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Facile synthesis of microporous carbons with three-dimensional honeycomb-like porous structure for high performance supercapacitors

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ABSTRACT

Microporous carbons (MPC) with three-dimensional (3D) honeycomb-like porous structure is synthesized by a simple and convenient carbonization method using polyvinyl alcohol (PVA) as carbon source and KOH as both activating agent and template. Benefiting from its large surface area, 3D interconnected honeycomb-like porous structure and high oxygen doping, the MPC-2 electrode exhibits a high specific capacitance of 367 F g^{-1} at 0.5 A g^{-1} and excellent electrochemical stability (99.7% of its initial capacitance after 10,000 cycles) in 6.0 M KOH aqueous electrolyte. More importantly, the assembled MPC-2 symmetric supercapacitor shows an energy density of 22.4 Wh kg^{-1} based on the total mass of active materials of the two electrodes in 1.0 M Na_2SO_4 aqueous electrolyte, as well as excellent electrochemical stability. Therefore, this work provides an easy, convenient way to design and large-scale produce 3D honeycomb-like porous carbon for high performance supercapacitors.

1. Introduction

Due to the rapidly increasing market for portable electronic equipment and energy needs, the development of electrochemical energy storage devices has attracted considerable attention [1]. Among energy storage systems, supercapacitors (SCs) have attracted tremendous attention from both industry and academia in recent years, because of their ultrahigh power density, long operating life, fast charge/discharge rate and environmental friendliness [2–6]. Based on the energy storage theory, supercapacitors can be classified into electrical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs store energy depending on the electrostatic adsorption of electrolyte ions onto the surface of electrode materials, while pseudocapacitors depend on the Faradaic reactions between electrolyte ions and electrode materials. Compared with pseudocapacitors, EDLCs have ultrahigh power density and superior electrochemical stability, which are attributed to the fast reversible adsorption and desorption of electrolyte ions in the double electric layers [7,8].

Carbon-based materials, especially porous carbons (PCs) have been widely used as electrode materials for EDLCs due to their large surface area, low cost, abundance of raw material and excellent mechanical stability [9–15]. It is widely known that the specific surface area and pore size distribution are two critical factors that decide the electrochemical performance of carbon materials [16,17]. Recently, PCs with a well-designed 3D structure have better permeability and can not only provide usable large active surface areas for the interfacial adsorption of ions for different pore sizes, but also shorten diffusion paths and thus favor the fast diffusion of electrolyte ions into the pores, have attracted more and more attention [18–25]. Consequently, a wide range of synthesis routes have been developed for obtaining novel 3D PCs, such as, using expensive zeolites or silica oxides as a sacrificial scaffold [26–28], using a metallic compound as a template [29,30]. However, these ways still suffer from some drawbacks such as complex synthesis processes, costly inorganic templates, which severely limit their application in large-scale production. Therefore, it remains a big challenge for the preparation of 3D interconnected porous carbon with an effective and convenient method.

Herein, we develop a novel, easy strategy to synthesize microporous carbons (MPC) with 3D honeycomb-like porous structure using polyvinyl alcohol (PVA) as the precursor and KOH as both the activating agent and template. The obtained carbon materials process unique 3D interconnected honeycomb-like porous structure, high oxygen doping and large surface area. As a result, the MPC-2 electrode delivers high specific capacitance, good rate performance and electrochemical stability. More importantly, the assembled MPC-2 symmetric supercapacitor exhibits an energy density of 22.4 Wh kg^{-1} based on the total mass of active materials of the two electrodes in 1.0 M Na_2SO_4 electrolyte, as well as good electrochemical stability.

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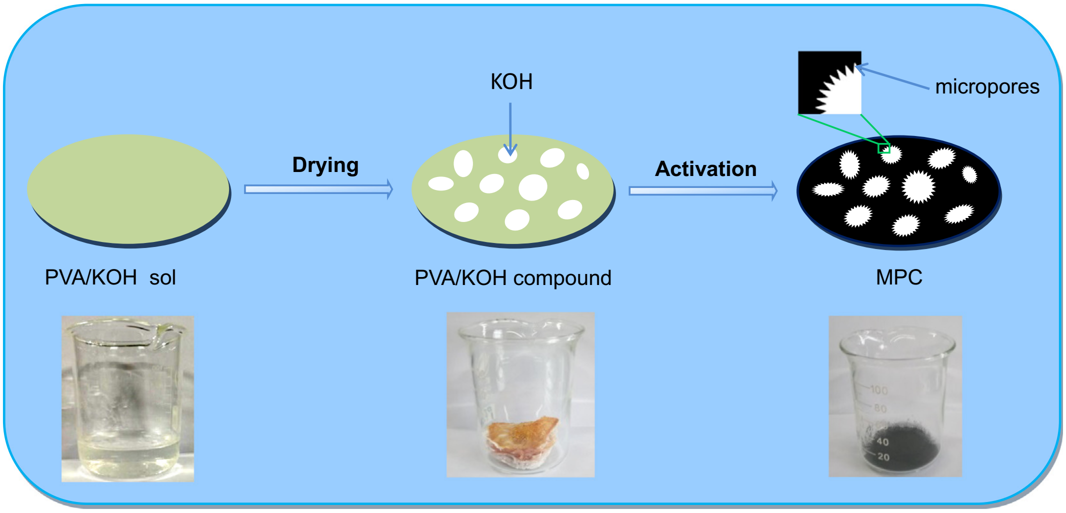

