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Polyaniline-Carbon Nanotubes@Zeolite Imidazolate Framework67-Carbon Cloth Hierarchical Nanostructures for Supercapacitor Electrode

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ABSTRACT

Polyaniline (PANI)-carbon nanotubes (CNT)@zeolite imidazolate framework-67 (ZIF-67) –carbon cloth (CC) (PANI-CNT@ZIF-67-CC) was constructed as supercapacitor electrode. Herein, the PANI-CNT@ZIF-67 was used as active materials and the flexible CC was employed as flexible collector electrode. The obtained PANI-CNT@ZIF-67-CC supercapacitor electrode was carefully characterized with scanning electron microscopy, N_2 adsorption-desorption isotherms, X-ray powder diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and electrochemical techniques. It was found that porous ZIF-67 was enclosed by a large number of CNT and partial CNT went through the ZIF-67, which improved the electroconductivity of the nanocomposites greatly. The CNT@ZIF-67 nanocomposites was covered by lots of PANI. Originating from the synergistic effect of PANI (including excellent electrical activity, well pseudo capacitance and good chemical doping/undoping) and CNT@ZIF-67-CC (including large specific surface area, hierarchical porous nanostructures and good electroconductivity), the obtained PANI-CNT@ZIF-67-CC supercapacitor electrode showed good performances. Under the sweep rate of 10 mV s^{-1}, the PANI-CNTs@ZIF-67-CC supercapacitor electrode exhibited a specific capacitance of 3511 mF cm^{-2}. At the current density of 0.5 mA cm^{-2}, the specific capacitance maintained 83% after 1000 charging/discharging cycles.

1. Introduction

Driven by the growing demand for the rapid solving of fossil energy and environmental problems, it is very necessary to develop renewable and clean energy resources [1,2]. Supercapacitors have been the focus of intense research interest and are supposed to be a good choice for alternate energy, because they possess the superiority combining large power density of traditional capacitors together with high specific capacity of batteries, exhibiting some potential advantages such as rapid charging and discharging rate, free from contamination, good reliability and good cycle stability [3–7].

Various materials such as conducting polymers (including polyaniline (PANI), polythiophene and polypyrrole), carbon nanomaterials (e.g. graphene, carbon nanotubes (CNT), porous carbon (PC)) and metal oxides (including Co_3O_4, MnO_2, NiO, etc) have been employed as electrode materials for improving the energy density of supercapacitors [8–16]. PANI is thought to be one of the most interesting materials, on account of the low price, convenient synthesis, excellent electrical activity, well pseudo capacitance and good chemical doping/undoping among these electrode materials [17–20]. To avoid some inevitable defects of the pure PANI, PANI were always combined with carbon materials to improve their performances [8], including increasing their specific capacitance, enhancing their thermal stability, increasing their electroconductivity, etc. For example, the specific capacitance of PC/CNTs/PANI nanocomposite could reach 1090 F g^{-1} with 97 Wh kg^{-1} specific energy density [17]. After PANI nanorods were supported on the graphene paper, the materials performed very well because there was no sticky additive hampering conductivity and wasting energy on unnecessary internal resistance [19].

Metal-organic frameworks (MOFs)/zeolite imidazolate frameworks (ZIFs) have attracted extensive attention for their high porosity and high surface area, combined with good thermal stability. However, people seldom had their relation in the conductivity application of MOFs-based materials because most single-phase MOFs were insulators. In order to overcome this difficulty, conductive nanomaterials including hierarchical porous carbons (HPCs) constructed of micropores, mesopores and macropores have been employed to combine MOFs into composites [21–

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28]. The surface area and pore structure have a significant effect on the specific capacitance of the carbon-based supercapacitor. Micropores can significantly enhance the specific surface area of composite materials and increase electrode capacitance. Mesopores provide channel for ion diffusion to improve electrochemical performance, while macropores serve as the ion reservoir and shorten the ion diffusion distance [28]. Among these HPCs, carbon cloth (CC) possesses many advantages including low cost, flexibility, chemical stability, good electrical conductivity, high porosity and light weight. More importantly, the inherent flexibility of CC makes it possible to impact mechanical elasticity, allow roll-to-roll convenient production and allow the foldable and transportable units. Hence, CC has widely used for supercapacitors [29–33]. For example, well-organized MnO_2 nanosheet arrays grown on CC directly were used for large-scale supercapacitor application [29]. In addition, vanadium oxide-PANI nanowire nanocomposites loading on CC by electrodeposition technology was employed for high performance supercapacitor [30].

In this work, PANI was electrodeposited on CNT@ZIF-67/CC as flexible supercapacitor electrode for the first time. The resulted flexible PANI-CNT@ZIF-67-CC supercapacitor electrode combined all the advantages of PANI, porous ZIF-67 and highly electroconductive CNTs together showing high specific capacitance. The obtained performances of the PANI-CNT@ZIF-67-CC supercapacitor electrode confirmed that the proposed supercapacitor electrode have promising future in energy storage utilizations.

