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Tunable porous structure of carbon nanosheets derived from puffed rice for high energy density supercapacitors

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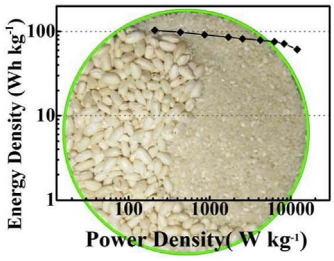
HIGHLIGHTS

- Rice derived, tunable micro/meso-pores structures of carbon nanosheets.
- Honeycomb-like architecture is induced by 'puffing effect'.
- The "puffing effect" avoiding organic solution usage, leading to green route.
- Ultrahigh S_{BET} of 3326 m^2 g^{-1} with optimized mesopores.
- Highest supercapacitors performance of 104 Wh kg^{-1} or 53 Wh L^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of green and clean synthetic techniques to overcome energy requirements have motivated the researchers for the utilization of sustainable biomass. Driven by this desire we choose rice as starting materials source. After the explosion effect, the precursor is converted into puffed rice with a honeycomb-like structures composed of thin sheets. These honeycomb-like macrostructures, effectively prevent the cross-linking tendency towards the adjacent nanosheets during activation process. Furthermore, tuneable micro/mesoporous structures with ultrahigh specific surface areas (S_{BET}) are successfully designed by KOH activation. The highest S_{BET} of 3326 m^2 g^{-1} with optimized proportion of small-mesopores is achieved at 850 °C. The rice-derived porous N-doped carbon nanosheets (NCS-850) are used as the active electrode materials for supercapacitors. It exhibites high specific capacitance specifically of 218 F g^{-1} at 80 A g^{-1} in 6 M KOH and a high-energy density of 104 Wh kg^{-1} (53 Wh L^{-1}) in the ionic liquid electrolytes. These are the highest values among the reported biomass-derived carbon materials for the best of our knowledge. The present work demonstrates that the combination of "puffing effect" and common chemical activation can turn natural products such as rice into functional products with prospective applications in high-performance energy storage devices.

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1. Introduction

Electrical double layer capacitors (DLCs) can store the electrostatical charge through reversible adsorption of ions at the interface of electrolyte and porous electrodes [1]. High surface area and appropriate pore distribution are the key factors for DLCs materials in-order to provide active sites and channels for sufficient number of electrolyte ions [2,3]. DLCs have attracted tremendous attention due to having higher specific power density and longer cycle life than li-ion batteries and fuel cells [4]. However, they still suffer from low energy densities (~8 Wh kg^{-1}), which has significantly limited their practical application [5]. Therefore, to fulfill the critical demands of energy, novel and advanced porous materials should be developed for highly efficient energy storage devices (DLCs) through a facile and clean synthesis technologies route [6].

In the past decade, novel electrode materials have been developed to simultaneously meet the requirements of: (i) high S_{BET} for more active sites to facilitates the charge storage [7–9], (ii) well-balanced nanoporous distribution that offer rapid ion transport with not only improved the rate capability but also boost the specific capacitance [10–12], (iii) nanosize-structures to reduce the diffusion pathways [13–15], and (iv) introduction of defects and heteroatoms to increase active sites for reaction as well as the ion-accessible surface area through excellent wettability [16–18].

Nano materials fabricated through templates with chemical activation showed superior performance *e.g.* the carbon nanocages (2561 $m^2 g^{-1}$) fabricated through MgO template method [19]; porous carbon nanosheets (3235 $m^2 g^{-1}$) produced from coal tar by $Mg(OH)_2$ template coupled with KOH activation [20]; flask-like hollow carbonaceous (2335 $m^2 g^{-1}$) [21] and hollow carbon nanospheres [22] (2225 $m^2 g^{-1}$) synthesized via soft templates using ribose and resorcinol as carbon precursor. These nano carbon materials are the most commonly used electrodes due to their high S_{BET}, good conductivities, abundant structures, and easily modified surface properties by doping and/or surface functionalization [7–22]. These supercapacitor materials exhibited good rate capability (200–230 F g^{-1}) at high scan rate (20 A g^{-1}) [19–22]. On the other hand, different researches synthesized functional carbon based materials directly from natural biomass [23–25]. With the aid of template chemicals and heteroatom-doped carbons, large S_{BET} can be obtained from various biomass, like cotton stalk [24], squid inks [25], soybeans [26], cellulose [27–29], seaweed [30], silk [31], wood [32], seedling [33], *etc*. Similarly, very recently, some new synthesis techniques have been explored for the direct fabrication of supercapacitors electrode materials by using yeast powder fermented rice with hydrothermal carbonization [34], and marking corn expansion through microwave popping [35] or steam-explosion [36]. These biomass materials were utilized as precursors, and could be transformed into porous structure that can exposed carbon atoms from the pore-making before the carbonization process.

