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Hierarchically porous nitrogen-doped carbon derived from the activation of agriculture waste by potassium hydroxide and urea for high-performance supercapacitors

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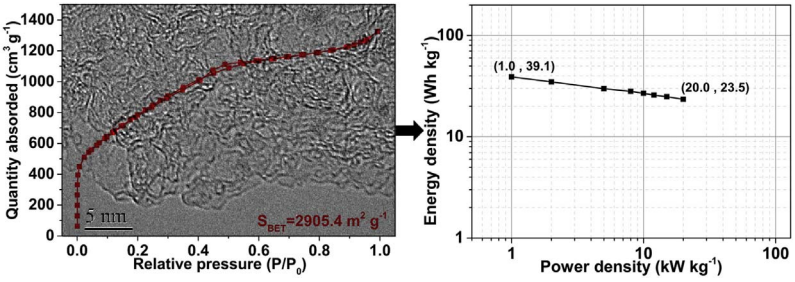
HIGHLIGHTS

- A green route for the scale preparation of hierarchically porous N-doped carbon (HPNDC).
- The HPNDC exhibits ultra-high specific surface area.
- The HPNDC shows an excellent electrochemical performance for supercapacitors.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen-doped carbon with an ultra-high specific surface area and a hierarchically interconnected porous structure is synthesized in large scale from a green route, that is, the activation of bagasse via a one-step method using KOH and urea. KOH and urea play a synergistic effect for the enhancement of the specific surface area and the modification of pore size of the as-prepared material. Benefiting from the multiple synergistic roles originated from an ultra-high specific area (2905.4 $m^2 g^{-1}$), a high porous volume (2.05 $mL g^{-1}$ with 75.6 vol% micropores, which is an ideal proportion of micropores for obtaining high specific capacitance), a suitable nitrogen content (2.63 wt%), and partial graphitization, the hierarchically interconnected porous N-doped carbon exhibits an excellent electrochemical performance with a high specific capacitance (350.8, 301.9, and 259.5 $F g^{-1}$ at 1.0 $A g^{-1}$ in acidic, alkaline, and neutral electrolytes, respectively), superior rate capability and excellent cycling stability (almost no capacitance loss up to 5000 cycles). Furthermore, the symmetric device assembled by this material achieves high energy densities of 39.1 and 23.5 Wh kg^{-1} at power densities of 1.0 and 20 kW kg^{-1}, respectively, and exhibits an excellent long-term cycling stability (with capacitance retention above 95.0% after 10 000 cycles).

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1. Introduction

Carbonaceous materials play significant roles as electrode materials for commercial supercapacitors (SCs) at present time because of its natural abundance and some attractive characteristics including high electrical conductivity, large surface area, and electrochemical stability [1–3]. Considerable efforts have been made aiming to synthesize different carbon-based materials, such as high specific area active carbon (AC) [4], carbon nanotube (CNT) [5,6], graphene [7–10], carbide-derived carbons [11,12] and carbon/metal oxide hybrid matetials [13,14] to improve the electrochemical performance of the assembled supercapacitors. However, their specific capacitances are largely restricted due to the physical charge storage mechanism of electric double layer capacitors (average specific capacitances are less than 300 F g^{-1}) [15,16] Therefore, it is of great importance to develop novel carbon-based materials to achieve higher specific capacitance (energy density) for EDLCs to meet the ever-growing requirement in energy storage devices. Investigation on functional carbon-based materials for SCs with enhanced energy and power density has been directed towards heteroatom-especially nitrogen-doped carbon (NDC) materials owing to their fascinating properties, such as high electronic conductivity, good wettability, and more active sites for energy storage [17,18]. Furthermore, NDC materials have been demonstrated to be effective in increasing the specific capacitance via surface faradaic pseudocapacitance without sacrificing the high rate capability and long cycle life in very recent years [19–29].

