



# Templated synthesis and activation of highly nitrogen-doped worm-like carbon composites based on melamine-urea-formaldehyde resins for high performance supercapacitors



Guanglin Sun<sup>a</sup>, Liya Ma<sup>a</sup>, Jiabing Ran<sup>a</sup>, Bing Li<sup>a</sup>, Xinyu Shen<sup>a</sup>, Hua Tong<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory of Analytical Chemistry for Biology and Medicine, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

<sup>b</sup> Suzhou Research Institute of Wuhan University, Suzhou 215123, People's Republic of China

## ARTICLE INFO

### Article history:

Received 14 January 2016

Received in revised form 3 February 2016

Accepted 7 February 2016

Available online 15 February 2016

### Keywords:

Nitrogen-rich carbon  
melamine-urea-formaldehyde resin  
hierarchical porous structure  
energy storage  
supercapacitor

## ABSTRACT

Nitrogen-rich carbon materials with hierarchical porosity were obtained by pyrolyzing melamine-urea-formaldehyde (MUF) resins between 650 and 850 °C with a mesoporous silica template, followed by KOH activation under N<sub>2</sub> atmosphere. In the synthesis process, the high nitrogen-containing MUF resins serve not only as carbon precursor but also as nitrogen source, and nitrogen content can be easily controlled by the carbonization temperature. The resulting MUF resins-derived porous carbon (MUF<sub>Cx</sub>) exhibits a high surface area (up to 2563.4 m<sup>2</sup> g<sup>-1</sup>) with nitrogen content varying from 14.25 to 11.68 at.%, respectively. As expected, electrochemical measurements show that the sample carbonized at 750 °C exhibits improved capacitance properties, such as an enlarged specific capacity (375 F g<sup>-1</sup> at 0.5 A g<sup>-1</sup>), excellent rate capability (272 F g<sup>-1</sup> at 10 A g<sup>-1</sup>), as well as excellent cycling retention (only 5% loss after 2000 cycles). Furthermore, an as-fabricated MUF<sub>Cx</sub>-based symmetric supercapacitor device shows a high energy density of 23.43 W h kg<sup>-1</sup> at a power density of 450 W kg<sup>-1</sup> operated in the voltage range of 0–1.8 V in 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Recently, supercapacitors have received considerable attention as alternative energy-storage systems with superior power density and long cycling durability compared to other conventional dielectric capacitors [1–4]. Based on the mechanism of energy storage, supercapacitors can be divided into pseudocapacitors and electrical double-layer capacitors (EDLCs). EDLCs have been extensively used in portable electronic devices because of high specific surface area and suitable pore size [5]. Activated carbons are regarded as the dominant electrode materials for commercial supercapacitors, owing to its large specific surface area, good conductivity, commercial availability and low cost [6–8]. However, more or less-severe drawbacks, such as the low specific capacitance and poor energy density, still preclude widespread and

practical use of pure carbon-based EDLCs in commercial supercapacitors.

To improve the specific capacitance of carbon electrode materials, the incorporation of heteroatoms (such as nitrogen or oxygen) into carbon materials turns out to be a promising approach [9]. In particular, it is known that the carbon materials with the nitrogen functional groups can introduce pseudocapacitance through redox reaction and improve the wettability of carbon materials to electrolyte solution, allowing these materials to increase the electric conductivity [10–12]. Therefore, much attention has been paid to the preparation of nitrogen-doped carbon electrode materials. In most cases, nitrogen-doped carbon materials are primarily prepared by post-treatment methods, in which the pure activated carbon is treated by ammonia gas/air or urea at a high temperature to introduce nitrogen into the carbon frameworks [13,14]. Another method is the direct carbonization of N-containing materials. For instance, Zhao and co-workers successfully synthesized nitrogen-doped hollow graphitic carbon spheres by direct pyrolysis of solid melamine-formaldehyde (MF) resin spheres, and the resulting materials exhibited some unique properties including excellent capacitance performance [15]. In addition, Liu et al. reported the synthesis of nitrogen-doped porous carbons by a template synthetic method with urea-formaldehyde

\* Corresponding author at: Key Laboratory of Analytical Chemistry for Biology and Medicine, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. Tel.: +86 2768764510; fax: +86 2768752136.

E-mail address: [sem@whu.edu.cn](mailto:sem@whu.edu.cn) (H. Tong).

(UF) resins as the precursor [16]. The synthesized carbons showed more superior rate capability and excellent long-term electrochemical stability. All of these works seem to suggest that the nitrogen-doped carbons can be used as precursors for high performance electrochemical supercapacitors.

Herein, we report a hard template strategy for the synthesis of hierarchical nitrogen-doped carbons with a high N content, using melamine-urea-formaldehyde (MUF) resins as the carbon and nitrogen source, respectively. The MUF resins have been widely used for particleboard industry, water-resistant particleboards, laminates and other commercial products in the past few years. To the best of our knowledge, it is the first time that MUF resins have been utilized for the construction of a hierarchical nitrogen-rich carbon. This strategy combines at least three dominant characteristics including its low cost, high atomic nitrogen content and widespread use in commercial products. By treating it as described below, the hierarchical porous carbons with high nitrogen contents were obtained after calcination at different temperatures. Owing to this unique structure, the resulting materials possess excellent capacitive performance, including low equivalent resistance, high specific capacitance, superior rate performance and excellent cycling stability in 6M KOH aqueous solution. Furthermore, a symmetric two-electrode cell assembled with nitrogen-doped hierarchical porous carbon showed a remarkable power and energy density, implying the great potential for future practical applications.

