Synthesis of Co₃O₄/NiO nanofilms and their enhanced electrochemical performance for supercapacitor application

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Abstract

Transition metallic oxides have attracted considerable attention for supercapacitor applications because of their superior electrochemical performance at relatively low cost. $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms were successfully prepared by calcination of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$. XRD, XPS, SEM and TEM techniques were used to characterize the composition and morphology of as-prepared samples. The results demonstrated that $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms presented graphene-like morphology with shrinkage and wrinkles. The Brunauer-Emmett-Teller (BET) measurement showed that specific surface area of $\text{Co}_3\text{O}_4/\text{NiO}$ was $176.5 \text{ m}^2/\text{g}$. Electrochemical properties tests indicated that the $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms had a higher specific capacitance and better rate capability than that of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ at high current density. As to the cycling performance, the specific capacitance of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode would first increase from 556 F/g to 710 F/g quickly at 2 A/g after 80 cycles and then remained stable. Therefore, compared with that of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$, the capacitance performance of as-prepared $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms was improved after calcination. The possible reason for the enhancement of capacitance performance was discussed.

Keywords: $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms, calcination, electrochemical, supercapacitor

1. Introduction

Recent years have witnessed increasing public concern on environmental issues caused by inappropriate industrial operations and unsustainable consumption of fossil fuel [1]. With the energy crisis emerging, seeking new-type green renewable energy is one of the most imminent problems. Supercapacitor is recently considered to relieve this issue because of its excellent electrical properties, such as the short charging time, long cycling life, high reliability, power and energy density [2-4]. The electrode materials, separator films and electrolyte can affect the performance of supercapacitor, and the electrode materials usually play the most important role among them [5]. The specific surface area, morphology, pore-size distribution and electrical conductivity of electrode materials have much effect on their electrochemical properties [6,7]. Therefore, design and preparation of electrode materials with excellent capacitance performance is still a challenging task.

Compared with carbonaceous and conducting polymer electrode materials, transition metallic oxide electrode materials are quickly favored by researchers because of their fast redox kinetics and good reversibility, which can realize large capacitance and ideal stability [8-10]. Cobalt-nickel double hydroxides or oxides, as an important part of transition metallic oxide materials, have recently been used as

catalyst for oxygen evolution reaction [11-13], isoniazid oxidation [14], ethanol oxidation [15], hydrogenation of *p*-nitrophenol [16] and adsorption of organic dyes [17-19]. In addition, some applications in electrode for cobalt-nickel double hydroxides or oxides have been reported [20,21]. Xu et al. synthesized Ni(OH)₂-Co(OH)₂ hollow microspheres through a microwave hydrothermal method, and they have enhanced reversibility and better retention of electrochemical capacitance in comparison with single Ni(OH)₂ and Co(OH)₂ [20]; Fan et al. prepared NiO/Co₃O₄ core/shell composites, which showed excellent cyclic performance and superior capacitive performance with large capacitance (510 F/g at 5 mA/cm²) [21].

Cobalt-nickel double hydroxides or oxides have very high ideal specific capacitance value, and the value of NiO, Ni(OH)₂, Co₃O₄ and Co(OH)₂ can be up to 2573 F/g [22], 2082 F/g [23], 3560 F/g [24] and 3500 F/g [25], respectively. However, their actual capacitance values are much lower than the ideal values in practical applications, which can be due to the poor crystallinity, electrical conductivity and redox reversibility. The recent research findings suggest that nanocomposites usually present better performance than single component in catalysis [26,27], biochemical sensing [28], gas sensing [29], through synergies. Oxides/hydroxides composed of two or three transition metal components often show enhanced electrochemical

performance too [30,31]. So far, various methods to synthesize cobalt-nickel double hydroxides or oxides have been reported, such as electrochemical deposition [32], hydrothermal method [33], template method [34], sol-gel method [35], thermal decomposition [36], chemical precipitation [37]. However, to the best of our knowledge, cobalt-nickel double oxides with high supercapacitor performance obtained by calcination are seldom reported.

Herein, we first prepared α -Co(OH)₂/ α -Ni(OH)₂ nanocomposites by chemical precipitation method, and then calcined it at 350 °C in nitrogen atmosphere to obtain graphene-like Co₃O₄/NiO nanofilms. The results indicated that the Co₃O₄/NiO nanofilms have a higher specific capacitance than that of precursor α -Co(OH)₂/ α -Ni(OH)₂ at high current densities, while the specific capacitance of Co₃O₄/NiO changed a little as the current density increased. As to the capacitance stability, the specific capacitance preserved well at 710 F/g after 500 times at constant current density of 2 A/g. Therefore, the capacitance performance of as-prepared Co₃O₄/NiO nanofilms was obviously improved after the precursor undergoing calcination. The enhanced electrochemical performance can be well explained by EIS measurement.

