

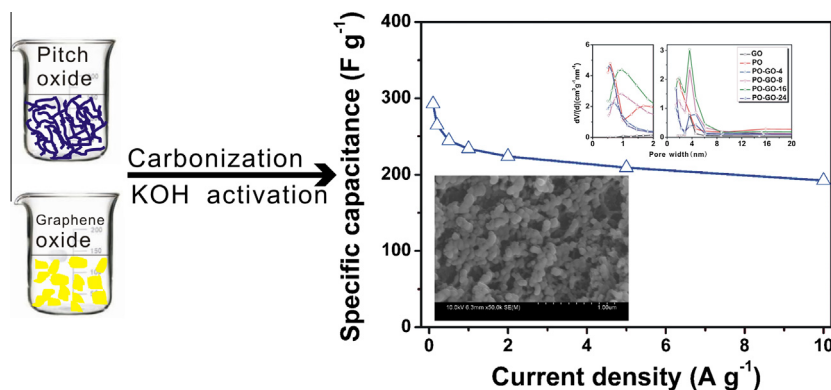
Nitrogen-doped hierarchical porous carbon with high surface area derived from graphene oxide/pitch oxide composite for supercapacitors



Yuan Ma, Chang Ma^{*}, Jie Sheng, Haixia Zhang, Ranran Wang, Zhenyu Xie, Jingli Shi^{*}

State Key Laboratory of Separation Membranes and Membrane Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, China

GRAPHICAL ABSTRACT



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ABSTRACT

A nitrogen-doped hierarchical porous carbon has been prepared through one-step KOH activation of pitch oxide/graphene oxide composite. At a low weight ratio of KOH/composite (1:1), the as-prepared carbon possesses high specific surface area, rich nitrogen and oxygen, appropriate mesopore/micropore ratio and considerable small-sized mesopores. The addition of graphene oxide plays a key role in forming 4 nm mesopores. The sample PO-GO-16 presents the characteristics of large surface area (2196 m² g⁻¹), high mesoporosity (47.6%), as well as rich nitrogen (1.52 at.%) and oxygen (6.9 at.%). As a result, PO-GO-16 electrode shows an outstanding capacitive behavior: high capacitance (296 F g⁻¹) and ultrahigh-rate performance (192 F g⁻¹ at 10 A g⁻¹) in 6 M KOH aqueous electrolyte. The balanced structure characteristic, low-cost and high performance, make the porous carbon a promising electrode material for supercapacitors.

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1. Introduction

Electrochemical capacitors (EDLC, known as ultracapacitors or supercapacitors) hold promise for a wide range of applications, including portable electric equipments, uninterruptable power sources, medical devices, load leveling and hybrid electric vehicles,

^{*} Corresponding authors.

E-mail addresses: fdoy_lt54@163.com (C. Ma), shijingli1963@163.com (J. Shi).

and so forth [1]. In recent years, great efforts have been made in developing better supercapacitor electrode materials. Porous carbon materials are widely used and studied as supercapacitor electrodes because of their relatively low cost, high specific surface area, good electric conductivity, rich source and excellent chemical stability [2].

In EDLCs, energies are stored by the electrostatic charge uptake at the electrolyte/electrode interfacial regions of porous carbons. The electrochemical performance of supercapacitors is greatly

dependent on high specific surface area (SSA) and a rational pore structure. Generally, carbon materials with higher SSA have a better capability for charge accumulation at the electrode/electrolyte interface. Recently, numerous researches have held that specific capacitance is not always linearly proportional to the SSA, especially for carbons with ultra-high SSA. This is because not all micropores in electrodes are necessarily accessible to the electrolyte ions, due to that closed pores or narrow bottle-necks may dramatically prevent or slow ion transport and impair the capacitive performance of supercapacitors. Hence, the micropore amount should be controlled at a particular level. The pores with bigger size have been reckoned more beneficial for convenient ion transportation and higher accessible surface. Hierarchical porous carbons, containing considerable mesopores or macropores, have inspired high hopes and been proved possess distinctive potential for high-performanced supercapacitors [3,4]. However, too many bigger pores or pores with too big diameter always lead to moderate even low surface area, which are obviously not conducive to high-performanced supercapacitors [5]. So, mesopores with relative small size should be introduced with an appropriate proportion. So far, great efforts have been made to gain well-designed hierarchical porous carbon materials for supercapacitors. Template method is most commonly used to create mesopores. A variety of templates, such as SiO_2 colloid, magnesium, nickel oxide, have been employed [6–8]. However, it always means that time-consuming washing process, introduction of impurity are unavoidable. These deficiencies hinder their practical applications. Hence, a simplified and convenient strategy to hierarchical porous carbons is still needed.

Besides pore structure, the surface functionalization of electrode materials is another crucial factor for the electrochemical performance [9]. In general, carbon materials are of poor surface wettability for electrolyte solution owing to the high temperature carbonization, which impedes the penetration of the electrolyte ions into the pores of carbons. Introduction of surface functionalization, especially nitrogen functionalizations, has been proven to be a promising approach to improve their surface wettability, electric conductivity and capacitance properties [10,11]. However, development of nitrogen functionalized electrode materials by a simple method is still required for further advancement in supercapacitors.

