Hydrothermal synthesis of cobalt oxide nanoparticles: Its optical and magnetic properties

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Abstract

Cobalt oxide (Co3O4) nanoparticles have been synthesized by hydrothermal method using mixture of cobalt(II)chloride, Triton X-100 and KOH in an autoclave at 180 °C for 6 h followed by heating at 400 °C for 3 h in air. The product have been characterized by Fourier transform infrared (FT-IR), UV-Vis spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Optical properties of the Co3O4 nanoparticles revealed the presence of two band gaps, viz. 2.9 and 2.4 eV. Data from vibrating sample magnetometer (VSM) confirm the purity of the product along with single phase paramagnetic behavior.

Keywords: Cobalt oxide; XRD; SEM; TEM; Optical properties.

Introduction

Cobalt oxide (Co3O4) nanoparticles exhibit interesting properties and applications when compared with their bulk, such as lithium storage [1], gas sensing [2] and electro-catalyst [3]. The most stable phase of cobalt oxides (Co3O4) with a direct band gap of 1.48-2.19 eV, is used as an n-type semiconductor and received considerable attention [1-5]. Various methods have been developed to synthesize Co3O4 nanoparticles, including the hydrothermal [4,5], microwave-assisted[6] and reverse micelles [7]. However, hydrothermal method is green and less expensive. Synthesis of Co3O4 nanoparticles via hydrothermal method generally requires reducing and precipitating agents. Until now, various nanoparticles of Co3O4 have been prepared by different methods [8-12]. Therefore, development of facile and rapid method to prepare high purity Co3O4 nanoparticles having various morphologies [1-14] is highly desirable. Recently, our group has been synthesized metal oxides nanoparticles via thermal decomposition method of transition metal Schiff base complexes [15,16]. Herein, we report synthesis, characterization and possible growth mechanism of Co3O4 nanoparticles by hydrothermal method.

Materials and Methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range 2θ = 4°-84°. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer.

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The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM. The transmission electron microscopy (TEM) images were obtained from a JEOL JEM 1400 transmission electron microscope with an accelerating voltage of 120 kV. Optical absorption spectra are recorded at room temperature on a Cary 100 UV-visible spectrophotometer (VARIAN EL 12092335) having wavelength range of 200–700 nm. A homogeneous suspension in distilled water, obtained through sonication (for 10 minutes) of well dispersed sample is used for UV-vis studies. Magnetic measurements are made at room temperature using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan).

**Preparation of Co$_3$O$_4$ nanoparticles**

Cobalt chloride (2.5 mmol) is dissolved in 40 mL distilled water and a certain amount of surfactant (1%, w/w, Triton X-100, Scheme 1) is added subsequently. Aqueous KOH and surfactant solutions are added drop wise until dark green solution is obtained. The resultant mixture is transferred into a 100 mL sealed teflon-lined autoclave and kept at 180 °C for 6 h. After cooling the autoclave to room temperature, the dark precipitate is obtained, filtered, washed with distilled water followed by absolute ethanol, and dried at 90°C for 6 h under vacuum. Thus obtained Co$_3$O$_4$ compounds labeled as MY-1. MY-1 is further heated at 400 °C for 3 h in presence of air and the product is labeled as MY-2.

**Results and Discussion**

Triton X-100, used as stabilizing agent in nanocolloidal system is absorbed on the surface of cobalt ion. H$_2$O$_2$ and KOH function as homogeneous precipitating agents. The probable chemical reactions are as follows:

- $\text{CoCl}_2 + 2 \text{KOH} \rightarrow \text{Co(OH)}_2 \downarrow + 2 \text{KCl}$
- $3 \text{Co(OH)}_2 \downarrow + \text{H}_2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 \downarrow + \text{H}_2\text{O}$

**FTIR spectra**

Figure 1a and 1b show FTIR spectra of Co$_3$O$_4$ nanoparticles (MY-1 and MY-2). The strong bands at 576 and 670 cm$^{-1}$ for MY-1 and 662 and 568 cm$^{-1}$ for MY-2, belonging to the spinel structure of Co$_3$O$_4$ [5]. The former peak at about 660–670 cm$^{-1}$ is attributed to the stretching vibration mode of Co–O in which Co is Co$^{2+}$ and is tetrahedrally coordinated. The latter one at 568-576 cm$^{-1}$ can be assigned to Co–O of octahedrally coordinated Co$^{3+}$. The two bands appeared at 3551 and 1610 cm$^{-1}$ have been assigned to the stretching and bending vibrations of absorbed water molecule on Co$_3$O$_4$ nanoparticles [4].

