Easy preparation of nitrogen-doped porous carbon nanospheres and their application in supercapacitors

Bin Xu [a,*], Shufang Yue [b], Ning Qiao [a], Mo Chu [b], Gang Wei [a]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China
[b] School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China

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ABSTRACT

An easy method for preparing porous carbon nanospheres is presented by using commercial spherical poly(vinylidene fluoride) (PVDF) as precursors. The PVDF nanospheres are simply converted to porous carbon nanospheres by a low temperature defluorination treatment with an organic alkali and followed high temperature carbonization. The as-prepared carbon exhibits monodispersed spherical morphology with size of ~ 170 nm, porous structure with a surface area of $523\ m^2\,g^{-1}$ and nitrogen-doped functionality, which affords a capacitance of $190\ F\,g^{-1}$ with good rate capability in $6\ mol\,L^{-1}$ KOH.

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1. Introduction

Spherical carbons have attracted great interests due to their potential applications as reinforcement materials for rubber, supports for catalysts and electrode materials for lithium ion batteries and supercapacitors [1]. Various approaches such as hydrothermal method [2], self-assembly template process [3] and chemical vapor deposition [4] have been used to prepare hollow or/and solid carbon spheres with different yields and sizes. However, it is still a challenge to develop a method which is easier, capable for large-scale production and have tunable sphere size.

Recent studies have shown the doped heteroatoms such as nitrogen [5–7], sulfur [8] and boron [9] play important roles in determining the properties of the carbons as they can modify the electronic and crystalline structures as well as surface chemistry of the carbon host. For example, introducing nitrogen into carbon frameworks can enhance the conductivity, basicity, oxidation stability and catalytic activity of the carbon, making the nitrogen-doped carbons very attractive in applications such as catalyst supports [5], CO_2 capture [6] and supercapacitors [7].

Here, we propose a novel, very simple route to prepare nitrogen-doped porous carbon nanospheres from commercial poly(vinylidene fluoride) (PVDF) spheres by a low temperature defluorination treatment and followed high temperature carbonization. The as-prepared carbons have monodispersed spherical

morphology, porous structure and nitrogen-doped functionality, making it an attracting material for supercapacitors.

2. Experimental

The commercial homogeneous PVDF (Kynar 761, Arkema Co.) and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), one of the strongest organic bases, were used as precursor and defluorination agent, respectively. The PVDF were defluorinated with DBU as the reported procedure [10]. Briefly, the PVDF powder by the amounts corresponding to the number ratio of DBU/(vinylidene fluoride unit)=4/1 were soaked in a dimethylformamide-ethanol solution of 1.0 M DBU at 70 °C for 18 h. The black solids deposited and the upper liquid becomes colorless. Then the powders were put in a tubular furnace and heated to 600–900 °C at a rate of $10\ ^\circ C\,min^{-1}$ under N_2 (99.999%) protection for 2 h. After cooled to room temperature, the PVDF-based porous carbon nanospheres (PCNSs) were obtained. The carbon sample prepared at a carbonization temperature of $x\ ^\circ C$ was denoted as PCNSx. The morphology of the carbons thus obtained were observed by field-emission scanning electron microscope (FESEM, S4800/E01-IOP), the porosity parameters were characterized by N_2 adsorption/desorption at 77 K (ASAP 2010), and the nitrogen functionality were characterized by X-ray photoelectron spectroscopy (XPS).

In order to evaluate the electrochemical performances of the PCNSs, a mixture of 87 wt% of carbon, 10 wt% of acetylene black and 3 wt% of polytetrafluoroethylene (PTFE) binder were pressed into pellet electrodes (11 mm in diameter), followed by drying at 120 °C for 6 h. The carbon loading in each electrode is about 10–13 mg.

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* Corresponding author. Fax: +86 10 64455013.
E-mail addresses: binxumail@163.com, xubinn@sohu.com (B. Xu).

Button-type capacitor was assembled into two-electrode system, among which two electrodes were same in both composition and mass, separated by polypropylene membrane using 6 mol L^{-1} KOH aqueous solutions as electrolytes. The electrochemical performances of the test capacitors were evaluated by cyclic voltammetry (CV) on a Solatron 1280B electrochemical workstation and galvanostatic charge/discharge between 0 and 1 V on an Arbin cell tester (CT2001A).

3. Results and discussion

As shown in Fig. 1a, the commercial homogeneous PVDF exhibits monodispersed spherical morphology with a diameter of ~180 nm, and the surface of the PVDF sphere is very smooth. Previously, by direct carbonization of PVDF we have obtained porous carbons with surface areas of ~1000 m^2 g^{-1} [11], which exhibit irregular particle morphology (Fig. 1b). The spherical morphology of PVDF has not reserved because PVDF is thermoplastic and the melting point (155–180 °C) is much lower than its decomposition temperature (~400 °C) [11].

