



Synthesis and characterization of porous cobalt oxide/copper oxide nanoplate as novel electrode material for supercapacitors

Shui-rong ZHANG¹, Zhi-biao HU², Kai-yu LIU¹, Yan-zhen LIU¹, Fang HE¹, Qing-liang XIE¹

1. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China;

2. College of Chemistry and Materials Science, Longyan University, Longyan 364012, China

Received 19 January 2015; accepted 6 June 2015

Abstract: A promising $\text{Co}_3\text{O}_4/\text{CuO}$ composite electrode material was successfully synthesized through a facile hydrothermal and calcination process. Effects of the surfactants hexadecyltrimethyl ammonium bromide (CTAB) and polyvinylpyrrolidone (PVP) on the morphology and electrochemical performance of the composite were investigated. Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption–desorption experiment were employed to characterize the microstructures and morphologies of the composite. Meanwhile, the electrochemical performances of the samples were studied using cyclic voltammetry (CV), galvanostatic charge–discharge test and electrochemical impedance spectroscopy (EIS). The results show that the porous $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB nanoplates own the best performance and exhibits a high specific capacitance of 398 F/g at 1 A/g with almost 100% capacitance retention over 2000 cycles, and it retains 90% of capacitance at 10 A/g.

Key words: cobalt oxide/copper oxide composite; hexadecyltrimethylammonium bromide (CTAB); polyvinylpyrrolidone (PVP); hydrothermal method; supercapacitors

1 Introduction

With the depletion of fossil fuel and the worsening of the environment, the development of clean, environmentally friendly and efficient energy storage systems has been stimulated [1]. Among various emerging energy storage technologies, supercapacitors (SCs) have received great attention due to high power density, excellent pulse charge and discharge characteristics, long cycle life and safe operation [2,3]. Supercapacitors can be classified as two kinds according to the charge–storage mechanism. One is electrical double-layer capacitor (EDLC), which is based on the electrical charge accumulation at the interface between the electrode and the electrolyte. Another is the pseudocapacitor (PC), which is based on the fast reversible Faradaic reactions on the surface or near the surface of active materials [4–7]. Until now, the major classes of the materials for supercapacitors are carbonaceous materials [8–10], transition-metal oxides (such as Co_3O_4 [11], NiO [12], MnO_2 [13] and CuO [14])

and conducting polymers [15–17]. Among them, transition-metal oxides have higher specific capacitance than the carbonaceous materials and conducting polymers [18]. Therefore, great efforts have been devoted to investigating the transition-metal oxides as the electrode materials for supercapacitors.

Recently, particular attention has been focused on exploring novel materials with rational design of multi-component combination, which improves the electrochemical performances of the materials for supercapacitors by the synergistic effect of all individual constituents [19]. For instance, $\text{Mn}_3\text{O}_4\text{--Co}_3\text{O}_4$ [20], $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ [21], $\text{Co}_3\text{O}_4\text{--GNS}$ [22], $\text{Fe}_3\text{O}_4/\text{rGO}$ [23] and $(\text{Ni--Co})(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{Ni}$ [24] composites have been developed with improved electrochemical performance. However, the electrochemical properties of these materials need to be further improved to meet the commercial applications.

Co_3O_4 has attracted tremendous interests and has been considered as one of the promising materials for supercapacitors due to many advantages such as high redox activity, reversibility, and theoretical capacitance

(~3560 F/g) [25–27]. Until now, there have been many reports about the synthesis of Co_3O_4 for supercapacitors. CAO et al [28] prepared hollow Co_3O_4 octahedra with a specific capacitance of 192 F/g at a current density of 1 A/g. ZHANG et al [29] reported the synthesis of Co_3O_4 nanoflake array films grown on nickel foams by a hydrothermal method. This material showed a specific capacitance of 289 F/g at a current density of 2 A/g. CuO can be another promising candidate for supercapacitors because of its abundant resources, low cost, non-toxicity, and easy preparation with various shapes [14,30]. WANG et al [30] prepared CuO nanosheet arrays freely standing on nickel foams by a template-free growth method. The CuO nanosheet arrays exhibit a specific capacitance of 569 F/g at a current density of 5 mA/cm² in 6.0 mol/L KOH. PENDASHTEH et al [14] reported anchored copper oxide nanoparticles on graphene oxide nanosheets via an electrostatic coprecipitation with the specific capacitance of 245 F/g at a current density of 0.1 A/g. While the individual chemical and physical properties of Co_3O_4 or CuO materials have been extensively investigated, there has been little study on the fabrication of $\text{Co}_3\text{O}_4/\text{CuO}$ composite as a possible supercapacitor material.

Herein, we have successfully synthesized porous $\text{Co}_3\text{O}_4/\text{CuO}$ nanoplate by a hydrothermal method and the effects of the surfactants hexadecyltrimethyl ammonium bromide (CTAB) and polyvinylpyrrolidone (PVP) on the morphology and electrochemical performance of the $\text{Co}_3\text{O}_4/\text{CuO}$ nanoplate were investigated. The porous $\text{Co}_3\text{O}_4/\text{CuO}$ nanocomposite exhibits high specific capacitance, good rate performance and long cycle life, indicating that the $\text{Co}_3\text{O}_4/\text{CuO}$ nanocomposite could be promising pseudocapacitance materials for supercapacitors. The $\text{Co}_3\text{O}_4/\text{CuO}$ nanocomposite modified by CTAB has the best electrochemical performance.

2 Experimental

2.1 Preparation of samples

All reagents used in the experiments are of analytical grade, and without any further purification.

