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3-Dimensional hierarchical porous activated carbon derived from coconut fibers with high-rate performance for symmetric supercapacitors

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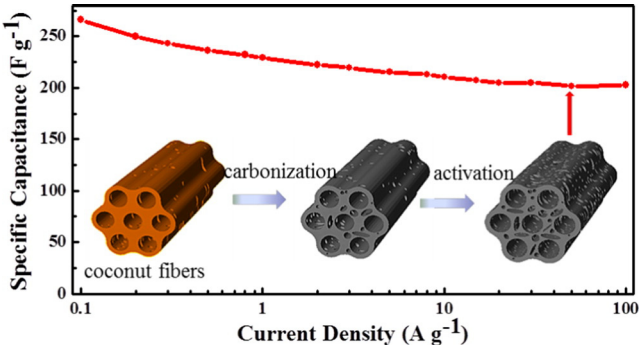
HIGHLIGHTS

- Coconut fibers with multi-tubular hollow structure were used to prepare activated carbon by carbonization and activation.
- Multi-tubular hollow structures were maintained and micro/mesopores were created on the wall.
- Special structures could shorten the diffusion paths resulting in high-rate performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Here we report a 3-dimensional hierarchical porous activated carbon (HPAC) prepared from coconut fibers with KOH activation, which exhibits high-rate performance for symmetric supercapacitors. At a 4:1 mass ratio of KOH to carbonized coconut fibers, the highest specific surface area of 2898 $m^2 g^{-1}$ with a pore volume of 1.59 $cm^3 g^{-1}$ (30% mesopores) is successfully achieved in a 3-dimensional HPAC. As a supercapacitor electrode combined with a 6 M KOH electrolyte, a high specific capacitance of 266 F g^{-1} at a current of 0.1 A g^{-1} is successfully achieved and an excellent rate performance up to 76% of its capacitance is retained at a high current of 100 A g^{-1}. Additionally, in $EMIMBF_4$ electrolyte, 3-dimensional HPAC electrode exhibit a high capacitance of 155 F g^{-1} at 0.1 A g^{-1} and 142 F g^{-1} at 10 A g^{-1}. Owing to its excellent rate performance, 3-dimensional HPAC can deliver a high energy density of 53 Wh kg^{-1} and a high power density of 8224 W kg^{-1}, which shows promising application potential in energy storage devices.

1. Introduction

Energy advancement promotes the development of our society, yet challenges still exist in the storage and delivery of energy. In these decades, people are trying to substitute sustainable technologies for conventional fossil fuel-based solutions by seeking renewable, low-cost and abundant energy resources, as well as developing new technologies of energy conversion and storage [1–4]. Rechargeable batteries are considered to be a promising solution for sustainable energy technologies, while their disadvantages of short cycle life (1000 cycles) and low power density prevent them from meeting the increasing demands

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of renewable technologies such as electrical vehicles [2]. Electrochemical supercapacitors, another example of an energy storage and conversion system, have become increasingly popular due to their high power density, excellent cycle stability, and compromise of the power/energy between traditional dielectric capacitors and batteries [1,5]. However, for some power applications, supercapacitors are mostly confined to a low energy density (<10 Wh kg^{-1}) in comparison with lithium-ion batteries (160 Wh kg^{-1}) [6,7].

Currently, activated carbon has been commercially utilized as an electrode material for supercapacitors, owing to their low cost versus other porous carbons (e.g. templated carbons and carbide derived carbons) [8]. For carbon-based electrical double layer capacitors (EDLCs), specific surface area, pore size distribution and structure, and electrical conductivity are critical parameters for the device's performance [9]. In certain cases, activated carbons with large micropore surface area only exhibit a finite growth of electric double-layer capacitance, ascribing to a tortuous path for electrolyte ions to access the inner pore surface area [10–12]. In addition, the restriction on diffusion velocity also makes the specific capacitance descend rapidly at high current densities [13,14]. Therefore, to enhance capacitance performance, it should be designed of high specific surface area activated carbons with the interconnected pores and short pore length, in which the amount of mesopores are critical to accelerate ion transport and raise the accessible surface area [14–18].

Compared with other synthetic routes, fabricating hierarchical porous carbon from natural plant and biomass waste has the advantages of high-yield, low-cost and less pollution [19]. Coconut generally grows in tropical and sub-tropical regions and produces a large quantity of coconut shell fibers although the year, yet only a small part is used for ropes, brushes, palm mattresses, etc. In this study, a simple and economic strategy is adopted to prepare hierarchical porous carbon by traditional KOH activation of carbonized coconut fibers. The experimental results prove that the coconut shell fibers, with a distinctive multitubular hollow structure, are a suitable raw material for preparing 3-dimensional hierarchical porous activated carbon (HPAC) possessing high specific surface area. As an electrode material for supercapacitors, the 3-dimensional HPAC delivers a large energy density and high rate performance. Hence, the coconut shell fibers could be adopted as a readily available, renewable and cost-effective raw material for supercapacitor electrodes possessing excellent electrochemical properties.

