



# Structure and electrochemical performance of nitrogen-containing nanoporous carbon from diphenylcarbazine via a template carbonization route



Xiang Ying Chen<sup>a,\*</sup>, Lei Zhang<sup>a</sup>, Liang Xiao Cheng<sup>a</sup>, Yuan Yuan He<sup>a</sup>, Zhong Jie Zhang<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, P. R. China

<sup>b</sup> College of Chemistry & Chemical Engineering, Anhui Province Key Laboratory of Environment-friendly Polymer Materials, Anhui University, Hefei 230601, Anhui, P. R. China

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## ABSTRACT

In this work, a simple template carbonization method has been developed to produce nitrogen-containing nanoporous carbon from diphenylcarbazine, using  $Mg(OH)_2$  as hard template. The carbonization temperature has a crucial role in determining the carbon structure. The **carbon-3:1-800** sample obtained with the mass ratio of diphenylcarbazine and  $Mg(OH)_2$  as 3:1 at 800 °C exhibits the optimum pore structure as well as the resultant best electrochemical performance. It has a large BET surface area of 1538.0  $m^2 g^{-1}$ , high pore volume of 3.48  $cm^3 g^{-1}$ , and hierarchical pore size distribution. As a result, it delivers superior electrochemical behaviors in a three-electrode system using 6 mol L<sup>-1</sup> KOH as electrolyte, whose specific capacitance calculated from galvanostatic charge-discharge curve can reach up to 517.4  $F g^{-1}$  at a current density of 1 A  $g^{-1}$ , which is much larger than most of the nanocarbons ever reported in the literature. The **carbon-3:1-800** sample also exhibits good cycling stability within 10000 cycles. Comparatively, the electrochemical test has also been carried out in a two-electrode system using [EMIm]BF<sub>4</sub>/AN as electrolyte. More importantly, the operation temperatures of 25/50/80 °C can greatly broaden the application scope of nanoporous carbon in the supercapacitor.

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## 1. Introduction

Nanoporous carbons have emerged as an important candidate for supercapacitor application, primarily due to its advantages of high surface area, large pore volume, good chemical stability, easy production and low cost [1,2]. The electrochemical performances of nanoporous carbon materials to a large extent depend on the raw material and their surface structure and porosity, but also on the heteroatoms incorporated into their structures [3]. As the most important and widely introduced heteroatom, nitrogen functionality can provide basic properties, improving the interactions between the carbon surface and acid molecules, such as dipole-dipole, hydrogen bonding, and covalent bonding [4]. For example, the ammonia-treated carbon monolith can greatly expand the micropore size-distributions and increase the

capacitance up to 246  $F g^{-1}$  from the nitrogen-free one (186  $F g^{-1}$ ), which is ascribed to the better surface wettability of nitrogen-containing carbon [5].

The incorporation of nitrogen species into carbon matrix can basically be realized by the following strategies: carbonizing the nitrogen-containing precursors, such as polypyrrole [6,7]; carbonizing the carbon precursor together with the nitrogen-additives, such as L-lysine [8],  $NH_4Cl$  [9]; post-treatment of carbon with nitrogen species, such as  $NH_3$  gas [10]. However, a major disadvantage existing in the above routes is that the porosities are commonly not high for supercapacitor application, owing to the lack of pore-forming agents. On the other hand, a template carbonization method has been proved to efficiently produce nanoporous carbons with enhanced surface area and pore volume [11]. The existence of hard/soft template in the carbonization process greatly favors for the incremental formation of pores, and of course this is propitious to achieving high performance supercapacitor. Examples include the urea formaldehyde resins [12], polyacrylamide [13], melamine-formaldehyde resin [14], natural prawn shell [15], coexistent with templates of  $Ca(OAc)_2 \cdot H_2O$  or

\* Corresponding author. Tel.: +86 551 62901450; fax: +86 551 62901450.

E-mail addresses: [cxyhfut@gmail.com](mailto:cxyhfut@gmail.com) (X.Y. Chen), [zhangzj0603@126.com](mailto:zhangzj0603@126.com) (Z.J. Zhang).

CaCO<sub>3</sub>. To date, exploring the nanoporous carbon exhibiting superior electrochemical behaviors remains challenging and fascinating toward material scientists.

We herein demonstrate a template carbonization method to produce nitrogen-containing nanoporous carbon, in which diphenylcarbazine and Mg(OH)<sub>2</sub> serve as carbon/nitrogen source and template, respectively. The influence of diphenylcarbazines and Mg(OH)<sub>2</sub> on the carbon structures were studied by means of several scientific techniques. The resultant electrochemical performance was investigated in a three-electrode system, and a two-electrode system, respectively.

## 2. Experimental

In present work, Mg(OH)<sub>2</sub> was selected as a hard template for producing nanoporous carbon materials, mainly because of the following reasons: (1) Mg(OH)<sub>2</sub> is commercially available, and used as received; (2) Mg(OH)<sub>2</sub> is inexpensive, making it possible for practical production of carbon materials in a large scale manner; (3) Mg(OH)<sub>2</sub> can decompose into MgO and H<sub>2</sub>O at elevated carbonization temperatures. As a matter of fact, the freshly produced MgO serves as hard template, favoring for the formation of porosity in carbon matrix, after removal by HCl solution. On the other hand, the H<sub>2</sub>O substance also benefits for carbon porosity; (4) The MgO *in-situ* produced is inert with carbon matrix, revealing its chemical and thermal stability; (5) The MgO *in-situ* produced can be readily removed by HCl solution, instead of other toxic or corrosive acids such as HF, which seems to be greener and more environmentally benign.

