layer capacitive materials are the most commonly employed electrode material for commercially available supercapacitors because of their good cycle lifetime and high maximum power density [1,5]. Recently, high specific capacitance (C_s) and energy density have also been achieved with some important carbon materials including graphenes, carbon nanotubes, and templated carbons via advanced synthesis methods [4,12–14]. However, these materials have a relatively high cost owing to complicated preparation processes and scarce raw materials, which considerably limits the potential for large-scale production and application of these carbon materials [15–17]. Therefore, it is highly desirable to synthesize lower cost carbon materials with comparable capacitive performance from ample and renewable natural resources for supercapacitor applications.

Bamboo has a particularly fast growth rate, short maturation cycle, and high production yield, making it abundant and renewable. Moreover, bamboo can be carbonized at high temperatures under a nitrogen atmosphere to produce low-cost carbon materials with interconnected, multichannel, and porous structures [18,19]. This porous structure can promote electrolyte access and ion diffusion, which gives bamboo-derived carbon materials high electrochemical activity. Accordingly, bamboo-derived carbon (BC) can also be employed as electrode materials for electrochemical applications such as supercapacitors, Li-ion batteries, lithium-sulfur batteries, and fuel cells [18,20–23]. In addition, heteroatom doping has been found to be an effective strategy to enhance the electrochemical activity of carbon materials [13,24–26]. Motivated by these interesting studies, we employed a two-step hydrothermal reaction involving KOH-activated BC (KBC), boric acid, and aqueous ammonia to successfully synthesize the first porous boron and nitrogen co-doped KBC (NBKBC). The NBKBC prepared by this hydrothermal co-doping process possesses higher surface area and more electrochemically active sites than those of un-doped KBC. Moreover, electrodes fabricated with the as-obtained NBKBC powder as an active material exhibit significantly enhanced C_s and energy density due to the high electrochemical activity promoted by the hierarchical porous structure and further endowed by boron and nitrogen co-doping relative to electrodes based on un-doped KBC, boron-doped KBC (BKBC), and nitrogen-doped KBC (NKBC). For NBKBC-based electrodes, the C_s values were as high as 281 $F g^{-1}$ in 1 M KOH and 318 $F g^{-1}$ in 1 M H_2SO_4, and the maximum energy

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density values were 37.8 Wh kg^{-1} in 1 M KOH and 42.1 Wh kg^{-1} in 1 M H_2SO_4. The best C_s obtained is larger than those of most previously reported BCs, boron and nitrogen co-doped carbons, and other typical biomass-based carbons. In addition, an asymmetric supercapacitor utilizing a negative electrode based on this novel NBKBC material demonstrated satisfactory energy density and electrochemical cycling stability.

2. Experimental section

2.1. Materials

Hydrochloric acid (37 wt%, HCl), sulfuric acid (98 wt%, H_2SO_4), and acetone were purchased from Shanghai Chemical Reagent Co., Ltd. (China). Potassium hydroxide (KOH), boric acid, aqueous ammonia (25 wt%, $NH_3 \cdot H_2O$), and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Corp. (China). Acetylene black (F-900, AB) was purchased from Tianjin Ebory Chemical Co., Ltd. (China). Bamboo powder (<150 μm) was donated by Zhejiang Longyou Mubang Chemical Co., Ltd. (China). All reagents were used as received.

2.2. Synthesis of porous KOH-activated bamboo-derived carbon

BC powder was prepared via high temperature pyrolysis of bamboo powder under an N_2 atmosphere in a tube furnace [27]. The temperature was increased from room temperature to 200 °C and then held at this temperature for 1 h to remove moisture, followed by a temperature increase to 750 °C at a rate of 3 °C/min with a dwell time at this temperature of 1 h to remove volatile organics and to carbonize the solid residues. A brown-black BC powder was obtained after allowing the material to cool to room temperature.

The BC powder was thoroughly mixed in a KOH solution (10 mol L^{-1}) with a BC/KOH ratio of 1:4 by weight, and then heated in an oven at 80 °C overnight until a black jelly-like slurry was formed [28,29]. The slurry was then heated in a tube furnace using the same high-temperature pyrolysis process described above for the original bamboo powder. The resulting sample was then washed thrice with 6 wt% HCl to remove soluble inorganic salts followed by washing with distilled water until pH neutrality was achieved. Finally, the material was dried in a vacuum oven at 100 °C for 12 h to provide KBC powder. These steps are illustrated by the left-hand side of Scheme 1.

