



## Full Length Article

# Biomass-derived nitrogen-doped porous carbons with tailored hierarchical porosity and high specific surface area for high energy and power density supercapacitors



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## ABSTRACT

Porous carbon materials with hierarchical structures attract intense interest for the development of high-performance supercapacitors. Herein, we demonstrate a facile and efficient strategy to synthesize nitrogen-doped hierarchically porous carbons with tailored porous structure combined with high specific surface area (SSA), which involves a pre-carbonization and a subsequent carbonization combined with KOH activation of silkworm cocoon precursors. Through adjusting the mass ratio of the activator (KOH) to pre-carbonized precursor in the activation process, the hierarchically porous carbon prepared at the mass ratio of 2 (referred to as NHPC-2) possesses a high defect density and a high SSA of  $3386 \text{ m}^2 \text{ g}^{-1}$  as well as the relatively high volumetric proportion of mesopores and macropores (45.5%). As a result, the energy density and power density of the symmetric supercapacitor based on NHPC-2 electrode are as high as  $34.41 \text{ Wh kg}^{-1}$  and  $31.25 \text{ kW kg}^{-1}$  in organic-solvent electrolyte, and are further improved to  $112.1 \text{ Wh kg}^{-1}$  and  $23.91 \text{ kW kg}^{-1}$  in ionic-liquid electrolyte.

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## 1. Introduction

The accelerating consumption of fossil fuel and the induced global warming put forward higher request to the development of sustainable energy storage techniques. As promising candidates for energy-storage devices, supercapacitors have triggered intense attention due to their high-impact characteristics, including fast response capabilities and high power densities [1,2]. Unfortunately, the commercialized supercapacitors suffer from low energy storage capabilities, which hinder their further practical application [3,4]. Nowadays, great efforts have been devoted to designing and optimizing various porous materials and electrolytes to improve the energy storage capabilities. Specific capacitance and voltage window are the two critical factors in controlling the energy density of capacitors [5]. The specific capacitance involves the electric double layer capacitance (EDLC) and pseudo-capacitance [6–8]. The former is determined by the quantity of the charges adsorbed along the electrode/electrolyte interface, while the latter is contributed from

the Faradaic reactions of the electrode material. Moreover, the voltage window that is dependent upon the stability of the electrolyte, can be efficiently expanded as the organic-solvent electrolyte or ionic-liquid electrolyte are adopted to replace aqueous electrolyte [9–11]. However, comparing with the aqueous electrolyte, organic-solvent electrolyte and ionic-liquid electrolyte possess larger ion size, higher viscosity and lower conductivity, resulting in a poor capacitive performance of the conventional electrode materials [12–14]. Therefore, the development of porous materials with numerous surface faradaic reaction sites, high specific surface area in combination with appropriate porosity is crucial for the improvement of the energy storage capabilities of the supercapacitors.

Porous materials are promising electrode materials for supercapacitors. Among them, porous carbon materials such commercial activated carbon have gained more and more attention for their appearing properties including developed porosity, low framework density, high chemical stability and good electrical conductivity [15]. However, the activated carbon based supercapacitors exhibit low specific capacitance especially under high current loads due to the poor diffusivity of the ions in the numerous ion-inaccessible tortuous and blind micropores of the activated carbons [16,17]. Various hierarchical porous carbons (HPC) with rich heteroatom doping and high defect density have been designed and synthesized [15,18,19] to replace the traditional activated carbons. The

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mesopore and macropore in HPC can shorten the diffusion path of the electrolyte ions to decrease the ESR caused by large ion size and high viscosity, and enhance the charge storage in micropores even at high current density [20,21]. Doping heteroatoms (e.g., N, O, S etc.) also can highly enhance the energy storage capabilities of supercapacitor by inducing the pseudocapacitance and improving the wettability of carbon electrodes [22,23]. In addition, the numerous defects on the carbon layers can change the surface structure to increase the EDLC [24].

Biomass materials are promising precursors that can be used to prepare hierarchically porous carbons with high defect density and rich heteroatom doping. In a general way, defects and heteroatoms can be generated by pyrolyzing the heteroatom-containing precursors [25–29], and the hierarchical porosity can be tailored by template or activation method [15,30]. As a natural bio-polymer, silkworm cocoon is mainly composed of protein with fibroin being enveloped by the glue-like sericin, and the rich heteroatoms including N atoms is beneficial for the preparation of nitrogen-doped carbons during pyrolysis [31]. Moreover, the trace inorganic salts dispersing in the silk is a natural template that is favorable for the homogeneously creation and expansion of pores through adjusting the activation condition during pyrolysis, facilitating the formation of hierarchically porous structure [32].

In this work, nitrogen-doped hierarchically porous carbons (NHPC) were successfully synthesized by a pre-carbonization and a subsequent KOH activation of silkworm cocoon. The porosity of the NHPC can be readily tailored via adjusting the mass ratio of KOH to the pre-carbonized precursor. The NHPC prepared at the mass ratio of 2 (referred to as NHPC-2) possessed a typical hierarchical porosity with a rational pore size distribution, a high SSA and a high defect density. As a result, the symmetric supercapacitors based on the NHPC-2 electrode exhibit high energy storage capabilities in organic-solvent and ionic liquid electrolytes.

