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Boron-doped ordered mesoporous carbons for the application of supercapacitors

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ABSTRACT

The boron-doped ordered mesoporous carbons (BOMCs) with different boron content are prepared by nanocasting approach using silica KIT-6, furfuryl alcohol and boric acid as the template, carbon and boron sources, respectively. The pore structure, morphology and surface physicochemical properties of the BOMCs samples are characterized by nitrogen adsorption/desorption isotherm, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results demonstrate that BOMCs inherit the ordered mesostructure of the pristine OMC and possess some boron-doped species on the surface. The electrochemical performances of the BOMCs are characterized by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) test, electrochemical impedance spectroscopy (EIS) and cycle life measurement. It has been found that with the increase of the boron content, the BOMC-0.05 shows high specific capacitance of 267.8 F g^{-1} at the scan rate of 5 mV s^{-1} and low resistance. At the same time, the symmetrical supercapacitor using BOMC-0.05 as electrode shows a specific capacitance of as high as 69.8 F g^{-1} and excellent cyclic stability with the specific capacitance retention of 92% even after 10000 consecutive cycles. The remarkable electrochemical behaviors demonstrate that the BOMCs will be a promising electrode material for the application of supercapacitors.

1. Introduction

With close attention paid to the world ecology and economy, people are observing the bountiful, low-cost, and clean energy from sun and wind which, in principle, should be able to satisfy the ever increasing and urgent demand. However, most of the renewable energy is intermittent and cannot meet the needs for casual use, except for converting to electricity [1–5]. Supercapacitors, which can bridge the gap between batteries and dielectric capacitors, are one of several promising energy storage devices with high power density and long cycling durability for fast storing the excess electrical energy [6].

According to the mechanism of electrical energy storage, the capacitive behavior of supercapacitors can be divided into two types: (1) using ion absorption (electrochemical double layer capacitors (EDLCs)), such as porous carbon, graphite and graphene; (2) by surface redox reaction (pseudocapacitors), such as metal-oxides and conducting polymers. Carbon materials have attracted very broad attention due to low cost, variety of form, ease of processability, chemistry stability and controllable porosity [7]. Consequently, carbon materials are extensively applied in supercapacitor devices, commonly exhibiting long life, high specific surface area and high dynamic of charge propagation [8]. However, the specific capacitance of carbon material is not exactly satisfactory as it is mainly produced by the quick formation of electrical double layer at electrode/electrolyte interface [9]. Therefore, great efforts have been dedicated to improve the supercapacitive performance of the carbon materials. Instead of enhancing the specific surface area, an alternative is to introduce pseudocapacitance by doping foreign atoms (such as nitrogen, boron, phosphorus and sulfur) in the carbon frameworks to tailor its electronic properties and chemical reactivity, and consequently tune its mechanical and electrochemical properties [10–15]. Among above doping elements, boron is a unique element that has been explored as substitution in carbon framework to promote the electrochemical capacitance of carbons [16,17]. Boron enters the carbon lattice by substituting for carbon at the trigonal sites and acts as electron acceptor because it has three valence electrons, causing a shift in the Fermi level to the conducting band and hence modifying the electronic structure of boron-doped carbon [18]. Furthermore, it can facilitate charge transfer between neighboring carbon atoms and thus enhance their electrochemical

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performance [19]. As a consequence, boron doping is an efficient and significant approach to modify the electrochemical capacitance of carbon materials, involving electric double layer capacitance and pseudocapacitance.

Due to the attractive influence of boron doping, several works have been reported about boron-doped carbon materials. For instance, Han et al. [20] reported that novel B-doped graphene nanoplatelets (borane-reduced graphene oxide, B-rG-O) were produced on a large scale via the reduction of graphene oxide by a borane-tetrahydrofuran adduct under reflux. Bo et al. [21] synthesized ordered mesoporous boron-doped carbons (BOMCs) by impregnating sucrose and 4-hydroxyphenylboronic acid into SBA-15 silica template and the BOMCs were acted as metal-free electrocatalysts for the oxygen reduction reaction (ORR) in alkaline solution. Besides, Ding et al. [22] proposed one-pot synthesis route with the combination of boron doping and fabrication of mesoporous carbon through sol-gel method using boric acid as the catalyst, dopant and pore-forming agent. All these previous reports demonstrate that boron doping is an efficient strategy for enhancing electrochemical performance of carbon materials. Additionally, ordered mesoporous carbons (OMCs) have received considerable attention owing to their large surface area, tunable pore structure, uniform and adjustable pore size, and good conductivity [23]. These outstanding features make them ideal candidates for supercapacitors application. In general, OMCs can be synthesized by either the soft template method or hard template method called nanocasting. Compared to soft template, the hard template method using mesoporous silica as template has many advantages over the soft template method such as controllability, pore regularity, thus it can produce highly ordered mesoporous structure for carbon materials. Up to now, various types of silica template, such as SBA-16, MCM-48, MSU-H, KIT-6, SBA-15, have been used to prepare different structure of OMCs by nanocasting [24–27]. In particular, mesoporous silica KIT-6 consists of two interwoven mesoporous subnetworks and can obtain much larger mean pore diameters [28]. Consequently, it is worthwhile to develop boron-doped ordered mesoporous carbons using KIT-6 as the hard template, which can take advantage of the physicochemical properties of OMCs and pseudocapacitance induced by boron-doped.

