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

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## Abstract

Cobalt oxide (Co3O4) nanoparticleshave 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 ºC 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 Co3O4nanoparticleshave revealed the presence of two band gaps, viz.2.9 and 2.4 eV. Data fromvibrating 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 ($Co_3O_4$) nanoparticlesexhibit 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 ($Co_3O_4$) with a direct band gap of 1.48-2.19 eV, is used asan*p*-type semiconductor and received considerable attention [1-5]. Various methodshave been developed to synthesize $Co_3O_4$ nanoparticles, including the hydrothermal [4,5], microwave-assisted[6] andreverse micelles [7]. However, hydrothermal method isgreen and less expensive. Synthesis of $Co_3O_4$ nanoparticles via hydrothermal method generally requires reducing and precipitating agents. Until now, various nanoparticles of $Co_3O_4$ have been prepared by different methods [8-12]. Therefore, development of facile and rapid method to prepare high purity $Co_3O_4$ nanoparticles havingvariousmorphologies [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 $Co_3O_4$ 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 $2\theta = 4^o–84^o$. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin–Elmer spectrophotometer.

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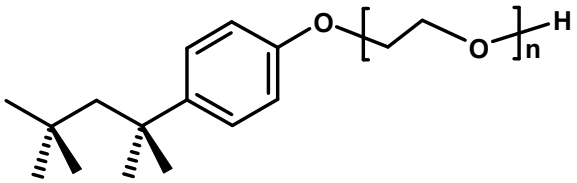


**Scheme 1.** Chemical structure of Triton X-100

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 $Co_3O_4$* 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 $Co_3O_4$compoundis labeled as MY-1. MY-1 is further heated at 400 ºC for 3 h in presence of air and the productis labeled as MY-2.

## Results and Discussion

Triton X-100, used as stabilizing agent in nano-colloidal system is absorbed on the surface of cobalt ion. $H_2O_2$ and KOH function as homogeneous precipitating agents. The probable chemical reactionsare as follows:

- $CoCl_2 + 2\ KOH \rightarrow Co(OH)_2 \downarrow + 2\ KCl$
- $3\ Co(OH)_2 \downarrow + H_2O_2 \rightarrow Co_3O_4 \downarrow + H_2O$

***FTIR spectra***

Figure 1a and 1b show FTIR spectra of $Co_3O_4$nanoparticles(MY-1 and MY-2). Thestrong 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 $Co_3O_4$[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 binding vibrations of absorbed water molecule on $Co_3O_4$nanoparticles [4].

***PXRD studies***

The as-prepared $Co_3O_4$ 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 $Co_3O_4$ and CoO phases. All diffraction peaks at $2\theta$ = 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 $Co_3O_4$ structure(JCPDS No. 43-1003). No characteristic peaks of other impure phases like CoO($2\theta$ = 20 (111), 23 (220), 37 (220) and 38 (311)) in the XRD od MY-1 could be detected, indicating that the $Co_3O_4$ products were of high purity.The average size of the $Co_3O_4$nanoparticleshave 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.