In the process, a mixture of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.399 g, 2 mmol), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.996 g, 4 mmol) and surfactant (CTAB or PVP, 0.1 g) in 60 mL deionized water was stirred for about 30 min. NaOH (0.72 g, 18 mmol) was added. The resulted mixture was stirred for another 15 min at room temperature, and then transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 373 K for 10 h. After being cooled down to room temperature naturally, the precipitates were collected by filtration, washed with

deionized water and ethanol, and dried at 333 K for 6 h under vacuum. The as-prepared precursors were calcinated at 673 K for 6 h in air. The as-prepared products modified by CTAB and PVP were labeled as $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB and $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP, respectively. Meanwhile, $\text{Co}_3\text{O}_4/\text{CuO}$ prepared without any surfactant was employed for comparison and labeled as $\text{Co}_3\text{O}_4/\text{CuO}$ -bare.

2.2 Structural characterization

The crystal structure of the as-prepared samples was analyzed by X-ray powder diffraction (XRD) (Rigaku) with Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$) at an operation voltage of 40 kV and a current of 250 mA. The morphology of the samples was studied by a Nova NanoSEM 230 field-emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) was performed on a JEM-2100F to further study the microstructure. Nitrogen adsorption-desorption experiment was carried out on a physisorption/chemisorptions analyzer (Quantachrome Nova Surface Area Analyzer). The specific surface area of the as-prepared samples was obtained using the Brunauer-Emmett-Teller (BET) equation, whereas the pore size distribution and volume were calculated using the Barrett-Joyner-Halenda (BJH) model from the desorption branch of the isotherm.

2.3 Electrochemical measurements

The electrochemical performances of the samples were investigated in a three-electrode system in 6 mol/L KOH. The Hg/HgO electrode and platinum foil were used as the reference electrode and counter electrode, respectively. A piece of nickel foam mesh coated with the samples was used as the working electrode, which is prepared as follows. A few drops of ethanol were added into the mixture of samples (85%), acetylene black (10%) and polytetrafluoroethylene (PTFE) binder (5%) to form homogeneous slurries. The slurries were coated on a nickel foam mesh, and dried at 333 K for 12 h under vacuum. The mass of active materials of working electrode is about 2 mg. Before the test, the working electrode was soaked in 6 mol/L KOH for 2 h. The cyclic voltammetry (CV) tests were carried out on a CHI 660D electrochemistry workstation. The galvanostatic charge and discharge tests were performed on a Land battery test system (Wuhan, China) in the potential range of 0–0.5 V (vs Hg/HgO). The electrochemical impedance spectroscopy (EIS) of the samples was analyzed by a PARSTAT 2273 electrochemical system (Princeton Applied Research) in the frequency range of 10^{-2} – 10^5 Hz with an AC amplitude of 5 mV in 6 mol/L KOH solution.

3 Results and discussion

3.1 Material characterization

The crystal phase and structure information of all the samples were obtained by XRD measurements. Figure 1 shows the XRD patterns of the samples prepared using different surfactants. All samples show similar XRD patterns, indicating that the surfactants will not change the phase of synthesized materials. By comparing the peak positions with the standard PDF files, it is easy to determine that all samples are composed of two phases, Co_3O_4 (JCPDS card No. 002–8158) and CuO (JCPDS card No. 001–6025). No peaks arising from possible impurities can be found in all XRD patterns, implying that the $\text{Co}_3\text{O}_4/\text{CuO}$ composites are pure. Moreover, the diffraction peaks are relatively wide, which is possibly due to the small size of the particles or the low degree of crystallinity of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites.

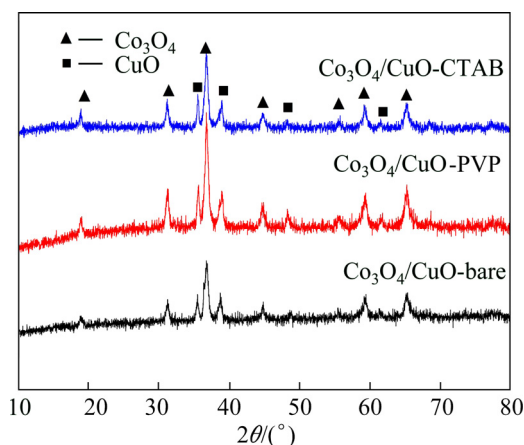


Fig. 1 Powder XRD diffraction patterns of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites

SEM was employed to investigate the surface morphologies of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites. The SEM images of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare are shown in Fig. 2. All $\text{Co}_3\text{O}_4/\text{CuO}$ composites have nanoplate morphology. As seen from Figs. 2(a) and (b), $\text{Co}_3\text{O}_4/\text{CuO}$ -bare synthesized without any surfactant displays aggregation. On the contrary, in Figs. 2(e) and (f), $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB does not exhibit aggregation and is well-dispersed. The lateral size of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB nanoplate is about 140 nm. In Figs. 2(c) and (d), $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP has a medium dispersion. It is clear that CTAB is more effective than PVP in controlling the morphology of the material, which can be attributed to the following factors [31]: CTAB is an ionic surfactant, and PVP is a nonionic surfactant. PVP and CTAB have different stabilization mechanisms, i.e., electrostatic stabilization and steric

hindrance stabilization. CTA^+ is easy to be adsorbed to the particle surface by electrostatic interaction to form electriferous films. However, PVP is adsorbed to the particle surface through hydrogen bonds to form macromolecular protective films. Though both electriferous films and macromolecular protective films can reduce aggregation, the effect of electriferous films is much stronger than that of macromolecular protective films.

TEM tests were conducted to investigate $\text{Co}_3\text{O}_4/\text{CuO}$ composites. The HRTEM image shown in Fig. 3 clearly reveals two different lattice fringes. The distances of the interplanar distance between adjacent lattice planes are about 0.252 nm and 0.242 nm, which are indexed as the $(\bar{1}11)$ plane of the CuO and the (311) plane of the Co_3O_4 , respectively, implying the successful synthesis of $\text{Co}_3\text{O}_4/\text{CuO}$ composite.

