



Simple and scalable synthesis of phosphorus and nitrogen enriched porous carbons with high volumetric capacitance



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ARTICLE INFO

Article history:

Received 16 January 2014

Received in revised form 21 April 2014

Accepted 11 May 2014

Available online 27 May 2014

Keywords:

Supercapacitors

Carbonization temperature

Nitrogen/phosphorus co-doping

Volumetric capacitance

Cycling stability

ABSTRACT

Phosphorus and nitrogen enriched porous carbons were fabricated by direct heat treatments of the honeycomb-patterned H_3PO_4 /polyacrylonitrile composite precursors obtained through solvent evaporation. Surface chemistry analysis showed that high surface concentrations of phosphorus and nitrogen as well as the desirable chemical structures can be achieved by controlling the carbonization temperature. Electrochemical measurements in 1 M H_2SO_4 aqueous electrolyte showed that the gravimetric capacitance and the volumetric capacitance reached as high as 205.7 F g^{-1} and 261 F cm^{-3} at 0.5 A g^{-1} , respectively. In particular, the capacitance showed no degradation even after 8000 charge/discharge cycles, clearly demonstrating a robust long-term stability. The excellent electrochemical performance makes the electrode material a promising candidate for supercapacitors.

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1. Introduction

Supercapacitors, which possess high-power delivery capability and long-cycle life, are becoming more and more important for sustainable and clean energy storage owing to the rapid development of portable electric devices, electric vehicles, and bulk electricity storage at power stations [1–3]. Among the numerous materials, porous carbons are the most attractive electrode materials for supercapacitors due to their reasonably high conductivity, large surface area and moderate cost [2,4]. The capacitance and rate capability of porous carbons highly depend on the surface area, pore size distribution and pore structure [5–7]. The high surface area of activated carbons endows them with high gravimetric capacitance (C_g), but their energy storage and rate capability are limited by the poorly developed pore structure [2]. Templated carbons, which exhibit well controlled narrow pore size distribution, ordered pore structure and large surface area, can overcome the disadvantages of activated carbons [8–10]. However, the control of pore structure cannot drastically enhance the capacitance [11]. Therefore, it is imperative to develop a more effective approach to enhance the capacitance of carbon materials.

The introduction of heteroatoms (such as B [12], N [13], O [14] or P [15]) into carbon frameworks is found to be an effective way to

improve the capacitance by providing so-called pseudocapitance, which is derived from the Faradic reactions of the heteroatom functionalities [16]. The introduction of nitrogen seems to be the most effective route for the preparation of high-capacitance electrode materials [17–22]. Nitrogen-containing polymers precursors, such as polyacrylonitrile (PAN) [17,23] and polyaniline (PANi) [24,25], have been particularly widely used in the investigation of nitrogen-doped carbons due to their many advantages. For instance, *in situ* generation of nitrogen by using nitrogen-containing polymer precursors can simplify the preparation procedure in contrast to other methods such as ammoxidation [26,27]. More importantly, the nitrogen in the polymer scaffolds is always accommodated into the carbon frameworks during the carbonization process, thus keeping them stable even under harsh working conditions [18]. PAN as a suitable precursor for nitrogen-enriched carbons has been widely used to prepare electrode materials for high-performance supercapacitors [28–30]. Recently, our group has studied the effect of phosphorus content on the capacitive performance of PAN-based carbon nanofibers obtained through electrospinning technology, which shows that the phosphorus plays a positive role in enhancing the electric double layer (EDL) capacitance [31]. However, these preparation methods, such as template synthesis and electrospinning technology, are often high-cost and/or time-consuming, and thus a simple, scalable and low-cost method is highly desired.

In this work, we present a simple synthesis of phosphorus and nitrogen enriched porous carbons (P/N-PCs) through direct heat treatments of the honeycomb-patterned H_3PO_4 /PAN (HPP-PAN)

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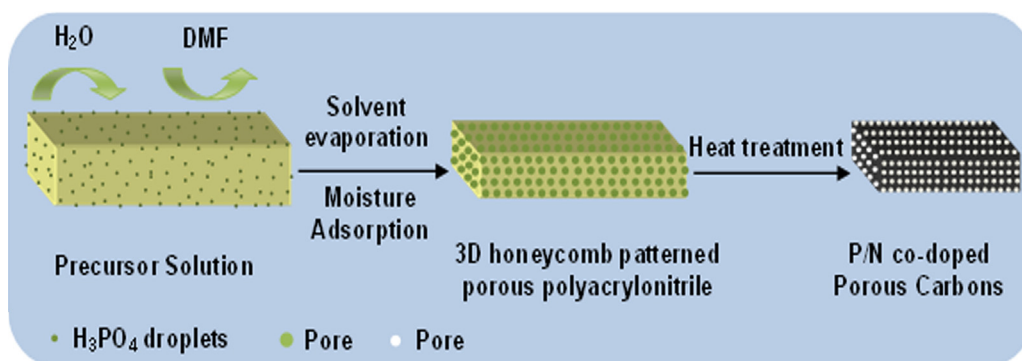


Fig. 1. Schematic illustration of the fabrication procedure of P/N-PCs series.

composite monolith prepared through solvent evaporation. The effect of temperature on the physicochemical and electrochemical properties of the P/N-PCs was investigated. The P/N-PCs-800 electrode materials obtained at 800 °C exhibited excellent electrochemical performance. It is worth noting that such a convenient synthesis approach can be easily scaled up.