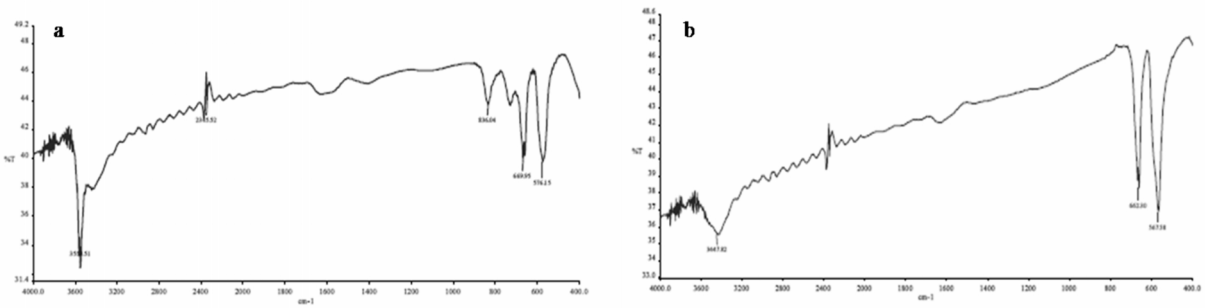


**Figure 1.** FTIR spectra of $Co_3O_4$nanoparticles MY-1 (a) and MY-2 (b).

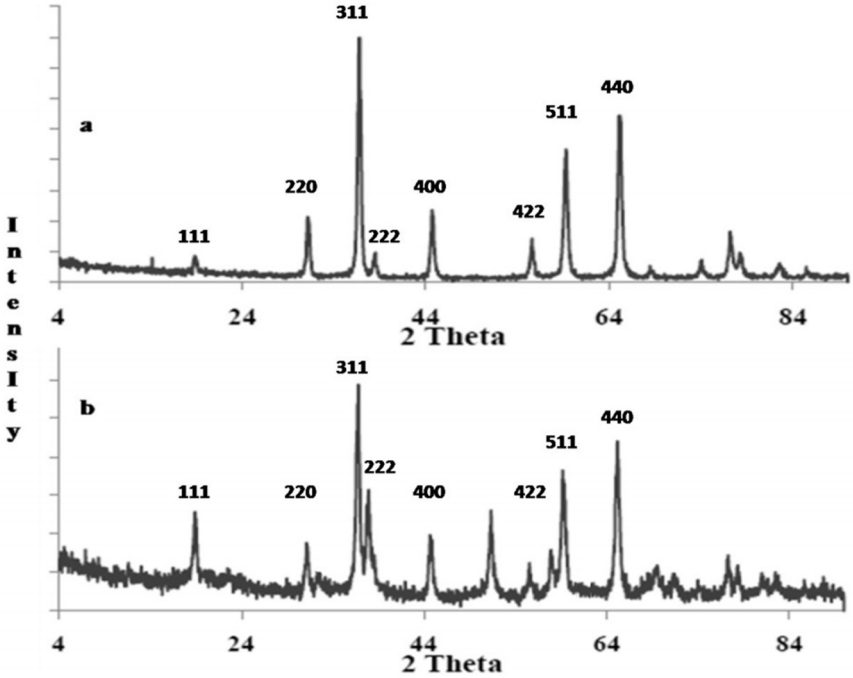


**Figure 2.** PXRD patterns of $Co_3O_4$nanoparticles: MY-1 (a) and MY-2 (b).

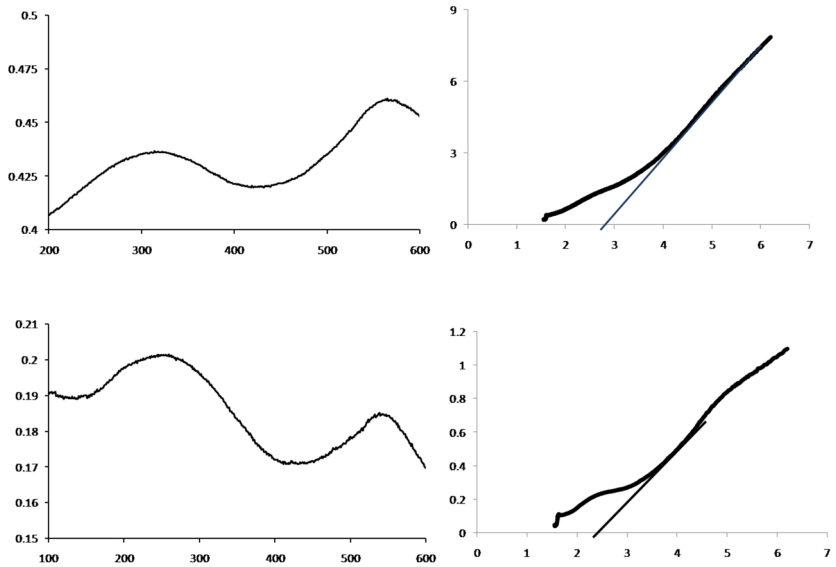

**Figure 3.** The UV-Vis and band gap of $Co_3O_4$nanoparticles: MY-1 (top) and MY-2 (bottom).

***Optical and VSM studies***

The optical absorption spectra of the $Co_3O_4$ 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 O2- $\rightarrow Co^{2+}$, respectively and are expected for $Co_3O_4$ [12]. The direct band gaps energy of the $Co_3O_4$ nanoparticles are 2.9 eV for MY-1 and 2.4 eV for MY-2 [17].

The magnetic behavior of the $Co_3O_4$ nanoparticles has been investigated at room temperature. The fine hysteresis loop in Fig. 4 is characteristics of paramagnetic behavior, although bulk $Co_3O_4$ 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 $Co_3O_4$ crystals are formed by aggregation of smaller crystallites during the