Herein, we demonstrate a facile strategy to nitrogen-containing hierarchical porous carbons through one-step KOH activation of pitch oxide/graphene oxide composite. With less KOH consumption and simpler process, the as-prepared carbon possessed high specific surface area ($2196 \text{ m}^2 \text{ g}^{-1}$), rich nitrogen (1.52 at.%) and oxygen (6.9 at.%), appropriate mesopore/micropore ratio (mesoporosity of 47.6%) and considerable small-sized mesopores (4 nm). As a result, an outstanding capacitive performance, including high capacitance (296 F g^{-1}) and ultrahigh-rate performance (192 F g^{-1} at 10 A g^{-1}) in 6 M KOH aqueous electrolyte was achieved.

2. Experimental

2.1. Material preparation

Pitch oxide (PO) was prepared by treatment of pitch (Isotropic pitch, Shanghai Dongdao Carbon Chemical Industry Co., Ltd.) using mixed acid. Firstly, 20 ml nitric acid and 80 ml sulfuric acid were blended and stirred in 40°C water bath for 10 min. The pitch was slowly added into the system in 30 min. After 2 min, 1000 ml deionized water was added into the mixture. Solid precipitate of the mixture was collected by repeated vacuum filtration. Subsequently, the collected solid precipitate and 1 g NaOH were

dissolved in 500 ml deionized water by stirring 2 h at 75°C water bath. The pitch oxide aqueous solution was obtained. Subsequently, solid content of the pitch oxide aqueous solution was measured.

Graphene oxide (GO) was prepared by oxidizing the natural graphite powder and subsequent exfoliation by ultrasonication by a modified Hummers' method [12,13]. Firstly, 1 g graphite powder (Qingdao Black Dragon Graphite Co. Ltd.) and 0.5 g sodium nitrate (Tianjin Kemiou Chemical Reagent Co., Ltd.) were mixed with 30 ml sulfuric acid (98%, Shanghai Macklin Biochemical Co., Ltd) in an ice bath under vigorous stirring. Then, 3 g potassium permanganate (Tianjin Kemiou Chemical Reagent Co., Ltd.) was slowly added into the system in 30 min while the temperature was kept from exceeding 20°C . After 2 h, the mixture was moved to 35°C oil bath and maintained for 12 h. Subsequently, 230 ml deionized water was slowly added, and then the mixture was heated to 98°C for 60 min. 150 ml deionized water and 20 ml hydrogen peroxide (30 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd.) were added into the mixture. After centrifugation and washing to remove residual salts, the graphite oxide aqueous solution was prepared. Then, the graphite oxide aqueous solution was ultrasonicated for 2 h and centrifuged at 8000 r min^{-1} . The supernatant colloidal substance was collected. Subsequently, solid content of GO aqueous solution was measured.

PO/GO compound was prepared by mixing pitch oxide aqueous solution and graphene oxide aqueous solution with different ratios under ultrasonic and stirring, followed by desiccation at 100°C . Then, the PO/GO compound was mixed with KOH at PO/GO:KOH = 1:1. Carbonization was conducted at 800°C for 1 h with a heating-rate of 3°C min^{-1} in high purity nitrogen. The product was washed using dilute HCl and deionized water repeatedly. The obtained solid was dried at 80°C to obtain porous carbons PO-GO-X (X means the ratio of PO/GO = 4, 8, 16, 24). The preparation process was displayed in Scheme 1. For comparison, PO and GO were activated by the same process, from which the resultant carbons were named PO and GO, respectively.

2.2. Materials characterizations

The morphology and structure of samples were examined by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The crystallographic structures of the materials were investigated by a Rigaku D/MAX-ga diffractometer with filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was measured by an X-ray photoelectron spectrometer (ESCALAB 250) to analyze the surface characteristics of the samples. Nitrogen adsorption and desorption isotherms was conducted at 77 K to investigate the porous texture of the samples on a Quantachrome ASMS analyzer. All samples were degassed at 200°C for 12 h before the measurement. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. Micropore size distribution was estimated by density functional theory (DFT), while mesopore size distribution by Barrett–Joyner–Halenda (BJH) model from adsorption branch isotherms. Pore volume was calculated from the adsorbed amount at a relative pressure $P/P_0 = 0.994$.

2.3. Electrochemical measurement

The working electrode was fabricated by mixing the active material, carbon black and polytetrafluoroethylene (PTFE) with the weight ratio of 80:10:10 and then dried in a vacuum oven at 100°C for 24 h. Finally, the electrode was pressed onto the nickel foam current collectors at 8 MPa for test. The weight of the electrode is 1.5–2.0 mg. The electrochemical performance of the electrodes was measured in three-electrode cells in 6 M KOH

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