



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: [www.elsevier.com/locate/jpowsour](http://www.elsevier.com/locate/jpowsour)

# Nitrogen-doped porous carbon with an ultrahigh specific surface area for superior performance supercapacitors

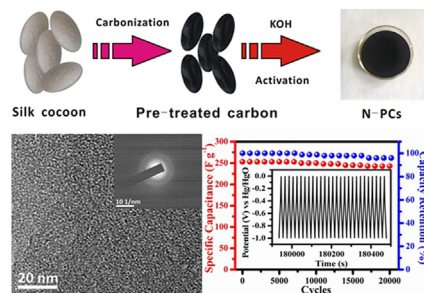
Chao Long, Yong Xiao, Mingtao Zheng<sup>\*\*</sup>, Hang Hu, Hanwu Dong, Bingfu Lei, Haoran Zhang, Jianle Zhuang, Yingliang Liu<sup>\*</sup>

Guangdong Provincial Engineering Technology Research Center for Optical Agriculture, College of Materials and Energy, South China Agricultural University, 483 Wushan Road, Guangzhou 510642, China

## HIGHLIGHTS

- A special staged KOH activation method was applied to synthesized Nitrogen-doped porous carbon materials via silk cocoon.
- We obtained an ideal Nitrogen-doped porous carbon with an ultrahigh specific surface area ( $3841 \text{ cm}^2 \text{ g}^{-1}$ ).
- The prepared sample displays superior electrochemical performance than many other Nitrogen-doped porous carbon materials.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 9 September 2015  
 Received in revised form  
 4 December 2015  
 Accepted 14 January 2016  
 Available online xxx

### Keywords:

Silk cocoon  
 Nitrogen-doped porous carbon  
 Ultrahigh specific surface area  
 Supercapacitors

## ABSTRACT

Owing to its abundant nitrogen content, silk cocoon is a promising precursor for the synthesis of Nitrogen-doped porous carbon (N-PC). Using a simple staged KOH activation, the prepared sample displays particular nanostructure with ultrahigh specific surface area ( $3841 \text{ m}^2 \text{ g}^{-1}$ ) and appropriate pore size, providing favorable pathways for transportation and penetration of electrolyte ions. Additionally, the doped nitrogen atoms ensure the samples with pseudocapacitive behavior. Those special characteristics endow N-PCs with high capacity, low resistance, and long-term stability, indicating a wonderful potential for application in energy-storage devices.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Supercapacitors, also known as electrochemical capacitors (EC), have been extensively developed due to their various advantages, such as high power energy, long service life and good stability

[1–5]. There are two types of supercapacitors based on the different charge-storage mechanism, electric double-layer capacitors (EDLCs) and pseudocapacitors. The energy storage principle of EDLCs is based on the separation of charged species in an electrical double layer across the electrode/solution interfaces [6]. Therefore, high surface area and suitable pores for electrolyte ions are significant to the EDLCs. On the other hand, pseudocapacitors can attain higher capacitance than EDLCs because they store and transport electrolyte ions by electrosorption, reduction-oxidation

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author.

E-mail addresses: [mtzheng@scau.edu.cn](mailto:mtzheng@scau.edu.cn) (M. Zheng), [tliuyi@scau.edu.cn](mailto:tliuyi@scau.edu.cn) (Y. Liu).

reactions, and intercalation processes. However, the inferior electrical conductivity and poor cycle stability result in a limitation for their practical applications.

As we all know, the surface area, pore size distribution, and surface microstructure of carbon materials are essential to the performance of supercapacitors. Therefore, many nanostructured carbon materials, including porous carbons (PCs) [7,8], carbon fibers [9], carbon aerogels [10] and carbon nanotubes [11], have been widely used in the EDLCs as electrode materials. Among all these carbon materials, PCs present numerous advantages than others, such as, low-cost, high surface area, adjustable pore structure, varieties of forms and ease of process ability. Those desirable merits ensure that many kinds of PC-based materials can be applied in the high performance supercapacitors [12–19].

Recently, for the purpose of further improving their applied performance, much effort has been devoted to synthesize and tailor the microstructures of PC materials. Among them, the nitrogen functionalized PCs is especially popular and important in the applications of adsorption and electrochemistry due to its specific structures and unique properties which can offer both high surface area for large amounts of potential active sites and channels for reactant/product transfer, respectively. Moreover, the doped nitrogen atoms endow the porous carbon with remarkable pseudocapacitive behavior. Most pathways for the production of nitrogen-containing PCs (N-PCs) rely on post-treatment of ammonia [20–22] or templating route combined with activation of nitrogen-rich carbon precursors [23–25]. Nevertheless, ammoxidation of PCs leads to a decrease in their surface area and pore volume, the nitrogen mainly distributed on the surface and often unstable, which limit their wide applications. In addition, templating route often suffers from these drawbacks such as time-consuming and severe synthetic conditions. Furthermore, most of the templates are based on surfactants and block-copolymers, which are rather expensive and non-renewable. One of the alternatives is to carbonize biomaterials, especially biomasses, to have nitrogen firmly incorporated in the carbon frame. For example, Senoz et al. reported the synthesis of microporous nitrogen-doped carbon materials from chicken feather fibers (composed of keratin, a fibrous structural protein also found in wool, hair, and some animal shells) [26]. Fan et al. reported on employing chitosan to produce nitrogen-containing microporous carbon materials [27]. Li et al. synthesized nitrogen-doped PCs by direct carbonization and activation of eggshell membranes [28]. In general, these were feasible methods to fabricate N-PCs, however, most of nitrogen-doped porous carbons obtained from above methods have comparatively low specific surface area ( $<2000 \text{ m}^2 \text{ g}^{-1}$ ), which impeded their applications to a considerable extent in supercapacitors electrode materials [29–32]. Therefore, it is still a challenge to develop a facile and benign method to synthesize N-PCs with ultrahigh specific surface area from simple available precursors.

