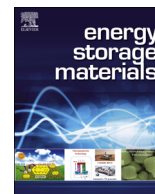




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Nitrogen-doped hierarchical porous carbon derived from block copolymer for supercapacitor

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ABSTRACT

Nitrogen-doped hierarchical porous carbon was successfully synthesized using block copolymers as precursor by a self-template method and subsequent KOH chemical activation. The self-template agent, polystyrene, promotes the formation of mesopores, which is favorable for the rapid transport of both electrons and electrolyte ions. The micropores of nitrogen-doped hierarchical carbons were then extensively developed by activation to provide large electrochemical double-layer capacitance. As the activation temperature increased from 600 °C to 900 °C, the specific surface area of the materials increased dramatically. Thus, the as-obtained nitrogen-doped hierarchical carbon (NHPC-800) possesses a high surface area of up to 2104.5 m²/g with nitrogen content of 5.79%. It exhibits a maximum specific capacitance of 257 F/g at a current density of 0.5 A/g in 6 M KOH aqueous electrolyte as measured in a three-electrode system. Furthermore, the nitrogen-doped hierarchical carbon electrode exhibits excellent rate capability with 128 F/g remaining at 20 A/g and good cycling stability of 90.38% retention over 10,000 cycles in a two-electrode system. The tunable porous structure and effective nitrogen doping via block polymer precursor shed a light for designing advanced electrode materials for a high-performance electrochemical energy system.

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1. Introduction

Supercapacitor is considered to be one of the promising energy storage devices with potential applications in consumer electronics, stand-by power systems and mobile electrical systems, due to its high power density, long cycle life and good safety character [1,2]. Activated carbons, especially hierarchical carbons, are the most widely used electrode materials for supercapacitor because of their excellent properties, including high surface area, appropriate pore size distribution, relative inert chemical properties, and low cost [3,4]. Consequently, a wide range of synthesis routes including metal-organic frameworks [5], protic ionic liquids and salts [6], template mediated synthesis [7,8], have been developed to obtain hierarchical carbons materials. However, these methods usually suffer from draw-backs such as complex preparation processes, difficult removal of cost inorganic templates [8–10], severely hindering their large scale applications in supercapacitor industry. Hence, developing cost-effective methods for the rapid

and low cost production of hierarchical activated carbons has become an urgent task.

Besides, the incorporation of heteroatom into active carbons has been proven to be an efficient and effective way to tune the intrinsic chemical and electrical properties of carbon [11,12]. Moderate N-doping can enhance the electrical conductivity and the wettability, consequently maximizing the electro-active surface area [13]. Meanwhile, nitrogen doping can also bring additional pseudocapacitance [14–16]. Therefore, nitrogen-enriched hierarchical carbons are proposed as ideal supercapacitor electrode materials. At present, there are a lot of methods to prepare nitrogen-doped porous carbon materials such as using nitrogen plasma process [17], chemical vapor deposition [18–20], and so on. However, most of these methods require post-doping process with high energy consumption.

Most recently, the block copolymer containing the source of carbon and a sacrificial block, is considered to be one kind of important precursor to prepare hierarchical activated carbon materials with high nitrogen content without post-doping route. High chemical and thermal stability of the block copolymer make it possible to maintain high contents of nitrogen species within the carbon matrix after carbonization and activation.

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In this paper, we report a simple method to synthesize nitrogen-doped hierarchical carbon materials with large surface area and high nitrogen content by KOH activation of the nitrogen-enriched block polymer which is synthesized by the polymerization of polyacrylonitrile (PAN) and polystyrene (PS) without hard templates. The introduced PS and the latter KOH activation play a crucial role in determining the structural characteristics and surface chemistry of porous carbons. Benefitting from high specific surface areas, convenient transport pathway for ions and electrons, high nitrogen content, the as-fabricated nitrogen-doped hierarchical carbon materials have exhibited excellent capacitive performances, including high specific capacitance, high rate performance and excellent cycling stability in 6 M KOH aqueous solution.

2. Experimental

2.1. Preparation of PS macro chain-transfer-agent (PS-cta)

1 g of chain transfer agent (3.55 mmol/L), 40 mL of styrene monomer (0.36 mol/L) and 100 mL DMF mixed in a 250 mL single necked flask equipped with magnetic stirring bar [21]. The flask was subjected to three freeze-pump-thaw (FPT) cycles and filled with Argon, then the flask was placed in an oil bath set at 100 °C for 6 h. The reaction was stopped by pouring the solution into ice methanol, and then it was washed three times with ethanol. After that, the solid products were dried in a vacuum oven at 40 °C.

2.2. Preparation of PS-*b*-PAN block copolymers

5 g of the above PS-cta (0.52 mmol/L) ($M_n=9700$, GPC), 18 mL of Acrylonitrile (AN) (86 mmol/L) and 100 mL DMF were mixed in a 250 mL single necked flask equipped with magnetic stirring bar. The flask was subjected to three freeze-pump-thaw (FPT) cycles

and filled with Argon. Then the flask was placed in an oil bath set at 70 °C for 6 h. The reaction mixture was dissolved in methanol and washed three times with ethanol. The solid products were dried in a vacuum oven at 40 °C.

