Hybrids of NiCo$_2$O$_4$ nanorods and nanobundles with graphene as promising electrode materials for supercapacitors

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Graphical abstract

Graphene/NiCo$_2$O$_4$ nanorods and nanobundles were facilely synthesized in one step. The porous NiCo$_2$O$_4$ nanobundle gives a higher specific capacitance of 1278 F/g at 1 A/g, even 719 F/g at a high current density of 20 A/g, showing a remarkable rate capability, could be a promising electrode material.

Abstract

High dispersion of NiCo$_2$O$_4$ nanorods and porous NiCo$_2$O$_4$ nanobundles decorated on RGO have been synthesized by a facile hydrothermal method, followed by calcination in one step. By adjusting the starting metal sources to realize the synthesis of different morphologies of NiCo$_2$O$_4$. The morphology and the microstructure of the as-prepared composites were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission electron microscope (TEM) techniques. Among them, the porous RGO/NiCo$_2$O$_4$ nanobundles gives a higher specific capacitance of 1278 F/g at 1 A/g and 719 F/g at 20 A/g, showing a remarkable rate capability. The excellent electrochemical performances could ascribed to the unique structural feature with higher surface area. It could be anticipated that the synthesized electrode material will gain promising applications in supercapacitors and other devices because of their outstanding characteristics of controllable capacitance and facilely synthesized.

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1. Introduction

Supercapacitors, due to their advantages of high power density, long cycle life, and small size have been gained rapidly attention...
were prepared similar to NiCoO₄ nanorods and NiCoO₄ nanobundles, excepted that 5 mg GO were firstly dispersed in the mixture of H₂O and ethylene glycol (1 mg/ml), then stirring and ultrasonific for at least 1 h to form a homogeneous aqueous dispersion. Then Co(NO₃)₂·6H₂O or Co (Ac)₂·4H₂O; Ni(NO₃)₂·6H₂O or Ni(Ac)₂·6H₂O and urea (0.36 g, 6 mmol) followed by stirring at room temperature. After stirring for several minutes, the clear solution was transferred into 40 ml Teflon-lined autoclave and keep in 180 °C for 12 h, the products were washed with deionized water and ethanol for several times, dried at 60 °C for 24 h. Then calcinated to 250 °C for NiCoO₄ nanorods and porous NiCoO₄ nanobundles, separately. The samples were denoted as RGO/NiCoO₄ NR and RGO/NiCoO₄ NB. The synthesis of NiCoO₄ on the graphene surface can be represented as follows: (see Scheme 1).

2.3. Material characterizations

Powder X-ray diffraction (XRD) patterns of all samples were carried out by a Rigaku D/max-2400 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Ka radiation (λ = 1.5418 Å) at a scanning rate of 5°/min in 2θ = 5–80°. The morphologies were analyzed on a Hitachi H-800 transmission electron microscope (TEM). Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (~196 °C). Before the measurements, the samples were degassed under vacuum condition at 120 °C for 8 h. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired at a relative pressure (P/P₀) range of 0.05–0.25. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t-plot method.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out in a conventional three-electrode system in 6 M KOH aqueous electrolyte at room temperature. The as-synthesized electrode materials, a platinum wire electrode and a silver/silver chloride electrode (Ag/AgCl) were used as working electrode, counter electrode and reference electrode, respectively. The working electrode was prepared by mixing sample (75 wt%) as active material with poly(tetrafluoroethene) (PTFE, 5 wt%) and carbon black (15 wt%) in ethanol to produce a homogeneous paste. Then the resulting mixture was coated onto the Ni foam substrate. The foam was dried at 80 °C in air for 12 h to remove the solvent. The electrochemical performances of the as-prepared material electrodes were tested using a cyclic voltammetry (CV) method, galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI 660D, Shanghai CH Instrument Company, China). The measurements were carried out in 6 M KOH aqueous electrolyte at room temperature. CV tests were done between 0 V and 0.5 V vs Ag/AgCl at scan rates of 2, 10, 20, 40, 50 and 100 mV s⁻¹. Galvanostatic charge/discharge curves were measured in the potential range of 0–0.4 V at different current densities, and the EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

3. Results and discussion

The formation of RGO–NiCo(OH)₃ can be explained as follows: metal cations were firstly adsorbed on GO surface, urea as
precipitator agent, then the reduction of GO and the formation of nickel and cobalt hydroxide happened in one step process by hydrothermal method. The formation of nickel and cobalt hydroxide can be illustrated as follows:

$$6\text{CO(NH}_2\text{)}_2 \rightarrow \text{C}_6\text{H}_6\text{N}_6 + 6\text{NH}_3 + 3\text{CO}_2$$ (1)

