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Design of rod-like NiCo₂O₄ with nanostructure derived from ZIF-67 as excellent material for supercapacitors

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MOF (metal-organic framework) is an ideal precursor for the synthesis of metal oxides owing to the high porosity and provision of redox sites. This study focused on the formation of NiCo₂O₄ rod-like nanostructure from Co-MOF by a simple hydrothermal method to overcome disadvantages of MOF such as low electrical conductivity and stability. Noticeably, NiCo₂O₄ with unique nanostructure could be obtained when the template removed after calcination. It was observed by SEM and TEM, the morphology of NiCo₂O₄ nanorods with a diameter was about 100 nm. Moreover, the morphology of Co₃O₄, which converted from MOF after calcination at 350 °C was similar to hexahedron. The synthesized rod-like NiCo₂O₄ electrode delivered specific capacitance of 1376 F/g at a current density of 1 A/g, indicating the excellent charge transfer ability in 6 M KOH solution. Therefore, this study presents a hydrothermal method to prepare the electrode materials based on MOF for supercapacitors effectively.

Keywords: Hydrothermal method; Co-MOF; NiCo₂O₄; Rod-like; Supercapacitor

1. INTRODUCTION

The increasing energy consumption and environmental problems provide the motivation for the study on storage device, such as batteries and supercapacitors with novel electrode materials[1]. Supercapacitors are divided into pseudocapacitors, electrochemical double-layer capacitors (EDLCs)

and hybrid supercapacitors based on energy storage mechanism, which have replaced existing rechargeable batteries in some fields due to their high power density, fast charge-discharge rate and excellent stability[2-4]. Metallic organic framework (MOF) is a kind of coordination supramolecular material, which is composed of coordination metal ions, nodes and organic ligands[5]. In order to meet the high electrochemical performance, MOFs were used as active materials for chemical capacitor, which can provide sufficient redox sites and accelerate ion diffusion rate[6]. However, the electrochemical performance of untreated single MOF is not desirable, because its inherent low conductivity and poor chemical stability lead to long charge and discharge time[7]. Using MOF as a template to synthesize new products can not only play the advantages of MOF, but also provide more active sites to enhance electrical conductivity[8].

MOF is an ideal precursor for the synthesis of metal oxides, because of its layered structure enables it to obtain more complete metal oxides with greater surface area and better electron conductivity[9, 10]. Zeolite imidazole framework (ZIF) is a kind of cluster or organic ligand composed of metal ions, wherein ZIF-67 is composed of Co^{2+} and organic compounds[11]. Metal oxides as supercapacitor materials have been attracted attention because of their multiple oxidation, which among, NiCo₂O₄ is rich in functional groups and has excellent electronic conductivity[12]. NiCo₂O₄ is at least two orders of magnitude higher than the oxides of nickel and cobalt[13, 14]. In addition, nanoplates NiCo₂O₄ has a large surface area, that can greatly improve the storage efficiency of metal ions[13]. Li et al. used hollow and porous three-dimensional nano-structured NiCo₂O₄ (derived from ZIF-67) with cage-like morphology as an electrode modifier to detect Hg²⁺ in the water quality detection[15]. Chen et al. fixed NiCo₂O₄ nanorods on the surface of Co₃O₄ to form porous Co₃O₄-NiCo₂O₄ nanorods, and the results indicated that the specific capacitance was 1041.2 F/g at the current density of 2 A/g[16]. Sennu et al. synthesized 3D NiCo₂O₄@Co₃O₄ composite material by two-step hydrothermal methods, and made asymmetric supercapacitor with double-layer formed activated carbon, the results showed that the battery maintained about 97% initial capacitance after 7000 cycles[17].

This article reports a simple hydrothermal method to synthesis different morphologies via changing the conditions of precursors, leading to various morphologies such as rod-like and sheet-like. Moreover, the prepared materials were applied as electrodes for electrochemical testing, indicating the excellent electrochemical performance. The study not only demonstrates a simple approach to obtain target products, but also proves the nanorod structure as electrodes would be beneficial for further development in the field of electrode materials.

