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Boron and nitrogen co-doped porous carbon with a high concentration of boron and its superior capacitive behavior

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ABSTRACT

In this work, boron and nitrogen co-doped hierarchical porous carbon (BN-HPC) with a relatively high contents of boron (3.97 wt%) and nitrogen (12.10 wt%) is synthesized by a method combined with template process and carbonization of hierarchical porous resin using melamine and boric acid as nitrogen and boron sources, respectively. The co-doping method achieves a high boron doping level (8 times of that of single boron doped sample) which is of great significance in increasing the doping efficiency of boron. The hierarchical porosity, structure and surface chemical properties are studied in detail via various means, such as Transmission Electron Microscopy, N_2 sorption, X-ray diffraction, X-ray photoelectron spectroscopy and elemental analysis, etc. Owing to the synergistic effect of hierarchical porosity and heteroatoms doping, BN-HPC exhibits greatly improved electrochemical capacitive performance of 304 F g^{-1} at a current density of 0.1 A g^{-1} and good rate capability (189 F g^{-1} remained at a current density of 10 A g^{-1}). The strategy of synthesis is facile and very effective.

1. Introduction

With the rapid development of modern society, there have been more urgent requirements for clean energy technologies. Among all energy storage devices, supercapacitors are one of the most attractive with their unique properties such as high power densities, long cycle life and short charging time [1–3]. Porous carbons are considered as the most promising electrode materials for supercapacitors due to their high surface area, chemical stability and low cost [1–5].

However, porous carbons generally suffer from limited electrochemically active sites and a low utilization of pore channels [6–8]. It is well known that the textural properties of the porous carbons, such as surface area, surface functionality, pore size distribution as well as structure of pores, play important roles in the electrochemical capacitance performance [6,9,10]. Thus, one solution to improve porous carbons is to prepare hierarchical porous carbons by hard or soft templates [6,11,12]. Recently, hierarchical porous carbons have been proved to possess distinctive potential for high-performance supercapacitor because mesoporous channels with larger pore size could serve as reservoirs of electrolyte and the expressway for ion transport, resulting in a decreased diffusion distance [11–13]. Another solution is to incorporate heteroatoms, such as nitrogen, boron and oxygen, which can considerably enhance the electrochemical performance of carbon electrode [6,8,10,11]. These heteroatoms can introduce pseudocapacitance through redox reaction and improve the surface wettability of carbon materials to electrolyte, ensuring a complete utilization of the exposed surface for charge storage [14–16]. Many works have demonstrated that nitrogen-doped carbons have better electronic properties than the related undoped ones [16–18]. This attracts researchers to prepare the boron-doped carbons. Boron can enter the carbon lattice by substituting carbon and act as electron acceptor due to its three valence electrons, leading to shifting the Fermi level to the conducting band and therefore modifying the electronic structure of doped carbon [19,20]. However, not similar as nitrogen-doping, boron-doping usually has a quite low doping efficiency by boric acid because inorganic boron compounds are usually lowly reactive [19,21,22]. Moreover, experimental conditions are strict for it is not easy to dope boron into carbon materials at temperatures below 1500 °C [23–25]. What's more, common dopants organic boron compounds are highly toxic [26–28]. Therefore, it remains a challenge to dope boron on carbons directly. To solve this problem, we propose to prepare boron and nitrogen co-doped porous carbons to make considerable improvements in terms of both the amount of boron and electrochemical

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performance.

Herein, we report a simple yet effective method for preparing boron and nitrogen co-doped porous hierarchical carbons (BN-HPC) with a relatively high contents of boron and nitrogen. The co-doping method can dramatically improve the doping efficiency of boron greatly and still well maintain the structural integrity of carbon frameworks well, even if the sample is heavily doped. Electrochemical studies show that BN-HPC shows greatly improved electrochemical performance and good rate capability as the active materials for supercapacitor. The effects of the heteroatom doping on the pore development, carbon framework, heteroatom contents and the electrochemical performance of the obtained samples are analyzed in detail.

2. Experimental

2.1. Sample preparation

Nano SiO_2 with an average diameter of 50 nm was purchased from Evonik Degussa Specialty Chemicals (Shanghai) Co., Ltd, other chemicals were purchased from Shanghai Chemical Reagents Company. All chemicals were used as received. The synthesis process of nitrogen doped hierarchical porous carbons (N-HPCs), BN-HPC and hierarchical porous carbons (HPC) is illustrated schematically in Fig. 1. Since the amount of dopants has a great impact on the electrochemical performance of carbon electrode and it is difficult to dope boron directly on the carbon (Table S1), nitrogen-doped hierarchical porous carbons (N-HPCs) were first prepared by direct pyrolysis of hierarchical porous resin (HPR) with different amount of melamine as a nitrogen source. The N-HPCs were analyzed in advance and worked as the reference to the mass ratio of melamine to HPR in the preparation of BN-HPC. BN-HPC was prepared by pyrolysis of HPR with melamine and boric acid as the nitrogen and boron sources, respectively. For comparison, dopant-free hierarchical porous carbon (HPC) was also prepared by direct pyrolysis of HPR only.

