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# Large-size graphene-like porous carbon nanosheets with controllable N-doped surface derived from sugarcane bagasse pith/chitosan for high performance supercapacitors

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ABSTRACT

The large-size graphene-like porous carbon nanosheets (LGPCN) with controllable N-doped surface are successfully prepared by using a simple and effective integrated “self-template” and “designing” strategy through KOH activation. Biomass-sugarcane bagasse pith and chitosan are used as self-template carbon source and controlled nitrogen source, respectively. The relationship between structure of the LGPCN-X (X represents the activation temperature) and its electrochemical performance at different activation temperatures is explored in detail. The large-size multiscale wrinkled nanosheets architecture, high surface area, and appropriate controllable surface nitrogen doping state of the LGPCN-800 shows the best electrochemical performance in 6 M KOH. The largest specific electrode capacitance is about 339 F $g^{-1}$ (at 0.25 A $g^{-1}$), which still as high as 280 F $g^{-1}$ at 100 A $g^{-1}$. The maximum energy density is about 11.77 Wh $kg^{-1}$ at a power density of 34.11 W $kg^{-1}$. The LGPCN-800 also shows an excellent cycling stability with 97.9% capacitance retention after 10,000 cycles.

## 1. Introduction

Energy and environment are the two major problems facing the human beings today. Therefore, development of sustainable and regenerative energy conversion and storage devices is one of the most important challenges [1–5]. In recent years, supercapacitors, with high power density, excellent cycling stability, good operational safety, high thermal stability and fast charge–discharge rates have received increased attention [6–8]. Among the different electrode materials of supercapacitors, carbon electrode materials have been extensively investigated due to high surface area, porosity, excellent electrical properties, good chemical stability, low cost, and flexible designability [9–12].

Based on the electrical double layer storage mechanism, the electrochemical performance of carbon electrode materials depends on the electrolyte ion-accessible surface area, electrolyte ion-transport channel, and electron transport path [13–17]. As is known, the electrolyte ion transport time ($\tau$) in the porous carbon electrode materials is defined by electrolyte ion transport distance ($L$) in the relationship of $\tau = L^2/D$ (where D is the electrolyte ion transport coefficient) [18]. Obviously, electrolyte ion transport kinetics is controlled mostly by electrolyte ion transport distance ($L$). Therefore, it is vital to engineer the nanoscale morphology of porous carbon electrode materials. Among all the nanostructured morphology of the novel carbon electrode materials, The porous carbon nanosheets is one of the most promising candidates as supercapacitor electrodes because of their high aspect ratios and open porous hierarchical architectures, which can offer high ions-accessible surface area for charge storage, open shortened diffusion distance for electrolyte ions-transport, and superior continuous conducting pathways for electrons transfer. To date, there are two different strategies for the preparation of advanced graphene-like porous carbon nanosheets electrode materials in my opinion, (i) “designing” strategy; (ii) “self-template” strategy.

In recent years, many ingeniously-designed porous carbon nanosheets materials [19–22] have been successfully prepared by using small organic molecules, macromolecules etc. as controlled carbon source. This “designing” strategy can precisely design and

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prepare advanced porous carbon nanosheets materials with fine structure. It is without doubt that these advanced carbon materials can help boost performance of carbon-based supercapacitors. However, the above-mentioned design-preparation process is not only time-consuming, costly, but also results in much environmental pollution. Therefore, the wide applications of advanced porous carbon nanosheets materials are limited by this complex and high-cost method. At the same time, biomass materials self-template carbonized electrode materials have been extensively investigated [23–26]. Generally speaking, in order to meet the specific needs of their biological functions, biomass materials from different organisms and even different parts or different periods of the same organism often exhibit distinctly different fine microstructures, pore structures, and even elemental composition. Therefore, biomass materials are the best self-template carbon sources to produce carbon-based electrode materials with unique micro-morphology and ingenious porous structures in my opinion. However, this strategy lacks controllability to some extent during the preparation of biomass material-based carbons with excellent electrochemical performance. Therefore, reasonable introduction of artificial control structure into the ingenious structure of biomass material-based carbons may be a feasible, facile, and effective preparation strategy of biomass material-based carbons with excellent electrochemical performance.

Sugarcane bagasse pith is the by-product obtained in sugarcane processing factories, which consists of approximately 50% cellulose, 25% hemicellulose and 25% lignin [27]. More importantly, Sugarcane pith predominantly exhibits a unique porous 3D honeycomb structure, which formed by parenchyma cell wall, in order to adapt to its physiological function of nutrients storing (mainly sucrose). Therefore, sugarcane bagasse pith is very suitable for use as a self-template carbon source of carbon nanosheets electrode materials. Furthermore, sugarcane bagasse pith can also be used as a hard template for controlled nitrogen sources (such as chitosan) to artificial control nitrogen-doped surface of carbon nanosheets, which can significantly enhancing the electrochemical properties of carbon nanosheets because N-doping can enhance the electronic conductivity and the surface wettability as well as provide extra pseudocapacitance. This dual-template role of sugarcane bagasse pith make it possible to control the morphology and surface chemical environment of the sugarcane bagasse pith-based carbon nanosheets during self-template carbonization process. Therefore, sugarcane bagasse pith may be able to produce advanced two-dimensional (2D) carbon electrode materials with excellent electrochemical properties using an integrated “self-template” and “designing” strategy.