2. EXPERIMENTAL

2.1. Chemicals

Ethanol (C₂H₅OH), potassium hydroxide (KOH), urea (CO(NH₂)₂) (\geq 99%) and isopropanol were obtained from Sinopharm Chemical Reagent Co., Ltd. 2-methylimidazole(C₄H₆N₂), Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (\geq 98%), Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) (\geq 99%), Polytetrafluoroethylene (5 µm), Acetylene black were purchased from Aladdin. All chemical reagents

were analytically pure, without further purification before using, and the experimental water was deionized water.

2.2. Materials preparation

2.2.1. Synthesis of ZIF-67 and Co₃O₄

In a typical procedure, 3.3 g 2-methylimidazole, 2.9 g $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 20 mL methanol respectively by stirring respectively and mixed together. The mixed solution was transferred to the 50 mL stainless steel autoclave for 12 h at the temperature of 100 °C. By centrifuging, the precipitate (ZIF-67) was collected and then dried at 60 °C for overnight. Under the air environment, the obtained above was calcined at 550 °C for 120 min with a heating rate of 1 °C /min, the final product was Co₃O₄.

2.2.2. Synthesis of NiCo₂O₄

In order to synthesize NiCo₂O₄, 0.2 g ZIF-67 as-prepared, 0.2908 g Ni(NO₃)₂·6H₂O, 0.5821 g Co(NO₃)₂·6H₂O and 0.3003 g urea were dissolved in 35 mL water. The mixed solution was transferred to the 50 mL stainless steel autoclave for 12 h at the temperature of 120 °C. The mixtures were washed three times with distilled water and ethanol, and dried at 60 °C for overnight. After carbonizing in the tube furnace at 350 °C for 2 h in air, NiCo₂O₄-2 with rod-like nanostructure was synthesized. The NiCo₂O₄-1 could be prepared by the hydrothermal method under the same step without adding Co(NO₃)₂·6H₂O. Similarly, urchin-like NiCo₂O₄-3 was synthesized without ZIF-67 addition.

Fig. 1 depicts the synthesis process of NiCo₂O₄ and the effect of different precursors on structures of NiCo₂O₄. Cobalt nitrate hexahydrate, 2-methyl imidazole and urea solutions were mixed to obtain ZIF-67. The as-prepared ZIF-67 by simple hydrothermal method was added to cobalt nitrate solution or mixed with cobalt nitrate, nickel nitrate solution to obtain different products. In the air atmosphere, the products prepared above could further transform into nanosheets and nanorods by annealing. Similarly, the precursor slowly to generated urchin-like structure without ZIF-67 in the hydrothermal process.

2.3. Characterizations

Scanning electron microscope (SEM, Zeiss Sigma 300) and Transmission Electron Microscope (TEM, JEOL JEM 2100) were used to analyze the samples. The substance contained in the composites were determined by X-ray diffraction (XRD, SmartLab 9kw, the scanning range of 2θ is 5-90°). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was applied to determine the chemical compositions of samples. Electrochemical tests including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) were carried out in electrochemical workstation (CHI760E).

2.4. Electrodes preparation

The electrode system was a three-electrode system, using nickel foam as the working electrodes, platinum sheet as a counter electrodes, saturated calomel as a reference electrodes, respectively. The asprepared material was mixed with carbon black and polyethylene in a ratio of 8:1:1, and 2 mL isopropyl alcohol was added to form the mixed solution, which was stirred thoroughly by ultrasonic shock. The obtained mixture was sprayed with 15 μ L onto the nickel foam (1 cm×1 cm) and dried at 60 °C for 12 h. The mass of the active material was about 0.3 mg.