2. Experimental

Chemicals

Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), polyvinyl pyrrolidone (PVP, K-30, M.W. 40000), sodium borohydride (NaBH_4 , 96 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). All the reagents are analytic grade and used as received without further purification.

2.1. Preparation of the samples

$\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ nanocomposites were firstly prepared according to our previous report (see supporting information) [16], and then a certain amount of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ nanocomposites was placed into a clean porcelain boat and transferred into a high temperature sintering furnace with quartz glass tube. After vacuuming, the precursor underwent 350 °C for 3 hours in nitrogen atmosphere with heating rate at 10 °C/min. After the quartz glass tube cooled down to ambient temperature, the porcelain boat was taken out. Black samples were collected.

2.2. Characterization

The X-ray diffraction (XRD) data were acquired on a Rigaku D/max-RA X-ray diffract meter ($\text{Cu K}\alpha$ radiation, $\lambda=0.15406$ nm) with 2θ value from 10° to 90° at a scanning rate of 4°/min. The spectra of X-ray photoelectron spectroscopy (XPS) was

performed by using a VG ESCA scientific theta probe spectrometer in constant analyzer energy mode with a pass energy of 28 eV and Al Ka (1486.6 eV) radiation as the excitation source. The morphology of the samples was analyzed by scanning electron microscopy (SEM, Hitachi S-4800, operating at 5.0 KV) and Transmission electron microscopy (TEM, Hitachi JEM-2100 instruments with an acceleration voltage of 200 KV). The specific surface area was calculated by using the Brunauer–Emmett–Teller method (BET, ASAP2020M, MICROMERITICS INSTRUMENT CORP. of U.S.). The electrochemical properties were tested on the electrochemical workstation A (CHI-660D). The electrochemical impedance spectroscopy experiment was conducted on the electrochemical workstation B (EIS, ZAHNER-Elektrik GmbH & Co. KG).

2.3. Electrode preparation and electrochemical measurement

Nickel foam was selected as the current collector in our experiment to test the electrochemical properties of samples. The nickel foam was firstly cut into a size of 1 cm×3 cm, and then soaked into acetone and diluted hydrochloric acid–ethanol, in turn, under ultrasonic to remove the oxide or organic impurities from its surface. The cleaned nickel foam was thoroughly dried in a vacuum box and its mass was weighed. The working electrodes were then prepared with the as-prepared active materials,

acetylene black (AB), polyvinylidene fluoride (PVDF) binder (5 %) with a weight ratio of 80:15:5. A small amount of N-methyl pyrrolidone (NMP) was then added to the mixture, followed by 30 min of grinding. The as-obtained slurry was then dipped onto the treated nickel foam (1cm×1cm) and dried at 70 °C in vacuum for 6 h to remove the solvent. Finally, the as-prepared electrode was weighed after pressed at 7 MPa. The reference electrode and counter electrode were Hg/HgO and platinum electrode, respectively, and the electrolyte was 6 M KOH aqueous solution. The electrochemical measurement was conducted in the electrochemical workstation at ambient temperature. The EIS measurements were performed with a signal of 5 mV from 0.1 Hz to 100 KHz in phosphate buffer saline (PBS) solution.

3. Results and discussion

3.1. Characterization of cobalt-nickel double oxides

To determine the crystalline phase of obtained product, XRD pattern of the product was recorded in a 2θ range of 10° - 90° with a scan rate of $4^\circ/\text{min}$ in Fig. 1. The three obvious diffraction peaks, located at 37.1° , 43.4° and 63.1° , can well be indexed to typical peaks of Co_3O_4 (JCPDS No. 42-1467) and NiO (JCPDS No. 44-1159), which indicates that $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ was transformed into $\text{Co}_3\text{O}_4/\text{NiO}$ by calcination.

Fig. 1. XRD pattern of cobalt-nickel double oxides.

Our previous report also indicated that $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ would transform into $\text{Co}_3\text{O}_4/\text{NiO}$ in the temperature range of 200 °C to 290 °C, and then maintained a platform of $\text{Co}_3\text{O}_4/\text{NiO}$ from 290 °C to 366 °C under the protection of nitrogen [16]. To obtain pure $\text{Co}_3\text{O}_4/\text{NiO}$, we chose 350 °C as the calcination temperature in our work. The TGA curve of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ is appended in Fig. S1 (see supporting information, SI).