2.1.1. Synthesis of HPR

The resol precursor was synthesized by a process reported [6,29–32]. In a typical experiment, 1.0 g of F127 was dissolved in 20.0 g of ethanol, then 0.5 g of nano SiO_2 and 5.0 g of the resol precursor in the ethanol solution containing 0.61 g of phenol and 0.39 g of formaldehyde was added under stirring. The resulting homogeneous solution was transferred to a dish and the ethanol evaporated at room temperature over 8 h. The sample was heated at 100 °C for 24 h in an oven to thermopolymerize the phenolic resin. Then it was calcined at 350 °C under nitrogen atmosphere for 5 h with a heating rate of 1 °C min^{-1} in the tube furnace to remove the F127. At last, the obtained products were treated by NaOH solution (2 M) at 80 °C for 2 h to remove the nano SiO_2 followed by washing and drying at 80 °C for 12 h.

2.1.2. Synthesis of N-HPC-X

X refers to the mass ratio of melamine to HPR. Each sample is prepared by 100 mg HPR saturated with melamine solution at a concentration of 0.1 g ml^{-1} For example, to prepare N-HPC-15, 1.5g melamine was dissolved in 15 ml dimethylsulfoxide, then 100 mg HPR was added and stirred for 10 h at 100 °C. Subsequently, the

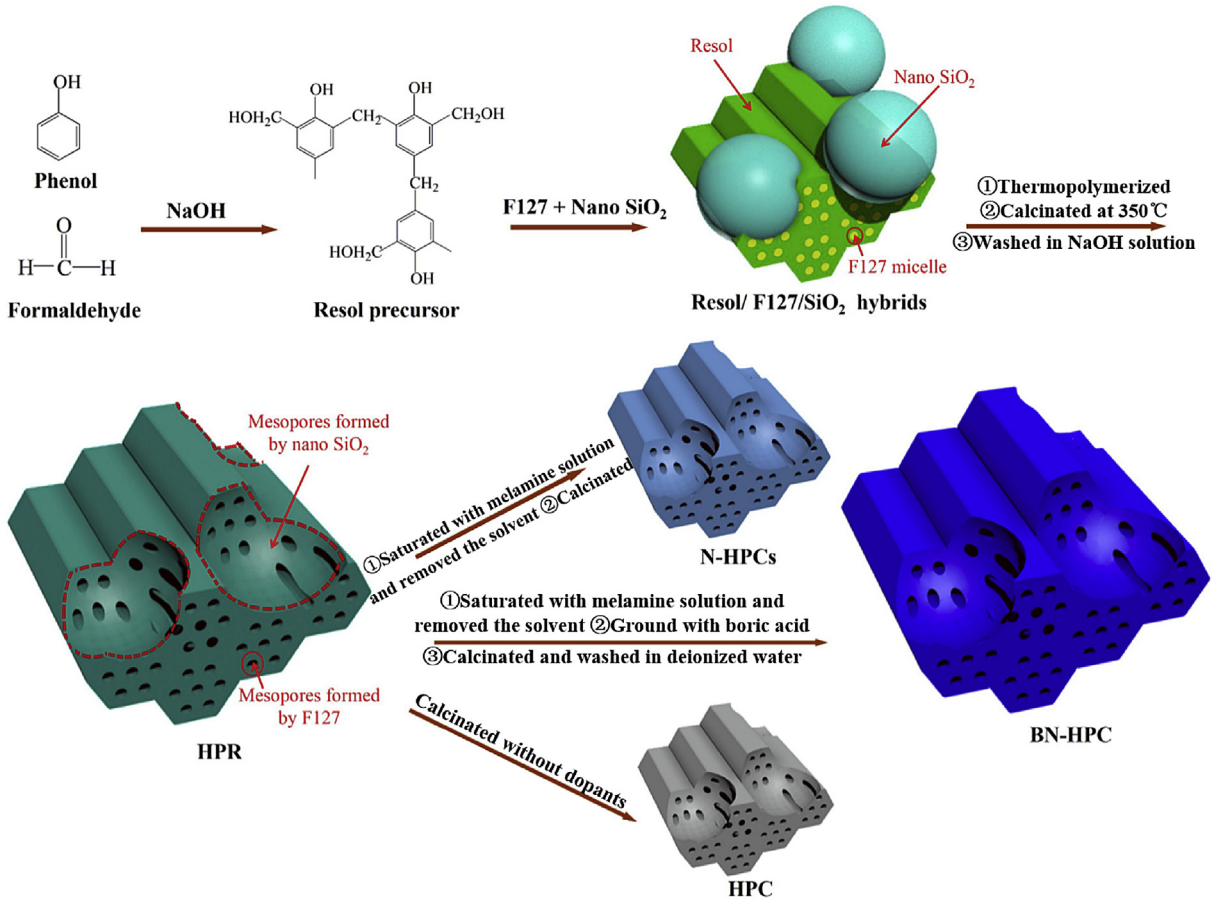

Fig. 1. Illustration of the synthesis process of HPC, N-HPCs and BN-HPC. (A color version of this figure can be viewed online.)