Hybrids of NiCo₂O₄ nanorods and nanobundles with graphene as promising electrode materials for supercapacitors

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GRAPHICAL ABSTRACT

Graphene/NiCo₂O₄ nanorods and nanobundles were facily synthesized in one step. The porous NiCo₂O₄ 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.

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ABSTRACT

High dispersion of NiCo₂O₄ nanorods and porous NiCo₂O₄ 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 NiCo₂O₄. 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/NiCo₂O₄ 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 facily 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

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[1–5]. However, the searching for electrode materials with higher electrochemical performance are still seriously needed, because of the practical application of supercapacitors are hindered by their low specific capacitance, poor cycling stability and so on. Over the past few years, lots of transition metal oxides and metal hydroxide such as MnO_2 , NiO , Co_3O_4 , $\text{Ni}(\text{OH})_2$, and NiAl-LDH [6–14], have been widely studied, because of their lower price and lower toxic nature. However, the intrinsic low conductivity of these metal oxides limited the performance of the supercapacitors. Great efforts have been paid to synthesis metal oxides with different morphologies or its composite material to improve the electrochemical performance of these materials. It is found the capacitance can be enhanced by incorporating carbon materials with pseudocapacitive materials.

Among the numerous carbon materials, graphene with one-atom thick layer 2D structure, is newly founded and has attracted plenty of interests for its unique characters, such as chemical stability, high electrical conductivity, and large surface area [15]. These encouraging characteristics provide such new materials a wide range of potential applications [11,16]. Recently, numerous works have been done on hybrid metal oxides-reduced graphene oxide (RGO), such as Mn_3O_4 , Co_3O_4 , NiO , Fe_2O_3 , and NiAl-LDH [17–22]. However, spinel transition metal oxides (AB_2O_4), with two metal elements provide the feasibility to tune the energy density and working voltage by varying the metal content, have less been developed [23–25]. Among the AB_2O_4 , it was reported that NiCo_2O_4 has high electron conductivity [26]. Wang et al. have reported the synthesis of NiCo_2O_4 -RGO composites, by heat treatment of NiCo hydroxides and GO, the material show an initial capacitance of 835 F/g at low current density [27]. He et al. synthesis NiCo_2O_4 nanowires loaded graphene using hexamethylenetetramine as surfactant; the capacitance is 737 F/g at a current density of 1 A/g [28]. Xiao et al. reported the electrochemical performance of NaCl -type $\text{Co}_x\text{Ni}_{1-x}\text{O}$ nanorods on reduced graphene oxide sheets [29]. However, it is found that the electrochemical performance of NiCo_2O_4 /RGO as supercapacitors need enhance urgently, and the synthesis method should be simplified for application.

So in the present work, NiCo_2O_4 nanorods and porous NiCo_2O_4 nanobundles/graphene/nanocomposites are facilely synthesized in one-step without any surfactant. By choosing appropriate temperature and the amount of ethylene glycol, NiCo_2O_4 nanorods and NiCo_2O_4 nanobundles can be obtained. By annealing, it is found NiCo_2O_4 nanobundles became porous structure. As result, these electrode materials show high capacitance, good cycling stability and excellent rate performance.

2. Experimental

2.1. Preparation of NiCo_2O_4 nanorods and NiCo_2O_4 nanobundles

Synthesis of NiCo_2O_4 nanorods: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.145 g, 0.5 mmol) and urea (0.36 g, 6 mmol) were added subsequently into the solution of H_2O and ethylene glycol. After stirring for several minutes, the clear solution was transferred into 40 ml Teflon-lined autoclave and keep in 180 °C for 12 h.

Synthesis of NiCo_2O_4 nanobundles: for the synthesis of NiCo_2O_4 nanobundles, the others are similar, except $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were replaced by $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (0.249 g, 1 mmol), $\text{Ni}(\text{Ac})_2 \cdot 6\text{H}_2\text{O}$ (0.125 g, 0.5 mmol), respectively.

2.2. Preparation of NiCo_2O_4 nanorods and NiCo_2O_4 nanobundles loads on graphene

Graphene oxide (GO) was prepared from natural graphite powder through a modified Hummers' method [30]. Graphene/ NiCo_2O_4

nanorods and NiCo_2O_4 nanobundles were prepared similar to NiCo_2O_4 nanorods and NiCo_2O_4 nanobundles, excepted that 5 mg GO were firstly dispersed in the mixture of H_2O and ethylene glycol (1 mg/mL), then stirring and ultrasonic for at least 1 h to form a homogeneous aqueous dispersion. Then $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{Ac})_2 \cdot 6\text{H}_2\text{O}$ 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 NiCo_2O_4 nanorods and porous NiCo_2O_4 nanobundles, separately. The samples were denoted as RGO/ NiCo_2O_4 NR and RGO/ NiCo_2O_4 NB. The synthesis of NiCo_2O_4 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 K α radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning rate of 5°/min in $2\theta = 5\text{--}80^\circ$. 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/P_0) 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(tetrafluoroethylene) (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- $\text{NiCo}(\text{OH})_x$ can be explained as follows: metal cations were firstly adsorbed on GO surface, urea as

Scheme 1. Schematic illustration of the synthesis of RGO/NiCo₂O₄ nanorods and RGO/NiCo₂O₄ nanobundles.