Fig. 2. XPS spectra of cobalt-nickel double oxides: (a) survey spectrum; (b) Co 2p region; (c) Ni 2p region and (d) O 1s region.

To further clarify the composition of the composites, the X-ray photoelectron spectroscopy (XPS) experiment was carried out. Fig. 2a is the survey spectrum with a scan region from 0 - 1100 eV, and the species of C 1s, O 1s, Co 2p and Ni 2p are detected. Fig. 2b shows the XPS spectrum of Co 2p. The peaks located at 780.6 eV and 796.3 eV can be respectively assigned to the binding energy of Co 2p_{3/2} and Co 2p_{1/2}, and two peaks at 786.1 eV, 802.8 eV correspond to their shake-up satellites, which is in agreement with previous reports of Co₃O₄ [38,39]. The XPS spectrum of Ni 2p_{3/2} in Fig. 2c split into two peaks around 854.6 eV and 855.6 eV, which could be

ascribe to the surface effect [40,41]. The peak located at 873.1 eV corresponds to Ni 2p_{1/2}. In addition, the Ni 2p have the classical shape of oxidized nickel “shake up effect” around 861.5 eV and 880 eV, which can further indicate the presence of NiO [42]. The presence of NiO and Co₃O₄ is in good agreement with the O 1s peak in Fig. 2d, where a doublet of 531.4 eV and 529.8 eV is observed [43].

Fig. 3. SEM and (HR)TEM images of Co₃O₄/NiO nanofilms: (a) SEM ; (b, c) TEM ; (d) HRTEM.

The morphology and nanostructure of the product were investigated by SEM and TEM analysis. The SEM images in Fig. 3a verified that the Co₃O₄/NiO sample remained the morphology of graphene-like as their precursor. However, compared with α -Co(OH)₂/ α -Ni(OH)₂ (Fig. S2, see SI), the membrane structure after

calcination appears large shrinkage, along with more wrinkles. The low-magnified TEM image in Fig. 3b, c confirmed the wrinkled morphology as the SEM images showed. In the HRTEM image of $\text{Co}_3\text{O}_4/\text{NiO}$ nanocomposites in Fig. 3d, the measured lattice fringe is 0.245 nm and 0.209 nm, matching well with the (311) plane of Co_3O_4 and (012) plane of NiO. These results are corresponding well with the XRD analysis in Fig. 1, indicating the successful preparation of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms.

3.2. BET measurement of cobalt-nickel double oxides

Fig. 4. Nitrogen adsorption and desorption isotherms of the as-synthesized $\text{Co}_3\text{O}_4/\text{NiO}$. The inset shows the pore-size distribution of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms.

A detailed analysis of the specific surface area and pore diameter distribution of cobalt-nickel double oxides nanocomposites has been performed by using Brunauer–Emmett–Teller (BET) gas adsorption-desorption measurements. The N_2 isotherms of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms shown in Fig. 4 are close to Type V with an evident hysteresis

loop in the 0.6 - 1.0 range of relative pressure, indicating the mesoporous structure of the $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms. BET specific surface area of the synthesized $\text{Co}_3\text{O}_4/\text{NiO}$ is $176.5 \text{ m}^2/\text{g}$ by calculation from N_2 isotherms at 77.3 K, which is smaller than that of $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ ($260.1 \text{ m}^2/\text{g}$) we reported before [16]. The pores of $\text{Co}_3\text{O}_4/\text{NiO}$ fall into the size range from 2 to 128 nm and pores around 30 nm are attributed to the interlayer spaces, determined by the Barrett–Joyner–Halenda (BJH) method (inset in Fig. 4).

3.3. Electrochemical measurement of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms

Cyclic voltammograms (C-V) test is a quick and efficient method to identify whether the sample can be used as capacitor materials [44,45]. Fig. 5a showed the C-V curves of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode at different scan rate in the potential range of 0 V-0.5 V (vs Hg/HgO) in 6 M KOH solution. It can be seen that the C-V curves of $\text{Co}_3\text{O}_4/\text{NiO}$

Fig. 5. (a) C-V curves of Co₃O₄/NiO electrode between 0 - 0.5 V; (b) C_{sp} of Co₃O₄/NiO (**Red**) and α-Co(OH)₂/α-Ni(OH)₂ (**Black**) electrodes as a function of scan rate; (c) Galvanostatic charge-discharge curves of Co₃O₄/NiO electrode at current density of 0.5 - 8 A/g; (d) C_{sp} of Co₃O₄/NiO (**Red**) and α-Co(OH)₂/α-Ni(OH)₂ (**Black**) electrodes as a function of current densities. The electrolyte is 6 M KOH.

