Materials Research Express

PAPER

Fabrication of NiFe$_2$O$_4$@CoFe$_2$O$_4$ core-shell nanofibers for high-performance supercapacitors

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Keywords: co-electrospinning, NiFe$_2$O$_4$@CoFe$_2$O$_4$, supercapacitors

Abstract

NiFe$_2$O$_4$@CoFe$_2$O$_4$ core–shell nanofibers were prepared by the co-electrospinning method. The prepared core–shell NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers electrode has the specific capacitance of 480 F g$^{-1}$ at a current density of 1 Ag$^{-1}$. After being cycled 2000 times at a current density of 5 Ag$^{-1}$, the capacity of NiFe$_2$O$_4$@CoFe$_2$O$_4$ core–shell nanofibers remained 87%. The electrochemical performance of the supercapacitor is improved by the synergistic action of the multi-metal and indicates that core/shell NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers are promising materials.

1. Introduction

As an important energy storage device, supercapacitor integrates the advantages of high power density, high cycle stability, wide voltage working window, fast charge and discharge. It is used in military fields such as electromagnetic ejection and electromagnetic guns, as well as energy vehicles and solar energy. The conversion of low-grade energy into high-grade energy and other civilian fields such as fields such as defense, aerospace has broad application prospects [1].

Transition metal oxides are typical pseudocapacitor electrode materials [2]. At present, there are mainly metal oxides such as cobalt oxides [3], manganese oxides [4], nickel oxides [5], iron oxides [6], etc Multi-metal oxides have also been studied intensively [7]. Electrode materials are the key to the development of high-performance supercapacitors. Spinel transition metal oxide (AB$_2$O$_4$) is an important pseudocapacitor material with two metallic elements [8, 9].

NiFe$_2$O$_4$ nanosheets were successfully synthesized via a facile hydrothermal method. Results showed that the specific capacitance could reach to 240.9 F g$^{-1}$ at the current density of 1 Ag$^{-1}$. The specific capacitance improved to 128% after 2000 cycles [9]. CoFe$_2$O$_4$ thin films are fabricated by aerosol-assisted chemical vapor deposition and show a capacitance of 540 mF cm$^{-2}$. Around 80% of the capacitance is retained after 7000 charge-discharge cycles [10]. CoFe$_2$O$_4$/NiFe$_2$O$_4$ nanocomposites were prepared via a facile hydrothermal method. The electrodes deliver a higher specific capacitance of 269 F g$^{-1}$ at a current density of 1 Ag$^{-1}$ and exhibit capacity retention of 81% after 10000 charge-discharge cycles [11].

One-dimensional nanostructured materials have unique advantages in energy storage. Nanofibers can obtain a high porosity with large surface area, extra surface-active sites, better permeability, faster electron and ion migration rates. all of which can incomparably increase the energy density, power density, and cycling performance for energy storage [12, 13]. MoO$_3$/Pd 1D nanorods nanocomposites have been synthesized by simple hydrothermal method with high specific capacitance of 501 F g$^{-1}$ at a current density of 1 mA g$^{-1}$, and the pure MoO$_3$ with high specific capacitance of 331 F g$^{-1}$ at a current density of 1 mA g$^{-1}$ [14]. The capacitance of MnO@Na$_2$Ti$_6$O$_13$ heterojunction nanowires which are attained by the in situ thermal decomposition method can reach a power intensity of 250 W kg$^{-1}$ at the energy density of 37.83 Wh kg$^{-1}$ [15].

On this basis, we propose to improve the material properties by forming core–shell nanofibers by co-electrospinning which using NiFe$_2$O$_4$ as the core layer and CoFe$_2$O$_4$ as the shell layer.

