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Research paper

Hierarchical mesoporous Co_3O_4/C@MoS_2 core–shell structured materials for electrochemical energy storage with high supercapacitive performance

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ABSTRACT

Hierarchical mesoporous Co_3O_4/C@MoS_2 core-shell structured materials are synthesized via a two-step calcination and a solvothermal method using cobalt metal-organic frameworks (cobalt-MOFs, ZIF-67) and $(NH_4)_2MoS_4$ as the precursors of Co_3O_4/C and MoS_2, respectively, which is a new class of core-shell materials as supercapacitor electrode materials. The obtained Co_3O_4/C@MoS_2 exhibits high specific capacitance (1076 F g^{-1} at 1 A g^{-1}), rate capability (76.9% capacitance retention at 10 A g^{-1}) and cyclic stability (64.5% capacitance retention after 5000 cycles at 10 A g^{-1}). Moreover, the content of MoS_2 greatly influences the electrochemical performances of the obtained core-shell materials. The results demonstrate that the as-synthesized ZIF-67 can be used as a promising candidate for designing Co_3O_4 based core-shell materials used in supercapacitors.

1. Introduction

Nowadays, energy problems have become the greatest focus attracting the world's attention and triggering great efforts for energy storage and conversion [1,2]. Owing to excellent cyclic stability, high energy density, superior power density and environmental friendliness, electrochemical capacitors (ECs) are considered as an ideal energy storage system [3,4]. ECs can be divided into electric double-layer capacitors and pseudocapacitors according to the mechanism of charge storage [5], and pseudocapacitors have attracted increasing attention due to their fast redox kinetics and large capacitance [6]. Recently, reduced graphene oxide (rGO)/transition metal oxides have been used for pseudocapacitors (e.g. rGO/Fe_2O_3 [7], rGO/CuO [8]). Among numerous transition metal oxide candidates, Co_3O_4 is known as an ideal electrode material for pseudocapacitors because of its ultrahigh theoretical capacitance (3560 F g^{-1}) and superior electrochemical performances [9]. However, in many cases, the observed specific capacitance (C_{sp}) of Co_3O_4 is far lower than the theoretical value on account of their large volume changes, low electronic conductivities and polarization during cycling [10]. One approach to circumvent this problem is to find effective supports such as various nanostructured carbon materials to uniformly disperse Co_3O_4 nanoparticles.

Metal-organic frameworks (MOFs) are a kind of organic-inorganic hybrid materials possessing large specific surface area and high porosity [11,12], and many research efforts have been focused on MOFs [13,14], MOFs-derived carbon [15–17], MOFs-derived sulfide [18] and their complexes [19–22] for electrochemical devices. Recently, cobalt-MOFs have been proved to be ideal sacrificial templates to fabricate porous carbon nanostructures or metal oxides via thermolysis in controlled atmospheres. The Co_3O_4 synthesized by this method exhibits special three-dimensional (3D) and open-framework structures, facilitating the transportation of electrolytes to attain enhanced capacitance. In addition, the Co_3O_4 derived from cobalt-MOFs owns favorable rate capability due to the maintained structure in the repeated charge-discharge process. As far as we are aware, the design and synthesis of Co_3O_4 based core-shell materials such as Co_3O_4@MnO_2, Co_3O_4@$Ni(OH)_2$ and Co_3O_4@$NiMoO_4$ have drawn great attention due to their excellent electrochemical performances when used as supercapacitor electrode materials [23–25].

MoS_2, a graphene-like 2D material, has shown unique structural and electronic properties [26]. MoS_2 is composed of covalently bonded S-Mo-S sheets combined by van der Waals force [27], and the structure of MoS_2 makes it a promising candidate as electrode material [28]. More importantly, MoS_2 coated 3D graphene networks or dispersed on amorphous carbon can facilitate the transportation of electrons [29,30]. Therefore, MoS_2 is considered to be a potential supercapacitor electrode material. Liang et al. [31]. have fabricated a MoS_2-Co_3O_4 composite via anchoring Co_3O_4 particles onto the surface of MoS_2 nanosheets, which

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shows significant increase in the capacitive performance compared with Co_3O_4 alone. Herein, we synthesize a Co_3O_4/C@MoS_2 core-shell structured material via a two-step calcination and a solvothermal method by using ZIF-67 and $(NH_4)_2MoS_4$ as the precursors of Co_3O_4/C and MoS_2, respectively. The obtained core-shell material exhibits high structural stability and fast transmission capacity for electrolyte ions and electrons.

2. Experimental

2.1. Reagents and apparatus

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), 2-methylimidazole and dimethylformamide (DMF) were purchased from Aladdin Chemicals Reagent Co., Ltd. (Shanghai, China). Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$) was received from J & K Chemical. All other reagents not mentioned were of analytical grade and used as received. All aqueous solutions were freshly prepared with ultrapure water (Milli-Q, Millipore).

