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P-type conductive polymer/zeolitic imidazolate framework-67 (ZIF-67) nanocomposite film: Synthesis, characterization, and electrochemical performance as efficient electrode materials in pseudocapacitors

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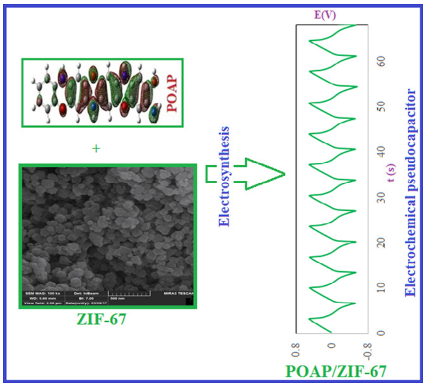
GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, zeolitic imidazolate framework (ZIF-67) was synthesized via chemical routes. For improving the electrochemical performance of the conductive polymer, POAP/ /ZIF-67 composite films were fabricated by POAP electropolymerization in the presence of ZIF-67 as active electrodes for electrochemical supercapacitors. The structural and the valance states of the prepared samples were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Different electrochemical methods, including galvanostatic charge discharge experiments, cyclic voltammetry, and electrochemical impedance spectroscopy, have been applied to study the system performance. The supercapacitive behavior of the composite film was attributed to the (i) high active surface area of the composite, the (ii) charge transfer along the polymer chain due to the conjugation form of the polymer, and finally, the (iii) synergism effect between the conductive polymer and ZIF-67.

1. Introduction

Supercapacitors (SCs) have been recently employed as energy storage devices owing to their unique properties such as high-power density, long life cycle, and fast charge/discharge (C/D), all of which has led to their introduction in different applications.

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The performance of SCs are based on two different methods, electrical double layer charge (EDLC) and pseudocapacitance [1–7].

Generally, carbon-based materials, [8–12] are classified as pseudocapacitors. Another procedure for obtaining higher performance includes hybrid supercapacitors as a hybrid of the two aforementioned methods that can provide a synergistic effect and remarkably increase the electrochemical features [13]. Different types of materials have been increasingly developed in the SCs for achieving high electrochemical behaviors. Owing to low toxicity, high thermal, chemical, and electrochemical stability as well as high ionic conductivity, ionic liquids (ILs) are promising materials for constructing electrodes [14–18].

Metal-organic frameworks (MOFs) are made by linking the inorganic and the organic units by strong bonds (reticular synthesis). The flexibility of the constituents' geometry, shape, functionality, and size, with a long range of variations, has led to different applications and investigations of MOFs within the past decade. In comparison to other classes of porous materials, MOFs with permanent porosity have been considered more extensive in their variety and multiplicity. These unique characteristics of MOFs set them apart from other traditional porous materials and have introduced them as an ideal candidate for the storage of fuels (hydrogen and methane), the capture of carbon dioxide, and catalysis applications and energy storage, etc. [19–23].

The framework structures and the extensive modulation of pore sizes introduced MOFs with extraordinary high surface areas of 43,000 $m^2\ g^{-1}$, with Langmuir surface areas of more than 10,000 $m^2\ g^{-1}$ [24]. To overcome poor electrical conductivity and steric hindrance to ion insertion in MOFs, Kang et al. [25] successfully synthesized a simple nickel-based MOF through the hydrothermal method as $Ni_3(btc)_2{\cdot}12H_2O$ with a structure composed of zigzag chains with both bridging and terminal Ni^{2+}ions. Each nickel center coordinated to four water molecules and were employed in an asymmetric supercapacitor as the positive electrode where the commercial activated carbon was fabricated as negative and obtained a high energy density of 16.5 Wh kg^{-1} in the KOH electrolytes, based on good pseudocapacitive behavior, and after only 1000 cycles, it lost nearly 6% of the initial capacitance to reach a specific capacitance of 726 F g^{-1}. Wang et al. [26] worked on the flexible solid-state supercapacitor based on a metal-organic framework interwoven by electrochemically deposited poly aniline (PANI) and they synthesized Co-based MOF crystals (ZIF-67) onto carbon cloth and further electrically deposited PANI to make a flexible conductive porous electrode (PANI-ZIF-67-CC) without altering the underlying structure of the MOF, thus obtaining a high areal capacitance of 2146 mF cm^{-2} at 10 mV s^{-1}. Hu et al. [27] cited redox-active organic molecules functionalized nitrogen-doped porous carbon derived from zinc based metal-organic framework (ZIF-8) as an efficient electrode material for a supercapacitor, which resulted in a high-performance asymmetrical SC with a high energy density (23.5 Wh kg^{-1}, 0.7 kW kg^{-1}) and a power density of 0.7 kW kg^{-1}. To further enhance the specific capacitance value, it is clear that morphology, particle size, surface area, and pore properties should be controlled and by forming composite materials, the conductivity can be improved. Composites not only embody the advantages of all the constituents but also overcome the drawbacks of the individual components.