Silkworm cocoon produced by the bombyx mori silkworm is one of the most abundant nontoxic protein-based biopolymer in nature, which is cultivated more than 480 000 ton per year all over the world [33]. Detailed investigations indicate that the silk consists of two main proteins, sericin and fibroin, which is rich in nitrogen and carbon elements. In recently years, however, compared with their widely used in fabrics, their potential applications in material science have attracted some attention, such as electrode materials. Liang and his group synthesized carbon microfibers with hierarchical porous structure from silk cocoon which could be used as electrodes of supercapacitors [34]. In addition, Yun et al. reported microporous carbon nanoplates from regenerated silk proteins for supercapacitors [35]. Recently, Hou and his co-workers have prepared hierarchical porous nitrogen-doped carbon nanosheets derived from silk for ultrahigh-capacity battery anodes and

supercapacitors [36]. Those researches clearly demonstrate that silk cocoon is a promising carbonaceous raw material for supercapacitor electrodes.

Herein, we reported a facile synthesis (staged KOH activation) of N-PCs with abundant micropores and mesopores as well as ultrahigh specific surface area ( $>3800 \text{ m}^2 \text{ g}^{-1}$ ) by silkworm cocoon. Using the as-prepared N-PCs as a charge storage material in supercapacitors, we have achieved a high specific capacitance of  $408 \text{ F g}^{-1}$  at a current density of  $0.5 \text{ A g}^{-1}$  and an excellent capacitance retention of 96% after 20 000 cycles at a high current density of  $25 \text{ A g}^{-1}$ . Those results clearly demonstrate that the electrochemical performance of N-PCs derived from silk cocoon is superior to that of most activated carbons used for commercial purposes.

## 2. Experimental section

### 2.1. Synthesis of N-PCs

Cocoons of *Bombyx mori* obtained from the South China Agriculture University in China were directly used as the starting material without any pretreatment. The schematic diagram for the synthesis of N-PCs derived from silk cocoon is shown in Scheme 1. In a typical process, the silk cocoon was first pre-carbonized in a tube furnace at  $400 \text{ }^\circ\text{C}$  under argon atmosphere for 2 h, and the heating rate was  $2 \text{ }^\circ\text{C min}^{-1}$ . Then, the carbonized sample was ground into powder and thoroughly mixed with KOH, the mass ratio of KOH to carbonaceous materials is about 3:1. At last, the mixture was activated at different temperature ( $600 \text{ }^\circ\text{C}$ ,  $700 \text{ }^\circ\text{C}$ ,  $800 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$ ) for 2 h under argon atmosphere with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . Moreover, during the activation process, the samples were pre-activated at  $400 \text{ }^\circ\text{C}$  for 1 h. The black products were then treated with 2 M HCl aqueous solution and then washed with deionized water. The final product was dried at  $80 \text{ }^\circ\text{C}$  overnight. The as-resulted N-PCs were named as N-PC-x, where x represents for the activation temperature.

### 2.2. Electrochemical measurements

The test was firstly performed by using a three-electrode system in 6 M KOH aqueous electrolyte solution at room temperature. The working electrode was fabricated as follows. The mixture containing 8 mg of N-PC materials, 1 mg of acetylene black and 1 mg of PTFE was thoroughly mixed to form slurry, then, the slurry was pressed onto a foam nickel substrate (12 M Pa) that served a current collector and dried at  $80 \text{ }^\circ\text{C}$  for 12h. In a three-electrode cell, the above loaded nickel foam, a Pt plate and Hg/HgO were used as the working, counter and reference electrodes, respectively. The electrochemical performance of N-PCs was studied by using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. Using the electrochemical system (ZAHNER Im6ex), EIS test was conducted at open circuit voltage in the frequency range of 100 kHz to 0.01 Hz with the AC voltage amplitude of 5 mV. The CV and GCD tests were carried out on a CHI660e electrochemical workstation (Chenhua Instrument Co., Shanghai).

The specific capacitance was calculated from CV and GCD test results according to the following equations:

$$C = \frac{1}{mv(U_2 - U_1)} \int_{U_1}^{U_2} I(U) dU \quad (1)$$

where  $C$  ( $\text{F g}^{-1}$ ),  $m$  (g),  $v$  ( $\text{V s}^{-1}$ ),  $U_1$  and  $U_2$ , and  $I(U)$  are the specific capacitance, mass of the active materials in the electrode, potential

Download English Version:

<https://daneshyari.com/en/article/7728618>

Download Persian Version:

<https://daneshyari.com/article/7728618>

[Daneshyari.com](https://daneshyari.com)