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Synthesis of Single-Crystalline Octahedral Co3O4 with Solid-State Thermal Decomposition

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Abstract

In this paper, single crystalline octahedral Co_3O_4 with dimensions about 100–500 nm and smooth surface has been prepared by solid-state thermal decomposition of cobalt(II) Schiff base complex $Co((3,4\text{-MeO-ba})_2en)Cl_2$ as new precursor at 450ºC under air atmosphere for 3.5 h. Surface morphology of the products were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: *Octahedral, Schiff base, Co_3O_4, Thermal decomposition.*

Introduction

Cobalt oxide nanocrystals are important for various applications and properties such as catalyst [1], supercapacitor materials [2-4], optical and magnetic properties [5-7] and etc [8-10]. Five different oxidation states formed for cobalt oxide, out of which, Co_3O_4 and CoO are stable [11]. The preparation of Co_3O_4 nanoparticles by thermal decomposition of complexes becomes increasingly important due to easy control of particle size and purity [12-16]. Among the various transition metal oxides, cobalt oxide (Co_3O_4), a p-type semiconductor, has attracted considerable interest in recent years owing to its broad application and properties [1-11]. Until now, various nanostructures of Co_3O_4 such as nanowires, nanorods, nanoparticles, nanocubes and etc have been prepared by using different synthesis methods [12-21]. The controllable synthesis of single crystalline octahedral structure of transition metal complexes is still much needed [22-24]. Recently, X. Wang and co-workers synthesized octahedral cages Co_3O_4 by the carbon-assisted carbothermal method [22].

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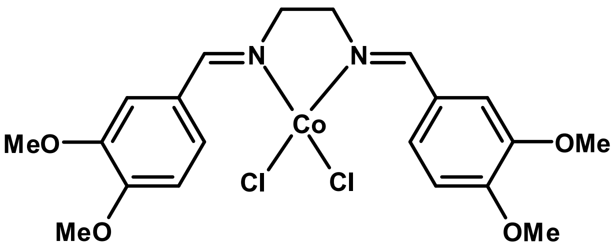
This paper reports the single crystalline Co3O4 crystals with well-defined octahedral structure were synthesized from the cobalt (II) Schiff base complex Co((3,4-MeO-ba)$_2$en)Cl$_2$ (Scheme 1) by using a solid-state thermal decomposition method. This method is simple, low-cost, green and reproducible process for the preparation of other transition metal complexes.



Scheme 1. Chemical structure of Co(II) Schiff base complex Co((3,4-MeO-ba)$_2$en)Cl$_2$.

Experimental

Materials and characterization

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM.

Synthesis of Co((3,4-MeO-ba)$_2$en)Cl$_2$

A methanolic solution of CoCl$_2$•6H$_2$O (0.01 mol in 2 mL) was added to stirred solution of (0.01 mol) (3,4-MeO-ba)$_2$en in methanol (15 mL). The mixture was stirred at room temperature for 1 h. The green solid was obtained after the solvent was evaporated slowly for several days at room temperature, then the products were collected by filtration, and dried in vacuum. FT-IR (KBr pellet, cm^{-1}): 1625 (C=N).

Preparation of Octahedral CO$_3$O$_4$

The cobalt(II) Schiff base complex Co((3,4-MeO-ba)$_2$en)Cl$_2$ was loaded in to a crucible and then was placed in oven and heated at a rate of 10°C/min in air. Single crystalline octahedral Co3O4 with dimensions about 100–500 nm were synthesized at 450 °C after 3.5 h, washed with methanol and dried at room temperature. The synthesized were characterized by FT-IR and SEM.

Results and Discussion

Figure 1 shows FT-IR spectra of single crystalline octahedral Co3O4 were formed via solid-state thermal decomposition of Co((3,4-MeO-ba)$_2$en)Cl$_2$ at 450C°. As shown in Figure 1, two peaks observed at 660 (is Co^{2+} and is tetrahedrally coordinated) and 565 cm^{-1} (is Co^{3+} and is octahedrally coordinated), are characteristic of the Co-O band vibrations which confirm the spinel structure of Co_3O_4 [1,13-16]. Existence of free precursor is ruled out due to the absence of stretching vibrations of CH, C=N and other groups of the ligand.

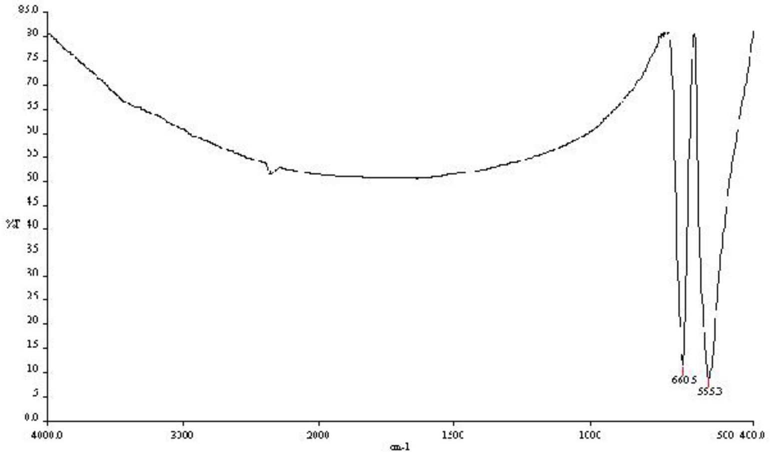


Figure 1. FT-IR spectrum of octahedral Co_3O_4.