FT-IR spectra were recorded on a FTIR-8400S spectrometer (Shimadzu, Japan). X-ray diffraction (XRD) analysis was carried out on a Rigaku D/max 2500PC diffractometer. The morphologies of Co_3O_4/C and Co_3O_4/C@MoS_2 were characterized by transmission electron microscopy (TEM) using a JEM 2100 transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA). Brunauer-Emmett-Teller (BET) specific surface areas and pore size distribution were determined using an ASAP 2010 specific surface area and pore size analyzer (Micromeritics, USA). Thermogravimetry (TG) and differential thermogravimetric (DTG) analysis were carried out on a TG209F3 thermal analyzer (Netzsch, Germany). The electrochemical properties of the materials were evaluated using a CHI 660D electrochemical workstation (China).

2.2. Preparation of ZIF-67 and Co_3O_4/C

ZIF-67 was prepared according to the procedures previously reported [32]. Typically, 0.9 g $Co(NO_3)_2{\cdot}6H_2O$ and 11 g 2-methylimidazole were dissolved in 6 mL and 40 mL of ultrapure water, respectively, and then the two solutions were mixed and magnetically stirred for 6 h at room temperature. The precipitated purple products were centrifuged and collected, washed with ultrapure water/ethanol successively and repeatedly, and finally dried at 80 °C for 24 h.

Co_3O_4/C was prepared via a two-step calcination method. The synthesized ZIF-67 was firstly calcined at 700 °C for 5 h in N_2 atmosphere for the preparation of Co/C, and then the obtained Co/C was calcined at 270 °C for 15 h in air atmosphere for the preparation of Co_3O_4/C.

2.3. Preparation of Co_3O_4/C@MoS_2

Different amounts of $(NH_4)_2MoS_4$ (10, 20, and 30 mg) were dissolved respectively in 50 mL of DMF to form homogeneous solutions, and then three samples of 50 mg Co_3O_4/C were dispersed to the above solutions under sonification. Next, the resultant mixture was solvothermally treated in a stainless steel autoclave at 200 °C for 10 h. After that, the mixture was centrifuged at 4000 rpm. The obtained products denoted as Co_3O_4/C@MoS_2-10, Co_3O_4/C@MoS_2-20 and Co_3O_4/C@MoS_2-30 were thoroughly washed with ultrapure water/ethanol several times and then dried at 60 °C. For a control experiment, MoS_2 was prepared from 20 mg $(NH_4)_2MoS_4$ according to the similar procedures for Co_3O_4/C@MoS_2 except the addition of Co_3O_4/C.

2.4. Electrochemical measurements

All electrochemical experiments were carried out at room temperature in a conventional three-electrode system consisting of a glassy carbon electrode (GCE, 3 mm in diameter) modified with the active materials as the working electrode, a platinum foil as the counter electrode and a KCl saturated Ag/AgCl electrode as the reference electrode. 2 M KOH aqueous solution was used as the electrolyte. The working electrode was fabricated as follows. First, 4 mg of the active materials (MoS_2, Co_3O_4/C, Co_3O_4/C@MoS_2-10, Co_3O_4/C@MoS_2-20 or Co_3O_4/C@MoS_2-30) was dispersed in 2 mL of ultrapure water. Next, 5 μL of the dispersion was dropped onto the surface of GCE and allowed to dry in ambient air (mass loading: 142 μg cm^{-2}). Cyclic voltammograms (CVs) of these electrodes were collected over the potential range from 0 to 0.7 V, and the galvanostatic charge/discharge (GCD) measurements were carried out over the potential range from 0 to 0.5 V. Cycling stability test was performed by repeating the GCD measurements at a current density of 10 A g^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out at −0.1 V in the frequency range from 10^6 to 0.01 Hz with an alternating sinusoidal signal of 5 mV. The equivalent circuit of the Nyquist plots was simulated by the ZSimpWin software.

$$C_{sp} = \frac{I \times t}{m \times V}$$

$$C_{sp} = \frac{\int IdV}{mvV}$$

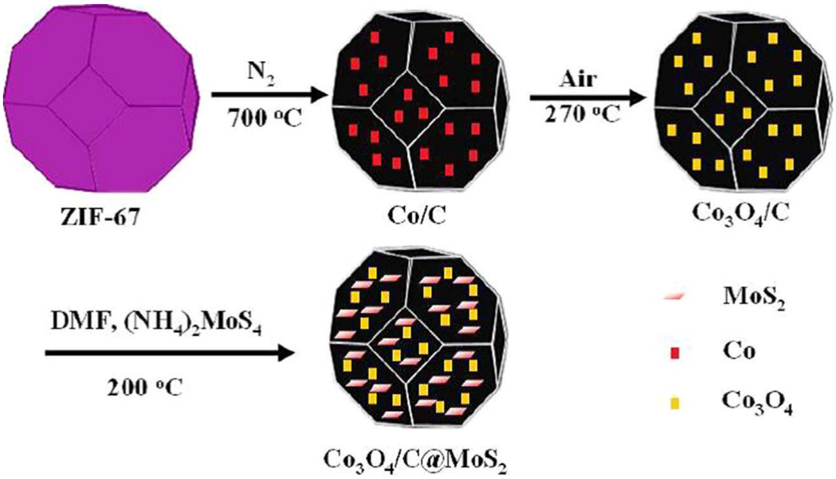

Fig. 1. Schematic illustration showing the preparation of Co_3O_4/C@MoS_2.