Generally, specific surface area and total pore volume play important roles in affecting the electrochemical properties of materials. Therefore, nitrogen adsorption–desorption experiment was measured to investigate the surface area and porous structure of $\text{Co}_3\text{O}_4/\text{CuO}$ composites. The N_2 adsorption–desorption isotherms of $\text{Co}_3\text{O}_4/\text{CuO}$ composites are shown in Fig. 4. The insets are the pore size distribution curves calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. All the isotherms have an obvious hysteric loop which is the characteristic of the type IV isotherm, indicating the existence of mesopores in $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites. From the insets, all the $\text{Co}_3\text{O}_4/\text{CuO}$ composites have several peaks, implying that they have different sizes of pores. Table 1 summarizes the textural parameters derived from the N_2 adsorption–desorption experiments of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites. It is obvious that $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite displays the highest specific surface area and the largest total pore volume. Thus, the CTAB is more effective in modifying the surface morphology and microstructure than PVP. The large pore volume and rich pores can ensure that enough electrolyte ions have easy access to the surface of the active materials. It is known that the redox reactions only occur in a very thin surface layer of the active materials [32], therefore, the as-prepared materials meet the basic requirements for high electrochemical performance supercapacitors.

3.2 Electrochemical properties

To explore the potential application of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites for supercapacitors, the composites were fabricated as electrodes and investigated by CV and galvanostatic charge–discharge measurements.

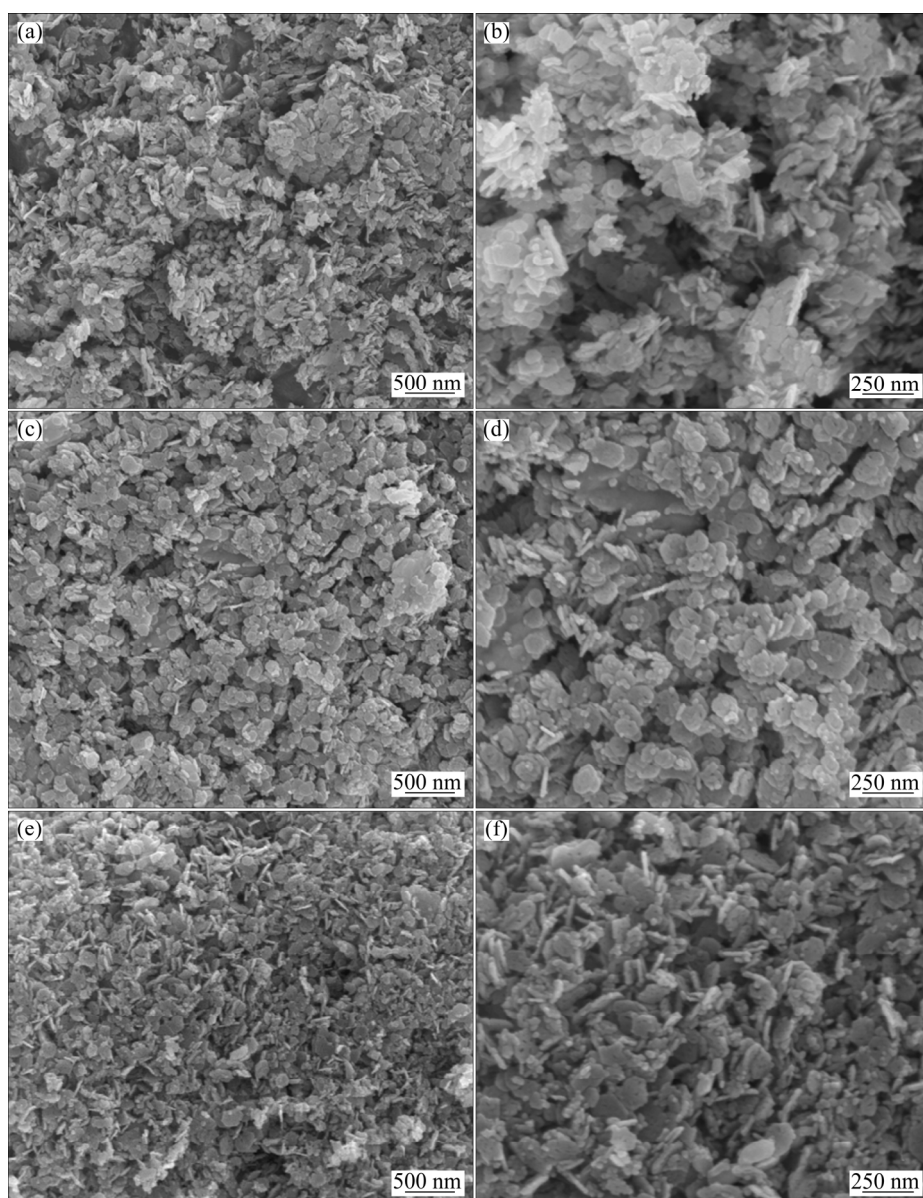


Fig. 2 Typical SEM images of $\text{Co}_3\text{O}_4/\text{CuO}$ -bare (a, b), $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP (c, d) and $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB (e, f)

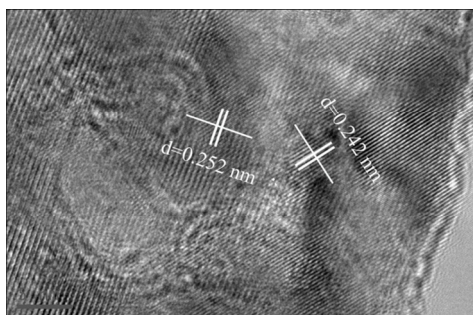
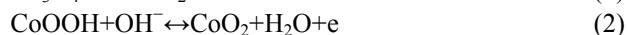