## 2. Experimental section

### 2.1. Materials

Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) and poly(tetrafluoroethylene) (PTFE) were purchased from Aldrich Chemical Company Inc. Tetraethylorthosilicate (TEOS, 98 wt%), formaldehyde aqueous solution (37 wt%), hydrochloric acid, hydrofluoric acid, ammonia, melamine and urea were purchased from Shanghai Chemical Corp. All the chemicals were used as received without further treatment.

### 2.2. Sample preparation

#### 2.2.1. Synthesis of hard-templated mesoporous carbon

The mesoporous silica template SBA-15 was synthesized according to the procedures reported previously. The detailed experimental procedure can be found in the literature [17]. In a typical synthesis of MUFC, 0.6 g calcined SBA-15 powder was impregnated with 10 g of 37 wt% formaldehyde aqueous solution. After ultrasonication for 30 min, 0.1 g of urea was added to the mixture and magnetically stirred at room temperature for 15 min. Then, 1 g of melamine was dissolved in the solution, followed by heating up to 100 °C for 15 min under vigorous stirring. The obtained stable suspension was subsequently cooled to room temperature and adjusted with ammonia until the pH of the mixture was about 9, followed by reaction for 4 h. Finally, the as-prepared sample was placed in a drying oven for 12 h at 100 °C to evaporate the unreacted formalin solution. The carbonization of the MUF was completed by pyrolysis with heating to 650 °C, 750 °C and 850 °C for 1 h in a tubular furnace under N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup>. The resulting dark solid was ground to powder, washed with hydrofluoric acid (HF, 10 wt.%) to remove silica template, and dried at 100 °C in air.

#### 2.2.2. Activation of nitrogen-rich mesoporous carbon

Activation was performed by impregnating mesoporous carbon with KOH agent with a weight ratio of 2:1 in a tube furnace under flowing N<sub>2</sub>, and then heated to the desired temperature of 700 °C

with a heating rate of 5 °C min<sup>-1</sup> and maintained for 1 h. Finally, the obtained product was washed consecutively with 0.1 M HCl solution at room temperature and then with deionized water until the pH of the mixture was about 7.0. The resultant samples were dried at 60 °C for 12 h and denoted as MUF<sub>Cx</sub>, where x indicates the carbonization temperature.

### 2.3. Characterization methods

The morphology of the prepared samples before and after KOH activation were characterized by field emission scanning electron microscopy (Sigma, Zeiss, Germany) and transmission electron microscopes (Tecnai G2, FEI, Netherlands and 2010FEF, JOEL, Japan). Raman spectroscopy carried out on a Raman microspectrometer (LabRam HR800, Jobin Yvon, France) with the 632.8 nm line of a He-Ne laser as excitation source. Small-angle and wide-angle X-ray diffraction (XRD) patterns were analyzed by an X-ray diffractometer (X'pert PRO, Panalytical, Holland) with CuK<sub>α</sub> radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA. The N<sub>2</sub> adsorption and desorption isotherms of the samples were determined on a Micromeritics Tristar 3000 system (USA) at 77 K. All of the samples were degassed in a vacuum at 200 °C before the measurements. Specific surface area was calculated using the Braunauer-Emmett-Teller (BET) equation and the pore size distribution plot was determined by the methods of non-local density function theory (NLDFT) and Barrett-Joyner-Halenda (BJH). X-ray photoelectron spectroscopy was collected on Thermo ESCALAB 250 using a monochromic Al X-ray source.

### 2.4. Electrochemical measurements

The electrochemical tests of the prepared carbon materials were conducted in a three-electrode electrochemical cell with 6M KOH aqueous solution or 1M H<sub>2</sub>SO<sub>4</sub> as the electrolyte. Platinum foil and Hg/HgO were used as the counter and reference electrodes, respectively. The working electrodes were prepared by mixing electroactive material, carbon black and polytetrafluoroethylene (PTFE) binder in a mass ratio of 80:10:10 to obtain a homogeneous black slurry. After coating the above slurry on the nickel foam, the electrodes were then dried at 100 °C in an oven overnight. The mass loading of the active material in working electrode was about 4 mg, and the thickness of the electrodes was set in a range of 100~150 μm. Furthermore, a symmetric two-electrode system composed of two identical electrodes was also used to characterize the capacitive and energy-storage properties of MUFC-based materials using 1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as electrolyte. All of the above electrochemical measurements were carried out by a CHI 660E electrochemical testing system. The cyclic voltammetry (CV) tests of individual electrode were obtained in the potential range of -1.0-0V vs. Hg/HgO by varying the scan rate from 5 to 100 mV s<sup>-1</sup>. Galvanostatic charge-discharge was performed at different current densities varying from 1.0 to 10 A g<sup>-1</sup> in the same potential range as the CV tests. The CV tests of symmetric cell were performed from 0 to 1.8V. The specific capacitance of the electrode was calculated by using the formula of

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

$$C_V = C_S \times \rho \quad (2)$$

$$\rho = \frac{1}{V_{total} + 1/\rho_{carbon}} \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/183111>

Download Persian Version:

<https://daneshyari.com/article/183111>

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