In this work, electrochemically synthesized POAP/ZIF-67 electrode at room temperature is presented as an efficient potential candidate for supercapacitor application. Our goals in this paper involved increasing the capacitance of the POAP electrode by using ionic liquid-assisted ZIF-67 to form a composite electrode, and moreover, enhance the cycle ability of the electrode. The capacitive behavior of the composite was tested by cyclic voltammetry, galvanostatic charge discharge, and impedance spectroscopy techniques.

2. Experimental

2.1. Reagent and materials

All the chemical reagents used were from their analytical grades. Inorganic salts such as $LiClO_4$ with >99% purity percentage were all purchased from the Merck Company. Double-distilled water was used throughout the experiments.

2.2. Characterization

The three-electrode system included carbon paste (C) as a working electrode, Ag/AgCl (Argental, 3 M KCl) as reference electrode, and a Pt electrode as a counter electrode. Electrochemical modes including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry were performed with a potentiostat/galvanostat (Ivium V21508, Vertex). All the experiments were conducted at 25 ± 2 °C. The transmission electron microscope (TEM) images of the samples were recorded with a Philips EM 208 microscope at 100 kV. Field-emission scanning electron microscopy (FESEM) (Tescan Mira 2) was applied to gain the data morphology of the samples. In addition to the above performance, and before dealing with FESEM measurements, the sample surface was covered with a thin gold film to prevent charge buildup. Powder X-ray diffraction patterns were documented at 298 K on a PANalytical (X'Pert Pro MPD) system using a Cu anode in the range of $2\theta = 20–80°$. To estimate the electrical capacity of the synthesized composite, the electrical charge/discharge method was evaluated using techniques such as chronopotentiometry at different electrical currents.

2.3. Synthesis of ZIF-67

ZIF-67 nanocrystals were synthesized via a hydrothermal previously reported process [26]. Briefly, 0.9 g of cobalt nitrate hexahydrate was dissolved in 6 mL of deionized (DI) water; then 11 g of 2-methylimidazole (HMIM) was dissolved in 40 mL of DI water. These two solutions were mixed ($Co_2 + HMIM{:}H_2O = 1{:}58{:}1100$) and stirred for 6 h at room temperature. Then, the resulting purple precipitates were collected by centrifugation; these precipitates were subsequently washed with water and ethanol thrice, and finally dried under vacuum at 80 °C for 24 h.

2.4. Preparation of POAP/ZIF-67

POAP/ZIF-67 composites were synthesized via electropolymerization in a solution consisting of 0.01 M monomer, 0.5 M $HClO_4$, 0.1 M $LiCO_4$, 5.0×10^{-3} M sodium dodecyl sulfate (SDS), and 3% of ionic liquid (1-methyl-3-butylimidazolium bromide) and ZIF-67 on the surface of the modified working electrode. Electropolymerization was conducted in 40 consecutive cycles at a sweep rate of 50 mV s^{-1} in a potentials range of −0.2 to 0.9 V [28–34].

3. Result and discussion

3.1. Surface analysis

The X-ray diffraction (XRD) results of ZIF-67 and POAP/ZIF-67 are shown in Fig. 1. It can be seen that fabricated material here match the corresponding simulated patterns, demonstrating that the products are pure-phase ZIF crystals. The X-ray diffraction patterns show sharp peaks for ZIF-67 nanoparticles, depicting their crystalline nature. An enlarged FE-SEM image (Fig. 2) clearly shows that the synthesized ZIF-67 and POAP/ZIF-67 nanostructure consists of interconnected nanoparticles.