



Nitrogen-doped porous carbon derived from citric acid and urea with outstanding supercapacitance performance



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ARTICLE INFO

Article history:

Received 31 May 2015

Received in revised form 22 July 2015

Accepted 3 August 2015

Available online 5 August 2015

Keywords:

porous carbon

citric acid

urea

N-doping

KOH activation

supercapacitor

ABSTRACT

In this work, we presented a novel approach to synthesize nitrogen-doped porous carbon materials *via* a three-step fabrication process using citric acid as the carbon source and urea as the nitrogen source. Firstly, hydrochar was synthesized by a microwave-assisted hydrothermal method using citric acid and urea and as the reactants. The hydrochar was then subjected to high-temperature carbonization in Ar atmosphere followed by KOH activation, giving nitrogen-doped porous carbon materials. The morphology, structure, and textural properties of the carbons were investigated by SEM, TEM, N₂ sorption isotherms, and XPS. The as-prepared porous carbon possesses a high BET surface area of 2397 m² g⁻¹ and an average pore size of 1.8 nm. Such N-rich porous carbon shows outstanding capacitive performance (365 F g⁻¹ at 0.5 A g⁻¹), good rate capacitive behavior, and excellent cycling stability, indicating a great potential for supercapacitors.

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1. Introduction

Supercapacitors have recently attracted significant attention because of their high power density, rapid charge/discharge capacity, and long life-cycle stability. Based on the electrode design, supercapacitors can be divided into two main categories including electric double-layer capacitors (EDLCs) with carbon electrodes and pseudocapacitors with metal oxide or conducting polymer electrodes [1–4]. In general, EDLCs rely on charge separation at electrode/electrolyte interfaces to store energy, while capacitance generation in pseudocapacitors is based on the Faradaic charge transfer reactions between the electrolyte and electroactive species on the electrode surface [5,6]. Activated carbons (ACs) with high surface area are the most commonly used materials in EDLCs because of their low cost, good chemical stability, and high electrical conductivity [7]. Although ACs possess large specific surface area (>1000 m² g⁻¹) and pore volume (>0.5 cm³ g⁻¹), only about 10–20% of the “theoretical” capacitance was observed due to the presence of electrochemically inaccessible micropores [8]. On the other hand, very large pores also reduce the capacitance as often noticed in carbon activation studies. The ideal pores should be slightly larger than the size of the de-solvated ions.

It is important to match the pore size of the ACs to the specific electrolyte and that not only high surface area is needed, but also narrow and controlled pore size distribution (PSD) [6]. In order to achieve high capacitance, many efforts have been devoted to the synthesis of ACs with tailored PSD, pore structures, and surface functionalities.

Up to now, various carbon precursors including fossil materials [9,10], polymers [11–14], biomass materials [15–20], and organic small molecules [21,22] have been successfully used to prepare ACs. Among these, organic small molecules, by virtue of structure diversity and commercial availability, are of particular interest, which make them another candidate for producing ACs with enhanced capacitive performance. In particular, heteroatom-doped ACs can also be prepared by selecting suitable precursors. Previous studies have demonstrated that the surface N-containing functionalities can give ACs acid/base characters, therefore playing a critical role in enhancing capacitance performance by providing pseudocapacitance *via* reversible redox reaction together with improving wettability between electrodes and electrolytes [23–25]. Popular strategies for the synthesis of N-doped ACs (NACs) include the direct carbonization approach, in which N-rich carbon precursors are directly pyrolyzed at high temperature [26], and the post-treatment approach, which attempts to treat carbon with N-containing dopants (such as ammonia, amine, or urea) [11,25,27,28]. The latter approach can maintain the properties of

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the bulk material, but is time-consuming and results in heterogeneity of N-doping. In contrast, the direct carbonization approach allows homogeneous incorporation of N into the carbons with a controlled chemistry. More importantly, the versatility of N-rich carbon precursors (such as N-containing polymers, biomass, ionic liquids, and organic small molecules) also allows for regulating the final electrochemical properties of NACs, which may be dedicated by the chemical and physical characteristics of the precursors. From this point, direct carbonization method may be more feasible for certain applications and is viewed as closer to commercialization. Considering the potential scale of supercapacitor applications, the production of NACs starting from organic small molecules is a highly attractive subject in material chemistry. So far only a small portion of organic small molecules such as 3-amino-1,2,4-triazine [29], aminoglucose [30], quinolone [31], diaminobenzene [4], ethylenediamine/carbon tetrachloride [32], resorcinol/phloroglucinol [33], tannin/melamine [34], and ionic liquids etc. [13,35] are used as N-containing precursors for supercapacitor electrodes. The search for new N-containing precursors that are cheap, accessible and with potential creating significant economic valorization is still needed. With this in mind, we herein employ citric acid/urea as the precursors to synthesize NACs. Citric acid is a commodity chemical, and more than a million tons are produced every year by fermentation. In 2007, worldwide annual production stood at approximately 1600,000 tons, among which more than 50% of this volume was produced in China. Although citric acid/urea have been successfully used to produce N-doped graphene quantum dots, the relevant literature is very limited, in which Sun et al. [36] reported the preparation of N-doped graphene quantum dots using citric acid as the C source and different amines such as ethanolamine, diethylamine, ethylenediamine, and hexamethylenetetramine as the N source.