Fig. 3 TEM image of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB

Figure 5(a) shows the CVs of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites modified by different surfactants in 6 mol/L KOH solution at a scan rate of 20 mV/s within a potential range of 0–0.6 V. The obvious reduction and oxidation peaks in CVs suggest that the charge storage

of all the electrodes are mainly based on the redox mechanism. The cathodic and anodic peaks of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites have the same position, indicating that the $\text{Co}_3\text{O}_4/\text{CuO}$ composites prepared in different conditions have the same redox reaction. The peak couples correspond to the redox reactions of Co_3O_4 and CuO :



The potential difference between the anodic and cathodic peaks was used as a measure of the reversibility of the redox reaction. A smaller potential difference corresponds to a higher reversibility. From Fig. 5(a), all the $\text{Co}_3\text{O}_4/\text{CuO}$ composites have a small potential

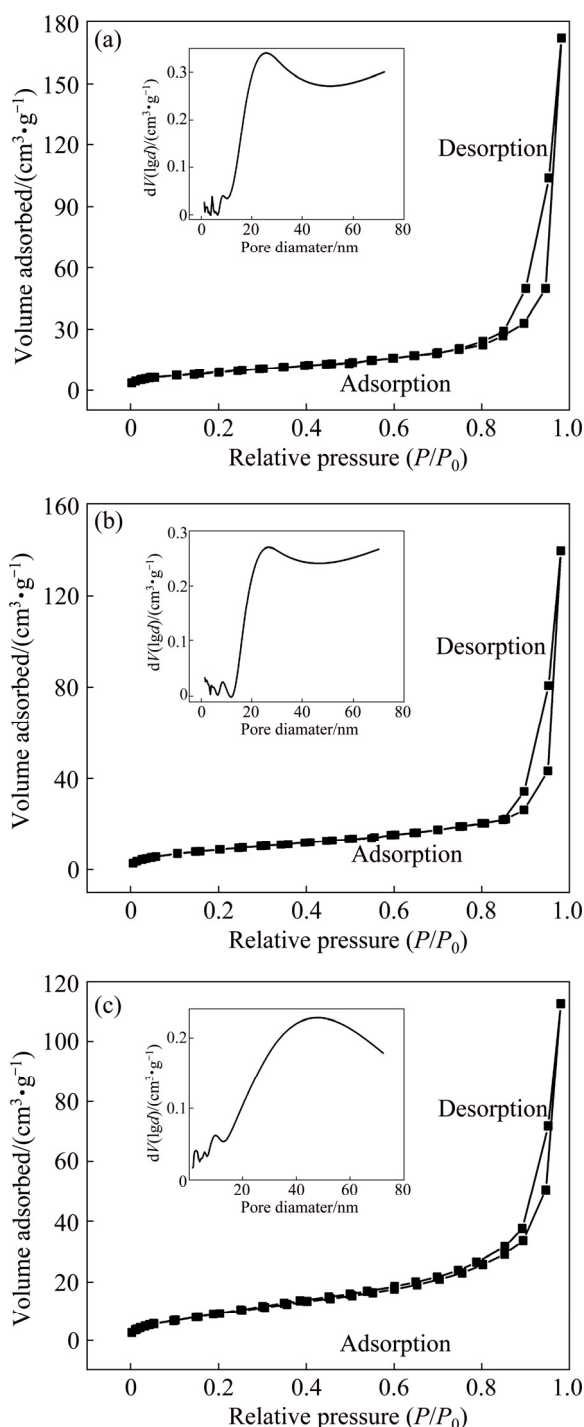


Fig. 4 Nitrogen adsorption and desorption isotherms of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites (Inset is their BJH pore size distribution curves)

Table 1 BET-specific surface area and BJH pore volume of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP, and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites

Sample	Specific surface area/($\text{m}^2\cdot\text{g}^{-1}$)	Total pore volume/($\text{cm}^3\cdot\text{g}^{-1}$)
$\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB	38.341	0.2660
$\text{Co}_3\text{O}_4/\text{CuO}$ -PVP	34.913	0.2156
$\text{Co}_3\text{O}_4/\text{CuO}$ -bare	34.401	0.1744

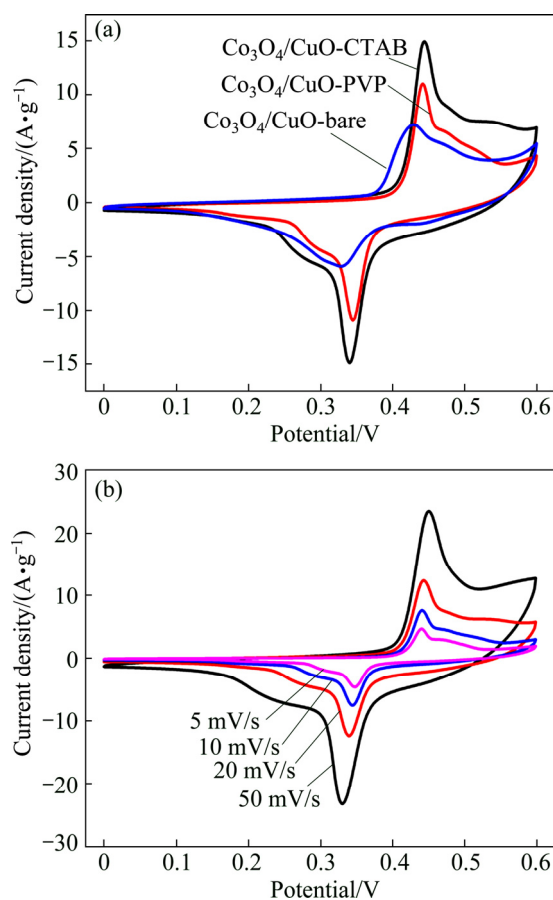


Fig. 5 Cyclic voltammograms of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composite electrodes recorded at scan rate of 20 mV/s (a) and $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite electrode recorded at various scan rates (b)

difference of about 100 mV, indicating that they have good reversibility. In addition, it is generally accepted that the specific capacitance of the materials is directly proportional to the integral area of the CV curve [33]. Evidently, the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite presents the largest specific capacitance, and the specific capacitance of $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composite is the smallest, which is deduced from the integrated area of the CV curves.

