Facile synthesis of porous Co_3O_4 nanoplates for supercapacitor applications

TAO GENG*, LI ZHANG, HONGYAN WANG, KEYING ZHANG and XIA ZHOU

Anhui Key Laboratory of Spin Electron and Nanomaterials, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Anhui 234000, China

Abstract. Porous tricobalt tetraoxide (Co_3O_4) nanoplates with large aspect ratio have been obtained by annealing $Co(OH)_2$ precursor nanoplates synthesized by a facile reflux method without the need for any template or surfactant. After the heat treatment, the as-obtained phase-pure Co_3O_4 nanoplates with a well-retained structure were applied as the electrode material for supercapacitors, and the sample exhibits excellent performance with a high specific capacitance of 225 F g^{-1} after 2000 charge–discharge cycles at 2 A g^{-1}, corresponding to a retention of 97% of the initial capacitance.

Keywords. Co_3O_4 nanoplates; $Co(OH)_2$ nanoplates; reflux; supercapacitors.

1. Introduction

In recent years, energy problems have received increasing attention and triggering tremendous efforts for energy storage and conversion. Supercapacitors are chosen as ideal energy storage systems. As an important magnetic p-type semiconductor, tricobalt tetraoxide (Co_3O_4) has attracted enormous research interest because of its unique energy storage,[1–4] catalysis,[5,6] sensors and other properties.[7–9] For high-performance supercapacitors, it is critical to possess a sufficiently large electroactive surface for the Faradic redox reaction and for enhancing the kinetics of ion and electron transport on the electrodes and the electrode–electrolyte interface. To achieve such requirements, various methods have been used for the preparation of nanoscale Co_3O_4 with diverse shapes including nanospheres,[10] nanowires[11–14] and nanobelts.[15] Some previous reports have demonstrated that Co_3O_4 nanowires can be synthesized by the hydrothermal method to precursor nanowires. After the heat treatment, the obtained Co_3O_4 nanowires exhibit excellent performance with a high specific capacitance of 240 F g^{-1}.[12] Although manifold Co_3O_4 nanostructures have been reported to be selectively synthesized, it still remains a challenge for different morphologies by changing experimental conditions, especially in a facile and environment-friendly way. Many efforts have been devoted into seeking for alternatively facile and efficient approaches to obtaining high-performance Co_3O_4 nanomaterials.

In this work, a facile reflux method to synthesize mono-dispersed $Co(OH)_2$ nanoplates and their transformation to Co_3O_4 nanoplates without using any template or surfactants was designed. Cobalt acetate tetrahydrate ($Co(CH_3COO)_2 \cdot 4H_2O$) and sodium carbonate ($Na_2CO_3$) were used as the reactants, and deionized water–ethylene glycol was used as the media. The intermediate compound, cobalt hydroxide ($Co(OH)_2$), is obtained after reflux. These $Co(OH)_2$ nanoplates are subsequently converted into Co_3O_4 nanoplates by annealing in air without causing any substantial changes in the morphology. When the Co_3O_4 nanoplates are applied for supercapacitors, they deliver a very high specific capacitance of 225 F g^{-1} after 2000 charge–discharge cycles, corresponding to an outstanding cyclic retention of 97%.

2. Experimental

2.1 *Materials' preparation*

The precursor $Co(OH)_2$ nanoplates are synthesized by a facile reflux method. All reagents and chemicals were analytically pure, bought from the Shanghai Chemical Company and used as-received without further purification. In a typical preparation process, 0.5 g $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved in 40 ml of a mixture containing 30 ml of deionized water and 10 ml of ethylene glycol. After stirring for about 10 min, a transparent solution was obtained. Then, 10 ml of aqueous solution of 20 mmol of Na_2CO_3 was added dropwise into the above solution, with vigorous magnetic stirring, to form a homogeneous solution. The resulting solution was subjected to refluxing at a fixed temperature of 120°C for 12 h. The heat treatments resulted in the formation of fluffy light pink colour

*Author for correspondence (szxygt@163.com)

solid precipitates. After autocooling the reaction mixtures to room temperature, the products were separated by centrifugation at 7000 rpm, with repeated washing with deionized water and ethanol for several times by centrifugation. Then the materials were dried in a vacuum oven at 60°C overnight. Finally, the samples were calcined at 300°C for 2 h at a ramping rate of 5°C min^{-1} to transform into Co_3O_4.