Electrochemical experiments were conducted in 6 M KOH at room temperature. The scan rate of the cyclic voltammetry was tested in a range from 5 to 80 mV/s. The measuring voltage range of charge and discharge was performed in a range from 0.1 to 0.35 V and the current of 1.0 A/g, 1.5 A/g, 2.0 A/g, 2.5 A/g and 3.0 A/g were applied. The specific capacitance (*Csp*) of electrodes are calculated by GCD measurements using the following equation:

$$Cs = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where Cs (F/g) is the specific capacitance, I (A) is the current, Δt is the discharge time, m (g) is the quality of electrode material, and ΔV (V) is the potential windows. The electrochemical impedance spectroscopy was measured under the range from 100 kHz to 0.01 Hz.



Figure 1. Schematic diagram of NiCo₂O₄ formation process.

3. RESULTS AND DISCUSSION

3.1. Structure characterization

3.1.1. XRD and XPS patterns

The crystal structure information of NiCo₂O₄-1, NiCo₂O₄-2, NiCo₂O₄-3, ZIF-67 and Co₃O₄ was confirmed by XRD. The XRD patterns of NiCo₂O₄-1, NiCo₂O₄-2 and NiCo₂O₄-3 are shown in Fig. 2a,

the vital diffraction peaks appear at 19.0° , 31.2° , 36.7° , 44.6° , 59.1° and 65.0° correspond to the (111), (220), (311), (400), (511), (440) planes of the NiCo₂O₄ phase (JCPDS 73-1702).



Figure 2. XRD patterns of (a) NiCo₂O₄-1, NiCo₂O₄-2, NiCo₂O₄-3, (b) ZIF-67, Co₃O₄.



Figure 3. (a) The full survey XPS spectrum of NiCo₂O₄-2, (b-d) XPS spectra for Co, Ni and O of NiCo₂O₄-2.

The reflection peaks of Co_3O_4 derived from ZIF-67 at 19.0°, 31.3°, 36.8°, 59.4° and 65.2° are shown in Fig. 2b, which can be well consistent with (111), (220), (311), (511) and (440) planes of Co_3O_4 (JCPDS 73-1701) respectively. All the results indicate that the products were prepared successfully[18].

The chemical oxidation states of Ni, Co, C and O could be explored by the XPS spectrum. As shown in Fig. 3a, the full survey XPS spectrum of NiCo₂O₄, proving the existence of Co, Ni and O to fit the Co 2p, Ni 2p, O 1s. It can be seen from Fig. 3b that the location of 779.1 and 793.9 eV were assigned to Co²⁺, while the other peaks at 781.0 and 795.3 eV could be attributed to Co³⁺[5]. The spectrum of Ni 2p in Fig. 3c shows two peaks at 853.3 and 871.2 eV assigned to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ respectively. Another two peaks fitted at 854.8 and 872.5 eV corresponded to Ni³⁺[19]. The high-resolution XPS spectrum for C is displayed in Fig. 3d, the metal-oxygen bonds and carboxylate groups can be found at 528.6, 529.1 and 530.5 eV[20, 21]. The main peak located at 529.1 eV is typical of metal-oxygen bond[22]. The other energy peaks were found at 528.6 and 530.5 eV often ascribed to defect oxygen or hydroxyl groups[23].