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:

An annealing treatment at 250 °C with a ramping rate of 5 °C min⁻¹ is utilized to convert the NiCo-precursor into spinel NiCo₂O₄ supported on the graphene sheets, as described by the simple oxidation reaction as follows:

To further investigate the formation of NiCo₂O₄, the power XRD patterns of graphene/NiCo₂O₄ nanocomposites are given in Fig. 1. The XRD spectra revealed that the graphene/NiCo₂O₄ nanocomposites with different morphologies are similar and these specimen could be indexed to the spinel structure of NiCo₂O₄ (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 NiCo₂O₄ and RGO–NiCo₂O₄ nanocomposites with different magnitudes (Fig. 2). As shown in Fig. 2a, the rod like NiCo₂O₄ nanocomposites with diameter of 10 nm and length up to around 70 nm can be clearly seen, while

Fig. 1. XRD patterns of RGO–NiCo₂O₄ nanocomposites after calcination.

NiCo₂O₄ nanorods and NiCo₂O₄ nanobundles with ultrafine structure are homogeneously anchored on the surface of RGO (Fig. 2c and g). There is no obvious morphology change of NiCo₂O₄ nanorods after calculation, which demonstrates excellent structural stability, however, a higher magnification TEM image shows in Fig. 2h further reveals that the NiCo₂O₄ nanobundles is actually a porous nanobundle composed of many small nanoparticles of 10–20 nm in diameter instead of conventional single-crystal nanobundle.

As is known that the electrochemical performances of a material partially depend on their specific surface area and pore size, the porous structure of the samples were characterized by nitrogen adsorption. These composites possess well-developed mesoporosity, reflected by their N₂ sorption isotherm. The pore size distributions of these four electrodes are not uniform and are different from each other (Fig. 3). As can be seen, RGO–NiCo₂O₄ nanobundles possess a uniform pore size distribution in range of 3–5 nm. Mesoporous RGO–NiCo₂O₄ 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–NiCo₂O₄ NB and RGO–NiCo₂O₄ NR electrode materials possess higher specific surface area than NiCo₂O₄ NB and NiCo₂O₄ NR (124.18 m² g⁻¹ and 96.32 m² g⁻¹), respectively. So it is expected these electrode will show well electrochemical performances.

The electrochemical behaviors of the obtained different RGO–NiCo₂O₄ nanocomposites are investigated by cycling (CV), galvanostatic charge/discharge and EIS measurements. Fig. 4a and b shows CV curves of RGO–NiCo₂O₄ NR and RGO–NiCo₂O₄ NB electrodes at a different scan rate in a 6 M KOH electrolyte between 0 and 0.5 V. The morphology of the NiCo₂O₄ nanocomposites loaded on graphene has a great influence on the integrated area of RGO–NiCo₂O₄ 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 Co₃O₄/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–NiCo₂O₄ electrodes. As

Fig. 2. TEM images of NiCo_2O_4 nanorods (a, b), RGO- NiCo_2O_4 nanorods after annealing (c, d), NiCo_2O_4 nanobundles (e, f) and RGO- NiCo_2O_4 (g, h) after annealing, respectively.

Fig. 3. Nitrogen adsorption/desorption isotherms (a) and BJH pore size distributions (b) for these electrode materials.

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, ΔV (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_2O_4 with different morphologies and RGO- NiCo_2O_4 nanoparticles [32,33]. Besides, the capacitance of RGO- NiCo_2O_4 NB at 1 A g^{-1}

(1278 F g^{-1}) is comparable to the reported binder free carbon textiles supported NiCo_2O_4 NW, as the capacitance is 1283 F g^{-1} at the same current density [34]. The values of RGO- NiCo_2O_4 NB have little difference to that of RGO- NiCo_2O_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_2O_4 NR and RGO- NiCo_2O_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_2O_4 NR and RGO- NiCo_2O_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

Fig. 4. CV curves of RGO-NiCo₂O₄ nanorods (a) and RGO-NiCo₂O₄ nanobundles (b) at different scan rates.

Fig. 5. (a) Charge–discharge behaviors of RGO-NiCo₂O₄ nanorods (a) and RGO-NiCo₂O₄ nanobundles (b) at different current densities; (c) capability test for RGO-NiCo₂O₄ nanorods and RGO-NiCo₂O₄ nanobundles at various current densities (1–20 A/g); (d) specific capacitance as a function of current density.

electrode materials for supercapacitors. The EIS of RGO-NiCo₂O₄ nanocomposites were carry out at open circuit potential with 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.

Table 1

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–NiCo ₂ O ₄ NB	1278	1221	1099	1030	963	851	719
RGO–NiCo ₂ O ₄ 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.

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 low frequency region is mainly characterized by purely capacitive behavior. The intersection of the semicircle on the real axis at high-frequency represents the equivalent series resistance (R_s) of the electrode, while the diameter of the semicircle corresponds to the charge-transfer resistance (R_{ct}) of the electrodes and electrolyte interface [35]. It is apparent that the values of R_s of RGO–NiCo₂O₄ NR is higher than that of RGO–NiCo₂O₄ NB. This result is because of lower conductivity of RGO–NiCo₂O₄ NR. The almost vertical shape, representing the swift ion diffusion in electrolyte and the adsorption onto the electrode surface, suggests the ideally capacitive behavior of the RGO–NiCo₂O₄ NB.

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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