Figure 5(b) shows CV curves of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite at various scan rates from 5 to 50 mV/s within the potential window of 0 to 0.6 V (vs Hg/HgO). The anodic and cathodic peaks are symmetrical in all the CV curves, and the peak separation of the redox peaks slightly increases with the increase of the scan rate, revealing that the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite has good redox reversibility. Moreover, the shapes of these CV curves exhibit almost no obvious change as the scan rate increases from 5 to 50 mV/s, which implies excellent electron conduction, improved mass transportation, and small equivalent series resistance within the composites [34].

The galvanostatic charge and discharge tests are the most direct approach to evaluate the performance of the electrode materials for supercapacitors. Figure 6(a) shows the galvanostatic charge and discharge of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites prepared by different surfactants at a current of 1 A/g in 6 mol/L KOH solution. The discharge curves of all electrodes exhibit a plateau which is characteristic of pseudocapacitance. This is in consistent with the results of CV curves. The discharge curves show two variation ranges, one is a linear variation of the time dependence of the potential, which is controlled by an electric double-layer capacitance behavior resulting from the charge separation between the electrode and electrolyte interface. Another is a slope variation of the time dependence of the potential, which indicates a pseudo-capacitance behavior mainly due to the redox reaction on the surface or near the surface of active materials [35]. The specific capacitances can be calculated from the charge and discharge curves using the following equation [4]:

$$C_s = \frac{It}{m(\Delta\phi)} \quad (4)$$

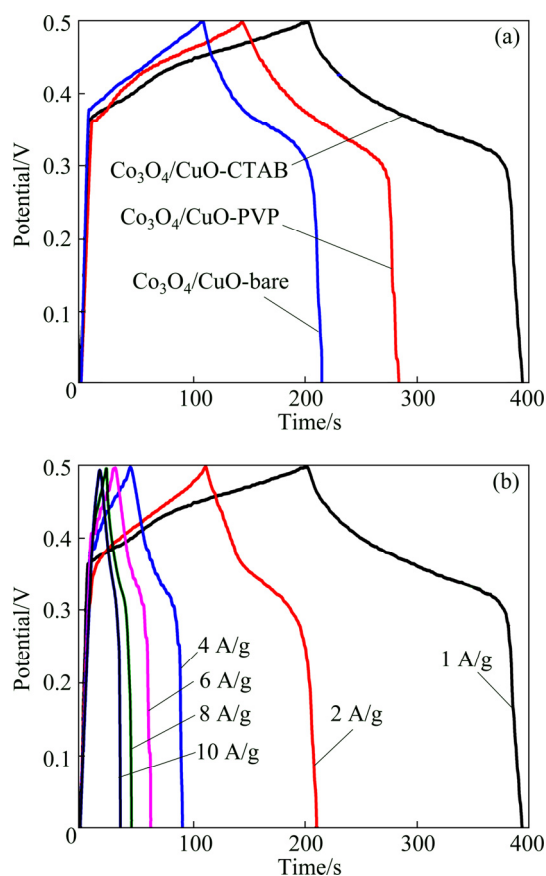


Fig. 6 Typical galvanostatic charge and discharge curves of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes recorded at current density of 1 A/g (a) and typical galvanostatic charge and discharge curves of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite electrode recorded at current densities of 1–10 A/g (b)

where C_s is the specific capacitance, $\Delta\phi$ is the potential drop during discharge process, m is the mass of the active material within the electrode, I is the discharge current, and t is the discharging time. The calculated specific capacitances are 398, 278, 210 F/g for $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes, respectively.

To further investigate the electrochemical performance of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite, galvanostatic charge and discharge tests of the composite electrode were performed at different current densities. Figure 6(b) displays the galvanostatic charge and discharge curves of the $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB at the current densities ranging from 1 to 10 A/g within the potential range of 0–0.5 V. The specific capacitances are 398, 394, 384, 372, 368, 360 F/g at the current densities of 1, 2, 4, 6, 8, 10 A/g, respectively. These values are much higher than those of $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites according to Fig. 6(b). From Fig. 7, it can be seen that all the composites electrodes have excellent rate performance. The capacitance retentions of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes at 10 A/g are 90%, 86.3% and 85.7%, respectively. It can be inferred that the excellent rate performance concerns the good dispersion, small size, high specific area and the porous structure of the composite, which can improve the active surface areas, shorten the electron and ion transport pathways, and reduce the diffusion resistance of the electrolytes.

