



# Soft templating synthesis of nitrogen-doped porous hydrothermal carbons and their applications in carbon dioxide and hydrogen adsorption



Pei-Wen Xiao <sup>a, b</sup>, Dan Guo <sup>a</sup>, Li Zhao <sup>a, \*</sup>, Bao-Hang Han <sup>a, \*</sup>

<sup>a</sup> CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, China

## ARTICLE INFO

### Article history:

Received 6 May 2015

Received in revised form

10 August 2015

Accepted 24 August 2015

Available online 1 September 2015

### Keywords:

Nitrogen-doped

Porous carbon

Hydrothermal carbonization

Hydrogen adsorption

Carbon dioxide adsorption

## ABSTRACT

Recent years, heteroatoms modified porous carbon materials have attracted particular attention due to their superior performance in adsorption, catalysis, or electrochemistry, *etc.* In this paper, we present a method to synthesize porous nitrogen-doped carbon materials *via* hydrothermal carbonization and soft templating process by using nitrogen-containing biomass derivative as precursor. The obtained materials possess relatively large Brunauer–Emmet–Teller specific surface area (up to 980 m<sup>2</sup> g<sup>-1</sup>), pore volume, as well as high nitrogen content (6.3 wt%). The morphology, porosity, and the functionalities were investigated by using scanning and transmission electron microscope, nitrogen sorption instrument, elemental analyzer, X-ray photoelectron spectroscope, and Fourier transform infrared spectrometer, *etc.* The effects of soft template concentration and the pH value on the properties of the obtained materials are discussed. Furthermore, the carbon materials exhibit relatively good properties for gas adsorption: the carbon dioxide adsorption capacities (3.7–4.7 mmol g<sup>-1</sup>) and the hydrogen adsorption capacity (up to 9.0 mmol g<sup>-1</sup>).

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## 1. Introduction

Porous carbons have attracted particular interests for their special properties [1,2], such as large surface area, surface hydrophobicity/hydrophilicity, large pore volume, chemical inertness, good mechanical and thermal stability, ease in handling, and low-cost preparation [3,4]. These materials have already been used and have great potential to be used in many important environmental and industry applications, such as heterogeneous catalysis [5,6], water and air purification [7,8], separation science [9], energy storage [10,11], and electrodes components [12,13].

By using traditional porous carbon synthetic methods, such as chemical activation, physical activation, and catalytic activation, porous carbons were obtained by activating carbon precursors with organometallic compounds or metal salts at high temperatures (approximately from 500 to 900 °C) [14–17]. Though these ways of

getting porous carbon are low-cost and easy for large-scale producing, the obtained products normally have inhomogeneous structure and wide spreading pore size distribution that limit their applications. Since Knox and his co-workers adopted hard template in the synthesis of porous carbon [18], porous carbon with homogeneous structure and uniform pore size has been synthesized by using different inorganic materials as hard templates, such as silica nanoparticles [19,20], zeolites [21], and anodic alumina membranes [22]. Hard templating synthesis of porous carbon always contains two procedures, the synthesis of regular hard template and the removal of the template under harsh condition, which make the process complicated and time-consuming [23]. Thus, this way does not conform to energy saving and green chemistry requirements. Using amphiphilic block-copolymers [24,25] or other supramolecular aggregates [26,27] as soft templates to synthesize ordered porous carbon is one way that overcomes some of the drawbacks mentioned above. However, the reported carbon precursors are mainly based on organic materials, which are not sustainable as compared to cheaper precursors, such as biomass [28]. As the hydrothermal carbonization (HTC) method possesses the features of mild reaction condition, low cost, controllable synthetic process, and meets the demands of green chemistry, it has already been

\* Corresponding authors. CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China, Tel./fax: +86 10 8254 5576.

E-mail addresses: [zhaol@nanocr.cn](mailto:zhaol@nanocr.cn) (L. Zhao), [hanbh@nanocr.cn](mailto:hanbh@nanocr.cn) (B.-H. Han).

proven to be a sustainable way to obtain carbon materials from biomass or biomass derived carbohydrates [29–34]. However, the directly hydrothermally carbonized materials do not have much porosity, and the specific surface areas of these materials are very small, which limit their applications. Employing block copolymers as soft template in the HTC synthetic process is a facile method that can introduce porous structure into the hydrothermal carbon materials. The soft template is easy to be formed in the HTC process without any intricate equipment. Kubo et al. have tried to combine the hydrothermal carbonization and the soft templating method together to synthesize ordered mesoporous hydrothermal carbons [35]. Besides the pore structure of the final products is easy to be controlled in the HTC process with the soft templating method, the economic saving and easy handling processes also make it a preferable method for synthesizing porous carbon materials.