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2. Experimental

2.1. Materials characterization

The crystal structure was characterized by powder x-ray diffraction (XRD, Bruker, D8-Advance) using Cu-Kα radiation. The morphologies and microstructures were tested using scanning electron microscope (SEM, Japan, JSM-6701F) with 5 kV of the field emission gun. and transmission electron microscopy (TEM, Japan, JMS-2010) equips with selected area electron diffraction (SAED). The electrochemical performance was studied by an electrochemical workstation (China, Wuhan Corrtest CS350).

2.2. Preparation of NiFe₂O₄@CoFe₂O₄ nanofibers

All chemicals are analytical grade and can be used without further purification. In this experiment, 0.58 g Ni(NO₃)₂·6H₂O, 1.6 g Fe(NO₃)₃·9H₂O and 3.5 g PVP were dissolved in 10 ml mixed solution including anhydrous ethanol and DMF (volume ratio is 1:1). After stirring at room temperature for 18 h as the precursor of core NiFe₂O₄. Weigh 0.58 g Co(NO₃)₂·6H₂O, 1.6 g Fe(NO₃)₃·9H₂O and 3.5 g PVP dissolved in 10 ml mixed solution of absolute ethanol and N,N-dimethylformamide (DMF) (volume ratio: 2:3), then continuously stir at room temperature for 18 h, which was the precursor of shell CoFe₂O₄. The two precursors were placed in two 10 ml syringes and placed on two boosters. Adjust the distance between the coaxial metal needle and the collecting plate at 16 cm, the spinning voltage was 16 kV, and the core NiFe₂O₄ precursor fluid booster speed was set to 0.35 ml h⁻¹, the shell CoFe₂O₄ precursor fluid booster speed was 0.38 ml h⁻¹. The spinning diagram is shown in figure 1.

Put the precursor fibers which were dried at 60 °C for 8 h into a clean porcelain boat and kept them at 600 °C for 4 h. Then, the NiFe₂O₄@CoFe₂O₄ core–shell nanofibers were prepared.

2.3. Electrochemical measurements

The electrochemical performance (CV, GCD, EIS) of the material in 3 mol l⁻¹ potassium hydroxide solution (KOH) was studied by an electrochemical workstation. The obtained material was used as a working electrode, one piece of Pt was used as the counter electrode and the saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was prepared as follows: 4 mg of the sample, 0.5 mg of the acetylene content, and 0.5 mg of the polyvinylidene fluoride (PVDF) were added to N-methyl-2-pyrrolidone (NMP). A slurry was formed after stirring. Then, the slurry was applied to a foamed nickel substrate (1 cm * 1 cm) with a spatula and dried at 60 °C for 12 h. The dried foamed nickel is pressed at a pressure of 10 MPa for 60 s.

3. Result and discussion

Figure 2 is an XRD pattern of one-dimensional NiFe₂O₄@CoFe₂O₄ nanofibers obtained by heat treatment at 600 °C, and of spinel-structured NiFe₂O₄ and CoFe₂O₄ crystals (111), (220), (311), (400), (422), (511) and (440) crystal faces (PDF#74-2081, PDF#22–1086) are basically coincident, and since the lattice parameters of NiFe₂O₄ and CoFe₂O₄ are very similar, the 2θ angle corresponding to the same crystal face. The results are basically the same, so the same crystal plane diffraction peaks of NiFe₂O₄ and CoFe₂O₄ measured by the experiment are not clearly separated, but overlap. There are no other obvious peaks in the spectrum, so the pure phase spinel structure NiFe₂O₄ and CoFe₂O₄ core–shell crystals were obtained.

Figure 3(a) is the SEM image of the calcined NiFe₂O₄@CoFe₂O₄ nanofibers. It can be seen that the NiFe₂O₄@CoFe₂O₄ forms a good one-dimensional structure, and the nanofibers are elongated and closely interwoven. It also shows the existence of the structure at the break of the nanofibers, and the interface is obvious. Figure 3(b) shows the energy spectrum of NiFe₂O₄@CoFe₂O₄ nanofibers. The appearance of the C
element is the reason why the test sample sticks to the conductive adhesive. According to the atomic composition analysis, the atomic ratio of Ni: Co is close to 1:1, and the atomic ratio of Co: Ni: Fe is close to 1:1:4.