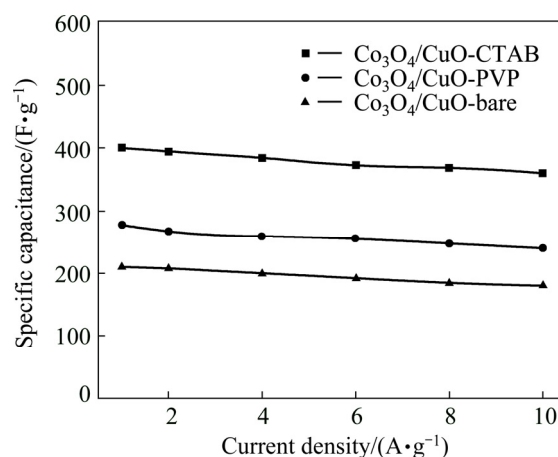


Fig. 7 Plots of specific capacitance vs current density for $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes

Cycling life tests of the $\text{Co}_3\text{O}_4/\text{CuO}$ composites electrodes were also carried out by galvanostatic charge and discharge experiment at the current of 1 A/g and the results are shown in Fig. 8. It is noticed that the specific capacitance increases rapidly at the first 100 cycles, which is probably due to an electrochemical activation of the $\text{Co}_3\text{O}_4/\text{CuO}$ composite electrode. Furthermore,

according to Fig. 8, we can know that all the $\text{Co}_3\text{O}_4/\text{CuO}$ composites electrodes prepared by different surfactants have a remarkable cycling life. This may be due to the nanoplate morphology and the combination of the CuO and the Co_3O_4 . In general, this demonstrates that the $\text{Co}_3\text{O}_4/\text{CuO}$ composite could be one of the promising candidates as electrode materials for high performance supercapacitors.

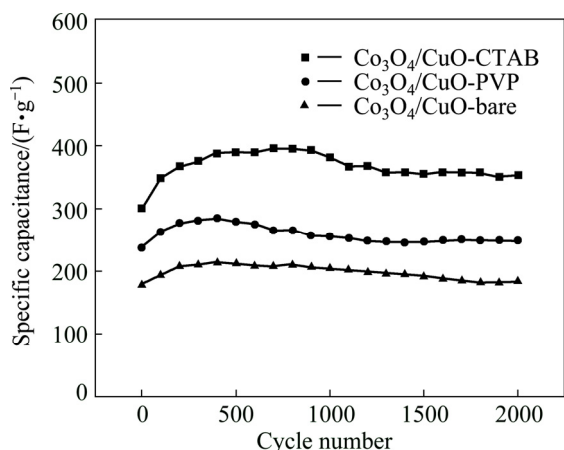


Fig. 8 Electrochemical stability tests for $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes

In order to get more information about the samples, EIS experiments were carried out in 6 mol/L KOH solution. Figure 9 displays the simulated Nyquist impedance plots and corresponding equivalent circuit. R_s represents the resistance closely related to the ionic conductivity of the electrolyte and electronic conductivity of the electrodes, R_{ct} is charge transfer resistance, CPE_1 and CPE_2 are constant-phase elements, which are denoted as the double layer capacitance and ionic diffusion process resulting in Warburg behavior in the electrode, respectively [36]. According to Table 2, we can know that the R_s and R_{ct} of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite electrode are the smallest, indicating that the

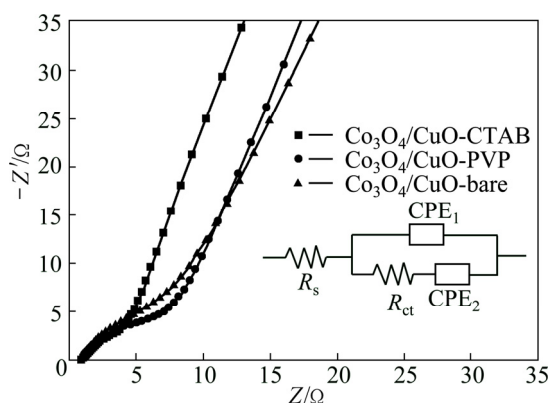


Fig. 9 Nyquist impedance plots of $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB, $\text{Co}_3\text{O}_4/\text{CuO}$ -PVP and $\text{Co}_3\text{O}_4/\text{CuO}$ -bare composites electrodes (The inset is the equivalent circuit)

$\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB composite has the highest electronic conductivity and the lowest charge transfer resistance. The result further supports that the porous structure fabricated by CTAB is more favorable to the diffusion process of ions.

Table 2 Calculated values of R_s and R_{ct} from ZSimpWin fitting of experimental impedance spectra based upon equivalent circuit

Sample	R_s/Ω	R_{ct}/Ω
$\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB	0.89	8.06
$\text{Co}_3\text{O}_4/\text{CuO}$ -PVP	0.97	9.12
$\text{Co}_3\text{O}_4/\text{CuO}$ -bare	1.09	10.91

4 Conclusions

1) The $\text{Co}_3\text{O}_4/\text{CuO}$ nanoplates were successfully synthesized by a facile hydrothermal method.

2) The surface morphology and microstructure of $\text{Co}_3\text{O}_4/\text{CuO}$ composite were modified by CTAB and PVP. However, the structure and electrochemical performance studies imply that CTAB is more optimal than PVP.

3) The $\text{Co}_3\text{O}_4/\text{CuO}$ composites modified by CTAB possess a high capacitance of 398 F/g at of 1 A/g and capacitance retention of 90% at 10 A/g. Moreover, the charge-discharge tests illustrate that the $\text{Co}_3\text{O}_4/\text{CuO}$ composite modified by CTAB has a good electrochemical stability with almost no degradation over 2000 cycles.