**PXRD studies**

The as-prepared Co$_3$O$_4$ nanoparticles have been characterized by X-ray powder diffraction (XRD) (Fig. 2). The XRD patterns of MY-1 and MY-2 are slightly different, because MY-2 is a mixed Co$_3$O$_4$ and CoO phases. All diffraction peaks at 20 = 19 (111), 31 (220), 37 (311), 39 (222), 45 (400), 56 (422), 59 (511) and 66 (440) displayed on the PXRD pattern of MY-1 and MY-2 can be indexed to the cubic Co$_3$O$_4$ structure (JCPDS No. 43-1003). No characteristic peaks of other impure phases like CoO (20 = 20 (111), 23 (220), 37 (220) and 38 (311)) in the XRD od MY-1 could be detected, indicating that the Co$_3$O$_4$ products were of high purity. The average size of the Co$_3$O$_4$ nanoparticles have been determined using the Debye-Scherrer formula ($D = 0.9 \lambda / \beta \cos \theta$), found as 26.6 nm for MY-1 and 21.3 nm for MY-2.

![Figure 1](image-url)
Optical and VSM studies

The optical absorption spectra of the Co$_3$O$_4$ nanoparticles have been carried out using UV-vis spectroscopy. The optical absorption profile (Fig. 3) shows two bands at 560 and 315 nm for MY-1 and 550 and 250 nm for MY-2, which indicating ligand-metal charge transfer events $O^2- \rightarrow Co^{3+}$ and $O^2- \rightarrow Co^{2+}$, respectively and are expected for Co$_3$O$_4$ [12]. The direct band gaps energy of the Co$_3$O$_4$ nanoparticles are 2.9 eV for MY-1 and 2.4 eV for MY-2 [17].

Figure 2. PXRD patterns of Co$_3$O$_4$ nanoparticles: MY-1 (a) and MY-2 (b).

Figure 3. The UV-Vis and band gap of Co$_3$O$_4$ nanoparticles: MY-1 (top) and MY-2 (bottom).

The magnetic behavior of the Co$_3$O$_4$ nanoparticles has been investigated at room temperature. The fine hysteresis loop in Fig. 4 is characteristics of paramagnetic behavior, although bulk Co$_3$O$_4$ shows anti-ferromagnetic behavior.

SEM and TEM images

SEM and TEM images of MY-1 and MY-2 (Figs. 5 and 6, respectively) indicate that the Co$_3$O$_4$ crystals are formed by aggregation of smaller crystallites during the
synthesis process and the morphology of \( \text{Co}_3\text{O}_4 \) nanoparticles is much uniform.

**Conclusion**

Two \( \text{Co}_3\text{O}_4 \) nanoparticles, MY-1 and MY-2 with similar morphology are prepared successfully by hydrothermal method using cobalt nitrate and/or acetate in

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**Figure 4.** \((\alpha h\nu)^2 vs. (h\nu)\) of \( \text{Co}_3\text{O}_4 \) nanoparticles: MY-1 (left) and MY-2 (right).

**Figure 5.** SEM images of \( \text{Co}_3\text{O}_4 \) nanoparticles: MY-1 (a) and MY-2 (b).

**Figure 6.** TEM images of \( \text{Co}_3\text{O}_4 \) nanoparticles: MY-1 (a) and MY-2 (b).
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presence of Triton X-100 as surfactant, and KOH and H$_2$O$_2$ as homogeneous precipitating agents. The Co$_3$O$_4$ nanoparticles are spherical shaped with an average size 26.6 nm (MY-1) and 21.3 nm (MY-2). They are characterized by FTIR, XRD, SEM and TEM techniques. Optical properties of the Co$_3$O$_4$ nanoparticles have revealed the presence of two band gaps 2.9 and 2.4 eV. The vibrating sample magnetometer (VSM) experiments confirm the purity, single phase and paramagnetic behavior.

References