Journal of Alloys and Compounds 471 (2009) 268–271

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Facile synthesis, characterization and electrochemical properties of cuspate deltoid CoO crystallites

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A R T I C L E I N F O

Article history:
Received 3 October 2007
Received in revised form 17 March 2008
Accepted 20 March 2008
Available online 2 May 2008

PACS:
81.16.Be
81.07.Vb
75.20.En
81.20.Fw

Keywords:
CoO
Electrochemical properties
Capacitance

A B S T R A C T

Cuspate deltoid cobaltous oxide (CoO) crystallites with an average grain size of 3 μm were obtained via developing the Co_3O_4 nanoplatelets under the KCl/NaCl flux atmosphere. The as-synthesized products were characterized by powder X-ray diffraction, transmission electron microscopy, field-emission scanning electron microscope and selected area electron diffraction. The electrochemical properties of the products were investigated by an Electrochemical Workstation device at room temperature. It has been found that the final prepared cubic CoO crystallites are of uniform cuspate deltoid morphology. The results of electrochemical tests indicate that the CoO shows acceptable capacitive behavior with specific capacitance about 88 F/g.

1. Introduction

As one kind of transition-metal monoxides, cobaltous oxide (CoO) has attracted much attention due to its interesting and distinctive structures and properties [1–5], and thus has been widely used for lithium-ion battery, cemented carbide, catalyst and many electronic components [6–8]. Up to the present, considerable researches have been devoted to study the preparation methods of new shaped and structured CoO. Common methods for preparing the CoO powders include wet chemical process, combustion of metal cobalt in air or vapor, and heating the hydroxide, carbonate or oxalate of cobalt in isolated air at high temperature. For instance, decomposition of cobalt acetate tetrahydrate in argon to produce the rocksalt CoO was studied with time resolved neutron diffraction and thermo gravimetric analysis [9]. CoO in the zinc blende structure was prepared by decomposing Co acetate in a nitrogen atmosphere [10]. Risbud et al. [11] used the thermolytic decomposition of $Co(acac)_2$ in refluxing benzyl ether to obtain CoO with fcc-Co phase while decomposition of $Co(acac)_3$ (acac = acetylacetonate) in oleylamine was also applied to synthesize wurtzite CoO [12]. Moreover, different CoO nanocrystals, such as nanoparticles [13–16], nanorod [17], nanoplatelet [18] have also been reported. However, to our best knowledge, there is no report on the preparation of pure cuspate deltoid CoO crystallites by decomposition of Co_3O_4 under molten salt atmosphere.

The possibility of CoO being a candidate for capacitor application was explored by Lin et al. [19], who prepared cobalt oxide xerogels using a sol–gel technique, followed by a heating step to different temperatures. The materials exhibit excellent cycle life with no significant change in the cyclic voltammogram (CV). In this work, we report the process of preparing CoO crystallites with new morphology by means of developing Co_3O_4 nanoplatelets in the molten salt, the capacitance of the prepared product was calculated and insight was gained into the capacitance capacity of the sample. Meanwhile, the factors affecting the growth morphology of the CoO crystallites were also discussed, in order to enrich the research of crystallite growth theory in molten salt.

2. Experimental

All chemical reagents were AnalaR (AR) grade and used without further purification. In a typical experiment, the procedure employed for preparing Co_3O_4 precursor is as follows: 8.73 g $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water to form a 30 mL solution ($[Co^{2+}] = 1.0$ mol/L), precipitate immediately appeared as soon as excessive

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doi:10.1016/j.jallcom.2008.03.074