References

- [1] LIU Chang, LI Feng, MA Lai-peng, CHENG Hui-ming. Advanced materials for energy storage [J]. *Advanced Materials*, 2010, 22(8): E28–E62.
- [2] WANG Guo-ping, ZHANG Lei, ZHANG Jiu-jun. A review of electrode materials for electrochemical supercapacitors [J]. *Chemical Society Reviews*, 2012, 41(2): 797–828.
- [3] WEI W F, CUI X W, CHEN W X, IVEY D. Manganese oxide-based materials as electrochemical supercapacitor electrodes [J]. *Chemical Society Reviews*, 2011, 40(3): 1697–1721.
- [4] CONWAY B E. *Electrochemical supercapacitor scientific fundamentals and technological applications* [M]. New York: Kluwer Academic/Plenum Publishers, 1999.
- [5] SIMON P, GOGOTSI Y. Materials for electrochemical capacitors [J]. *Nature Materials*, 2008, 7(11): 845–854.
- [6] XIA Xin-hui, TU Jiang-ping, WANG Xue-li, GU Chang-dong, ZHAO Xin-bin. Hierarchically porous NiO film grown by chemical bath deposition via a colloidal crystal template as an electrochemical pseudocapacitor material [J]. *Journal of Materials Chemistry*, 2011, 21(3): 671–679.
- [7] LIU Jin-ping, JIANG Jian, CHENG Chuan-wei, LI Hong-xing, ZHANG Ji-xuan, GONG Hao, FAN Hong-jin. Co_3O_4 Nanowire/ MnO_2 ultrathin nanosheet core/shell arrays: A new class of high-performance pseudocapacitive materials [J]. *Advanced*

Materials, 2011, 23(18): 2076–2081.

- [8] FRACKOWIAL E, BEGUIN F. Carbon materials for the electrochemical storage of energy in capacitors [J]. Carbon, 2001, 39(6): 937–950.
- [9] DOU Yuan-yun, LUO Min, LIANG Sen, ZHANG Xue-ling, DING Xiao-yi, LIANG Bin. Flexible free-standing graphene-like film electrode for supercapacitors by electrophoretic deposition and electrochemical reduction [J]. Transactions of Nonferrous Metals Society of China, 2014, 24(5): 1425–1433.
- [10] DOU Yuan-yun, LUO Min, LIANG Sen, ZHANG Xue-ling, DING Xiao-yi, LIANG Bin. Flexible free-standing graphene-like film electrode for supercapacitors by electrophoretic deposition and electrochemical reduction [J]. Transactions of Nonferrous Metals Society of China, 2014, 24(5): 1425–1433.
- [11] WANG Ya-ping, PAN An-qiang, ZHU Qin-yu, NIE Zhi-wei, ZHANG Yi-fang, TANG Yan, LIANG Shu-quan, CAO Guo-zhong. Facile synthesis of nanorod-assembled multi-shelled Co_3O_4 hollow microspheres for high-performance supercapacitors [J]. Journal of Power Sources, 2014, 272: 107–112.
- [12] YANG Ze-heng, XU Fei-fei, ZHANG Wei-xin, MEI Zhou-sheng, PEI Bo, ZHU Xiao. Controllable preparation of multishelled NiO hollow nanospheres via layer-by-layer self-assembly for supercapacitor application [J]. Journal of Power Sources, 2014, 246: 24–31.
- [13] LIU Kai-yu, ZHANG Ying, ZHANG Wei, ZHENG He, SU Geng. Charge-discharge process of MnO_2 supercapacitor [J]. Transactions of Nonferrous Metals Society of China, 2007, 17(3): 649–653.
- [14] PENDASHTAH A, MOUSAVI M F, RAHMANIFAR M S. Fabrication of anchored copper oxide nanoparticles on graphene oxide nanosheets via an electrostatic coprecipitation and its application as supercapacitor [J]. Electrochimica Acta, 2013, 88: 347–357.
- [15] SNOOK G A, KAO P, BEST A S. Conducting-polymer-based supercapacitor devices and electrodes [J]. Journal of Power Sources, 2011, 196(1): 1–12.
- [16] LU Xiao-feng, ZHANG Wan-jin, WANG Ce, WEN T C, WEI Y. One-dimensional conducting polymer nanocomposites: Synthesis, properties and applications [J]. Progress in Polymer Science, 2011, 36(5): 671–712.
- [17] LONG Yun-ze, LI Meng-meng, GU Chang-zhi, WAN Wei-xiang, DUVAIL J L, LIU Zong-wen, FAN Zhi-yong. Recent advances in synthesis, physical properties and applications of conducting polymer nanotubes and nanofibers [J]. Progress in Polymer Science, 2011, 36(10): 1415–1442.
- [18] HUANG Ming, ZHANG Yu-xin, LI Fei, ZHANG Li-li, WEN Zhi-yu, LIU Qing. Facile synthesis of hierarchical $\text{Co}_3\text{O}_4/\text{MnO}_2$ core-shell arrays on Ni foam for asymmetric supercapacitors [J]. Journal of Power Sources, 2014, 252: 98–106.
- [19] XU Kai-bing, ZOU Ru-jia, LI Wen-yao, XUE Ya-fang, SONG Guo-sheng, LIU Qian, LIU Xi-jian, HU Jun-qing. Self-assembling hybrid $\text{NiO}/\text{Co}_3\text{O}_4$ ultrathin and mesoporous nanosheets into flower-like architectures for pseudocapacitance [J]. Journal of Materials Chemistry A, 2013, 1(32): 9107–9113.
- [20] PANG Huan, DENG Jia-wei, DU Ji-min, LI Su-juan, LI Juan, MA Ya-hui, ZHANG Jiang-shan, CHEN Jing. Porous nanocubic $\text{Mn}_2\text{O}_3/\text{Co}_3\text{O}_4$ composites and their application as electrochemical supercapacitors [J]. Dalton Transactions, 2012, 41(34), 10175–10181.
- [21] WU Hao-bin, PANG Huan, LOU Xiong-wen. Facile synthesis of mesoporous $\text{Ni}_{0.3}\text{Co}_{2.7}\text{O}_4$ hierarchical structures for high-performance supercapacitors [J]. Energy & Environmental Science, 2013, 6(12), 3619–3626.
- [22] ZHANG W F, LIU F, LI Q Q, SHOU Q L, CHENG J P, ZHANG L, J. NELSON B, ZHANG X B. Transition metal oxide and graphene nanocomposites for high-performance electrochemical capacitors [J]. Physical Chemistry Chemical Physics, 2012, 14(47): 16331–16337.
- [23] CHENG J P, SHOU Q L, WU J S, LIU F, DRAVID V P, ZHANG X B. Influence of component content on the capacitance of magnetite/reduced graphene oxide composite [J]. Journal of Electroanalytical Chemistry, 2013, 698: 1–8.
- [24] GONG Xue-fei, CHENG Ji-peng, LIU Fu, ZHANG Li, ZHANG Xiao-bin. Nickel-cobalt hydroxide microspheres electrodeposited on nickel cobaltite nanowires grown on Ni foam for high-performance pseudocapacitors [J]. Journal of Power Sources, 2014, 267: 610–616.
- [25] ZHENG Ming-bo, CAO Jian, LIAO Shu-tian, LIU Jin-song, CHEN Hui-qin, ZHAO Yu, DAI Wei-jie, JI Guang-bin, CAO Jie-ming, TAO Jie. Preparation of mesoporous Co_3O_4 nanoparticles via solid-liquid route and effects of calcination temperature and textural parameters on their electrochemical capacitive behaviors [J]. The Journal of Physical Chemistry C, 2009, 113(9): 3887–3894.
- [26] MEHER S K, RAO G R. Ultralayered Co_3O_4 for high-performance supercapacitor applications [J]. The Journal of Physical Chemistry C, 2011, 115(31): 15646–15654.
- [27] MEHER S K, RAO G R. Effect of microwave on the nanowire morphology, optical, magnetic, and pseudocapacitance behavior of Co_3O_4 [J]. The Journal of Physical Chemistry C, 2011, 115(51): 25543–25556.
- [28] CAO Y B, YUAN F L, YAO M S, BANG J H, LEE J H. A new synthetic route to hollow Co_3O_4 octahedra for supercapacitor applications [J]. Cryst Eng Comm, 2014, 16(5): 826–833.
- [29] ZHANG Y Q, LI L, SHI S J, XIONG Q Q, ZHAO X Y, WANG X L, GU C D, TU J P. Synthesis of porous Co_3O_4 nanoflake array and its temperature behavior as pseudo-capacitor electrode [J]. Journal of Power Sources, 2014, 256: 200–205.
- [30] WANG Gui-ling, HUANG Ji-chun, CHEN Shu-li, GAO Yin-yi, CAO Dian-xue. Preparation and supercapacitance of CuO nanosheet arrays grown on nickel foam [J]. Journal of Power Sources, 2011, 196(13): 5756–5760.
- [31] KONG Ling-bin, LU Chao, LIU Mao-cheng, LUO Yong-chun, KANG Long. Effect of surfactant on the morphology and capacitive performance of porous NiCo_2O_4 [J]. Journal of Solid State Electrochemistry, 2013, 17(5): 1463–1471.
- [32] CHANG Jie, SUN Jing, XU Chao-he, XU Huan, GAO Lian. Template-free approach to synthesize hierarchical porous nickel cobalt oxides for supercapacitors [J]. Nanoscale, 2012, 4(21): 6786–6791.
- [33] STOLLER M D, RUOFF R S. Best practice methods for determining an electrode material's performance for ultracapacitors [J]. Energy & Environmental Science, 2010, 3(9): 1294–1301.
- [34] YAN Jun, FAN Zhuang-jun, SUN Wei, NING Guo-qing, WEI Tong, ZHANG Qiang, ZHANG Ru-fan, ZHI Lin-jie, WEI Fei. Advanced asymmetric supercapacitors based on $\text{Ni}(\text{OH})_2/\text{graphene}$ and porous graphene electrodes with high energy density [J]. Advanced Functional Materials, 2012, 22(12): 2632–2641.
- [35] ZHAO Dan-dan, BAO Shu-juan, ZHOU Wen-jia, LI Hu-lin. Preparation of hexagonal nanoporous nickel hydroxide film and its application for electrochemical capacitor [J]. Electrochemistry Communications, 2007, 9(5): 869–874.
- [36] XU Hui, ZHUANG Jun-xia, CHEN Yong, WU Jun-xia, ZHANG Jun-long. Preparation and performance of $\text{Co}_3\text{O}_4/\text{NiO}$ composite electrode material for supercapacitors [J]. RSC Advances, 2014, 4, 15511–15517.