2. Experimental

2.1. Fabrication of HPP-PAN

In a typical preparation, 2.0 g PAN ($M_w = 100,000 \text{ g mol}^{-1}$, UK Courtaulds Co.) and 1.3 g phosphoric acid (H_3PO_4 , 85 wt% in water, Beijing Chemical Co.) were dissolved into 18 mL N, N-dimethylformamide (DMF). Then the obtained precursor solution was dropped into a clean petri dish and kept for 24 h under the environment of $\sim 35^\circ\text{C}$ temperature and $\sim 60\%$ humidity. Finally, three-dimensional (3D) HPP-PAN was obtained after the complete evaporation of the solvent. For comparison, 2.0 g PAN was dissolved into 18 mL DMF and then the cast film of pure PAN was prepared by the same process as HPP-PAN.

The general mechanism for the formation of HPP-PAN is as follows. Solvent evaporation induces the growth of the phosphoric acid droplets into microspheres, and meanwhile induces chain entanglements of PAN molecules, which prevent the phosphoric acid microspheres from further growth and lock in the phosphoric acid microspheres. Thus, a honeycomb-patterned structure can be formed after the complete evaporation of the solvent. It should be noted that the water absorption of phosphoric acid would enlarge the pore size.

2.2. Fabrication of P/N-PCs series

The as-prepared HPP-PAN was placed in an electric furnace, heated up at a rate of 3°C min^{-1} and kept at 280°C in air for 2 h for the oxidative stabilization of PAN. Then, the stabilized samples were carbonized at a heating rate of 5°C min^{-1} and finally soaked at a controlled temperature (700, 800, or 900°C) for 2 h under N_2 atmosphere. The as-prepared P/N-PCs series are denoted as P/N-PCs-700, P/N-PCs-800, and P/N-PCs-900, where the number represents the carbonization temperature. For comparative purpose, pure PAN-based carbons (PP-Cs-800) were prepared in the same conditions as P/N-PCs-800. Fig. 1 schematically shows the typical fabrication procedure of P/N-PCs series.

2.3. Structure and surface chemistry analysis

The morphology of the obtained P/N-PCs series was characterized using a Supra55 field emission scanning electron microscope (FE-SEM) from Carl Zeiss. Energy dispersive X-ray spectroscopy

(EDX) analysis was carried out on the same FE-SEM. The X-Ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker NEW D8 Advance, Germany) with a Lynx eye high-speed strip detector and Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 40 mA, $\lambda = 0.154 \text{ nm}$). N_2 adsorption and desorption isotherms were performed using Autosorb-iQ2-MP Gas Adsorption Analyzer (Quantachrome) at 77 K. The surface area was determined by Brunauer-Emmett-Teller (BET) theory and Barrett-Joyner-Halenda (BJH) method. Also, CO_2 adsorption and desorption isotherms were carried out using Tristar II 3020 (Micromeritics) at 273 K, and the micropore surface area was determined by Dubinin-Radush-Kevich method. The surface elemental composition of all samples was analyzed by X-ray photoelectron spectroscopy (XPS, EscaLab 250, Thermo Fisher Scientific).

2.4. Electrochemical measurements

To prepare the working electrodes, a mixture of the as-prepared materials, polyvinylidene fluoride (PVDF) binder and acetylene black with the weight percent ratio of 80:10:10 was dispersed in 1-Methyl-2-pyrrolidone (NMP) and smeared onto the platinum current collectors. Then, the electrodes were dried at 120°C for 24 h in a vacuum oven. The typical mass loading was some $2.0 \sim 2.4 \text{ mg cm}^{-2}$. The electrochemical measurements were separately carried out in a three-electrode system and in a two-electrode system with 1 M H_2SO_4 as the electrolyte. For the three-electrode device, Ag/AgCl was used as the reference electrode and a platinum foil as the counter electrode. Cyclic voltammetry (CV, at different scan rates from 10 to 100 mV s^{-1}) measurements and electrochemical impedance spectroscopy (EIS, frequency from 10 mHz to 100 kHz) were conducted on an electrochemical analyzer system (Metrohm Autolab PGSTAT 302 N, Netherlands). The galvanostatic charge/discharge measurements (at current densities from 0.5 to 10 A g^{-1}) were carried out on a LANDCT2001A tester (China). The tests were performed in the potential range of -0.9 to 0.1 V in a three-electrode system. In a sandwich two-electrode system, CV and galvanostatic charge/discharge measurements were carried out in the potential range of 0 to 1.0 V . The C_g was calculated based on the mass of the samples within the electrodes.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 2 shows the SEM images of the cross-section of HPP-PAN, pure PAN film and P/N-PCs series. HPP-PAN (Fig. 2a) clearly demonstrates a honeycomb-patterned structure with a narrow pore size distribution from 5 to $8 \mu\text{m}$, while the pure PAN film (Fig. 2b) is observed to be nonporous. The honeycomb-patterned structure can be successfully retained in the P/N-PCs series after carbonization

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