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$$ (2)

$$\text{Ni}^{2+} + 2\text{Co}^{2+} + 6\text{OH}^- \rightarrow \text{NiCo}_2(\text{OH})_6$$ (3)

An annealing treatment at 250 °C with a ramping rate of 5 °C min$^{-1}$ is utilized to convert the NiCo-precursor into spinel NiCo$_2$O$_4$ supported on the graphene sheets, as described by the simple oxidation reaction as follows:

$$\text{NiCo}_2(\text{OH})_6 + 1/2\text{O}_2 \rightarrow \text{NiCo}_2\text{O}_4 + 3\text{H}_2\text{O}$$ (4)

To further investigate the formation of NiCo$_2$O$_4$, the power XRD patterns of graphene/NiCo$_2$O$_4$ nanocomposites are given in Fig. 1. The XRD spectra revealed that the graphene/NiCo$_2$O$_4$ nanocomposites with different morphologies are similar and these specimen could be indexed to the spinel structure of NiCo$_2$O$_4$ (JCPDS card no. 20-0781). However, RGO peaks are not clearly present in both samples. This may be because of the lower carbon content or crystallinity.

TEM study gives the morphologies of NiCo$_2$O$_4$ and RGO–NiCo$_2$O$_4$ nanocomposites with different magnitudes (Fig. 2). As shown in Fig. 2a, the rod like NiCo$_2$O$_4$ nanocomposites with diameter of 10 nm and length up to around 70 nm can be clearly seen, while NiCo$_2$O$_4$ nanorods and NiCo$_2$O$_4$ nanobundles with ultrafine structure are homogeneously anchored on the graphene sheets. The shapes of these four electrodes are not uniform and are different from each other (Fig. 3). As can be seen, RGO–NiCo$_2$O$_4$ nanobundles possess a uniform pore size distribution in range of 3–5 nm. Mesoporous RGO–NiCo$_2$O$_4$ nanobundles consist of lots of nanoparticles, possessing numerous mesoporous convenient for ions transfer, which may lead to a well electrochemical performance. Addition of proper amount of metal nanoparticles is beneficial to the peeling of graphene sheets, so it is seen RGO–NiCo$_2$O$_4$ NB and RGO–NiCo$_2$O$_4$ NR electrode materials possess higher specific surface area than NiCo$_2$O$_4$ NB and NiCo$_2$O$_4$ NR (124.18 m$^2$ g$^{-1}$ and 96.32 m$^2$ g$^{-1}$), respectively. So it is expected these electrode will show well electrochemical performances.

The electrochemical behaviors of the obtained different RGO–NiCo$_2$O$_4$ nanocomposites are investigated by cycling (CV), galvanostatic charge/discharge and EIS measurements. Fig. 4a and b shows CV curves of RGO–NiCo$_2$O$_4$ NR and RGO–NiCo$_2$O$_4$ NB electrodes at a different scan rate in a 6 M KOH electrolyte between 0 and 0.5 V. The morphology of the NiCo$_2$O$_4$ nanocomposites loaded on graphene has a great influence on the integrated area of RGO–NiCo$_2$O$_4$ electrodes, which is directly related to the capacitance of the electrodes. However, the shapes of CV curves are typical pseudocapacitive behavior, which is distinct from electric double-layer capacitance characterized by nearly rectangular CV curves. Distinct pairs of redox peaks can be observed in the anodic and cathodic curves within 0.05–0.45 V (vs Ag/AgCl) in all CV curves. Such peaks can be ascribed to the redox couples of Co$_3$O$_4$/CoOOH and NiO/NiOOH [31]. As the increasing of the scan rate, the peak current increases, while the shapes of these CV curves do not significantly change as the scan rate increases from 2 to 100 mV S$^{-1}$, revealing the fast redox reactions for electrochemical energy storage.

Galvanostatic charge/discharge tests of these electrodes were conducted in 6 M KOH in a voltage range of 0–0.4 V with current densities ranging from 1 to 20 A g$^{-1}$, to further investigated the electrochemical performances of RGO–NiCo$_2$O$_4$ electrodes. As
shown in Fig. 5. As is shown in Fig. 5a, the plateaus at around 0.3 V in the charge–discharge curves suggests the typical pseudocapacitive characteristics, which is in good agreement with the CV curves. The specific capacitances \( C_s \) of the electrodes can be calculated according to the following equation:

\[
C_s = \frac{It}{\Delta V m}
\]