2.2 *Materials' characterization*

The chemical composition of the samples was determined by X-ray powder diffraction (XRD), Shimadzu XRD-6000 X-ray diffractometer equipped with CuKα radiation ($\lambda = 0.154060$ nm), employing a scanning rate of 0.02° s^{-1}. Field scanning electron microscopy (FESEM) images of the product were obtained on Hitachi S-4800 field-emission scanning electron microscope, employing the accelerating voltage of 5 and 15 kV, respectively. Transmission electron microscopy (TEM) images of the product were carried out on an FEI Tecnai G^{20} high-resolution transmission electron microscope (HRTEM), employing an accelerating voltage of 200 kV.

2.3 *Electrochemical measurements*

The electrochemical measurements were performed with CHI 440A electrochemical analyzer (Chen Hua Instruments Co. Ltd., Shanghai, China) in a conventional three-electrode cell. The working electrode was prepared by mixing 80 wt% of the synthesized Co_3O_4, 15 wt% of acetylene black and 5 wt% of binder (polyvinylidene difluoride, PVDF, Aldrich). This mixture was then pressed onto the nickel foam electrode (1 cm^2) and dried at 60°C overnight. The electrolyte used was a 2 M KOH aqueous solution. Cyclic voltammetry (CV) and chronopotentiometry

measurements were carried out in a three-electrode cell with a Pt foil serving as the counter electrode and a Hg/HgO as the reference electrode.

3. Results and discussion

XRD patterns of the precursor sample were obtained, which revealed the phase of the precursor sample as shown in figure 1a. All the identified peaks can be assigned to pure hexagonal phase $Co(OH)_2$ (JCPDS card number 74-1057). The absence of peaks due to other phases indicates the high purity of the synthesized material. The very high peak intensity suggests that the material is well crystallized. The XRD pattern of figure 1b confirms that the heat-treated sample contains only pure cubic phase Co_3O_4 (JCPDS card number 74-1656). This indicates the complete transformation of $Co(OH)_2$ into the Co_3O_4 phase. The reactions in the precursor could be described as follows

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow,$$

$$Co(CH_3COO)_2 + 2NaOH \rightarrow$$
$$Co(OH)_2\downarrow + 2CH_3COONa.$$
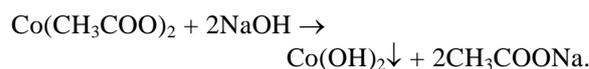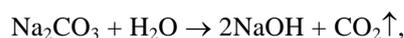
FESEM images of $Co(OH)_2$ are shown in figure 2a and b, from which petaloid microstructures with a relatively smooth surface and $Co(OH)_2$ nanoplates with sizes in the order of approximately 8 μm can be observed. FESEM images of Co_3O_4 are shown in figure 2(c and d). The FESEM image indicates that nanoplates have rough and porous surfaces consisting of many primary nanoparticles, and nanoplates with a thickness of about 100 nm. FESEM analysis confirms successful thermal conversion to Co_3O_4 without substantial change in morphology.

