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Hierarchical structured carbon derived from bagasse wastes: A simple and efficient synthesis route and its improved electrochemical properties for high-performance supercapacitors

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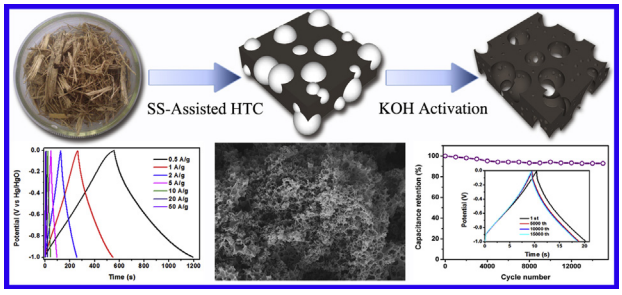
HIGHLIGHTS

- Bagasse-derived hierarchical structured carbon (BDHSC) was synthesized.
- Sewage sludge was employed to regulate the morphology and porosity of BDHSC.
- The BDHSC-based electrode exhibits excellent supercapacitive performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Bagasse-derived hierarchical structured carbon (BDHSC) with tunable porosity and improved electrochemical performance is prepared via simple and efficient hydrothermal carbonization combined with KOH activation. Experimental results show that sewage sludge acts as a cheap and efficient structure-directing agent to regulate the morphology, adjust the porosity, and thus improve the supercapacitive performance of BDHSC. The as-resulted BDHSC exhibits an interconnected framework with high specific surface area (2296 $m^2\ g^{-1}$), high pore volume (1.34 $cm^3\ g^{-1}$), and hierarchical porosity, which offer a more favorable pathway for electrolyte penetration and transportation. Compared to the product obtained from bagasse without sewage sludge, the unique interconnected BDHSC exhibits enhanced supercapacitive performances such as higher specific capacitance (320 $F\ g^{-1}$), and better rate capability (capacitance retention over 70.8% at a high current density of 50 $A\ g^{-1}$). Moreover, the BDHSC-based symmetric supercapacitor delivers a maximum energy density of over 20 $Wh\ kg^{-1}$ at 182 $W\ kg^{-1}$ and presents an excellent long-term cycling stability. The developed approach in the present work can be useful not only in production of a variety of novel hierarchical structured carbon with promising applications in high-performance energy storage devices, but also in high-value utilization of biomass wastes and high-ash-content sewage sludge.

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1. Introduction

Supercapacitor, as a promising candidate for energy storage system, has attracted tremendous attention not only owing to their high power density, long cycle life, good reversibility, but also due to its potential applications in the fields of hybrid electrical vehicles, electronic devices, and power management in renewable-energy-based smart grids [1–5]. According to the energy storage mechanism, supercapacitors can be classified into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors. It is well known that EDLCs store charges in the double layers by charge accumulation between the surfaces of electrodes, while pseudocapacitors are based on the redox reactions used in their charge-storage mechanism, which are often unstable during the cycling process and cannot achieve power-density performances as high as those of EDLCs [5,6]. Because of the pure electrostatic charge accumulation between the electrode/electrolyte interface, EDLCs usually possess higher power density and longer cycling stability compared to the pseudocapacitors, but it usually suffers from the low capacitance and energy density [3]. In order to achieve high supercapacitive performances, the electrode material used for ideal EDLCs should be featured: (1) high specific surface area for charge storage, (2) appropriate pore size distribution for specific capacitance and rate capability, (3) good electrical conductivity for rate capability and power density, (4) better electrochemical and mechanical stability for good cycling performance [7]. In recent years, porous carbon (PC) has attracted broad interest as an electrode material for energy storage and conversion because of its low cost, high specific surface area, excellent electrical conductivity and chemical stability, environmental friendliness, and long cycling life [8–10]. However, most PC materials, especially activated carbons (AC), usually exhibit microporous characteristic with a narrow micropore distribution ranging from 0.5 to 1.1 nm [11]. It has been reported that the specific capacitance undergoes a sharp increase in carbons with pore sizes of less than 1 nm [12]. However, this type of porosity severely limits the transport of ions in large particles, and undermines the supercapacitive performance especially at high current densities [13–15].