where \( m \) (g) is the mass of the active material in the film electrode, \( I \) (A) is the discharge current, \( \Delta V \) (V) is the potential window, \( t \) is the discharge time, and \( C_s \) (F g\(^{-1}\)) is the specific capacitance. Table 1 lists the charge/discharge data of the electrode materials calculated from the above equation at different current density. And the results were compared with the former reported NiCo\(_2\)O\(_4\) with different morphologies and RGO–NiCo\(_2\)O\(_4\) nanoparticles [32,33]. Besides, the capacitance of RGO–NiCo\(_2\)O\(_4\) NB at 1 A g\(^{-1}\) (1278 F g\(^{-1}\)) is comparable to the reported binder free carbon textiles supported NiCo\(_2\)O\(_4\) NW, as the capacitance is 1283 F g\(^{-1}\) at the same current density [34]. The values of RGO–NiCo\(_2\)O\(_4\) NB have little difference to that of RGO–NiCo\(_2\)O\(_4\) NR, and the capacitance decreased with the increasing of current density, because the transfer of electric charges was out of sync with current rates. At a faster charge–discharge, only outer active surface of electrode material is utilized for charge storage. The rate performance of RGO–NiCo\(_2\)O\(_4\) NR and RGO–NiCo\(_2\)O\(_4\) NB electrodes at various current density were compared in Fig. 5c. During these cycles at each current density from 1 to 20 A g\(^{-1}\), no obvious specific capacitance loss is observed. Besides, supercapacitors are required to have a long cycle life for large scale application. The long-term cycling performances of RGO–NiCo\(_2\)O\(_4\) NR and RGO–NiCo\(_2\)O\(_4\) NB electrodes are shown in Fig. 6 at a current of 5 A g\(^{-1}\).

Electrochemical impedance spectroscopy (EIS) is an important parameter determining the fundamental behavior of the
electrode materials for supercapacitors. The EIS of RGO–NiCo$_2$O$_4$ nanocomposites were carried out at open circuit potential with an ac perturbation of 5 mV in the frequency range of 1000 kHz–0.01 Hz. Fig. 7 gives the Nyquist plots of these electrodes. As seen, in the high frequency region, a semicircle due to charge transfer resistance on the electrode/electrolyte interface is observed.

Fig. 4. CV curves of RGO–NiCo$_2$O$_4$ nanorods (a) and RGO–NiCo$_2$O$_4$ nanobundles (b) at different scan rates.

Fig. 5. (a) Charge–discharge behaviors of RGO–NiCo$_2$O$_4$ nanorods (a) and RGO–NiCo$_2$O$_4$ nanobundles (b) at different current densities; (c) capability test for RGO–NiCo$_2$O$_4$ nanorods and RGO–NiCo$_2$O$_4$ nanobundles at various current densities (1–20 A/g); (d) specific capacitance as a function of current density.
The region between the high frequency and regions is called Warburg region and this is a combination of both resistive and capacitive behavior characterized by diffusive resistance. The intersection of the semicircle on the real axis at high-frequency represents the equivalent series resistance (Rs) of the electrode, while the diameter of the semicircle at low frequency region is mainly characterized by purely capacitive behavior. The high-frequency region and this is a combination of both resistive and Warburg region. The region between the high frequency and low frequency regions is called the so-called faradaic behavior. The intersection of the semicircle on the real axis at 0.1 Hz at room temperature.

The specific capacitance values of electrodes calculated from charge–discharge curves measured at different current densities.

| Sample                  | 1 A/g | 2 A/g | 3 A/g | 4 A/g | 5 A/g | 10 A/g | 20 A/g |
|-------------------------|-------|-------|-------|-------|-------|--------|--------|
| RGO–NiCo2O4 NB          | 1278  | 1221  | 1099  | 1030  | 963   | 851    | 719    |
| RGO–NiCo2O4 NR          | 933   | 908   | 850   | 807   | 768   | 696    | 627    |

Fig. 6. Cycling performances of these electrode materials at 5 A/g.

Fig. 7. EIS plots of these nanocomposites in the frequency range between 100 K and 0.1 Hz at room temperature.

4. Conclusions

In conclusion, RGO-NiCo2O4 nanorods and RGO-NiCo2O4 nanobundles were successfully decorated on RGO without any surfactant by hydrothermal method and combined with a simple post-annealing treatment. The starting metal salts play an important role in the synthesis of NiCo2O4 nanobundles with a higher specific surface area, which leads to a higher capacitance. The RGO-NiCo2O4 nanobundles electrode material has an excellent supercapacitance (1278 F g⁻¹ at 1 A g⁻¹), even at a higher current density 20 A g⁻¹, it also possess a capacitance of 719 F g⁻¹. Besides, the specific capacitance of RGO–NiCo2O4 nanobundles decayed by less than 5% after 1000 cycles at current density of 5 A g⁻¹. The higher capacitance of RGO–NiCo2O4 nanobundles than RGO–NiCo2O4 nanorods should be attributed to the mesoporous structure of RGO–NiCo2O4 nanobundles after annealing treatment. Thus, the simple preparation method and excellent chemical performances leads RGO–NiCo2O4 nanobundles to be attractive electrode materials for supercapacitor.

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