### 2.1. Typical synthesis procedure for carbon-3:1-700/800/900 samples.

Diphenylcarbazine and Mg(OH)<sub>2</sub> with mass ratio of 3:1 were first poured into absolute ethanol, stirred for 2 h and then evaporated in air at 80 °C, resulting in red precipitate. It was ground, and then placed in a porcelain boat, flushing with Ar flow for 30 min, and further heated in a horizontal tube furnace up to 700, 800, or 900 °C at a rate of 5 °C min<sup>-1</sup> and maintained at this temperature for 2 h under Ar flow. The resultant product was immersed with dilute HCl solution to remove soluble/insoluble substances, subsequently washed with adequate deionized water. Finally, the sample was dried under vacuum at 120 °C for 12 h to achieve the **carbon-3:1-700/800/900** samples.

### 2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX2500V with Cu K $\alpha$  radiation. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S-4800 scanning electron microscope. High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were performed with a JEM-2100F unit. X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB MK II X-ray photoelectron spectrometer with an exciting source of Mg K $\alpha$  (1253.6 eV). The specific surface area and pore structure of the carbon samples were determined by N<sub>2</sub> adsorption-desorption isotherms at 77 K (Quantachrome Autosorb-iQ) after being vacuum-dried at 150 °C overnight. The specific surface areas were calculated by a BET (Brunauer-Emmett-Teller) method. Cumulative pore volume and pore size distribution were calculated by using a slit/cylindrical nonlocal density functional theory (NLDFT) model.

### 2.3. Electrochemical measurements

Detailed electrochemical measurements employed in present work are given in **Supporting Information** section and schematic illustration of a supercapacitor cell is shown in Fig. S1.

## 3. Results and discussion

The unit structure of diphenylcarbazine involved in this work is depicted in Fig. 1a. Interestingly, it is symmetrical in structure and the phenyl group can lead to carbon formation under carbonization conditions. The high nitrogen content (23.14%) of the pristine diphenylcarbazine makes it conceivable to produce carbon materials doped with nitrogen species. More importantly, in order to improve the porosity of the carbon materials, certain amount of Mg(OH)<sub>2</sub> substance, acting as hard template, was introduced.

When carbonizing the mixture of diphenylcarbazine and Mg(OH)<sub>2</sub> with mass ratio of 3:1 at 800 °C under Ar flow, weakly black powder occurs in the porcelain boat. The XRD pattern of the **carbon-3:1-800** sample before washing with HCl solution is shown in Fig. 1b. In the 2 theta scope of 4 ~ 90°, several diffraction peaks can be observed, which are ascribed to cubic MgO (JCPDS card No. 65-0746). As for the broad and low-intensity peak located at 20 ~ 25°, it corresponds to amorphous carbon. Clearly, the MgO substance derives from the thermal decomposition of Mg(OH)<sub>2</sub>, whereas the carbon roots in the carbonization of diphenylcarbazine.

For closer observation of the **carbon-3:1-800** sample before washing with HCl solution, HRTEM technique was also adopted. Fig. 1c indicates the HRTEM image, and the intermediate carbon/MgO composite basically takes on flake-like structures. The magnified HRTEM image is shown in the inset of Fig. 1d, whose lattice fringes are uniform and apparent. The two lattice spacings of 0.25 and 0.15 nm can be indexed as {111}, and {110} planes of cubic MgO. Together with the SAED pattern in the inset of Fig. 1d, it is discerned that the amorphous carbon and MgO are actually incorporated in the intermediate carbon sample. By all appearances, the *in-situ* produced MgO substance essentially serves as hard template for nanoporous carbon synthesis [16]. Of course, the H<sub>2</sub>O substance produced by the thermal decomposition of Mg(OH)<sub>2</sub> also benefits for creating carbon porosity to some extent.

After the removal of MgO substance by washing with HCl solution, a series of **carbon-3:1-700/800/900** samples can be achieved. The corresponding XRD patterns are comparatively indicated in Fig. 2a, and all of which exhibit one broad diffraction peak centered at 23.2°. This peak can be attributed to (002) plane of graphite. Furthermore, the low-intensity of these peaks reveals that the **carbon-3:1-700/800/900** samples are amorphous in nature with low degrees of graphitization. Besides, compared with (002) plane of the standard graphite (2 theta usually at 26.6°), the present ones at 23.2° have obviously shifted to low degree direction. This further support the fact that the carbon lattices within the **carbon-3:1-700/800/900** samples have been expanded (*i.e.* disordered in structure).

Intrinsic features of the **carbon-3:1-700/800/900** samples were determined by Raman technique as well as the deconvoluted ones by OriginPro Lorentzian method, as shown in Fig. 2b-d. All of them exhibit two distinct peaks in the wavenumber scope of 500 ~ 2000 cm<sup>-1</sup>, regardless of the variation of carbonization temperatures. The D band usually correlates with breathing vibrations of sp<sup>2</sup> rings, characterizing A<sub>1g</sub> symmetry disallowed in graphite or the double-resonance Raman process in disordered carbon, and the G band thanks to graphite in-plane vibrations with E<sub>2g</sub> symmetry [17]. Besides, the integral area ratios of D band and G band of the **carbon-3:1-700/800/900** samples, indexed as I<sub>D</sub>/I<sub>G</sub>, are also

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