Fig. 1. Schematic diagram of the formation process of MPC.

2. Experimental

2.1. Materials

KOH, polyvinyl alcohol and hydrochloric acid were acquired from Tianjin Yongda Chemical Reagent Co., Ltd. All chemicals and reagents are of analytical grade and were used without any further treatment.

2.2. Preparation of porous carbon materials

KOH (2 g) and polyvinyl alcohol (2 g) were mixed in 30 mL distilled water (85 °C) with stirring until the mixture became limpid. Then, the mixture was dried in a vacuum oven. The resulting product was pyrolyzed in a quartz tube furnace at 700 °C for 2 h under N_2 atmosphere. Then, the obtained example was thoroughly rinsed using dilute hydrochloric acid solution and distilled water several times, and dried in a vacuum oven. For comparison, the different masses of KOH (1 g, 4 g) were also investigated under the above process. The obtained samples were named as MPC-x (which x relates to the mass of KOH). The PVA was directly pyrolyzed at 700 °C for 2 h under N_2 flow, and the obtained example was named as CP. The CP and KOH were mixed with the mass ratio of 1:1, and pyrolyzed at 700 °C for 2 h under N_2 flow, the product was named as ACP. All carbonized samples were rinsed with dilute hydrochloric acid and distilled water several times, and dried in a vacuum oven.

2.3. Material characterizations

The microstructure and morphology of carbon materials were determined by scanning electron microscope (SEM, JEOL JSM-7500F) and transmission electron microscope (TEM, JEOL JEM2010). The crystal structures of carbon materials were checked by X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 0.15406$ nm). Raman analysis was conducted with a Jobin-Yvon HR800 Raman spectroscopy. The surface chemical characteristic of the sample was measured by X-ray photoelectron spectroscopy (XPS) using a PHI5700ESCA spectrometer with a monochromated Al Kα radiation. The specific surface area of samples was tested by N_2 adsorption-desorption isotherms using Barrett-Emmett-Teller (BET) method. The pore size distribution was derived from the adsorption branch of isotherm by density functional theory (DFT) model.

2.4. Electrochemical characterization

Electroactive material, carbon black and poly (tetrafluoroethylene) with a mass ratio of 75:20:5 coated onto the nickel foam current collector (1 cm × 1 cm), and the mass loading was ~3 mg cm^{-2}. The electrochemical measurements of the individual electrode were carried out in 6 M KOH aqueous electrolyte with a three-electrode cell. The prepared electrode acted as the working electrode, platinum foil and Hg/HgO electrode served as counter and reference electrode. The cyclic voltammetry (CV) and galvanostatic charge-discharge tests of the three-electrode system were carried out between −1 and 0 V in 6.0 M KOH aqueous electrolyte. Electrochemical impedance spectra (EIS, Nyquist plots) were evaluated at the frequency range from 100 KHz to 0.01 Hz under an open circuit potential. The symmetric supercapacitor was built using two electrodes with exactly the same mass in 1.0 M Na_2SO_4 aqueous electrolyte, and the electrochemical tests were carried out in a voltage window of 1.8 V. All of the above electrochemical measurements were tested by a CHI 660E electrochemical work station at room temperature.

The specific capacitance (C) was calculated with the following equations:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

$$C = \frac{\int IdV}{vmV} \tag{2}$$

where I is the response current density, Δt is the discharge time, m is the active mass of the electrode materials. ΔV is the voltage range, and ν is the potential scan rate.

The energy density (E) and power density (P) were calculated based on the following formulas:

$$E = 1/2CV^2 \tag{3}$$

$$P = \frac{E}{t} \tag{4}$$

where t is the discharge time (s).

3. Results and discussion

3.1. Structural characterization

The preparation process of MPC is illustrated in Fig. 1. KOH and polyvinyl alcohol were mixed in 85 °C distilled water with stirring until the mixture became limpid, and then dried in a vacuum oven. The