electrode showed a pair of redox peaks in each cycle scanning, revealing that the capacitance mainly results from the reversible faradaic reactions. In addition, as the scan rate increasing, the redox current are gradually increasing and the anodic peaks shifted toward positive potential, while the cathodic peaks shifted toward negative potential, indicating more serious electrochemical polarization. The reason may be explained by the diffusion of OH⁻ ions into the interlayer space of Co₃O₄/NiO nanofilms. At high scan rate, the OH⁻ ions can only access the outer active sites due to

shorter time period, which resulting the low utilization rate of active materials of Co₃O₄/NiO [34,46]. All the C-V curves are almost symmetric, suggesting the fine reversibility of the oxidation and reduction processes. The redox reactions of nanofilms are given below [47,48].

From the C-V loops, the specific capacitance can be calculated according to equation:

$$C_1 = \frac{\int_{V_a}^{V_c} I(V) dV}{mv(V_a - V_c)}$$

Where m is the mass of the active materials (g), v is the scan rate of C-V curves (V/s); (V_a-V_c) represents the potential window (V); I is the discharge current (A). The obtained specific capacitance values of Co₃O₄/NiO electrode are 739.8 F/g, 737.3 F/g, 699.4 F/g, 600.3 F/g, 564.7 F/g and 528.0 F/g at the sweep rate of 5 mV/s, 10 mV/s, 15 mV/s, 20 mV/s, 25 mV/s and 30 mV/s, respectively, while that of α-Co(OH)₂/α-Ni(OH)₂ electrode are 771.1 F/g, 755.6 F/g, 620.9 F/g, 570.1 F/g, 418.2 F/g and 344.0 F/g at the sweep rate of 2.5 mV/s, 5 mV/s, 7.5 mV/s, 10 mV/s, 12.5 mV/s and 15 mV/s, respectively, as shown in Fig. 5b.

Galvanostatic charge–discharge test is another method for determining the specific capacitance of electrode materials under constant conditions. Fig. 5c showed the charge–discharge curves at different current densities. It can be seen that the charge-discharge curves of Co₃O₄/NiO electrode are not symmetric and the voltage is non-linear with time. In addition, the discharge curve appears an approximate platform, indicating the measured capacitance is mainly based on the surface redox reaction of electrode material, which corresponds well with the results obtained from the C-V curves. The equivalent series resistance (ESR) of the electrode gives rise to initial drop (iR drop) of the discharge voltage, which remains until the constant capacitive performance is reached. Notably, the higher current density gives the larger iR drop, which coincides with Xiao et al.'s result [49]. The subsequent potential decline of discharge curves to 0.2 V with slope variation should be ascribed to the domination of faradic redox reaction of electrode materials, while the sharp decline of discharge curves below 0.2 V with linear slope is ascribed to pseudocapacitance coming from the surface properties [50,51]. The current density dependent specific capacitance can be calculated from the discharge curves according to the equation:

$$C_2 = I\Delta t / m\Delta V$$

, Where I is the discharge current (A), Δt is the discharge time (s), m is the mass of the electrode material (g) and ΔV is the potential range (V). Fig. 5d

showed the specific capacitance values of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode are 604 F/g, 572 F/g, 556 F/g, 534 F/g and 457.6 F/g, while that of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode are 719.3 F/g, 505.7 F/g, 429.7 F/g, 373.1 F/g and 276.6 F/g, at the current density of 0.5 A/g, 1 A/g, 2 A/g, 4 A/g and 8 A/g, respectively. The C-V curves and galvanostatic charge-discharge curves of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode are appended in Fig. S3 (see SI).