2.3. Preparation of carbon precursor

2 g of the polymer powder was stabilized at 250 °C for 90 min under air flow (80 mL/min) with a heating rate of 2 °C/min, then the as-obtained black powder was carbonized at 600 °C for 2 h under Argon flow (80 mL/min) with a heating rate of 2 °C/min, and then final product was named as nitrogen-doped mesoporous carbon (NMC).

2.4. KOH Activation of carbon precursor

The KOH was added to the NMC and mechanically mixed with mass ratio of KOH/NMC=3. Then the mixture was placed on the nickel crucible and the activated process was carried out at 600, 700, 800, 900 °C for 1 h under Argon flow (60 mL/min) with a rate of 4 °C/min. The resultant activated carbon was washed with 5% HCl and then with distilled water to neutral pH, and finally dried in a vacuum oven at 100 °C. The resultant product was named NHPC-*x*, where *x* represents the activation temperature.

2.5. Characterization of carbon material

The morphology of the as-obtained products was characterized by scanning electron microscopy (SEM, JEOL JSM-700). Transmission electron microscopy (TEM) observation of the samples was carried out with a JEOL 2100F microscopy operating at 200 kV. X-ray diffraction was measured on a X-ray diffractometer (Rigaku, D/Max-2400, Japan). X-ray photoelectron spectroscopy spectra were obtained on an AXIS Ultra DLD spectrometer with an excitation

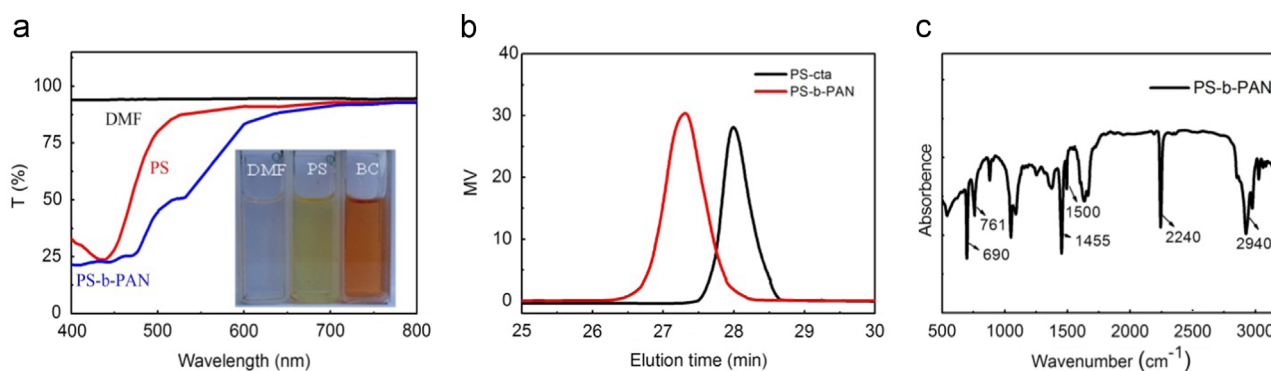


Fig. 1. (a) UV-vis spectra of DMF, and PS-cta, PS-b-PAN in DMF, inset is the optical images. (b) GPC of the PS-cta, PS-b-PAN in THF. (c) FT-IR of the PS-b-PAN solid.

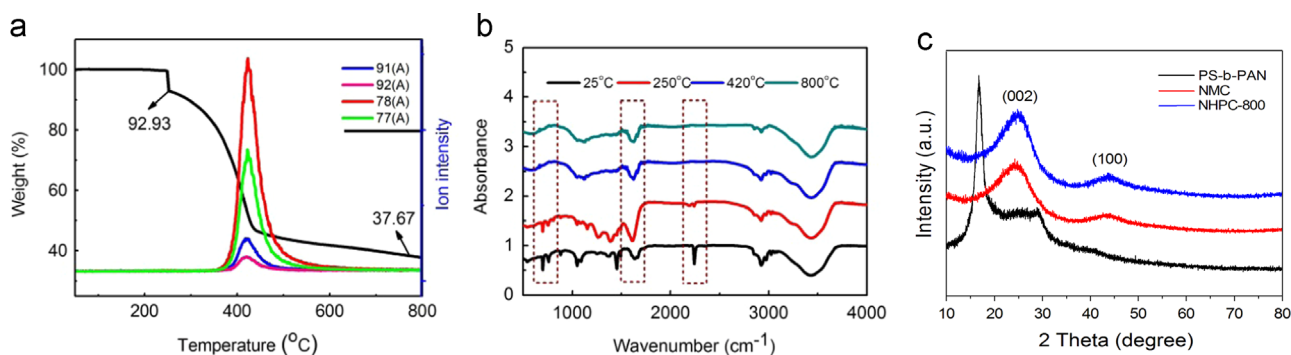


Fig. 2. (a) TG and in-situ MS spectrum analysis of PS-b-PAN; (b) FT-IR spectrum of PS-b-PAN during the carbonization; (c) XRD patterns of PS-b-PAN, NMC and NHPC-800.

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