Previous research works have also demonstrated that the optimization of the pore structure, including pore volume, pore size, and pore size distribution, is a highly effective approach to improve the electrochemical performance of the carbon and/or NDC-based materials for SCs [30–37]. In this regard, the hierarchical porous NDC-based nanomaterials possessing micro- and meso-pores are considered as a promising candidate for high performance SCs, The micropores can be used as the accommodation sites for charge storage, and the mesopores can used as electrolyte reservoirs that in turn enable the rapid transport of ions [33,38]. The existence of macropores usually produces a low packing density in the NDC-based nanomaterials and may result in a small volumetric capacitance and consequently low volumetric energy and power density for the corresponding supercapacitors [6]. However, this drawback can be overcome via the fabrication of the practical electrode, in which the macropores can be compressed under certain pressure [24]. To achieve a better performances for SCs, various synthesis methods including template methods, the combination of carbonization and activation, and molten salt synthesis route, had been developed for the synthesis of NDCs with a hierarchically porous architecture, high specific surface areas and appropriate pore size distributions. For example, Zhao et al. prepared the hierarchical nitrogen-doped carbon nanocages (hNCNCs) with a specific surface area of 1794 $m^2 g^{-1}$ and a nitrogen content of 7.9 wt% by an in situ MgO template method, The obtained SC show a specific capacitance of 313 F g^{-1} (at a current density of 1 A g^{-1}) in 6 M KOH electrolyte [39]. Hu et al. prepared a hierarchical N,S-codoped carbon with a high surface area of 3068 $m^2 g^{-1}$ via the activation of the pre-carbonization amino acid-rich swim bladders by a large amount of KOH addition. The assembled SCs exhibit the specific capacitances of 300 and 250 F g^{-1} (at a current density of 1 A g^{-1}) in 1 M KOH and 1 M H_2SO_4 electrolytes, respectively [40]. Ouyang et al. reported a one-step synthesis of a 3-D nitrogen-doped porous carbon (NPC) material by using tofu as the nitrogen-containing carbon source via a molten salt synthesis method. The SCs with NPC displayed a specific capacitance of 429 F g^{-1} in 6 M KOH electrolyte [41]. Xiong et al. reported the N-doped hierarchical porous carbon nanospheres (NHPCNs), with a specific area of 1725 $m^2 g^{-1}$ and a specific capacitance of 376 F g^{-1} (at a current density of 1 A g^{-1}) in KOH electrolyte. This can be achieved via the carbonization and KOH activation of mesoporous polydopamine nanospheres, which were prepared by the one-step self-polymerization of dopamine using Pluronic F127 as the soft template [42]. More recently, Zhang et al. have reported a N-superdoped 3D porous graphene network structure with a high N-doping level of 15.8 at% via a multi-steps route, The obtained capacitances were up to 320, 260, and 245 F g^{-1} (at a current density of 1 A g^{-1}) in 6 M KOH, 1 M H_2SO_4 and 1 M KCl electrolytes, respectively [43]. However, the above mentioned synthesis methods/routes still suffer from some obvious drawbacks such as complex preparation processes, expensive raw materials, the adoption of various templates, and high activation agent loading, which is make it very difficult to meet the demand for large-scale porous NCs production in practical applications. It is, therefore, highly necessary to develop a simple and cheap route for the preparation of hierarchical porous NCs with high electrochemical performance.

Considering the potential large-scale application of NCs for supercapacitors, the preparation of NCs with hierarchical porous nanoarchitectures for supercapacitors with high power density and energy density via direct pyrolysis and/or activation of renewable biomass and/or biomass wastes would be a sustainable route. In this respect, many efforts have been made to preparing NC-based electrode materials with high specific capacitance and excellent rate capability by enhancing the specific surface areas and optimizing the nitrogen content and pore size distribution [44–52]. Sugar cane bagasse is an abundant and free renewable agricultural waste rooting from sugar industry, which has been used as a raw material for the preparation of porous carbon materials used in many fields [53–58]. More recently, carbonaceous materials derived from sugar cane bagasse have been used as electrode materials for supercapacitors [55–58]. However, most of them exhibit low specific capacitances (< 300 F g^{-1} at a current density of 1.0 A g^{-1}) because they have low specific areas with suitable pore structure and/or no heteratoms-doping (nitrogen-doping). Therefore, the fabrication of carbon-based materials with high specific surface area, appropriate pore size and pore size distribution, as well as nitrogen-doping from a cheap and green route, using sugar cane bagasse as a precursor, is still be a significant and urgent challenge.

Herein, we develop a facile and green method to fabricate nitrogen-doped carbon with an ultra-high specific area and a hierarchical porous structure (NDHPC) using sugar cane bagasse, KOH, and urea as a carbon precursor, an activation agent, and a nitrogen source, respectively, in which carbonization, activation, and nitrogen-doping occur simultaneously. Furthermore, the urea used in the preparation process can not only increase the specific surface area, but also regulate the pore size of the final NDHPC material and thus to achieve a better electrochemical performance. The as-prepared NDHPC displays an interconnected framework, an ultra-high surface area (2905.4 $m^2 g^{-1}$), a high porous volume (2.05 mL g^{-1}) and a hierarchical pore structure. Benefiting from the multiple synergistic effects originated from an ultra-high specific area, a high porous volume, suitable nitrogen content, and partial graphitization, the NDHPC exhibits a significantly excellent electrochemical performance with a high specific capacitance, superior rate performance and excellent cycling stability (almost no capacitance loss up to 5000 cycles). The symmetric supercapacitor based NDHPC achieves a high energy density of 39.1 Wh kg^{-1} (at a power density of 1.0 kW kg^{-1}) performed with an operation voltage of 2.0 V in the 2 M Li_2SO_4 electrolyte.

2. Experimental section

Raw materials: The synthesis (or adoption) of the sugar cane bagasse and urea used in this paper has been published elsewhere [25]. The nickel foam was purchased from Shenzhen Kejing Star Technology CO., LTD. And the thickness of nickel foam is 1.522 mm. Potassium hydroxide and hydrochloric acid (analytical grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemical reagents were used directly without further purification.