In the present study, we presented a facile approach to synthesize N-doped porous carbon with very high specific surface area via a three-step fabrication process using citric acid/urea as the precursors. Firstly, hydrochar was synthesized by a microwave-assisted hydrothermal method using citric acid/urea as the reactants. The hydrochar was then subjected to high-temperature carbonization in Ar atmosphere followed by KOH activation, giving N-doped porous carbons. Upon hydrothermal treatment, citric acid self-assembled into sheet structure and formed N-free graphite framework through intermolecular dehydrolysis reaction. In the presence of amine, hydrothermal process promoted the formation of amide between NH_2 and COOH . The consequent intramolecular dehydrolysis between neighbour amide and COOH groups led to the formation of pyrrolic-N in the graphene framework [36]. Further high-temperature carbonization and subsequent KOH activation produced N-doped porous carbon. The resultant porous carbon shows a very high specific surface area of $2397 \text{ m}^2 \text{ g}^{-1}$, excellent capacitive performance (365 F g^{-1} at 0.5 A g^{-1}) due to the dual O, N-doping. Such a low-cost, high-performance electrode material is potentially useful for high-power supercapacitors.

2. Experimental

2.1. Preparation of N-doped porous carbons

In a typical process, 8.75 g (41.7 mmol) citric acid and 7.5 g (125 mmol) urea were dissolved in 20 mL of water. Subsequently, 20 mL of the solution was sealed in a 35 mL microwave tube and heated with a maximum microwave irradiation power of 800 W for 5 min (optimized conditions) using a microwave system (CEM MARS6). The resulting carbonaceous solid, denoted as hydrochar, was recovered by filtration, washed with distilled water, and dried.

The dried hydrochar (2 g) was then carbonized at 700°C in a tubular furnace (GSL-1700X, Hefei Kejing Materials Technology

Co., Ltd., China) under Ar flow for 2 h. The product was denoted as CU- x , standing for carbon prepared from citric acid and urea, where x ($x=700$) stands for the carbonization temperature.

KOH activation of the CU- x was as follows: briefly, CU-700 (500 mg) and KOH aqueous solution (2.0 M, 9.0 mL) were placed in a 25 mL flask. The mixture was stirred for 2 h at ambient temperature. After evaporating to dryness, the mixture was dried at 120°C for 5 h and transferred to a nickel crucible followed by heat-treatment at 800°C for 2 h (heating rate: 4°C min^{-1}) under Ar atmosphere. Finally, the product was repeatedly washed with deionized water until a pH value of 7 was reached and followed by drying at 120°C for 5 h. The products were denoted as CUA- x , standing for activated carbon prepared from citric acid and urea, where x ($x=00, 800, \text{ or } 900$) stands for the KOH activation temperatures.

2.2. Structural characterization

The morphologies of the obtained porous carbons were characterized by scanning electron microscopy (SEM, JEOL JSM-6610LV). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 microscope operating at 200 kV. The crystallographic information of the carbons was investigated by powder X-ray diffraction (XRD, Rigaku D/Max 2500PC). Raman spectra were collected on a Renishaw inVia Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a 1063 photoelectron spectrometer (Thermo Fisher Scientific, England) with $\text{Al-K}\alpha$ X-ray radiation as the X-ray source for excitation. The textural properties were characterized by N_2 sorption measurements at 77.3 K (Micromeritics TriStar II 3020). The specific surface area (SSA) was obtained by Brunauer-Emmett-Teller (BET) method. The total pore volume (V_{total}) was estimated from the adsorbed amount at a relative pressure p/p° of 0.99. Micropore volume (V_{micro}) was calculated using the t-plot method.

2.3. Electrochemical measurements

The working electrodes were typically fabricated by mixing the porous carbon as the active material (80 wt%), carbon black (acetylene black with a BET surface area of $65 \text{ m}^2 \text{ g}^{-1}$, 10 wt%), and polytetrafluoroethylene (PTFE, 10 wt%) in ethanol and then coated onto the nickel foam current collectors ($1 \text{ cm} \times 1 \text{ cm}$) with a spatula. The premade electrodes were pressed under a pressure of 10 MPa for 5 min and finally dried at 100°C for 12 h in an oven. The density and thickness of the loading composite on each electrode was controlled to be 1.63 g cm^{-3} , and $18.4 \mu\text{m}$, respectively, and the nickel foam and active material are 90 mg and 3.0 mg. The two symmetrical electrodes were separated using a glassy fibrous separator soaked with electrolytes (6 M KOH) in a CR2032 stainless steel coin cell.

The capacitive performance of single electrode was studied on a CHI760D electrochemical workstation (CH Instruments Inc., Shanghai, China) using a standard three-electrode system with platinum wire and Hg/HgO electrode as counter and reference electrodes, respectively, in 6.0 M KOH electrolyte at 25°C . Cyclic voltammetry (CV), galvanostatic charge-discharge (GC) technique and electrochemical impedance spectroscopy (EIS) were employed in the electrochemical investigations. CV tests of individual electrode were carried out between -1.0 and 0 V (vs. Hg/HgO). GC tests were performed at different current density varying from 0.5 to 20 A g^{-1} in the same potential range as the CV test. The specific capacitance based on GC was calculated using the equation: $C_g = I/(m dV/dt)$, where I is the constant current and m the mass of active materials, and dV/dt is calculated from the slope obtained by fitting a straight line to the discharge curve from the end of the voltage drop to the end of the discharge process. The

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