For better insights into the dimensionality of the Co_3O_4 nanoplates morphologies, TEM is used, and the respective micrographs are shown in figure 3. TEM shows that
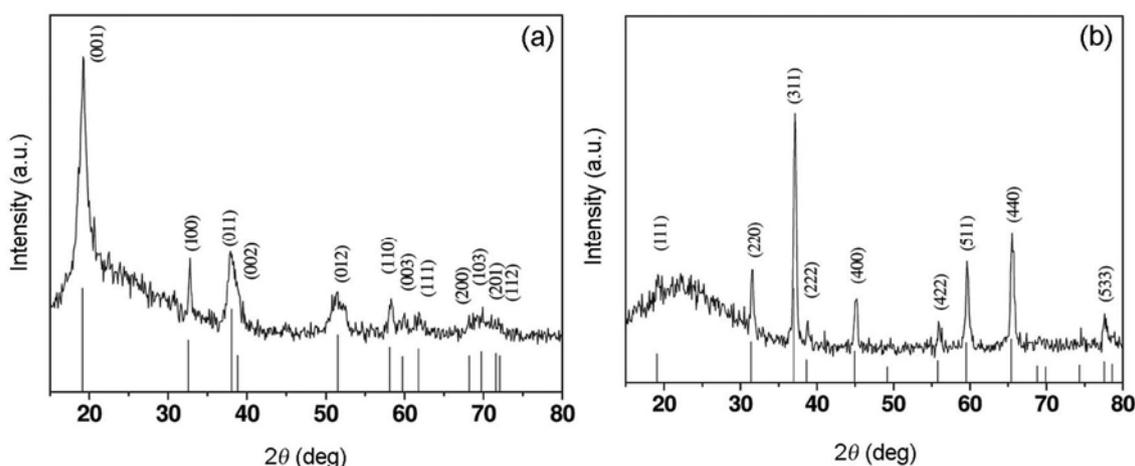

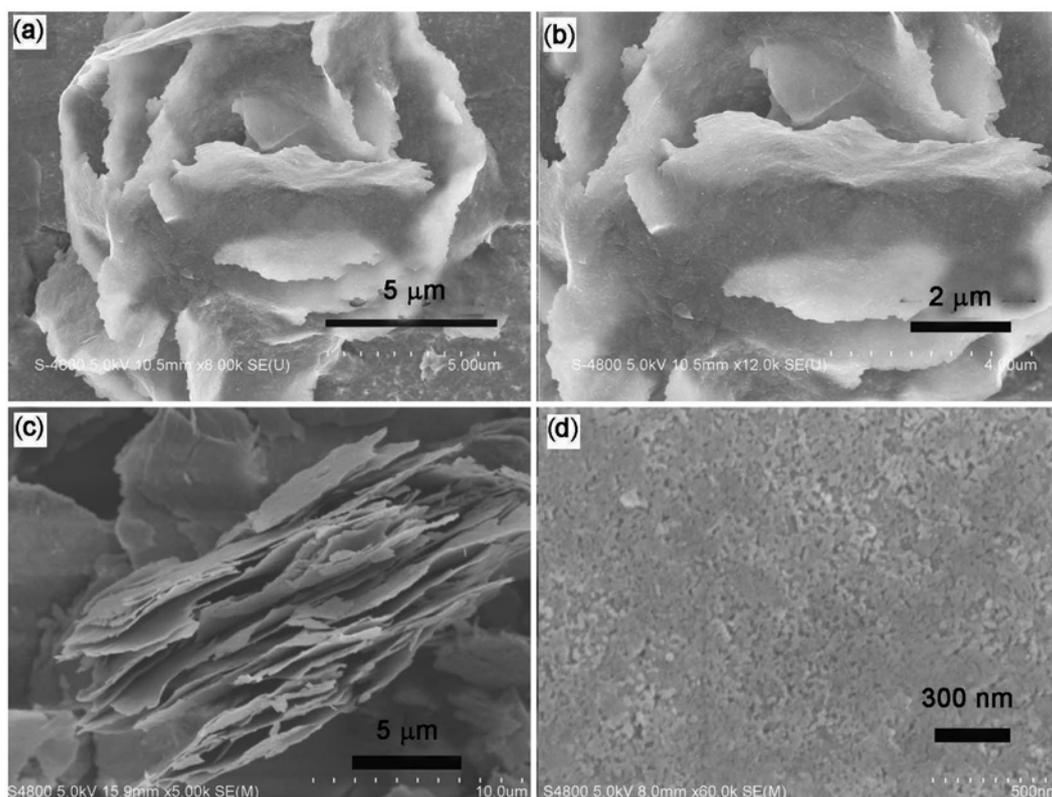**Figure 1.** XRD patterns of (**a**) $Co(OH)_2$ nanoplates and (**b**) Co_3O_4 nanoplates.