Figure 4(a) shows nanofibers which are a few microns in length, and the core–shell structure is obvious. The core NiFe$_2$O$_4$ has a diameter of about 100 nm and an overall diameter of about 250 nm. Figure 4(b) is a selected area electron diffraction image at the frame of figure 4(a). It shows the crystal faces corresponding to different diffraction rings. The diffraction pattern is a concentric ring, indicating that the test sample is polycrystalline.

Figure 5(a) shows the cyclic voltammetry curve of NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofiber electrode with the scan rate of 5, 10, 30, 50, 100 mVs$^{-1}$ and working window of 0 $\sim$ 0.5 V. The curve has an oxidation peak and a reduction peak, indicating that a reversible redox reaction occurred on the sample electrode we prepared. The faradic redox reactions are related to Co$^{3+}$/Co$^{2+}$, Ni$^{3+}$/Ni$^{2+}$, Fe$^{3+}$/Fe$^{2+}$ redox couples with the assistance of OH$^-$ [16–19]. As the scanning rate becomes larger, the current of the corresponding peak also becomes larger but does not affect the shape of the overall cyclic voltammogram, indicating that these samples have good cycle stability characteristics. Due to the internal resistance polarization of the electrode material, the oxidation peak and the reduction peak potential move to the positive and negative electrodes, respectively. Figure 4(b) is a comparison of cyclic voltammetry curves of NiFe$_2$O$_4$@CoFe$_2$O$_4$ and NiFe$_2$O$_4$ and CoFe$_2$O$_4$ nanofibers at a scan rate of 10 mVs$^{-1}$. It can be seen that the positions of the oxidation peak and the reduction peak of the three materials are slightly different, and the peak current of the cyclic voltammetry curve of NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers is the largest, and the area enclosed by the voltammetric curve is also largest. The larger the surrounding area of the CV curve means that the core–shell structure is efficiently improved the electrochemical performance [20].
Figure 5 (c) shows the galvanostatic charge-discharge curves of NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers at different current densities. The charge-discharge potential window is $0 \sim 0.4$ V. The charge-discharge curve is symmetric and the resistance drop is small, further confirming the excellent supercapacitor performance and the reversible faradic reaction. Figure 5 (d) is a comparison of the charge-discharge curves of NiFe$_2$O$_4$@CoFe$_2$O$_4$ with NiFe$_2$O$_4$ electrodes and CoFe$_2$O$_4$ electrodes at the same current density. It can be seen that the charge and discharge time of NiFe$_2$O$_4$@CoFe$_2$O$_4$ materials is the longest, which is consistent with the CV test results, the core–shell structure enhances electrochemical performance.

Figure 6 (a) is a comparison of the specific capacitance of NiFe$_2$O$_4$@CoFe$_2$O$_4$ fibers with NiFe$_2$O$_4$ and CoFe$_2$O$_4$. The specific capacitance of NiFe$_2$O$_4$ and CoFe$_2$O$_4$ nanofibers reached 286, 247, 199, 174, 149, 124,
95 Fg\(^{-1}\) and 305, 240, 196, 173, 146, 114, 96 Fg\(^{-1}\) at current densities of 1, 3, 5, 10, 20, 30, 40 Ag\(^{-1}\). The specific capacitance of NiFe\(_2\)O\(_4\) reached 480, 417, 348, 315, 278, 237 and 214 Fg\(^{-1}\) at the current densities of 1, 3, 5, 10, 20, 30, 40 Ag\(^{-1}\), showing a higher specific capacitance value respectively. Figure 6(b) shows the cycle performance of NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) for 2000 cycles at 5 Ag\(^{-1}\) current density.