5 M NaOH solution was slowly added into the $Co(NO_3)_2$ solution, the pH value was then modulated between 12 and 14 under constant stirring about 30 min, finally the mixed solution together with 10 mL distilled water were transferred to a Teflon-lined autoclave with about 50 mL capacity. The autoclave was sealed and maintained at 140 °C for 12 h and then cooled to room temperature naturally. The obtained Co_3O_4 precipitate was filtered off, washed with absolute ethanol and distilled water several times, and then dried in a vacuum at 60 °C for 4 h. For the preparation of CoO crystallites, the above-prepared Co_3O_4 precursor (1.0 g) was mixed with NaCl (2.0 g) and KCl (2.0 g) in an agate mortar, the mixture was then ground for several minutes into fine powders. The mixed sample was heated in an alumina crucible to 1000 °C and kept at that temperature for 3 h in the air atmosphere. The heating rate of the muffle furnace was maintained at 3 °C/min. Then the heat-treated sample was cooled gradually to room temperature, washed several times with distilled water in order to remove the NaCl/KCl flux, and finally filtered, dried in an oven at 90 °C for 3 h.

The obtained CoO powders were used to fabricate the electrode of electrochemical capacitor according to the previous report [20]. The electrode was prepared by mixing 80 wt% active CoO powders material, 15 wt% acetylene black and 5 wt% polyvinylidene fluoride (PVDF) as binder before pressed onto nickel grid (1.2×10^7 Pa) that serves as a current collector (surface is 1 cm^2).

The power X-ray diffraction (XRD) patterns were acquired in a 2θ range from 10° to 100° on a Bruker D8-ADVANCE X-ray powder diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å) at a scanning rate of 0.02° s^{-1}. The scanning electron microscopy (SEM) images of the prepared product were obtained on a LEO1530VP field-emission (FE) scanning electron microscope. Prior to the measurements, the sample was coated with gold for 3 min in an Anatech hummer 6.2 sputtering system operating at 40 mTorr. The transmission electron microscopic (TEM) images, the energy dispersive X-ray analyzer (EDX), and the selected-area electron diffraction (SAED) patterns of the sample were recorded using a TECNAI G2 20 S-TWIN, electron microscope, at an acceleration voltage of 200 kV. The sample was prepared by dispersing the calcined material in water at room temperature. A few drops of this dispersion were placed on a holey carbon-coated copper mesh and dried at room temperature. Electrochemical characterization was carried out in a conventional three-electrode electrochemical cell containing 2 M KOH aqueous solution as electrolyte. The freshly prepared CoO film on Ni substrate was used as the working electrode, a platinum foil (area 1 cm^2) was used as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The cyclic voltammetry and galvanostatic charge/discharge measurements were performed using a CHI660 model Electrochemical Workstation at room temperature.

3. Results and discussion

The typical XRD pattern of the Co_3O_4 precursor synthesized with hydrothermal route is shown in Fig. 1(a). The diffraction peaks presented identify the sample as typical cubic Co_3O_4 [$a = 8.094$ Å, space group: $Fd3m$ (2 2 7)], while no obvious peaks corresponding to other cobalt oxides are detected, indicating the high purity of the precursor. The well-resolved sharp diffraction peaks reveal the good crystallization of the Co_3O_4 precursor. Fig. 1(b) shows the XRD pattern of CoO crystallites sample prepared by developing Co_3O_4 precursor in KCl/NaCl flux at 1000 °C for 3 h. The well-resolved sharp diffraction peaks assigned to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes can be indexed to a typical cubic rock salt CoO phase (space group: $Fm3hm$), in good accordance with the results reported in the literature [21].

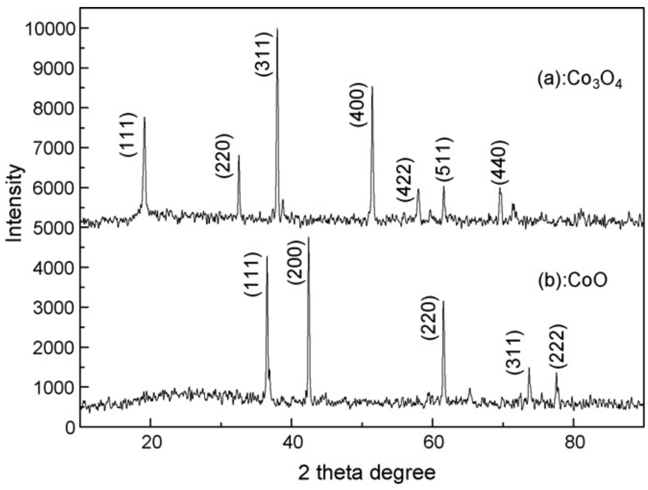

Fig. 1. XRD patterns of (a) the as-prepared Co_3O_4 precursor and (b) final developed CoO crystallites.