## 2. Experimental

### 2.1. Preparation of NHPCs

The NHPCs were prepared via a modified chemical activation method including a pre-carbonization and a subsequent carbonization combined with KOH activation of silkworm cocoon. Firstly, dried silkworm cocoon was pre-carbonized at 450 °C (heating rate: 5 °C min<sup>-1</sup>) for 0.5 h to transform the protein into sp<sup>2</sup>-hybridized aromatic structure and introduce additional oxygen-containing functional groups in the pre-carbonized product [33]. The numerous oxygen-containing functional groups in silkworm cocoon are helpful for the creation and expansion of the pores during the activation process [34,35]. Subsequently, the pre-carbonized precursor was mixed and grinded with KOH at a mass ratio of 0.5, 1 and 2. Then the mixture was heat-treated at 900 °C (heating rate 1 °C min<sup>-1</sup>) for 2 h in an Ar atmosphere. After that, the obtained samples were washed thoroughly with 5 wt.% hydrochloric acid (HCl) and deionized water until the pH values reached 7.0, and finally dried at 80 °C. The final products were named as NHPC-x, where x is the mass ratio of KOH to pre-carbonized precursor.

### 2.2. Characterizations

Scanning electron microscopy of JEOL 6701 was employed to characterize the morphologies of the NHPCs, while transmission electron microscopy of JSM-2100 was used to observe the microstructures of NHPCs. The nitrogen gas sorption measurement was carried out with the adoption of the Brunauer-Emmett-Teller (BET) model and nonlocal density functional theory (NLDFT) methods to calculate the SSA and the pore size distribution (PSD) of

NHPCs, respectively. The composition and chemical state of NHPCs were characterized on X-ray photoelectron spectrometer XPS of ESCALAB-250. The crystallographic features and microstructures of the NHPCs were tested by X-ray diffraction spectroscopy (XRD) by using K<sub>α</sub> radiation of Cu (λ = 1.54056 Å) and Raman spectroscopy (Raman, LabRam HR800).

### 2.3. Electrochemical measurements

All the capacitive measurements were conducted in an assembled symmetric system with a CR2032 coin-type cell on a CHI660e working station. The electrode was prepared via pressed the mixture of NHPC-x, conductor (acetylene black) and PTFE (80:15:5) onto the nickel foams (the active mass is approximately 2.0 mg cm<sup>-2</sup>) under the pressure of 10 MPa and dried at 120 °C in a vacuum oven overnight. A glass-fiber membrane was used as the separator. 1.0 M TEABF<sub>4</sub> in AN (2.5 V) and neat EMIMBF<sub>4</sub> (3.5 V) were used as the organic-solvent electrolyte and the ionic liquid electrolyte, respectively. Cyclic voltammetry (CV) curves of these samples were recorded at the rate of 20, 50, 100, 200 and 500 mV s<sup>-1</sup>. Galvanostatic charge-discharge (GCD) curves of the samples were recorded with various current densities of 5, 10, 20, 30, 50 A g<sup>-1</sup>. Finally, the electrochemical impedance spectroscopy (EIS) measurements carried out with a certain frequency range (100 kHz–10 mHz). The specific capacitance C (F g<sup>-1</sup>) based on the GCD was calculated according to the equation:

$$C = \frac{2I\Delta t}{m\Delta V} \quad (1)$$

where  $I$  (A),  $\Delta t$  (s) and  $m$  (g) are the discharge current, discharge time, and the effective mass loaded on a single working electrode, respectively.  $\Delta V$  (V) refers to the potential change excluding the voltage drop within  $\Delta t$ . The energy storage capabilities and rate including energy density  $E$  (Wh kg<sup>-1</sup>) and power density  $P$  (W kg<sup>-1</sup>) of the supercapacitor is dependent on the following two equations:

$$E = \frac{1}{2 \times 4 \times 3.6} C \Delta V^2 \quad (2)$$

$$P = \frac{3600E}{\Delta t} \quad (3)$$

The capacitance calculated from the EIS measurement can be illustrated as follows, in which  $C(\omega)$  is decided by the real part capacitance  $C'(\omega)$  and imaginary part  $C''(\omega)$  of the supercapacitors.

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (4)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \quad (5)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (6)$$

Where  $Z(\omega)$  is the complex impedance, which is determined by the real part impedance  $Z'(\omega)$  and the imaginary part  $Z''(\omega)$ .

## 3. Results and discussion

### 3.1. Physicochemical characterization

SEM and TEM images of NHPC-x exhibits their morphologies and porous structures. As shown in Fig. 1, the amount and size of pores in NHPC tends to increase as the mass ratio of KOH to the pre-carbonized precursor increases from 0.5 to 2. Among three samples, NHPC-2 exhibits a typical honeycomb-like porous structure with abundant interconnected mesopores and macropores. The well-defined hierarchical porosity of NHPC-2 indicates the critical role of KOH dosage in tailoring the porosity [36]. The

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