Figure 2. FESEM patterns of (**a** and **b**) Co(OH)$_2$ nanoplates and (**c** and **d**) Co$_3$O$_4$ nanoplates.
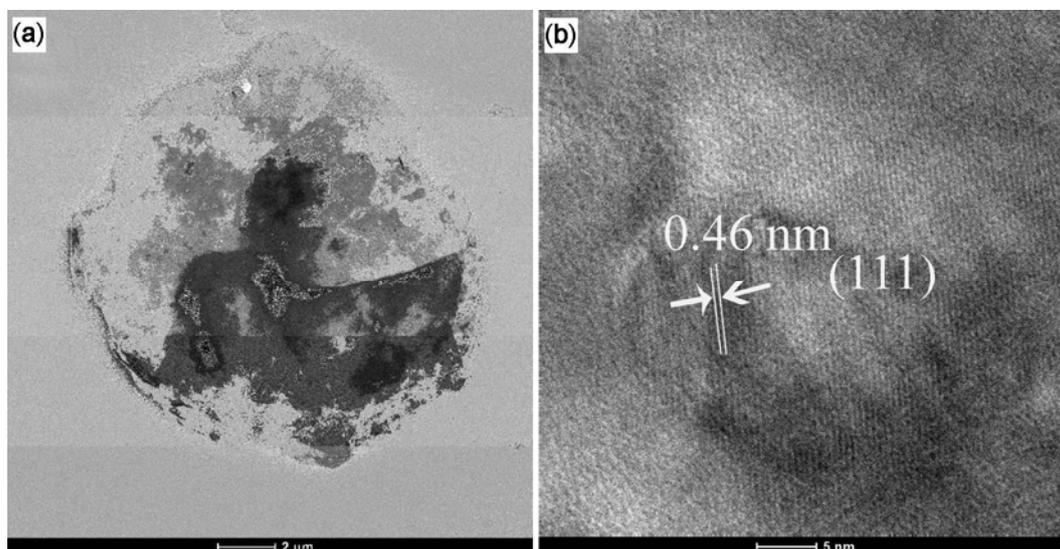

Figure 3. TEM patterns of (**a** and **b**) Co$_3$O$_4$ nanoplates.

the Co$_3$O$_4$ nanoplates appear as dark spots that are arranged randomly to form the nanoplate structures. The HRTEM image (figure 3b) shows some visible lattice fringes with an interplanar distance of 0.46 nm, corresponding to the (111) plane of Co$_3$O$_4$.

Thus, the electrochemical properties of the as-prepared Co$_3$O$_4$ nanoplates as the electrode material for superca-

