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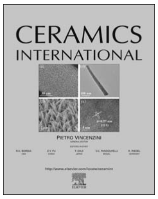

Synthesis of nitrogen-doped porous carbon from zeolitic imidazolate framework-67 and phenolic resin for high performance supercapacitors

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ABSTRACT

An one-pot method has been developed to synthesize a new type of composite material, which can be used as carbon source to produce electrode material for supercapacitors. Specifically, zeolitic imidazolate framework-67 (ZIF-67) crystal was synthesized firstly in 2-methylimidazol aqueous solution, then silica primary particles (from hydrolysis of tetraethylorthosilicate) and phenolic resin (from aggregation of resorcinol and formaldehyde) co-condensed on the surface of ZIF-67 crystal in the same system. The key to realize one-pot method is that 2-methylimidazol aqueous solution shows alkalescence, which can catalyze the hydrolysis of tetraethylorthosilicate and the aggregation of phenolic resin. After carbonization and remove of silica, the N-doped porous carbon (Carbon-ZSR) with high degree of graphitization, wide pore size distribution and maximum specific surface area was obtained. When it is used for supercapacitors as the electrode material, the Carbon-ZSR shows excellent electrochemical properties, large specific capacitance (305 Fg^{-1} at 1 Ag^{-1}), high rate performance (229 Fg^{-1} keeps at 10 Ag^{-1}) and excellent electrochemical stability (the specific capacitance maintains 98.4% after 5000 cycles at 10 Ag^{-1}), which suggest that the ZIF-derived nitrogen-doped porous carbon is an outstanding electrode material for energy storage devices.

1. Introduction

Supercapacitors, as a new type of energy storage devices, have received researchers' extensive attention due to their a lot of advantages, such as fast charge-discharge capability [1], long cycle life [2], maximum capacitance density [3] and environmental friendliness [4], etc. Based on the charge storage mechanism, supercapacitors can be divided into faradaic capacitor and electrical double layer capacitor (EDLC) [5]. Faradaic capacitor stores energy via redox reaction of electrode materials [6]. In general, these electrode materials contain conducting polymers [7] and transition metal oxides [8], etc. Electrical double layer capacitor undergoes electrostatic charges adsorb at the interface of electrolyte-electrode materials to store energy [9], and the electrode materials usually include grapheme [10], carbon nanotubes [11], activated carbons [12] and many other porous carbon materials [13]. So far, porous carbons are widely researched because of their large specific surface area [14], chemical inertness [15], low cost and high electrical conductivity [16]. When the porous carbons are used for electrode materials, micropores mainly store energy [17], while mesopores provide channels for electrolyte ions transmitting into micropores and increase the transmission rate of the electrolyte [18]. Hence, hierarchical porous carbon materials hold more excellent electrochemical performances.

In view of MOFs' advantages, maximum specific surface area and nitrogen-containing ligands [19–21], N-doped porous carbon materials with a great many outstanding properties could be acquired by carbonizing them directly. For example, Yamauchi's group pyrolyzed zeolitic imidazolate framework-8 (ZIF-8) at 900 °C to prepare nanoporous carbon [22], which shows large specific surface area (1250 $m^2 g^{-1}$) and excellent capacitive performance (214 Fg^{-1} at 5 mv/s). MOF-5, Ni-MOF-74 and many other MOFs have also been carbonized, and the results indicate that they are all promising electrode materials [23–26]. In order to further improve the performance of MOFs-derived carbon materials, many researchers co-carbonized additional carbon sources with MOFs. Cao's group found that the ZIF-derived carbon material prepared by co-carbonization of ZIF-7 and glucose at 950 °C exhibits larger specific capacitance (226.2 Fg^{-1} at 0.2 Ag^{-1}), larger specific surface area(783 $m^2 g^{-1}$) and wider pore size distribution than that prepared by direct carbonization of ZIF-7 [27], which indicates that adding additional carbon sources is an important strategy to enhance the performance of the carbon materials derived from MOFs. However, in many previous reports [28–31], multiple steps should be contained for preparing MOFs-derived compounds, which means that it is time-consuming and difficult to

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realize large-scale production. In consequence, it is necessary to find a simple and novel strategy to ameliorate the electrochemical properties of the carbon materials derived from MOFs.

In this work, an one-pot method has been developed to synthesize a new type of composite material from assembling ZIF-67, phenolic resin and silica, which can be used as carbon source to produce electrode material for supercapacitors. In 2-methylimidazol aqueous solution, ZIF-67 crystal was synthesized firstly, then silica primary particles (from hydrolysis of tetraethylorthosilicate) and phenolic resin (from aggregation of resorcinol and formaldehyde) co-condensed on the surface of ZIF-67 crystal. The key to realize one-pot method is that 2-methylimidazol aqueous solution shows alkalescence, which can catalyze the hydrolysis of tetraethylorthosilicate and the aggregation of phenolic resin [32,33]. Compared to previous multistep strategies, the one-pot method is capable of effectively simplify the synthetic steps and decrease the consuming time. For the composite material, ZIF-67 is the precursor, while adding phenolic resin and silica on the surface of ZIF-67 is to boost the specific surface area of ZIF-67 derived carbon material, and silica is the template to manufacture mesopores. After carbonization and remove of silica, the N-doped porous carbon with large specific surface area, wide pore size distribution, high degree of graphitization, fast ion pathways, high capacitance and excellent electrochemical stability was obtained.