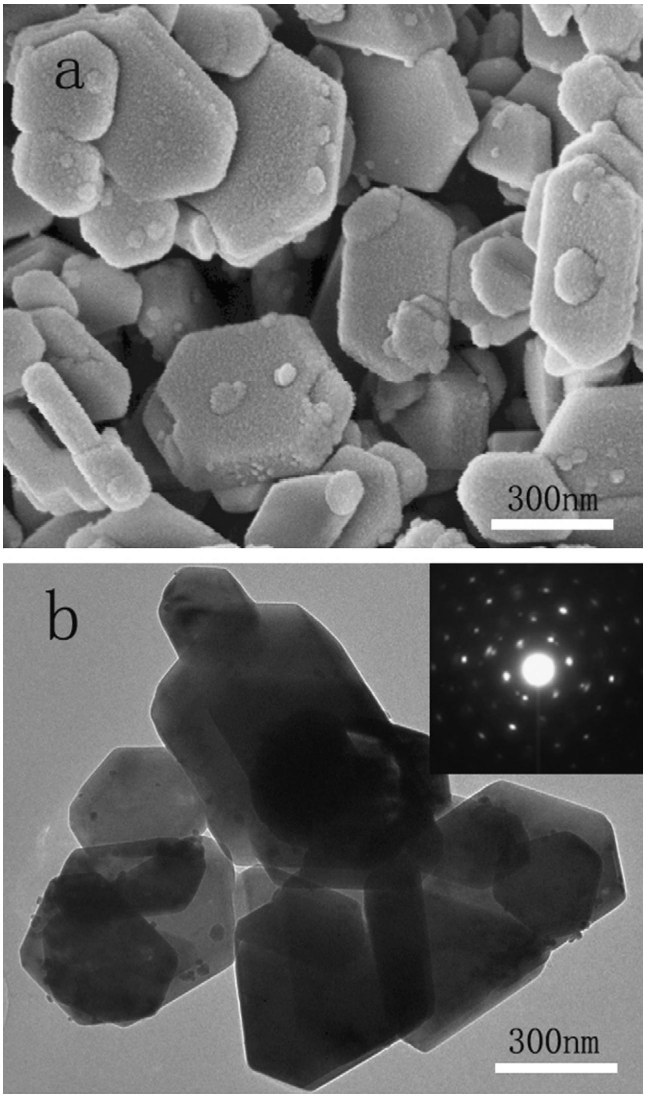

Fig. 2. FE-SEM image (a) and TEM image (b) of the as-prepared Co_3O_4 precursor. Inset is the SAED pattern, showing single crystal property for the product and being indexed onto the corresponding oxide crystal structure.

The morphology and microstructure of the obtained Co_3O_4 precursor can be observed in FE-SEM and TEM images. Fig. 2a shows FE-SEM image of the precursor obtained using hydrothermal synthesis route at 140 °C for 12 h. It can be seen that the precursor displays wafery sheets with an average thickness of ∼30 nm and diameter up to about 400 nm. TEM measurement of the Co_3O_4 precursor was performed as shown in Fig. 2b. The lamellar morphology observed is consistent with the results presented in the FE-SEM image. SAED pattern of the Co_3O_4 powders was obtained by focusing the electron bean on an individual crystal, typical single crystal pattern can be seen in the inset of Fig. 2b.

Fig. 3a shows typical FE-SEM image of the cubic CoO samples, it can be seen that nearly all of the growth planes of the crystallites display equilateral triangle with cuspate morphology, and crystal stocks with an average size about 3 μm are of the main crystal shape for the collision and connected growth of the crystallites in molten salt atmosphere. The partial magnified image with higher