In our previous work, 3D cubic-ordered mesoporous carbons (OMCs) were successfully synthesized by using silica KIT-6 as the template and furfuryl alcohol as the carbon source, and the specific capacitance of OMC-600 reached 256.86 F g^{-1} at the scan rate of 1 mV s^{-1} [29]. In order to further enhance the supercapacitive performance of the OMCs, boron-doped ordered mesoporous carbons (BOMCs) with different boron content are prepared by nanocasting approach using silica KIT-6, furfuryl alcohol and boric acid as the template, carbon and boron sources, respectively. And the physical and supercapacitive behaviors of BOMCs are extensively investigated in comparison with the pristine ordered mesoporous carbons.

2. Experimental

2.1. Synthesis

Furfuryl alcohol was purchased from Sigma-Aldrich. Boric acid and toluene-p-sulfonic were purchased from Shanghai Chemical Reagent Co. Ltd. China. All of the chemicals were analytical grade and used as received without further purification. The preparation strategy of BOMCs is schematically shown in Fig. 1. Mesoporous silica KIT-6 was used as the template and prepared according to the reported procedure [29]. BOMCs with different boron content were obtained by adjusting the mass ratio of boric acid to furfuryl alcohol (0.02, 0.05, 0.08). In a typical procedure, 1.0 g furfuryl alcohol solution which contains 0.02 g boric acid was impregnated into 1.0 g KIT-6 by nanocasting approach in the presence of 0.1537 g toluene-p-sulfonic acid for 1 h. In order to polymerize furfuryl alcohol completely, the mixture was cured in the oven at 80 °C and 160 °C for 2 h, 4 h respectively. Thereafter, the obtained mixture was carbonized in argon atmosphere at 600 °C for 3 h at a heating rate of 5 °C min^{-1}. Finally, the BOMCs were obtained by the removing of silica template using 5% HF aqueous and drying at

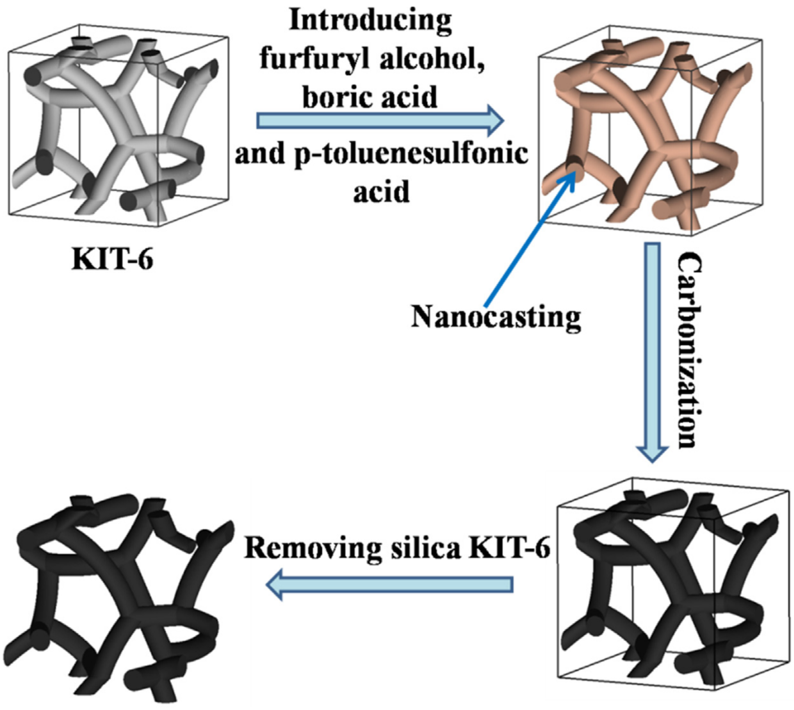

Fig. 1. A schematic mechanism of BOMCs formation.