



From weed to multi-heteroatom-doped honeycomb-like porous carbon for advanced supercapacitors: A gelatinization-controlled one-step carbonization



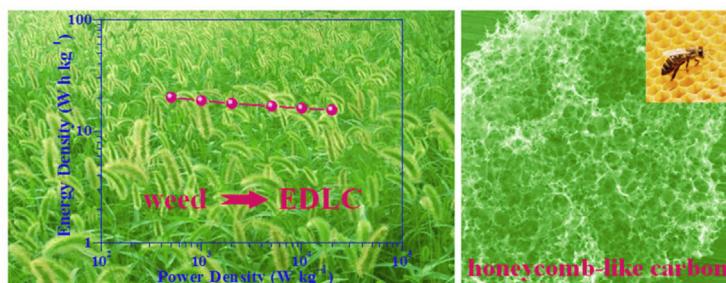
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HIGHLIGHTS

- Honeycomb-like porous carbon materials are prepared from green bristlegrass seeds.
- The texture of carbon products can be easily tailored by gelatinization pre-treatment.
- The obtained carbons have high surface area, hierarchical porosity and N/S/O-doping.
- The fabricated carbon-based electrodes exhibit excellent supercapacitive performance.
- The as-assembled symmetric supercapacitors deliver high energy and power densities.

GRAPHICAL ABSTRACT



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ABSTRACT

Biomass-derived porous carbon materials stimulate considerable research interest owing to the abundant resources, low cost, eco-friendliness and effective applications in electrochemical energy storage. Herein, N/S/O-doped honeycomb-like porous carbon materials are successfully controlled prepared from green bristlegrass seeds by one-step carbonization with assistance of gelatinization treatment. Benefitting from their three-dimensional interconnected honeycomb-like hierarchical porous architecture together with high specific surface area and multi-heteroatom doping, the as-synthesized carbon materials exhibit high specific capacitance of 391 F g^{-1} at a current density of 0.5 A g^{-1} with good rate capability (67.8% capacitance retention at 50 A g^{-1}) in 6 M KOH and outstanding cycling stability with a capacitance retention of 97.2% over 10000 cycles. Meanwhile, the symmetric supercapacitor device in 1 M Na_2SO_4 aqueous electrolyte is able to deliver a high energy density of 20.15 Wh kg^{-1} at a power density of 500 W kg^{-1} with a wide voltage window of 2.0 V. More impressively, it still retains a high energy density of 15.56 Wh kg^{-1} even at 20 kW kg^{-1} . In addition, the supercapacitor device also shows superior cycling performance with a 94.2% capacitance retention for 10000 cycles.

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1. Introduction

As an advanced energy storage system, supercapacitor has achieved significant attention due to its high power density, long cycling life and rapid dynamics of charge propagation [1,2]. Among various supercapacitor electrode materials, carbon-based materials are always dominant because of their good electrical conductivity, large surface area, electrochemical inertness, and good chemical stability, which make them the most commonly employed electrode material for alkali-metal-ion batteries [3–5] and commercial supercapacitors [6–9]. However, most commercially available activated carbons are prepared from non-renewable fossil fuel and lacked in control over pore size distribution, thus bringing about environmental unsustainability and low capacitance and energy density [10]. Generally, the performances of carbon-based electrical double layer capacitor (EDLCs) are primarily dependent on the structure and composition of carbon materials. Therefore, to develop high performance EDLCs, it is particularly preferred to synthesize the advanced carbon materials with novel hierarchical morphology, high specific surface area, desirable porous structure, good electrical conductivity, and rich functionalized heteroatoms [11–13].

In general, the large surface area of the carbon materials signifies the abundant sites for charge accumulation enabling the high capacitance, but the relationship between them is nonlinear. It has been found that the pore structure, such as pore geometry, pore size and pore size distribution, exhibits significant influence on the electrochemical performances of carbon-based EDLCs [14]. The micropores can offer high surface area enhancing the electric double layer capacitance, while the mesopores and macropores will facilitate the ion diffusion and charge propagation displaying the low-resistance [15]. In recent years, three-dimensional (3D) interconnected hierarchical architectures have been recognized as one of the most promising structures for supercapacitors, because they can provide not only the large surface area, but also the 3D continuous electron pathway for good electrical contact and the interconnected pores for fast electrolyte penetration and accessibility [16]. Another approach to optimize the electrochemical performance of carbon-based electrodes is the introduction of surface functional groups and/or doped heteroatoms, which are capable of enhancing electronic conductivity, improving surface wettability, and introducing pseudocapacitance [17]. Therefore, it is highly desirable to explore the simple, renewable and cost-effective strategies to fabricate 3D interconnected porous heteroatom-doped carbon materials [18,19].