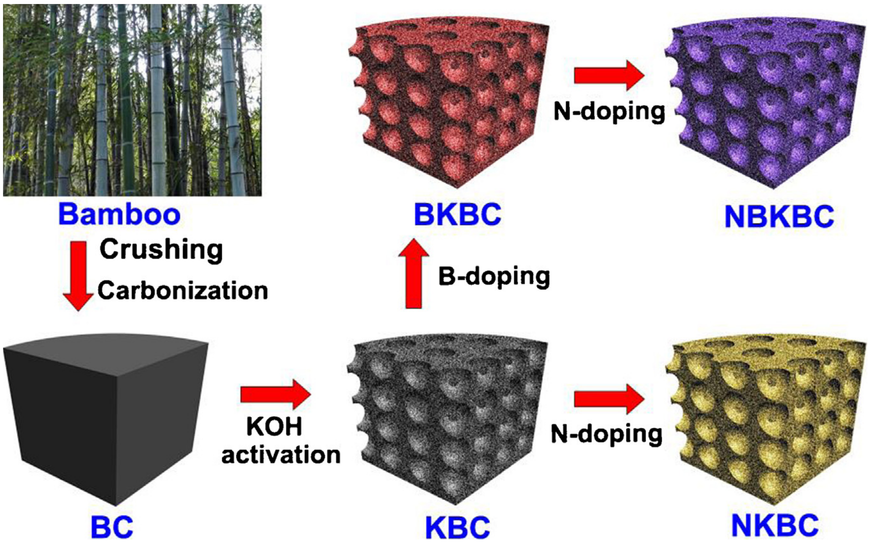
2.3. Synthesis of porous KOH-activated bamboo-derived carbon with heteroatom doping

Porous BKBC was prepared using a simple one-step hydrothermal process [26]. Typically, KBC (0.50 g) was immersed in a solution containing boric acid (2.50 g) and deionized water (50 mL), and, after being ultrasonically dispersed at room temperature for 30 min, was transferred to a 100 mL Teflon-lined autoclave. The autoclave was then sealed and maintained at 180 °C for 12 h to allow hydrothermal doping of boron. After cooling to room temperature, the product was centrifuged and washed with water and ethanol several times to remove excess boric acid and other residues followed by drying at 100 °C for 12 h to remove the adsorbed solvents, yielding a black BKBC powder.

Porous NKBC was prepared using a similar hydrothermal process by replacing the boric acid aqueous solution with ammonia solution (12.5 wt% in H_2O, 40.0 g) [30]. When BKBC and ammonia were used as the precursor and dopant, respectively, porous NBKBC was prepared by means of an equivalent hydrothermal process. These steps are illustrated by the right-hand side of Scheme 1.

2.4. Fabrication of electrodes

Nickel foam (110 pores per inch) and stainless steel mesh (400 pores per inch) were first successively pretreated with acetone, 2 M HCl, absolute ethanol, and deionized water each for 15 min to ensure a clean surface. A nickel hydroxide-manganese dioxide-reduced graphene oxide ($Ni(OH)_2$-MnO_2-RGO) composite was synthesized according to our previous report [10]. Electrodes based on BC, KBC, BKBC, NKBC, NBKBC, and $Ni(OH)_2$-MnO_2-RGO active materials were fabricated as follows. A mixture of sample powders, 23 wt% acetylene black (as the electrical conductor), 5 wt % polytetrafluorethylene (as the binder), and a small amount of water was prepared by milling to produce a homogeneous paste. This paste was then pressed onto nickel foam or stainless steel current-collectors to produce the electrodes. The loading densities of the active materials were about 6 mg cm^{-2} for all electrodes.



Scheme 1. The preparation process of bamboo-derived carbon (BC), KOH-activated BC (KBC), boron-doped KBC (BKBC), nitrogen-doped KBC (NKBC), and boron and nitrogen co-doped KBC (NBKBC).