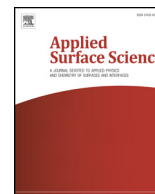




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Facile synthesis of hierarchical porous carbon nanorods for supercapacitors application



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ABSTRACT

A hierarchical porous carbon nanorods (HPCRs) with highly interconnected three-dimensional conductivity networks derived from metal-organic frameworks have been successfully synthesized via a simple carbonization method. The resultant HPCRs shows a stable porous structure with abundant micro/mesopore on two-dimensional squared shape carbon nanosheets and also between the closely cross-linked carbon sheets. The electrochemical measurements reveal that the HPCRs materials as electrodes for supercapacitor deliver a high specific capacitance of 274 F g^{-1} at 0.5 A g^{-1} with an enhanced rate capability in basic media. Moreover, a considerable energy density of 6.77 Wh kg^{-1} at power density of 100 W kg^{-1} are exhibited for solid-state symmetric supercapacitor. The assembled symmetric supercapacitor also works well under 0 and -20°C with a remarkable temperature endurance. The large-scale production of unique hierarchical porous carbon nanorods with high efficiency, low cost and one-step synthesis method will be effective electrode materials in energy storage applications.

1. Introduction

Due to the continuous consumption of fossil fuels, the sustainable and renewable energy sources coupling with various advanced electronic storage devices are urgently required to relieve the energy crisis [1–4]. Supercapacitors with high power density, long life and quick charge-discharge capability properties have been widely applied in different portable and hybrid electronic devices [5–10]. The electrochemical performance of supercapacitors is closely determined by the design of electrode materials. In recent years, the focus of researchers is to develop electrode materials for supercapacitors to obtain high power density and improved energy density. In this regard, metal-oxides, porous carbon and conducting polymers are proved to be promising [2,11–16]. The porous structure can offer many benefits such as shortening electrolyte ion diffusion distance and providing more surface area for charge storage. Among them, porous carbon materials have been regarded as a promising electrode material for supercapacitors, due to their outstanding features, such as high specific surface area, richly porous structure, high conductivity and good chemical stability [17,18].

To date, activated carbon with high specific surface area is highly

popular in the carbon-based supercapacitors [8,19]. But, its energy density still need to be further improved. To solve this, many researchers are trying to design other porous carbon materials with three-dimensional framework or heteroatom doping to boost the capacitance of carbon-based supercapacitors [15,20–22]. Zhu et al. reported that a 3D porous carbon obtained through activating graphene oxide with KOH as electrode material exhibited superior electrochemical capacitive performance [23]. However, the further development of carbon-based supercapacitors are also intensely restricted by some problems, such as high cost of raw materials, poor controllability of morphology and time-consuming of synthesis procedure. Hence, it is urgently desirable to develop a facile, low-cost and controllable method for the synthesis of porous carbon materials to enhance the electrochemical performance of carbon-based supercapacitors.

Metal-organic frameworks (MOFs) with open architectures have been deemed as perfect templates for the construction of porous carbon materials, because of their diverse open architecture, high specific surface area and distinguishingly meso/microporous structure [24–28]. During the direct carbonization approach, abundant micropore and mesopore will generate and the original three-dimensional porous framework of MOFs will also be mostly retained. In the past preparing

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process of porous carbon, silica or zeolite templates, carbon sources and activating agent were usually used with complex synthesis route [29,30]. In contrast, this method through the distinct carbonization of MOF precursors is simple. The porous carbon materials derived from MOFs have been popularly applied in various fields, such as Li-S batteries [27,31], hydrogen uptake [32,33] and sensing [34]. Due to high porosity and well-defined morphology, porous carbon materials derived from MOFs will be of great important in the energy storage fields, including supercapacitors [35,36].

Herein, we developed a simple and scalable approach to obtain hierarchical porous carbon nanorods (HPCRs) through direct carbonization of MOFs precursor. The as-prepared HPCRs consist of multi-layered well-preserved carbon sheets with abundant micropore on 2D squared-shape cross-sectional carbon sheets and well-defined mesopore between firmly interconnected carbon sheets. The HPCRs can well maintain the original morphology of MOF precursors. It is remarkable that the whole preparation process is appropriate for mass production with low cost and high efficiency. As electrode materials for supercapacitors, the small-sized micropore on carbon sheets will enhance the electrolyte penetration and provide more electrochemical active spots for a better capacitance performance. Meanwhile, the numerous mesopore between carbon sheets will facilitate ion diffusion and transport for an enhanced dynamic performance. Due to the synergetic effect of the interconnected conductive porous network and appropriate pore size, the obtained HPCRs exhibited superior electrochemical capacitive performance at room/low temperature.

2. Experimental section

2.1. Synthesis of hierarchical porous carbon nanorods (HPCRs)

The rod-like Al-MOFs were used as carbon precursor. The precursors were prepared through the hydrothermal reaction [34,37]. The mixed solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1,4-naphthalenedicarboxylate (1,4-H₂NDC) and H_2O (2.0 mmol, 1.0 mmol and 1.1 mol) was placed into 50 mL Teflon autoclave and then heated at 180 °C for 24 h. Then the yellow powder of Al-MOFs was annealed at 700, 800 and 900 °C for 5 h at a heating rate of 2 °C min⁻¹ by a N₂ gas flow. The obtained sample was treated with 10% HF aqueous solution for several hours and then washed with hot deionized water and alcohol to remove the Al impurities. After dried at 100 °C under vacuum, the hierarchical porous carbon nanorods were easily obtained and named as HPCR-x (x = annealing temperature).