3.1.2. SEM, EDS and TEM Results

Fig. 4a and Fig. 4b demonstrate the SEM images of Co₃O₄ and ZIF-67 (converted into Co₃O₄ after calcination at 350 °C). From Fig. 4b, it can be observed that the topography of ZIF-67 was rhombic polyhedron, which was broken into the hollow structure after calcination. Fig. 4c exhibits the SEM image of Co₃O₄ nanocubes, which lose its original structure and converted to nanosheets or nanorods. Obviously, the single nanorod has an average width of 100 nm, and the bottom was hexagonal. The rough surface allows electrolytes to enter the pores and pass out, which can generate large capacitance. As shown in Fig. 4e, synthesized NiCo₂O₄-3 in the shape of a urchin without MOF, and such structure can enlarge the surface area to make more active sites to participate the redox reaction[24]. The polyhedron ZIF-67 changed into flakes and sticks may be due to the decomposition of ZIF-67 blocks during the calcining process[25]. At the same time, after adding Ni and Co, the stick with hexahedral was formed on the basis of the polyhedron. The rod-like structure expanded the contact area of the active substance and the electrolyte[26]. As displayed in Fig. 4f, the EDS full spectrum confirms the elements of Co, Ni, C and O throughout the whole material, while the element of C was from ZIF-67 derived carbon skeleton[27], and the corresponding mass ratio are shown in Table 1. The rod-like structure of NiCo₂O₄-2 was further detected by TEM. Fig. 5 show well-resolved lattice fringes, which located at 0.47 nm, 0.20 nm, 0.24 nm and 0.16nm correspond to the NiCo₂O₄ (111), (400), (311) and (511), respectively[28].



Figure 4. The SEM imagines of (a) ZIF-67, (b) Co₃O₄, (c) NiCo₂O₄-1, (d) NiCo₂O₄-2, (e) NiCo₂O₄-3, (f) the EDS mapping images of NiCo₂O₄-2, (g) the EDS mapping of Co, Ni, O and C elements in NiCo₂O₄-2.



Figure 5. TEM (a-b) and HRTEM (c-d) images of NiCo₂O₄-2.

Element	Weight percent/%	Atomic percent/%	
С	37.15	59.80	
Co	29.85	9.75	
Ο	22.23	26.86	
Ni	10.77	3.55	

Table 1. The elements distribution in NiCo₂O₄-2

3.2. Electrochemical performance

Table 2. Comparison of the electrochemical performance of NiCo₂O₄ derived from ZIF-67 in this work with previously reported studies.

Electrode Material	Test Solution	Specific capacitance/(F/g)	Current density/ (A/g)	Reference
NiCo ₂ O ₄	2 M KOH	902	1	[29]
3D rGN/NiCo ₂ O ₄	1 M KOH	708.36	1	[30]
NiCo ₂ O ₄	3 M KOH	1366	2	[31]

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Ni@NiCo ₂ O ₄	3 M HCl	597	1	[32]
NiCo ₂ O ₄	2 M KOH	1367	1	[33]
NiCo ₂ O ₄	3 M KOH	1650	1	[34]
NiCo ₂ O ₄	6 M KOH	1376	1	This
				WOIK



Figure 6. CV curves of (a) Co₃O₄, NiCo₂O₄-1, NiCo₂O₄-2, NiCo₂O₄-3 at a scan of 5 mV/s, (b) NiCo₂O₄-2 with different scan rates.



Figure 7. Charge and discharge curves of (a) Co₃O₄, (b) NiCo₂O₄-1, (c) NiCo₂O₄-2. (d) NiCo₂O₄-3 in 6 M KOH solution with different current densities.

Fig. 6(a-b) shows the CV curves of several electrodes at the scan rate of 5 mV/s in 6 M KOH solution, respectively. Fig. 6a displays the area under CV curve is the largest for NiCo₂O₄-2 than that for other electrodes at the scan rate of 5 mV/s suggesting a higher specific capacitance of NiCo₂O₄-2. As shown in Fig. 6b, when the scan rate was increased from 5 to 80 mV/s, the area of anode peak current and cathode peak current increased, owing to the active materials in the electrode could react with OH⁻ quickly[35]. The main peaks accompanied by a small hump were observed mainly due to a reversible Faradic reactions of M^{2+} or M^{3+} (M=Co or Ni) [36]. The appearance of oxidation and deoxidation peaks in the CV curve reveals the capacitance of the electrode material, and the reactions are as follows[37-39].