To inherit the spherical morphology of PVDF, an organic alkali DBU was used as defluorination agent to stabilize the PVDF at 70 °C, a temperature much lower than its melting point before high temperature carbonization [10]. After defluorination, the white PVDF powders were converted to black char. SEM (Fig. 1c) indicates the char has reserved the spherical morphology of PVDF. XPS analysis indicates the atom ratio of C/F has increased from the pristine 1:1 of PVDF to 4.3:1 of the defluorinated char, implying that most of the fluorin atoms in PVDF have been removed by DBU during the defluorination period, making it has a much improved thermal stability and can endure the followed high temperature carbonization. SEM observation (Fig. 1d) indicates the carbonized products are highly monodispersed spheres with a diameter of ~170 nm, while XPS analysis indicates no fluorin atoms are detected in the carbonized products, proving the PVDF nanospheres have been simply converted to carbon nanospheres by defluorination pretreatment and followed carbonization. Moreover, XPS analysis indicates some nitrogen atoms have been introduced in the char during defluorination by DBU. The nitrogen content in the
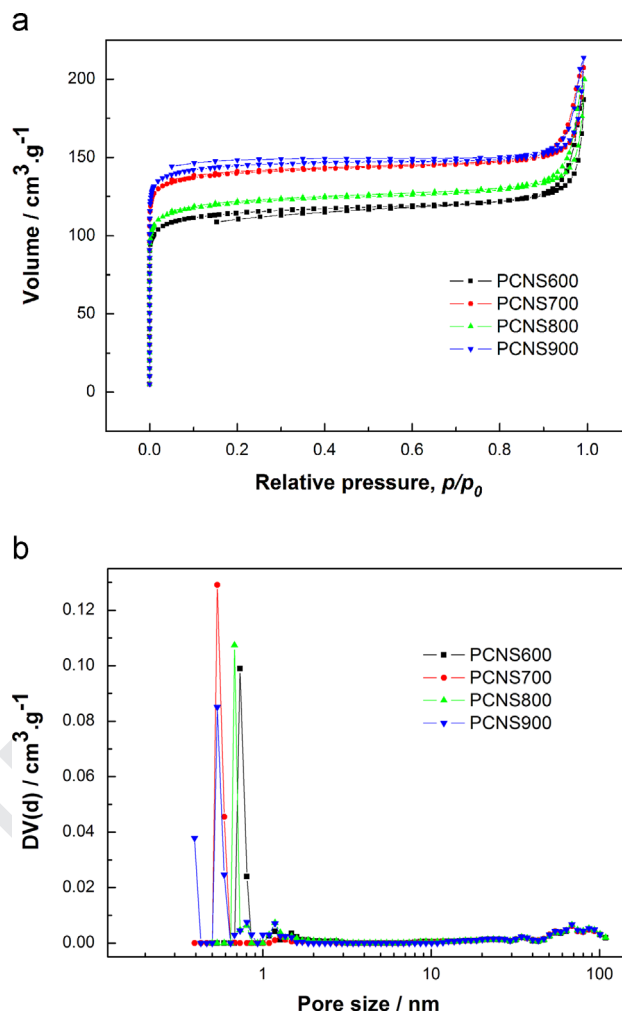
Fig. 2. Nitrogen adsorption/desorption isotherms (a) and pore size distribution (b) of the PVDF-based porous carbon nanospheres prepared by defluorination and followed carbonization.
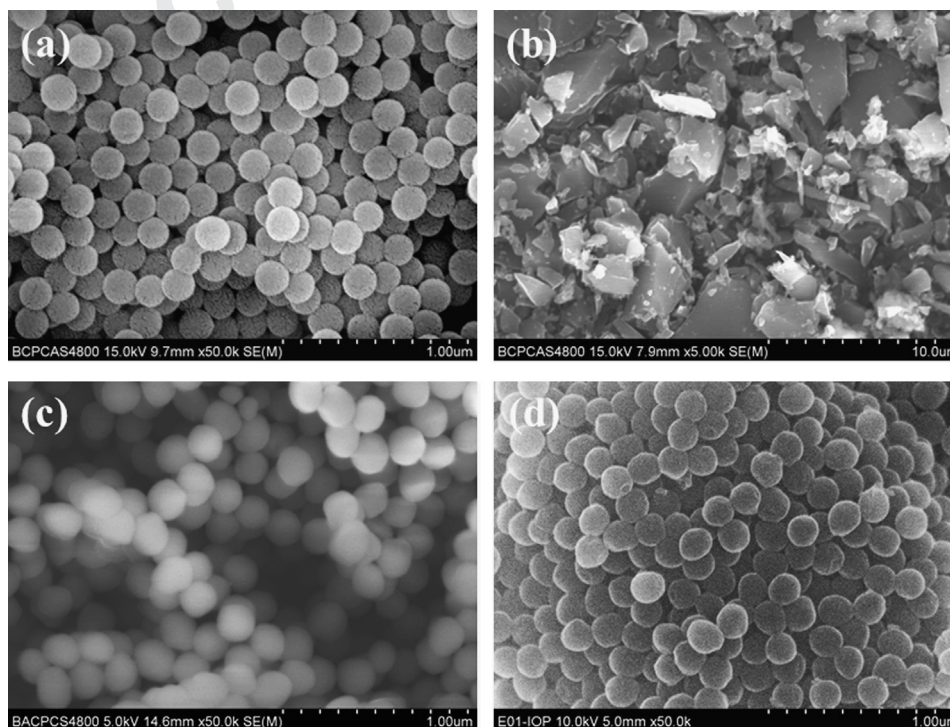
Fig. 1. SEM images of the PVDF (a), PVDF-based carbon prepared by direct carbonization of PVDF (b) and PVDF-based carbon nanospheres prepared by defluorination and followed carbonization (c) an (d).