On the other hand, to meet demands for special applications and improve the performance of the porous carbon, surface functionalization is required [36–41]. Heteroatoms, such as the group III and group V elements, could be introduced to the system [42–50]. Among these, nitrogen-doped carbons have attracted particular interest. Nitrogen-doped carbons were typically obtained by the treatment of carbons in nitrogen-containing gases or carbonization of organic nitrogen-containing compounds [51]. As discussed before, the HTC method is a sustainable way to obtain carbonaceous materials from biomass. Zhao et al. have synthesized nitrogen-doped carbons from chitosan and glucosamine *via* HTC process [36]. As expected, the porosity of these materials is very low. Thus, to find some methods to synthesize porous nitrogen-doped carbons from these nitrogen-containing biomass related precursors is interesting. As discussed before, soft templating method is a facile process that can be combined with HTC to introduce pores into the hydrothermal carbon materials, thus we would like to add soft template into the HTC process to obtain nitrogen-doped porous carbon materials, which could be used in some important applications in environmental fields, such as carbon dioxide sequestration or hydrogen storage, *etc.*

Hereby, a series of porous nitrogen-doped carbons were synthesized *via* HTC and soft templating process, where the glucosamine was used as carbon and nitrogen precursor, while a triblock copolymer P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) as the soft template. It is found out that the pore structure of the resulting materials varies by changing the ratio of soft template to carbon precursor and the pH value. The morphology, surface area, pore structure, and the content of the carbon materials were investigated. The largest Brunauer–Emmett–Teller (BET) specific surface area is up to 980 m<sup>2</sup> g<sup>-1</sup>. Furthermore, these kinds of materials show relatively high adsorption capacities for carbon dioxide (3.7–4.7 mmol g<sup>-1</sup>) and hydrogen (up to 9.0 mmol g<sup>-1</sup>).

## 2. Experimental

### 2.1. Materials

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, average molecule weight 5800) and D-(+)-Glucosamine hydrochloride (GA) (>99.0% crystalline) were purchased from Sigma–Aldrich Co. Glucose, hydrochloric acid (A. R., 36–38%) and anhydrous ethanol were purchased from Beijing chemical works, China. The Millipore–ELIX water purification system was employed to obtain ultra-pure water (18.2 MΩ cm). All the chemicals were used without further purification.

### 2.2. Synthesis

A certain amount of P123 was dissolved in 30 mL ultra-pure water (P123 solution), and hydrochloric acid was used to adjust the pH of P123 solution. The solution containing a certain amount of D-(+)-glucosamine hydrochloride with 30 mL ultra-pure water was added to the P123 solution dropwise. The mixture was stirred for 3 h at a constant temperature of 40 °C and then sealed into a glass vial inside a PTFE inlets autoclave followed by hydrothermal treatment at 180 °C for 20 h. The obtained black powder was washed and filtered by water and ethanol for several times, then the materials were dried at 80 °C overnight. Finally, the materials were calcined at 600 °C in the nitrogen flow to remove the soft template. The obtained hydrothermal porous nitrogen-doped carbons were named as HPNC-x (HPNC-1: P123 of 0.50 mmol and pH value of 7.0, HPNC-2 to HPNC-4 with the molar amount of P123 from 0.25 to 1.0 and pH value of 2.0 (Table S1 in the Supplementary file)). As a control experiment, a nitrogen-free carbon material (HPC-3) was synthesized by using glucose as precursor through the same synthetic process as HPNC-3 material.

### 2.3. Characterizations

Nitrogen and hydrogen sorption isotherms were obtained with a Micromeritics ASAP 2020 M + C (Micromeritics, USA). Carbon dioxide adsorption isotherm was obtained with a Micromeritics TriStar II 3020 surface area and porosity analyzer (Micromeritics, USA). The samples were degassed at 393 K overnight before measurement. The nitrogen and hydrogen sorption isotherms were measured at 77 K, while the carbon dioxide adsorption at 273 K. The specific surface area is calculated with BET method. The scanning electron microscopy (SEM) observations were carried out on a Hitachi S4800 microscope (Hitachi Ltd., Japan) at an accelerating voltage of 4 kV. Transmission electron microscopy (TEM) observations were performed with a Tecnai G<sup>2</sup> F20 U–TWIN microscope (FEI, USA) at an accelerating voltage of 200 kV. Infrared (IR) spectra were recorded by using a Spectrum One Fourier transform infrared (FTIR) spectrometer (Perkin–Elmer Instruments Co., Ltd. USA). X-ray photoelectron spectroscopy (XPS) surface experiments were taken by using a Thermo Scientific ESCALAB 250Xi electron spectrometer (Thermo Fisher, USA) with a monochromatic Al source ( $h\nu = 1486.6$  eV, 15 kV primary energy, 30 mA emission intensity), with an analysis area of 500 × 500 μm<sup>2</sup>. Solid-state <sup>13</sup>C CP/MAS NMR measurements were performed on a Bruker Avance III 400 spectrometer (Bruker, Switzerland). Elemental analysis was carried out by a FLASH EA1112 elemental analyzer (Thermo Quest, Italy). Thermogravimetric analysis (TGA) was performed using a Pyris Diamond Thermogravimetric (Perkin–Elmer Instruments Co., Ltd. USA) at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>.

## 3. Results and discussion

### 3.1. Synthesis and characterizations of porous nitrogen-doped carbons

#### 3.1.1. Supposed mechanism and morphology

As we know, the P123 composes of EO and PO segments, and the EO segments are more hydrophilic than PO segments, thus micelle is apt to be formed in water [4]. When glucosamine is added to P123 solution, the functional groups of GA, like hydroxyl groups, are helpful to make the biomass-derived precursor arrange along the P123 micelle through the hydrogen bond. During the sol–gel process, the soluble biomass derived carbohydrates interact with the EO moieties of the P123 chain *via* hydrogen bond and co-assemble [52]. Under the HTC condition of 180 °C, the carbohydrates, which

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