$$Co_3O_4 + OH^- \leftrightarrow CoOOH + e^-$$
(2)

$$NiCo_2O_4 + OH^- + H_2O \leftrightarrow NiOOH + CoOOH + e^-$$
(3)
$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^-$$
(4)

$$OOH + OH \leftrightarrow CoO_2 + H_2O + e \tag{4}$$

The electrochemical properties of Co_3O_4 and $NiCo_2O_4$ were further investigated by galvanostatic charge-discharge texts at a different current density from 1 to 3 A/g. The GCD curves were shown in Fig. 7(a-c) ranging from 0.1 to 0.35 V. It can be seen from Fig. 7, the appearance of nonlinear shape with obvious discharge platforms represent typical pseudocapacitance characteristic [40]. Obviously, the current density gradually increased while the charge-discharge time decreased at the same time, leading to the active materials in the electrodes could not complete the Faraday electrochemical reaction at high current density[41]. Fig. 6c NiCo₂O₄-2 shows the longest charge and discharge time among the three electrodes, indicating NiCo₂O₄-2 had better capacitance performance as a whole.

The results of special capacitance and electrochemical impedance spectroscopy are shown in Fig. 8. The specific capacitance of Co_3O_4 , NiCo₂O₄-1, NiCo₂O₄-2 and NiCo₂O₄-3 acquired from the GCD curves are 540, 872, 1376 and 432 F/g at a current density of 1 A/g. The Co particles in ZIF-67 interact with adjacent carbon or oxygen atoms to form tight bonds, thereby altering the electronic configuration of carbon frameworks and generating additional active sites[42]. The capacity obtained for NiCo₂O₄-2 from ZIF-67 showed its superior capacity, which was higher than the other working electrodes in this work.



Figure 8. The special capacitance (a) and the electrochemical impedance spectroscopy of (b) NiCo₂O₄, Co₃O₄.

As shown in Fig. 8b, there was an incomplete semicircle in the high-frequency region and a line in the low-frequency region. In theory, the slopes of the lines represent the resistance of ion diffusion (*Rs*), while the semicircle represents the resistance of charge transfer (*Rct*) [43]. However, it is not obvious to see a completed semicircle in the high-frequency region, which may be mainly determined by the pseudo capacitance of the hydroxide[2]. The internal resistances of NiCo₂O₄-2, NiCo₂O₄-1, Co₃O₄ and NiCo₂O₄-3 are 0.624 Ω , 0.689 Ω , 0.715 Ω and 1.028 Ω . The *Rct* of NiCo₂O₄-2 were estimated to be about 2.739 Ω , which were lower than that of NiCo₂O₄-1 (2.844 Ω), Co₃O₄ (3.265 Ω) and NiCo₂O₄-2 2 possesses steeper inclined line than that of other electrochemical performance. Moreover, the NiCo₂O₄-2 possesses steeper inclined line than that of other electrodes, indicating a stronger diffusion rate of ions. The reasons for these can be explained as follows: the excellent specific capacitance of NiCo₂O₄-2 henefit by the synergistic effect between bimetallic nanoparticles; sheet-like NiCo₂O₄-1 can entanglement more OH⁻ and expose more active sites thus shows a high specific capacitance; NiCo₂O₄-2 nanorods serve as highly conductive cores can storage more active sites, because interleaved nanoparticles in its internal structure strengthen contact between the electrodes and the electrolytes.

4. CONCLUSION

In summary, NiCo₂O₄ with various nanostructures were successfully synthesized through the effective hydrothermal method. The NiCo₂O₄-2 with rod-like nanostructure derived from ZIF-67 possessed a high specific capacitance of 1376 F/g at a current density of 1 A/g. Furthermore, NiCo₂O₄-3 was synthesized by changing the conditions of the precursor. The obtained NiCo₂O₄ was applied in the electrochemical oxidation, and the results demonstrated the NiCo₂O₄ nanorods possess better electrochemical performance with the features of high specific capacity in 6 M KOH solution than the other electrodes. The rod-like structure expanded the contact area of active substance and the electrolyte, providing a faster rate of electron transfer. Therefore, all these results fully prove the potential of NiCo₂O₄ electrode material based on MOF in the energy storage application.

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