2.2. Materials characterization

The whole morphology and microstructure of materials were characterized by scanning electron microscope (SEM, S-4800) and transmission electron microscope (TEM, G2F20). X-ray power diffraction (XRD) was recorded using CuK α radiation from Smartlab 9. N₂ adsorption/desorption isotherms were obtained with Brunauer-Emmett-Teller (BET) method and pore distribution was calculated with Density Functional Theory model by ASAP 2020. X-ray photoelectron spectrometer (XPS, K-ALPHA 0.5EV) was used to characterize the element component. The Raman spectra was characterized by Horiba LabRAM HR Evolution.

2.3. Fabrication of HPCRs working electrode and solid-state asymmetric supercapacitor device

The working electrode was made by homogeneously mixing 80 wt% as-prepared HPCR, 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) with N-methyl-2-pyrrolidone (NMP) as solvent. The obtained black slurry was coated on the half of nickel foam (10 mm * 20 mm) and dried in a vacuum oven at 100 °C for 10 h to remove NMP. Then the electrode was pressed at 8 MPa. The mass

loading of HPCR-700, HPCR-800 and HPCR-900 on the electrodes was about 2.4, 2.5 and 2.4 mg, respectively.

The solid-state symmetric supercapacitors devices were fabricated with the two identical electrodes and KOH/PVA gel electrolyte. The preparing process of KOH/PVA gel electrolyte was shown as following: 2 g PVA was soaked in 20 mL deionized water for several hours and heated at 90 °C under stirring. The as-synthesized 6 M KOH solution (10 mL) was dropwisely added into above clear solution. The mixing solution was continued to heat at 90 °C under intensely stirring to get a homogeneous gel solution. The two electrodes with the same mass were submerged by the KOH/PVA solution for 5 min and pressed together until the water was vaporized. The total mass loading of active material on two working electrodes was about 5.0 mg.

2.4. Electrochemical measurement

The electrochemical performance of each electrode was measured in 6 M KOH solution using a typical three-electrode system, consisting of Pt foil as counter electrode, Hg/HgO electrode as reference electrode and as-prepared electrode as working electrode. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy measurements (EIS) were tested using Zennium electrochemical workstation (Zahner, German) at 20 °C. The cycling stability was tested on the LAND CT2001A battery test system.

According to GCD curves, the specific capacitance was calculated via $C = I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time, m is the mass of active material on each electrode, and ΔV is the working voltage change. For two electrodes, the specific capacitance was determined from GCD via the formula $C = I\Delta t/M\Delta V$, where M is the total mass of active material on two electrodes. The energy density (E) and power density (P) were estimated by $E (\text{Wh kg}^{-1}) = C\Delta V^2/2$ and $P (\text{W kg}^{-1}) = E/t$, where C is the specific capacitance of the two-electrode device [21].

3. Results and discussions

The synthesis route of the HPCRs with layered porous structure was illustrated in Fig. 1. First, a certain mole ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1, 4-H₂NDC and DDI H₂O were mixed and heated in Teflon autoclave. Then the light yellow precursor was obtained through the hydrothermal reaction. According to the previous literature [37], the three-dimensional structure of Al-MOF precursors for the electroneutrality balance in water as green solvent was made up of corner-sharing octahedral Al(OH)₂O₄ with infinite chains, where the Al³⁺ was connected with four oxygen atoms of 1,4-naphthalenedicarboxylate along a and b axis, and two hydroxyl groups along c axis. The interconnecting network of Al³⁺ and naphthyl groups resulted in the forming of stable and highly square-shaped pore channel. The infinite linking between Al³⁺ and hydroxyl groups in *trans* position generated the growth of nanorods. During high temperature calcination, the multilayered porous carbon sheets were formed due to the dehydration reaction of MOF precursors.

To investigate the morphology and microstructure of HPCRs samples, the SEM images of HPCRs at different carbonization temperature were shown in Fig. 2. The HPCRs samples (Fig. 2a, c, e and Fig. S1) had rod-like morphology with squared cross-sectional surface, which kept consistent with the original morphology of Al-MOF precursors (Fig. S2). These rod-like HPCRs consisted of various two-dimensional squared shape cross-sectional carbon sheets with side length of 300–500 nm (Fig. 2b, d, f). Compared with the MOFs precursors with smooth surface and straight rod-like morphology (Fig. S2), the surface of HPCRs presented a layered structure and the shape of HPCRs bent and even fractured, suggesting that the precursors gradually transformed into highly hierarchical porous carbon nanorods during high temperature calcination and the stress variation and non-uniformly convergence between carbon sheets generated the slightly change of shape. The fracture surface became rough (Fig. 2b), indicating the carbon sheets

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