To overcome the limit of the ion-transport kinetics in microporous carbons, many efforts have been devoted to the design and fabrication of carbon-based electrode materials with a hierarchical porous structure combining macropores, mesopores, and micropores, in which macropores can serve as the ion-buffering reservoirs in the interior of carbon materials, mesopores as channels for accelerating the rapid transport of ions, while micropores as the locations for charge accommodation [16,17]. Hierarchical porous carbons with high specific surface area and suitable pore size distribution can achieve an enhanced supercapacitive performance. Many strategies, including template methods, pyrolysis and carbonization of various carbon precursors, have been developed for the synthesis of carbon hierarchical structures [18–24]. For example, Hao and co-workers have synthesized nitrogen-rich carbon via temperature-dependent crosslinking of terephthalonitrile monomers [22]. Hierarchical porous carbon has been prepared via a modified chemical activation route with polypyrrole microsheets as precursor and KOH as activating agent [23]. However, these methods still suffer from some drawbacks such as complex synthesis processes, high cost of templates and raw materials, and difficulty to regulate the porosity, which severely hinder their scalable production and practical applications. Therefore, researchers have paid increasing attention to employing green, reproducible biomass or its derivatives, and renewable materials to prepare hierarchical porous carbons [25–28].

Bagasse, which is an industrial biomass waste produced from sucrose extraction in sugar plants, have been used as precursor for preparing carbonaceous materials [29–40]. Currently, bagasse-derived carbonaceous materials have been employed as absorbent in environmental fields to remove heavy metal ions and organic pollutants [29–35]. More recently, the energy storage application of bagasse-derived carbons as electrode materials has also aroused growing interest [36–40]. However, most bagasse-derived carbonaceous materials exhibit specific surface areas lower than 2100 $m^2\ g^{-1}$ and narrow pore size distribution which restrains their electrochemical performance (i.e. specific capacitance<300 F g^{-1}, energy density<10 Wh kg^{-1}). Therefore, it still remains a great challenge to develop simple and cost-effective methods for preparing hierarchical pore structured carbon from bagasse with high specific surface area and excellent supercapacitive performance.

Herein, we report a simple and cost-effective method for the synthesis of hierarchical structured carbons via hydrothermal carbonization (HTC) combined with KOH activation process, in which bagasse wastes were used as carbon precursor and high-ash-content sewage sludgy (SS) as the additive. The employed sewage sludge contains abundant inorganic components such as silica which could act as the natural template to regulate the pore structure of bagasse-based porous carbon and thus to achieve a better capacitance performance. The as-prepared bagasse-derived hierarchical structured carbon (BDHSC) exhibits interconnected framework, high surface area (2296 $m^2\ g^{-1}$), and hierarchical pore size distribution. Benefiting from the unique hierarchical structure, the as-resulted BDHSC presents a higher surface area utilization rate than other bagasse-derived porous carbons, high specific capacitance (320 F g^{-1}), excellent rate capability, and long-term stability. In order to investigate the practical applications of the as-resulted BDHSC, a symmetric supercapacitor was also assembled in a 1 M Na_2SO_4 aqueous electrolyte, and the BDHSC-based supercapacitor delivers a maximum energy density of over 20 Wh kg^{-1}.

2. Experimental section

2.1. Preparation of three-dimensional BDHSC

The bagasse after extracting sugarcane juice by crushing and squeezing was collected from Guangzhou, China. The employed SS with initial moisture content of approximately 85% used was collected from Liede Sewage Treatment Plant, Guangzhou, and dried naturally. The potassium hydroxide (KOH) was purchased from Guangzhou Chemical Reagent Factory, China. In a typical process, 2.0 g of bagasse and 2.0 g of SS powder were mixed and grounded in an agate mortar into fine powder. The powder was then dispersed into 40 ml of deionized water, and then transferred into a teflon-sealed autoclave, which was subsequently placed in an oven followed by heating at 220 °C for 3 h. After that, the autoclave was cooled down naturally. The solid product was dried in 105 °C oven for 3 h and then mixed with KOH at a KOH/C ratio of 3:1. The activation was carried out in a fixed-bed reactor at a slow heating rate of 10 °C/min from room temperature to the 700 °C under a nitrogen (N_2, 99.99%) atmosphere (flow rate of 20 ml min^{-1}) and held for 3 h. The system was then cooled down under a N_2 atmosphere and the product was washed with 3 M HCl and then rinsed with deionized water until the pH of washing effluent reached 6–7. Finally, the product was dried at 105 °C for 6 h, and the activated sample was named as BDHSC-1. To further investigate the effect of the addition of SS, the porous carbons derived from SS without bagasse and bagasse in the absence of SS through the similar treatment were prepared and named as SAC and BAC, respectively. In addition, BDHSC samples derived from bagasse with the mass ratios of SS/bagasse of 3:1 and 4:1 were also prepared and labeled