2. Experimental section

2.1. Materials

2-methylimidazol (purity 98%) was purchased from Aladdin Chemical Co., Ltd. Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, purity 99%), tetraethylorthosilicate (TEOS), formaldehyde aqueous solution (37 wt%), hydrofluoric acid (HF, 40 wt%) and resorcinol (purity 99.5%) were purchased from Chuandong Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

2.2. Preparation of ZIF-67

ZIF-67 was prepared by the method reported previously [34]. 2-methylimidazole (5.5g) was dissolved in deionized (DI) water (20 mL), then $Co(NO_3)_2{\cdot}6H_2O$ (0.45g) in 3 mL of water was added into above solution under vigorous stirring at room temperature. 6 h later, the product was obtained by centrifugation and dried at 60 °C for 12 h.

2.3. Preparation of ZIF-67/SiO_2/RF-M from ZIF-67

The prepared ZIF-67 (0.3g) was added into the solution of 2-methylimidazole (5.5g) in deionized (DI) water (20 mL), then the mixture was sonicated for 2 h. After ZIF-67 dispersing in the solution sufficiently, TEOS (1.72 mL), resorcinol (0.448g) and formaldehyde (0.626 mL) were added into the mixture under vigorous stirring. 24 h later, the product was obtained by centrifuged and dried at 60 °C for 12 h, which is named ZIF-67/SiO_2/RF-M.

2.4. Preparation of ZIF-67/SiO_2/RF via one-pot method

2-methylimidazole (5.5g) was dissolved in deionized (DI) water (20 mL), then $Co(NO_3)_2{\cdot}6H_2O$ (0.45g) in 3 mL of water was added into above solution under vigorous stirring at room temperature. 6 h later, TEOS (1.72 mL), resorcinol (0.448g) and formaldehyde (0.626 mL) were added into last mixture and the system was kept stirring for 24 h, then the product was obtained by centrifugation and dried at 60 °C for 12 h, which is named ZIF-67/SiO_2/RF.

2.5. Preparation of ZIF-67/RF

The preparation of ZIF-67 is the same to (2.2). But before the product was centrifuged and dried, resorcinol (0.448g) and formaldehyde (0.626 mL) were added into the mixture and the system was kept stirring for 24 h. The composite is named ZIF-67/RF.

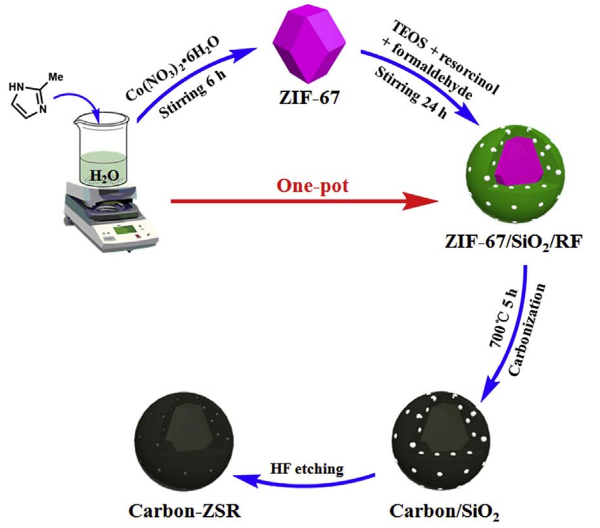

Fig. 1. Schematic illustration of the synthesis of Carbon-ZSR.

2.6. Preparation of SiO_2/RF

2-methylimidazole (5.5g) was dissolved in deionized (DI) water (20 mL), TEOS (1.72 mL), resorcinol (0.448g) and formaldehyde (0.626 mL) were added into the solution, and the system was stirred at room temperature for 24 h. Then, the product (SiO_2/RF) was obtained by centrifuged and dryed at 60 °C for 12 h.

2.7. Preparation of Carbon-ZSR, Carbon-ZSR-M, Carbon-Z, Carbon-ZR, Carbon-SR

The prepared ZIF-67/SiO_2/RF, ZIF-67/SiO_2/RF-M, ZIF-67, ZIF-67/RF and SiO_2/RF were placed in porcelain combustion boat, respectively, then heated in tube furnace at 700 °C with a heating rate of 5 °C min^{-1} under a flow of N_2. After that, the products were washed with (HF, 5%), then dried at 60 °C in vacuum drying oven for 12 h. The obtained carbons were respectively named Carbon-ZSR, Carbon-ZSR-M, Carbon-Z, Carbon-ZR, and Carbon-SR.

2.8. Characterization

Field-emission scanning electron microscope (FE-SEM, JEOLJSM-6335F) was used to investigate morphologies of the samples. X-ray diffraction (XRD) patterns were analyzed by PANalytical Empyrean diffractometer with Cu (Ka) radiation at 40 kV and 30 mA. Raman spectroscopy was carried out on LabRAM HR evolution Raman spectrometer. FTIR (Fourier Transform Infrared Spectroscopy) spectra were tested via FTIR spectrophotometer (NICOLET-5700) from 4000 to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was performed by ESCALAB 250 system with a monochromatized Al-Kα radiation.

2.9. Electrochemical characterization

The electrochemical measurements were tested with a three-electrode system in H_2SO_4 (1 mol/L) solution. In this system, a Pt plate and saturated calomel electrode (SEC) were used as counter electrode and reference electrode, respectively. The working electrodes were prepared from the mixture of electroactive materials (16 mg), acetylene black (2 mg), PTFE (2 mg) and N-methylpyrrolidone