It can be seen from Fig. 5b and Fig. 5d that the specific capacitance value of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode is larger than that of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode at low scan rate or current density, however, rapidly decreased when the scan rate or current density increased, and ultimately became much smaller than that of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode. Thus, compared with $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode, $\text{Co}_3\text{O}_4/\text{NiO}$ electrode showed better rate capability. The worse rate capacity of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode can be attributed to the declined utilization ratio of active sites of electrode material at high scan rate or current density, which can be further ascribed to its worse electrical conductivity and low diffusion resistances of electrolyte ions, compared with that of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms. The specific capacitance is summation of pseudocapacitance from the surface properties and faradaic capacitance from redox reaction of electrode materials [52]. It is known that

pseudocapacitance from the surface properties is usually independent of the scan rates [53], while faradaic capacitance relies on the charge transfer rate of electrode material and the diffusion ability of electrolyte ions [54]. Under low scan rate, the contribution of pseudocapacitance from the surface properties is big for $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ because of its high specific surface area of electrode material; and both $\text{Co}_3\text{O}_4/\text{NiO}$ and $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ have high utilization ratio for the generation of faradic capacitance through redox reaction. The higher specific capacitance for $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode may be ascribed to the contribution of pseudocapacitance from the surface properties. However, when the scan rate or current density increases, the transfer of OH^- ions will increase as well, and OH^- ions can not make full use of the inner active sites of electrode material due to the decreased time period, which results in the rapid decline of faradaic capacitance of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode, while the faradaic capacitance of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode can preserve well because of its better electrical conductivity and lower diffusion resistances of OH^- ions, thus leading to the larger specific capacitance for $\text{Co}_3\text{O}_4/\text{NiO}$ electrode. In addition, the EIS performance (see section 3.4) indicated that $\text{Co(OH)}_2/\text{Ni(OH)}_2$ electrode has larger resistance than that of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode. At low scan rate or current density, the iR drop caused by resistance is little, and high

capacitance value is reserved. However, capacitance loss associated with iR drop can be very prominent at high scan rate or current density for $\text{Co}(\text{OH})_2/\text{Ni}(\text{OH})_2$ electrode, thus resulting to the worse rate capability than that of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode [50].

In present literatures, some works about Co_3O_4 or NiO being used as electrode materials of supercapacitor have been reported. Herein, we have listed some of them (Table 1), and $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms in our work showed excellent capacitance performance. Thus, $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms can be a good electrode material for supercapacitor application.

Table 1. The specific capacitance of materials based on Co_3O_4 and NiO as supercapacitor electrode.

Active material	Specific capacitance (F/g)					Electrolyte	Ref.
	5 mV/s	10 mV/s	15 mV/s	20 mV/s	25 mV/s		
$\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms	739.8	737.3	699.4	600.3	564.7	6 M KOH	This work
$\text{Co}_3\text{O}_4/\text{Carbon}$ composites	290	230	205	190	-	2 M KOH	[55]
sample-II-350 Co_3O_4 NPs	350	330	320	-	-	6 M KOH	[56]
Co_3O_4 nanocapsules	495.6	451.3	-	-	388.1	1 M KOH	[57]
Magnetic field	695	440	-	~330	-	6 M KOH	[58]

assisted NiO

3.4. Comparison of electrochemical properties between $\text{Co}_3\text{O}_4/\text{NiO}$ and $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$.

In order to compare the electrochemical properties of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms and their precursor, the electrochemical impedance spectroscopy (EIS) experiment was conducted to elucidate the difference in their electrical conductivity and electrolytic ion diffusion rate. Fig. 6a shows Nyquist plots obtained with $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$

Fig. 6. (a) Isotropic EIS curves of the as-synthesized $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ nanocomposites and $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms in the frequency range between 0.1 Hz and 100 KHz at room temperature; (b, c) Bode curves based on EIS; (d) C-V curves of $\text{Co}_3\text{O}_4/\text{NiO}$ and $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ at the same scan rate (10 mV/s)

and $\text{Co}_3\text{O}_4/\text{NiO}$ electrodes. Each Nyquist plot shows a semicircle in the

high-frequency region and a straight line in the low-frequency region. The semicircle in the high frequency region is related to charge transfer resistance (R_{ct}) caused by faradic reaction, and the smaller semicircle of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode means the better electrical conductivity in charge-discharge processes. The straight line corresponds to diffusion resistance of electrolyte ions within the electrode, and the higher slope for $\text{Co}_3\text{O}_4/\text{NiO}$ electrode than that of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode indicates its lower diffusion resistance of ions and improved electrolyte ions diffusion ability [59, 60].