pacitors were further studied. Cyclic voltammogram (CV) was conducted in a 2 M KOH aqueous electrolyte between 0 and 0.6 V (*vs.* Hg/HgO). The representative CV curves at various scan rates of 2, 5, 10, 20 and 50 mV s^{-1} are shown in figure 4a. A distinct pair of current peaks can be clearly identified during the cathodic and anodic sweeps. At a low scan rate of 5 mV s^{-1}, one current peak
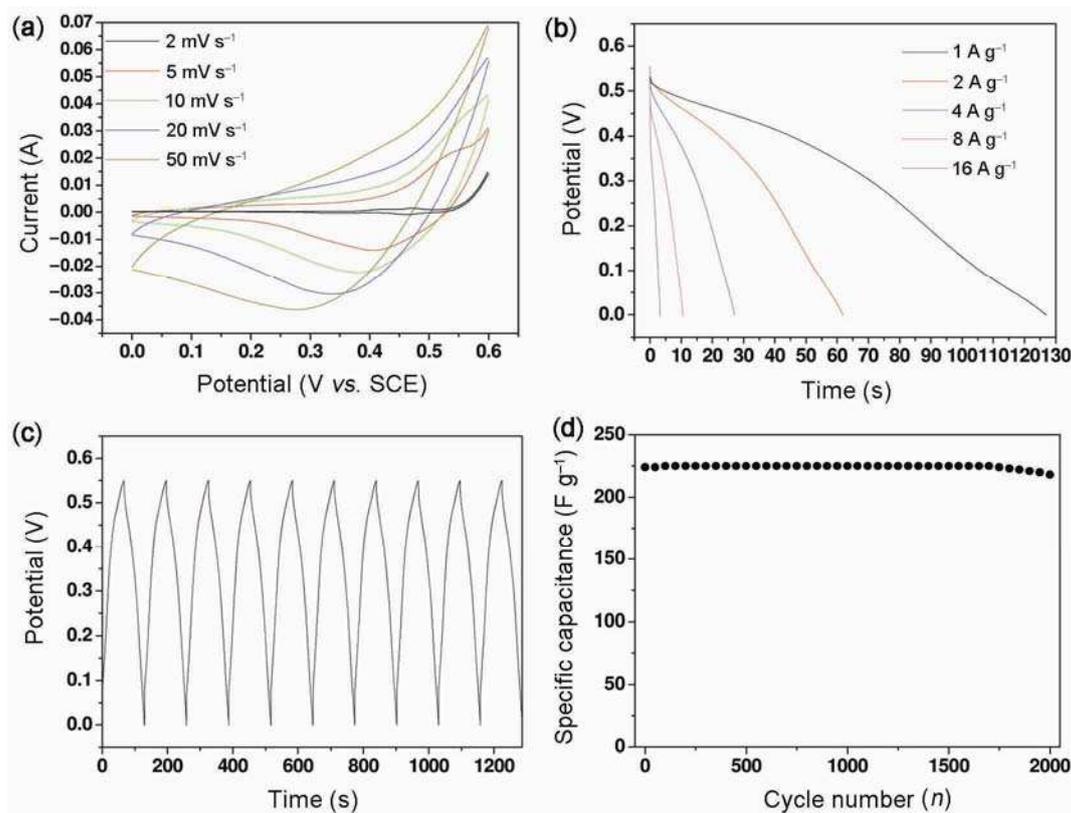
Figure 4. Electrochemical characterization of the Co_3O_4 nanoplates' electrodes measured in 2 M KOH solution. (**a**) CV curves at scan rates of 2, 5, 10, 20 and 50 mV s^{-1}. (**b**) Galvanostatic discharge curves at different current densities. (**c**) Galvanostatic charge and discharge voltage profiles at a current density of 2 A g^{-1}. (**d**) Cycling performance at a current density of 2 A g^{-1}.

can be clearly identified at 0.42 V during the cathodic sweep, but one broad oxidation peak at 0.53 V is observed during the anodic sweep. It can be attributed to the following reversible redox reaction[16]

$$Co_3O_4 + OH^{-1} + H_2O \leftrightarrow 3CoOOH + e^-, \quad (1)$$

$$CoOOH + OH^{-1} \leftrightarrow CoO_2 + H_2O + e^-. \quad (2)$$
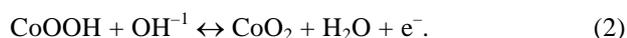
The specific capacitances of the Co_3O_4 electrodes were obtained by constant current charge–discharge tests in the potential range between 0 and 0.55 V. Figure 4b shows the constant current discharge curves of the as-prepared Co_3O_4 nanoplates, which means that the Co_3O_4 nanoplate electrodes have excellent electrochemical capability. The specific capacitance can also be calculated based on the following equation[16]