2. Experimental

2.1. Chemicals and reagents

The CNTs (the diameter: 20–40 nm and the length was less 5 μm) was obtained from Shenzhen Nanotechn Port Co., LTD (Shenzhen, China). $Co(NO_3)_2$&903;$6H_2O$ was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). N-methyl pyrrolidone, 2-methyl imidazole (Hmim), polyvinylpyrrolidone (PVP) and aniline were purchased from Aladdin Chemistry Co., Ltd. Aniline was distilled under reduced pressure. Acetylene black and polyvinylidene fluoride were supplied by Kaisai Chemical Factory. Methanol and potassium chloride were provided by Tianjin Chemical Reagent factory (Tianjin, China). Other reagents of analytical grade were obtained from Shanghai Reagent Co., Ltd (Shanghai, China). Ultra-pure water (18.2 MΩ cm) was used throughout the whole experiment.

2.2. Apparatus

Scanning electron microscopy was performed with a HITACHI S-3400N at an accelerating voltage of 15 kV. Electrochemical experiments were carried out by CHI 660C (Shanghai, China) in 3 M KCl solution using three-electrode systems where the PANI-CNT@ZIF-67-CC, PANI@ZIF-67-CC and PANI-CC were used as the working electrodes, saturated calomel electrode (SCE) was the reference electrode and Pt plate was used as the auxiliary electrode. Galvanostatic discharge/charge tests were tested at different current density at the potential window between 0 V and 1.0 V.

2.3. Preparation of CNT@ZIF-67 and ZIF-67

ZIF-67 was synthesized using the following procedures. 0.9 g $Co(NO_3)_2$&903;$6H_2O$ and 11 g Hmim were firstly dissolved into 6 mL and 40 mL of H_2O, respectively. Then, they were mixed together with water (volume ratio of $Co(NO_3)_2$&903;$6H_2O$: Hmim: H_2O = 1:58:1100) and reacted for 6 h in air. After that, the precipitate was separated with centrifuging, washed for three times with water and methanol respectively, finally put into the oven to dry at 80 °C for 24 h.

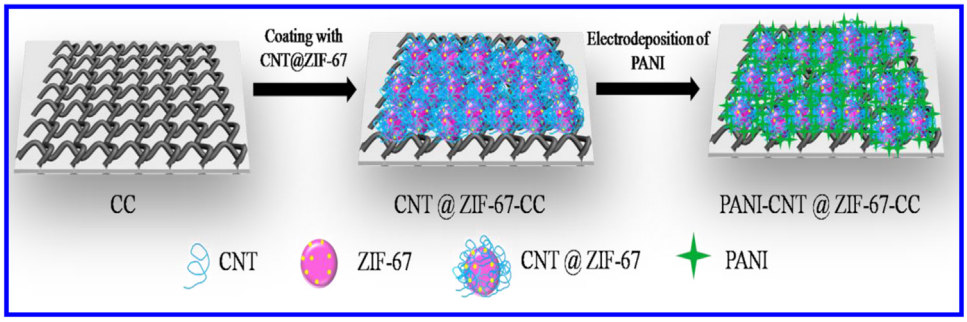
For the preparation of CNT@ZIF-67, 1.1 g Hmim was dissolved into 4 mL H_2O and 0.09 g $Co(NO_3)_2$&903;$6H_2O$ was dissolved in 0.6 mL H_2O to form cobalt nitrate solution. 120 mg PVP was dispersed in 60 mL methanol, then 0.04 g CNTs were added, the mixture were immersed in an ultrasound bath for 1 h. The excess PVP were separated out by centrifugation, and the resulted precipitate was dispersed into 12 mL water. Then, Hmim solution was added to the CNT dispersion liquid firstly, and the solution of cobalt nitrate was slowly added to the above solution and stirred in air for 6 h, After that the product was centrifugated and isolated, washed for three or four times using water and methanol, respectively, finally put into the oven and dried under 80 °C for 24 h.

2.4. Preparation of CNT@ZIF-67-CC and ZIF-67-CC

The CC was cut into pieces with an area of $1 \times 2\ cm^2$, immersed in an ultrasound bath for 30 min with acetone, ethanol, water, respectively, then dried at 60 °C. After that, 70% of the mass fraction of the active materials (CNT@ZIF-67 or ZIF-67), 20% of acetylene black as a conductive agent and a binder of 10% PVDF in NMP as the slurry were continuously stirred to form the gummy material and then coated on the CC evenly, drying under 120 °C for 12 h, to form target electrode (CNT@ZIF-67-CC or ZIF-67-CC). The preparation process of CNT@ZIF-67-CC was illustrated in Scheme 1.

2.5. Preparation of PANI-CNT@ZIF-67-CC and PANI- ZIF-67-CC

PANI was electrochemically polymerized on the surface of the resulted CNT@ZIF-67-CC and ZIF-67-CC electrode. Mixture of 0.1 M aniline and 3 M KCl was used as the electrolyte. Under the optimal conditions, about 3 mg PANI was electrodeposited on the CNT@ZIF-67-CC surface. The experiment was performed during −0.2 ∼ 1 V (*vs.* SCE) with the sweep rate of 10 mV s^{-1}, and the number of



Scheme 1. Schematic illustration of the two-step fabrication process of PANI-CNT@ZIF-67-CC supercapacitor electrode.