2. Experimental section

2.1. Material synthesis

A typical preparation procedure consists of two steps. First, the ground coconut fibers (CF, Haikou, China) were carbonized by heating with a rate of 3 °C min^{-1} to 700 °C and maintaining this temperature for 1 h under a nitrogen atmosphere. Second, the CF carbonized materials (referred to as CFC) were mixed at different ratios of KOH (Guangzhou Chemical Reagent Corp. China) and activated by heating at a rate of 3 °C min^{-1} to 850 °C and maintaining this temperature for 1 h under a nitrogen atmosphere, followed by washing with dilute HCl solution (2%, Shanghai Chemical Reagent Co., Ltd., China) and then deionized water until pH ≈ 7. Finally, the samples were dried at 120 °C for 12 h. The resultant samples were denoted as HPAC-X, where X represents the mass ratio of KOH to CFC. The preparation process can be illustrated by the following schematic of Fig. 1.

2.2. Characterization methods

N_2 (77 K) adsorption/desorption (JW-BK122W, Beijing JWGB Sci. & Tech. Co., China) were used to measure the specific surface area and the porosity of CFC and HPAC, and the Brunauer-Emmett-Teller (BET) method and non-localized density function theory (NLDFT) were implemented to calculate the specific surface area and pore size distribution, respectively, in which all samples were degassed in vacuum at 120 °C for 4 h before measurements. The morphology and microstructure were characterized via field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan), transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) at an operating voltage of 200 kV.

2.3. Electrochemical measurements

A symmetrical two-electrode cell was used to measure the electrochemical performance of HPAC, as shown in Fig. 2. Briefly, the as-prepared samples were mixed with Ketjen black (Lion Corp., Japan) and polytetrafluorethylene (PTFE, 60% dispersion in water, Sigma-Aldrich, USA) at a mass ratio of 80:15:5 to form a paste, which was pressed into a film with a roller and cut into 10 mm diameter pieces. Then the pieces were pressed on the current collector (12 mm in diameter) at a pressure of 10 MPa (30 s), and then dried at 110 °C for 6 h in

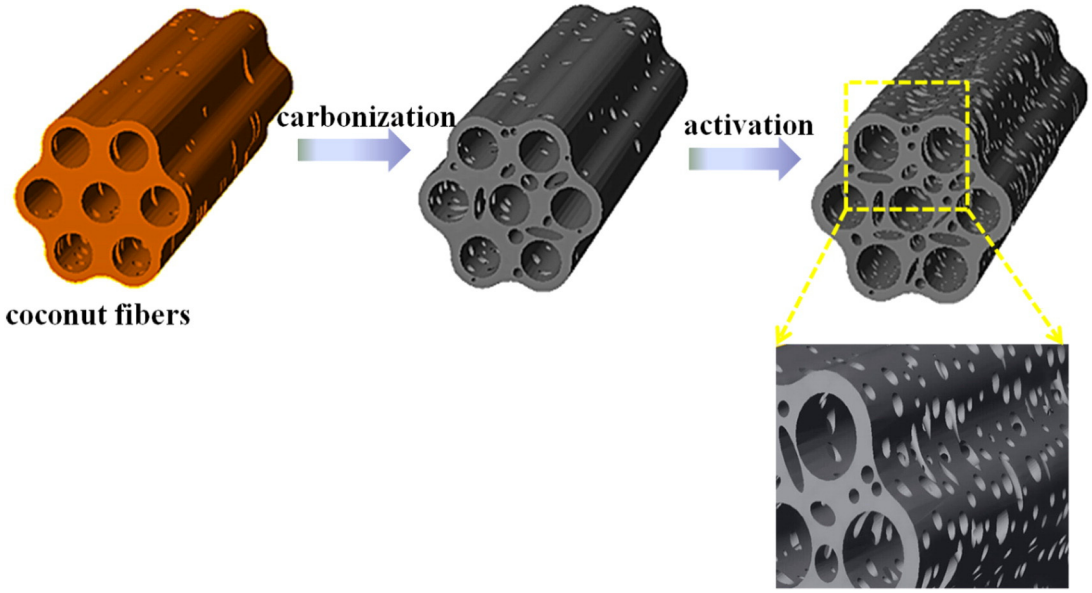

Fig. 1. Schematic illustration of the synthesis of 3-dimensional HPAC from coconut fibers.