As a renewable source, natural biomasses from plants, animals or waste residues have received considerable attention for their promising applications in the preparation of carbon-based materials due to their high abundance, easy availability, low-cost and eco-friendliness [20,21]. Moreover, the microstructure of bio-inspired carbon materials are usually dependent on the inherent structure and composition of the biomass precursor. Thus, a variety of porous carbon materials with controlled morphologies and textures together with heteroatom doping can be prepared from natural biomass precursors and are of continuously increasing interest for supercapacitors, which can achieve the dual goals of environmental sustainability and energy storage [22–24]. Green bristlegrass, a common crabgrass, is one of the most abundant weeds which widely spreads not only into cropland, fallow land and pastures, but also onto rights-of-way, roadsides, parks, forestry and other areas. These weeds would compete with crop plants for soil nutrient, water and sunlight, resulting in substantial losses in yields. Therefore, it should be of central importance to convert these worthless weeds into high additional value materials.

In this work, green bristlegrass seeds (GBS) are successfully developed as the new biomass precursors to prepare carbon materials. Under the assistance of gelatinization pre-treatment, 3D interconnected honeycomb-like porous carbon materials with multi-heteroatom doping, high specific surface area and hierarchical porous structure can be controlled synthesized by a one-step pyrolysis carbonization. Fig. 1

illustrates the synthesis process of the honeycomb-like porous carbon materials derived from GBS. As a typical 3D interconnected porous architecture, honeycomb-like carbons have been prepared from various nature materials, such as wheat flour [25,26], wheat bran [27], rice bran [28], pomelo peel [29], soybean residue [30], plane tree fluff [31], and *Ailanthus altissima* stem [32]. However, to the best of our knowledge, green bristlegrass has never been employed as the precursor to prepare advanced carbon materials. Thanks to the unique porous structure and multi-heteroatom doping, the green bristlegrass seeds-derived honeycomb-like carbon materials exhibit outstanding electrochemical performances as electrodes for supercapacitors.

2. Experimental section

2.1. Preparation of honeycomb-like porous carbon from GBS

The spikes of green bristlegrass were collected naturally and the detached seeds were directly used as the precursor. In a typical synthesis, the GBS were rinsed with deionized water in ultrasound bath for several times to remove the dirt, and then dried in oven at 80 °C. The cleaned GBS were soaked in KOH aqueous solution with different mass ratios of GBS to KOH (1:0, 1:2, 1:4, and 1:6) for 24 h, and the gel could be formed. Afterwards, the gel was fully dried at 80 °C in air and transformed into xerogel, as revealed in Fig. 1. Subsequently, the xerogel was loaded in a nickel crucible and pyrolyzed in a horizontal tubular furnace at different carbonization temperatures (600 °C, 700 °C, 800 °C, 900 °C) for 2 h with a heating rate of 10 °C min⁻¹ under high purity Ar flow. After being cooled to ambient temperature, the resulting carbon products were ground into powder with a manual agate mortar. Finally, the carbon samples were dispersed in deionized water, centrifuged and repeatedly washed with abundant deionized water, until the pH value reached about 7.0, and then dried at 80 °C overnight to achieve the honeycomb-like porous carbon materials.

2.2. Sample characterizations

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) elemental mapping measurements were performed on a Quanta 200F environmental scanning electron microscope (FEI, Netherlands). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) patterns were taken from a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) patterns were recorded on a PANalytical Empyrean diffractometer with Cu K α_1 radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were measured by a LABRAM-HR confocal laser micro-Raman spectrometer (Jobin-Yvon, France) in the backscattering configuration excited with the 514.5 nm line of an Ar⁺ ion laser. X-ray photoelectron spectroscopy (XPS) tests were carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer with Al K α monochromatic radiation at a constant pass energy of 1486.6 eV (Thermo Fisher, USA). The nitrogen adsorption-desorption isotherms were measured by nitrogen physisorption at 77.35 K using Quantachrome ASiQwin-Autosorb iQ Station 1 (Quantachrome Instruments v4.01, USA).

2.3. Electrochemical tests

To investigate the electrochemical performance of the obtained carbon materials, the working electrodes were prepared by pasting the slurry composed of 80 wt% carbon sample, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride binder in absolute ethanol solvent onto one side of carbon cloth (WOS 1002, CeTech CO., Ltd., China) with an active area of $1 \times 1 \text{ cm}^2$, which were finally dried at 60 °C for a day. The mass loading of the active materials in each carbon electrode was about 2.2–2.5 mg cm⁻².

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