In this study, we report a simple and effective construction method of large-size graphene-like porous carbon nanosheets (LGPCN) with controllable N-doped surface using sugarcane bagasse pith, chitosan, and KOH as self-template carbon source, controlled nitrogen source, and activating agent, respectively. The different activation temperatures (600 °C, 700 °C, 800 °C, and 900 °C) were used to study the effect on the structural and electrochemical performance of the samples. As the activation temperature increases, the structural morphology, thickness, and surface nitrogen doping state of the LGPCN change obviously. At an activation temperature of 800 °C, the LGPCN-800 with multiscale wrinkled nanosheets architecture, appropriate surface nitrogen doping state, and high specific surface area of 1786.1 $m^2\ g^{-1}$ exhibits the best electrochemical performance in 6 M KOH. The specific electrode capacitance is up to 339 F $g^{-1}$ at a current density of 0.25 A $g^{-1}$. Even if the current density increased by 400 times to 100 A $g^{-1}$, the specific electrode capacitance can still retain a value of 280 F $g^{-1}$. The maximum energy density is about 11.77 Wh $kg^{-1}$ at a power density of 34.11 W $kg^{-1}$. When the power density is further increased to 24.32 kW $kg^{-1}$, the LGPCN-800 still retained an energy density of 7.68 Wh $kg^{-1}$. LGPCN-800 also displays excellent cycling stability (97.9% of its initial capacitance after 10,000 charge-discharge cycles).

## 2. Experimental section

### 2.1. Synthesis of graphene-like porous carbon nanosheets (LGPCN)

Sugarcane bagasse pith after extracting sugarcane juice by squeezing was obtained from the sugarcane (purchased from a supermarket). Initially, In order to remove the residual sucrose, the never-dried sugarcane bagasse pith was repeated rinsed with distilled water for about one week. Following the never-dried sugarcane bagasse pith (5 g) were suspended in 500 ml of distilled water containing 1 wt% glacial acetic acid, and then chitosan (2.14 g) was added with continuous stirring until chitosan was completely dissolved. The mixed suspension was stirred for about 4 h at room temperature, and dried at 80 °C in a conventional oven. Sugarcane bagasse pith/chitosan composite carbon precursors were first pre-carbonized in a tube furnace for 1 h at 700 °C in Ar atmosphere (about 40 ml $min^{-1}$) with ramp rate of 3 °C $min^{-1}$. Then the pre-carbonized materials were impregnated with KOH in an aqueous solution (the mass ratios of pre-carbonized materials to KOH was 1:4) by magnetic stirring, and dried at 100 °C in a conventional oven. Activation was performed at 600 °C, 700 °C, 800 °C, and 900 °C for 1 h in Ar atmosphere (about 40 ml $min^{-1}$) with ramp rate of 3 °C $min^{-1}$. The resulting carbon materials were ground to powder, washed with 0.5 M HCl solution and distilled water until reached a neutral pH. Finally, the graphene-like N-doped porous carbon nanosheets were dried for 12 h in a vacuum oven at 100 °C. The obtained samples were named LGPCN-X where X represents the activation temperature.

### 2.2. Material characterization

The morphology evolution of the LGPCN-X with the increase of activation temperature was observed with field emission scanning electron microscopy (FESEM, JSM-7001F) and Transmission electron microscopy (TEM, JEM-2100). The structure of the LGPCN-X was investigated by X-ray diffraction (XRD, D8 ADVANCE) with Cu K$\alpha$ 1 radiation ($k = 0.15406$ nm) at 40 kV and 40 mA. The surface elemental characterization of the LGPCN-X was performed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) with a monochromatic Al Ka source. The specific surface area and pore size distribution of the samples were characterized by $N_2$ adsorption analyses (BELSORP-Mini II) at 77 K. The samples were outgassed at 150 °C for 12 h under a vacuum. The Barrett-Emmett-Teller (BET) method was used to evaluate specific surface area. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model. Raman spectra were recorded on a HORIBA Scientific LabRAM HR Evolution Raman spectrometer system with an excitation wavelength of 532 nm.

### 2.3. Supercapacitors preparation and electrochemical measurements

The electrochemical performances of the LGPCN-X were evaluated in a symmetrical two-electrode system. The electrode materials were prepared by mixing LGPCN-X (85 wt%), acetylene black (10 wt%), and PTFE binder (5 wt%) in ethanol. The obtained electrode materials were coated onto the nickel foam. The premade electrodes were dried at 100 °C for 12 h in a vacuum oven. After drying, the electrodes were pressed under a pressure of 10 MPa for 1 min. Two symmetrical electrodes were separated by