$$C_m = I \times \Delta t/(\Delta V \times m),$$

where C_m (F g^{-1}) is the specific capacitance, I (A) the applied current, Δt (s) the time taken during discharge, ΔV (V) the voltage window, and m (g) the mass of the active material. Therefore, the specific capacitance can be calculated to be 231, 225, 210, 175 and 126 F g^{-1} at the discharge current densities of 1, 2, 4, 8 and 16 A g^{-1}. Figure 4c illustrates the charge–discharge voltage profiles

of the sample at a discharge current density of 2 A g^{-1} for the first 10 cycles, and clearly a Coulombic efficiency of nearly 100% can be reached. Figure 4d shows the SC variation for Co_3O_4 nanoplate electrodes of cycle number at a current density of 2 A g^{-1}. It is obvious that the sample can deliver a high specific capacitance of 218 F g^{-1} at the end of 2000 charge–discharge cycles. This corresponds to a cyclic retention of 97%, reveals an excellent electrochemical stability of Co_3O_4 nanoplates electrode materials.

4. Conclusions

In summary, Co_3O_4 nanoplates have been synthesized by a facile reflux process and subsequent thermal decomposition at atmosphere. This method uses $Co(CH_3COO)_2 \cdot 4H_2O$ as the precursor in a deionized water–ethylene glycol mixed solvent with Na_2CO_3 as additive. The as-synthesized $Co(OH)_2$ nanoplates can be facilely converted into phase-pure Co_3O_4 nanoplates via thermal annealing. Electrochemical studies on the Co_3O_4 nanoplate samples show high rate capability and good capacity retention of ~97% after 2000 continuous charge–discharge cycles. These encouraging results confirm that properly tailored

Co$_3$O$_4$ nanoplates can serve as electrode materials for high-performance supercapacitors.

References

1. Lu Q, Chen J G and Xiao J Q 2013 *Angew. Chem. Int. Ed.* **52** 2
2. Chen J S, Zhu T, Hu Q H, Gao J J, Su F B, Qiao S Z and Lou X W 2010 *ACS Appl. Mater. Interfaces* **2** 3628
3. Larcher D, Sudant G, Leriche J B, Chabre Y and Tarascon J M 2002 *J. Electrochem. Soc.* **149** A234
4. Meher S K and Rao G R 2011 *J. Phys. Chem. C* **115** 15646
5. Zhang Y, Rosen J, Hutchings G S and Jiao F 2014 *Catal. Today* **225** 171
6. Bai B Y and Li J H 2014 *ACS Catal.* **4** 2753
7. Lou X W, Deng D, Lee J Y and Archer L A 2008 *J. Mater. Chem.* **18** 4397
8. Li Y G, Tan B and Wu Y Y 2008 *Nano Lett.* **8** 265
9. Hu L H, Peng Q and Li Y D 2008 *J. Am. Chem. Soc.* **130** 16136
10. Ge D H, Geng H B, Wang J Q, Zheng J W, Pan Y, Cao X Q and Gu H W 2014 *Nanoscale* **6** 9689
11. Yang L, Cheng S, Ding Y, Zhu X, Wang Z L and Liu M 2012 *Nano Lett.* **12** 321
12. Wang B, Zhu T, Wu H B, Xu R, Chen J S and Lou X W 2012 *Nanoscale* **4** 2145
13. Xia X H, Tu J P, Zhang Y Q, Mai Y J, Wang X L, Gu C D and Zhao X B 2012 *RSC Adv.* **2** 1835
14. Rakhi R B, Chen W, Cha D and Alshareef H N 2012 *Nano Lett.* **12** 2559
15. Wang Q, Xia Y P, Jiang C L and Bang J H 2014 *CrystEngComm* **16** 9721
16. Cao Y B, Yuan F L, Yao M S, Bang J H and Lee J H 2014 *CrystEngComm* **16** 826