Fig. 6b revealed that both the two electrodes preserved constant impedance at high frequency ($> 10^4$ Hz), indicating the capacitive properties. In the low frequency range, $\text{Co}_3\text{O}_4/\text{NiO}$ electrode showed lower frequency impedance than that of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode (Fig. 6b), demonstrating a more conductive behavior and lower ion diffusion resistance for sample $\text{Co}_3\text{O}_4/\text{NiO}$, coinciding well with the EIS results. The corresponding phase angle curves (Fig. 6c) demonstrated that these electrodes had two time constants; one was in the frequency range from 100 to 1000 Hz and another one was at lower frequencies (~ 0.1 Hz). Furthermore, the diameter of the capacitive semicircle at high frequencies of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode was smaller than that of $\alpha\text{-Co(OH)}_2/\alpha\text{-Ni(OH)}_2$ electrode, which indicated the former had lower resistance [61-63]. All the analysis above displays that the $\text{Co}_3\text{O}_4/\text{NiO}$ electrode has

lower charge transfer resistance and ion diffusion resistance than that of α -Co(OH)₂/ α -Ni(OH)₂ electrode.

The C-V tests of Co₃O₄/NiO and α -Co(OH)₂/ α -Ni(OH)₂ electrode were performed under the same scan rate, and the results are showed in Fig. 6b. It can be seen that both of the two samples occurred reversible redox reaction when they were used as electrode, and the faradic capacitance was formed. The closed geometric curve area of Co₃O₄/NiO electrode is much larger than that of α -Co(OH)₂/ α -Ni(OH)₂ electrode, indicating a superior capacitance performance of sample after precursor undergoing calcination. In addition, the better symmetric shape of C-V curves for Co₃O₄/NiO electrode is observed, as well as a smaller potential difference (ΔE) between oxidation peak and reduction peak (0.20 V vs 0.24 V), suggesting Co₃O₄/NiO electrode has a better redox reversibility than that of α -Co(OH)₂/ α -Ni(OH)₂ electrode [34,46,64].

3.5. Charge/discharge cycling test of Co₃O₄/NiO nanofilms

Electrochemical stability is one of the most important factors to evaluate the usefulness of supercapacitors in commercial applications [65]. Fig. 6 presents the specific capacitance retentions of the Co₃O₄/NiO electrode in the potential range of 0 V to 0.5 V for 500 respective charge–discharge cycles at a current density of 2 A/g in

6 M KOH. The specific capacitance gradually increased up to about 710 F/g at 80 cycles and remained stable afterward, reflecting the good long-term cyclability of our $\text{Co}_3\text{O}_4/\text{NiO}$ electrode. Previous work reported that the gradual increase in specific

Fig. 7. Charge/discharge cycling test of $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms as electrode at constant current density of 2 A/g. The concentration of electrolyte is 6 M KOH.

capacitance during the cycling may be ascribed to activation of the electrode, as electrolyte ions in general require a certain period of time to penetrate the entire inner space of the electrode material [66,67]. $\text{Co}_3\text{O}_4/\text{NiO}$ electrode in our work can be activated within 80 cycles, which is much faster than that of single Co_3O_4 electrode reported by Cao et al. (1200 cycles) [48]. The good cyclability may be attributed to the graphene-like structure of $\text{Co}_3\text{O}_4/\text{NiO}$, which can enable the full exposure of the active area to the electrode, and thus enhancing the utilization of the materials and the

long-time cyclability is obtained.

4. Conclusions

In summary, graphene-like $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms have been successfully prepared by $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ calcination. XRD, XPS, SEM and TEM measurements have been used to characterize the composition and morphology. BET analysis showed the specific surface area of $\text{Co}_3\text{O}_4/\text{NiO}$ was $176.5 \text{ m}^2/\text{g}$. The electrochemical properties tests indicated that the $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms have a higher specific capacitance and better rate capability than that of $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ nanocomposites at high current densities. As to the capacitance stability, the specific capacitance value of $\text{Co}_3\text{O}_4/\text{NiO}$ electrode preserved well at 710 F/g after 500 cycles at 2 A/g . Therefore, the capacitance performance of as-prepared $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms was improved after calcination of $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$ nanocomposites. The enhanced electrochemical performance can be attributed to the high electrical conductivity and low diffusion resistances of electrolyte ions.

Acknowledgements

This work is supported by the National Science Foundation of China (NSFC) (Grants

21471001, 21275006), and Natural Science Foundation of Anhui Province (Grant no.1508085MB22), Financed by the 211 Project of Anhui University, and The Key Laboratory of Functional Inorganic Materials Chemistry of Anhui Province.

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Graphical Abstract

Graphene-like $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms were successfully prepared by simple calcination of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$. The as-synthesized $\text{Co}_3\text{O}_4/\text{NiO}$ nanofilms had better rate capability and capacitance performance than that of precursor $\alpha\text{-Co}(\text{OH})_2/\alpha\text{-Ni}(\text{OH})_2$, and could be used as an excellent electrode material for supercapacitor.