Herein, with the help of “puffing and thermal effect”, rice grains was turned into a specific open micro/nano-structure material. The “puffing effect” has the merit of additional solutions un-requirement, which is an extension of green chemical method [37], and offers a clean, rapid, eco-friendly and more efficient fabrication route. Importantly, puffed rice's volume is 25 times larger than rice particles mainly arising from the open honeycomb-like macrostructure from the bombing process (Scheme 1 and Fig. 1). The main ingredients of rice are, carbohydrate (70–80%), moisture (10–15%), and protein (~8%), carbohydrate work as the main carbon source and protein work as nitrogen source. Therefore, in this report, natural rice-derived porous N-doped carbon nanosheets (NCS-X) with adjustable ultrahigh specific surface areas and porosity, controllable nitrogen doping level (0.88–1.62 at. %) was produced via the “puffing effect” method and regulated by activation temperature. The synthetic strategy of NCS-X is schematically depicted in Scheme 1. The high S_{BET} (3326 $m^2 g^{-1}$) with optimized mesopores volume (31% for mesoporous volume) is achieved at 850 °C. The excellent textural properties have the optimum capacitance performance of 218 F g^{-1} at 80 A g^{-1} in 6 M KOH. Most importantly, the energy density reached to 104 Wh kg^{-1} (53 Wh L^{-1}) in ionic liquid electrolyte, which is the highest among the ever-reported biomass derived carbon materials for the best of our knowledge. Thus, the fitted empirical routines provide guidelines for materials designing and structural optimization for high-performance carbon materials.

2. Experimental section

2.1. Materials

In this study, rice is purchased from shop in Jiangsu Province, China. Potassium hydroxide (KOH) and hydrochloric acid (HCl) are bought from Sinopharm Chemical Reagent Co., Ltd. 1-Ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$ > 99%, water content < 100 ppm) is bought from Jiangsu Guotai Super Power New Materials Co., Ltd.

2.2. Fabrication of rice-derived porous carbon nanosheets

Firstly, the rice is heated in a sealed container, after the thermal effect of steam the pressure reached to 5–10 atm. The rice cracked to form puffed rice after the releasing of pressure through the sudden opening of container cover lid. Secondly, the white puffed rice is pre-carbonized in inert atmosphere at 500 °C for 1 h with the heating rate of 3 °C min^{-1}. Thirdly, pre-carbonized puffed rice (PPR-500, 200 g) are mixed with KOH (3 times PPR-500 wt) and further activated at a rate of 3 °C min^{-1} up to 750, 800, 850, and 900 °C for 1 h with the protection of nitrogen. Then as-prepared materials were washed with 1 M HCl solution to remove inorganic impurities and further washed with distilled water until the pH was around 7. Finally, the samples are dried at 120 °C for 8 h. The fabricated samples are named as NCS-X, where X represents the activation temperature.

2.3. Characterization

The porosity and surface area of the samples are measured by nitrogen (77 K) adsorption, performed at relative pressure P/P^0 of 4.8×10^{-7}-0.9981, utilizing the Micromeritics ASAP 2020. The samples are degassed at 300 °C for 6 h before measurements. The BET surface areas (S_{BET}) are calculated according to the Brunauer-Emmett-Teller (BET) method. The pore size distributions are obtained using the density functional theory (DFT). The surface morphology of the prepared samples is performed using Hitachi field-emission scanning electron microscopy (FE-SEM S-4800) and TEM (Tecnai G2 F30 S-Twin, FEI). The Raman system and X-ray powder diffraction (XRD) (AXS D8 ADVANCE, Bruker) are operated to analyze the crystal structure and graphitic degree of the as-prepared samples. HAADF-STEM and the corresponding EDX elemental mapping are conducted to analyze the element distribution. The elemental analysis and XPS presented the content of heteroatoms in the prepared samples.

2.4. Electrochemical measurements

The electrochemical performances of the prepared materials are examined using cyclic voltammetry (CV), Galvanostatic charge/discharge and AC impedance spectroscopy (EIS) on the CHI660E electrochemical workstation by two-electrode system. The NCS-X was grounded into powder for 20 min. The honeycomb-like macrostructure lead to macrospores which are also grounded and compressed, which reduced the volume and increased the tap density. The calculated densities of electrode materials are provided in Fig. S3. The electrodes are prepared by mixing the prepared samples (NCS-X), carbon black and PTFE binder (86: 10: 4) weight ratio into chip with 11 mm diameter, aluminum mesh with $EMIMBF_4$ and stainless steel mesh with