新型多孔 $\text{Co}_3\text{O}_4/\text{CuO}$ 纳米片的制备及其超级电容器的性能

张水蓉¹, 胡志彪², 刘开宇¹, 刘艳珍¹, 何方¹, 谢清亮¹

1. 中南大学 化学化工学院, 长沙 410083;

2. 龙岩学院 化学与材料学院, 龙岩 364012

摘 要: 通过水热法成功合成 $\text{Co}_3\text{O}_4/\text{CuO}$ 复合物, 并探索十六烷基三甲基溴化铵(CTAB)和聚乙烯吡咯烷酮(PVP)对其形貌和性能的影响。用 X 射线衍射仪(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和氮气吸附-脱附测试表征其微观结构和表面形貌。采用循环伏安、恒流充放电和交流阻抗测试等方法研究样品的电化学性能。结果表明, 多孔 $\text{Co}_3\text{O}_4/\text{CuO}$ -CTAB 纳米片具有最好的电化学性能, 在电流密度 1 A/g 下的比容量达 398 F/g , 而在 10 A/g 时其比容量仍能保持 90%。此外, 该复合物具有很好的循环稳定性, 在 2000 次循环后容量几乎没有衰减。

关键词: 氧化钴/氧化铜复合物; 十六烷基三甲基溴化铵(CTAB); 聚乙烯吡咯烷酮(PVP); 水热法; 超级电容器

(Edited by Xiang-qun LI)