Figure 2 shows the XRD patterns for the CO_3O_4 nanoparticles obtained from solid-state thermal decomposition of Co((3,4-MeO-ba)$_2$en)Cl_2. All of the diffraction peaks can be clearly indexed to the monoclinic structured CO_3O_4. No other impurities were detected by XRD analysis, indicating the high phase purity of the CO_3O_4 nanoparticles [22-24].

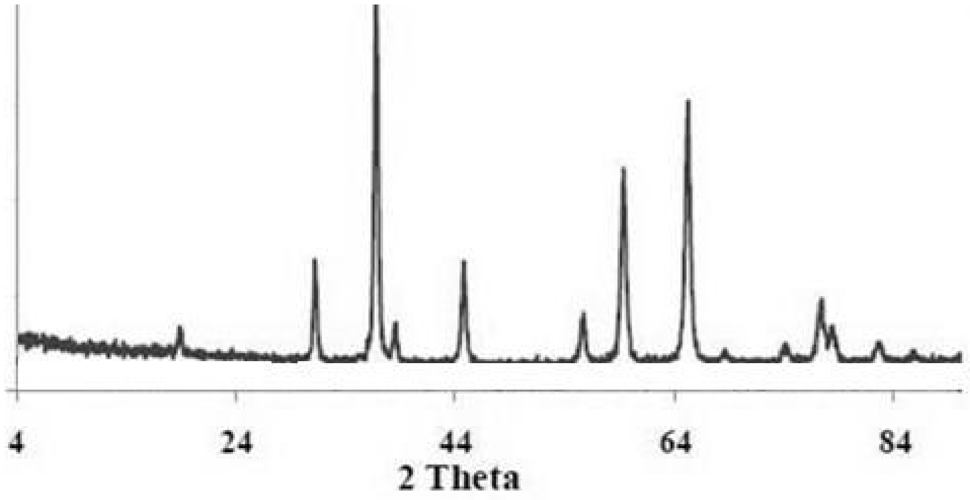


Figure 2. XRD patterns of the as-prepared Co_3O_4 nanoparticles.

The morphology of the single crystalline octahedral Co_3O_4 is examined by SEM (Figure 3). As shown in Figure 3, it was observed that the single crystals were octahedral, which particles were uniform. It is noticed that the yield of the single crystalline octahedral is as high as 95% in our work.

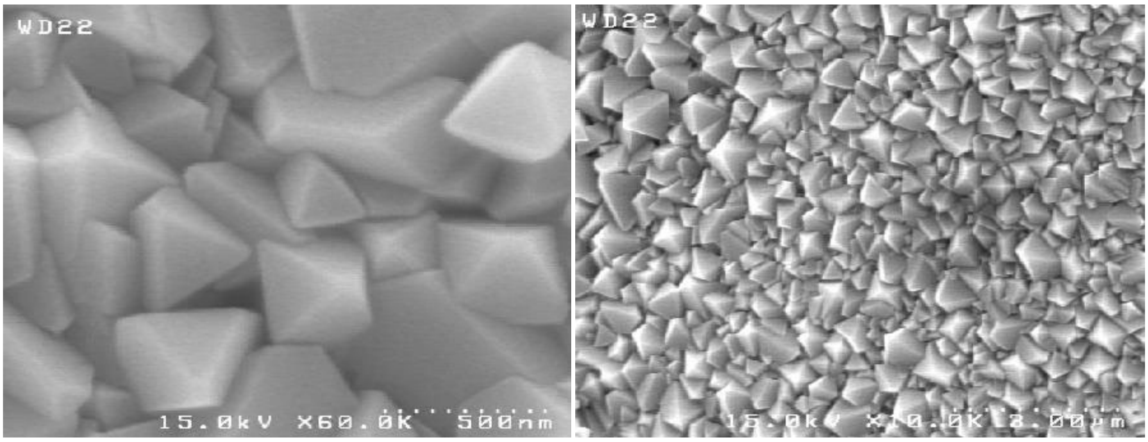


Figure 3. SEM images of octahedral Co_3O_4.

Conclusion

In summary, we have successfully prepared single crystal octahedral CO_3O_4 by solid-state thermal decomposition of cobalt (II) Schiff base complex Co((3,4-MeO-ba)$_2$en)Cl$_2$. This method is facile, inexpensive, nontoxic and can be extended for preparation of other transition metal oxide nanoparticles.

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