The specific capacitance of NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\) reached 480, 417, 348, 315, 278, 237 and 214 Fg\(^{-1}\) at the current densities of 1, 3, 5, 10, 20, 30, 40 Ag\(^{-1}\), showing a higher specific capacitance value respectively. Figure 6(b) shows the cycle performance of NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\) for 2000 cycles at 5 Ag\(^{-1}\) current density. The remaining capacity of NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\) is 87%, the NiFe\(_2\)O\(_4\) electrode is about 83% retention, CoFe\(_2\)O\(_4\) electrode is about 94% retention. The NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\) has a robust structure, CoFe\(_2\)O\(_4\) protects the morphology of NiFe\(_2\)O\(_4\) nanostructures from damage.

Figure 7 is the EIS spectrum of each electrode. Table 1 cross-link the impedance values fitted according to the Zview software. From the graph, it shows the Nyquist plots for the impedance spectra of electrodes and the equivalent model which includes the Warburg impedance of the bulk solution resistance (Rs), the charge transfer resistance (Rct), and diffusive resistance (W) \(^{[21]}\). It can be analyzed that the impedance Rs of

### Table 1. NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\) and NiFe\(_2\)O\(_4\),

| Impedance values | Rs (Ω) | Rct (Ω) |
|------------------|--------|---------|
| NiFe\(_2\)O\(_4\) | 0.7231 | 0.4054  |
| CoFe\(_2\)O\(_4\) | 0.6628 | 0.3809  |
| NiFe\(_2\)O\(_4\)@CoFe\(_2\)O\(_4\) | 0.6881 | 0.3512  |
NiFe$_2$O$_4$@CoFe$_2$O$_4$ is smaller than the $R_s$ value of NiFe$_2$O$_4$, and the slope of NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanocomposite in the low-frequency region is significantly larger than the other two. This indicates that the overall impedance value of NiFe$_2$O$_4$@CoFe$_2$O$_4$ is smaller than the NiFe$_2$O$_4$ and CoFe$_2$O$_4$ monomers. Therefore, these studies show that NiFe$_2$O$_4$@CoFe$_2$O$_4$ electrodes have lower interfacial charge transfer resistance and lower impedance.

Electrochemical test results show that the excellent electrochemical properties of NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers electrodes can be attributed to three contributions. First, NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers serve as a backbone, providing multiple channels for the faradic reaction, enhancing charge transport and ion diffusion. Enhances charge transport and ion diffusion in the electrolyte/electrode material region [22]. At the same time, the two-component NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanocomposite can further improve the utilization of electroactive materials because of the feasible oxidation states and the synergistic effect [23]. Finally, the NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanocomposite realized a robust structure, which protected the morphology of NiFe$_2$O$_4$ nanostructures from damage.

4. Conclusions

Using the co-electrospinning method and heat treatment process, the NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers were prepared. After their characterization and electrochemical performance test, the following results were obtained: after calcination at 600 °C, the NiFe$_2$O$_4$@CoFe$_2$O$_4$ with good crystallinity of pure phase was obtained. The nanofibers are continuous and smooth and cross-link into a more stable three-dimensional network structure. A clear core–shell structure can be seen from the TEM test. Due to the core–shell synergistic effect, the nanofibers of the structure are tougher and not easily broken, thereby maintaining a good nanofiber structure. This stable structure can increase the contact area of the electrode material with the electrolyte, thereby making the reaction with the electrolyte more adequate during the test. From the results of electrochemical performance test, the NiFe$_2$O$_4$@CoFe$_2$O$_4$ nanofibers have the highest specific capacity, the best cycle stability, and the conductivity is improved. In summary, the core–shell structure changes the morphology of the electrode material, and the electrochemical performance of the supercapacitor is improved by the synergistic action of the multi-metal.

Acknowledgments

This work was financed by the National Natural Science Foundation of China (Grant No. 11664023) and supported by the HongLiu first-class disciplines Development Program of Lanzhou University of Technology.

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