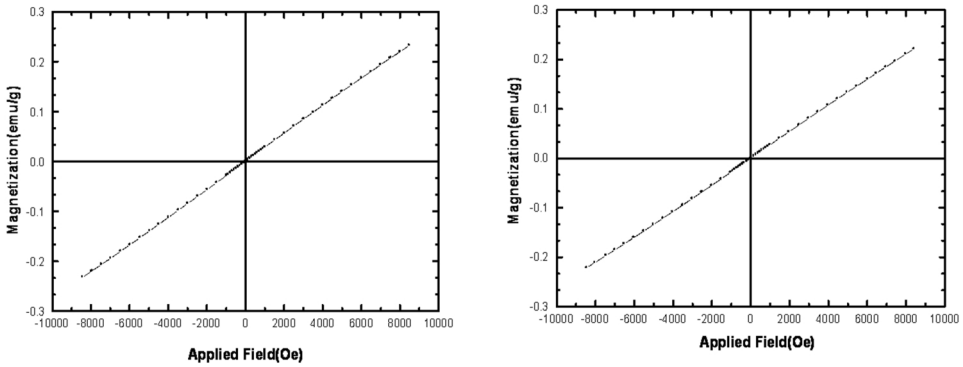


**Figure 4.** $(\alpha h\nu)^2$ *vs.* $(h\nu)$ of $Co_3O_4$nanoparticles :MY-1 (left) and MY-2 (right).

synthesis process and the morphology of $Co_3O_4$ nanoparticles is much uniform.

***Conclusion***

Two $Co_3O_4$ nanoparticles, MY-1 and MY-2 with similar morphology are prepared successfully by hydrothermal method using cobalt nitrate and/ acetate in

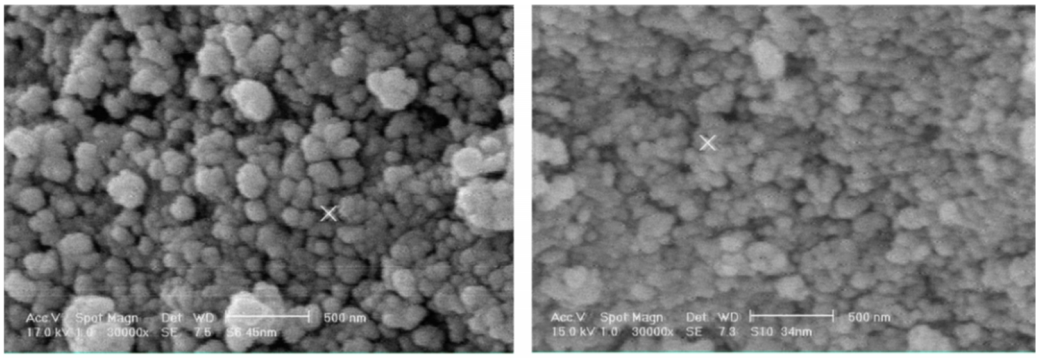


**Figure 5.** SEM images of $Co_3O_4$nanoparticles: MY-1 (a) and MY-2 (b).

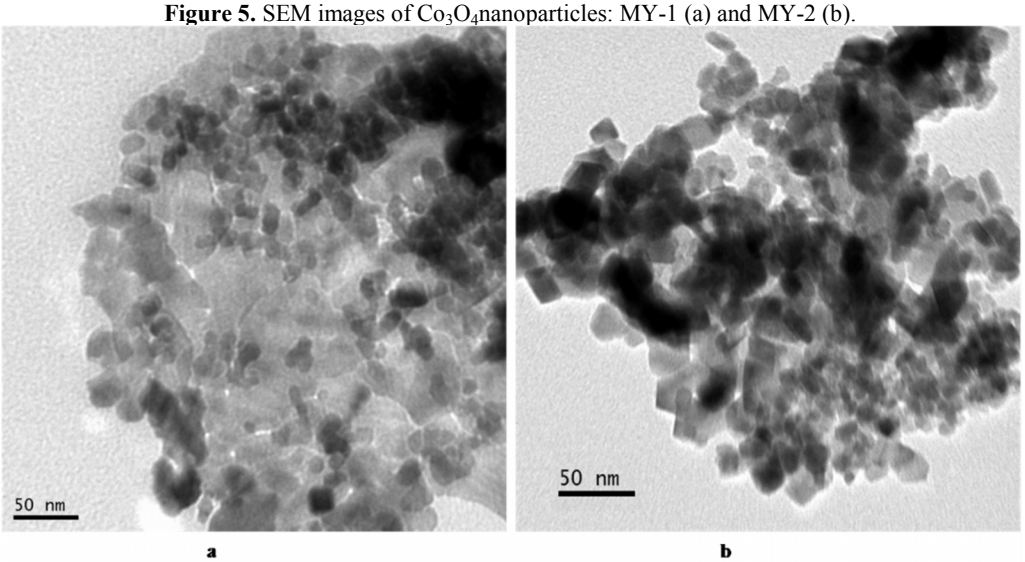


**Figure 6.** TEM images of $Co_3O_4$ nanoparticles: MY-1 (a) and MY-2 (b).

presence of Triton X-100 as surfactant, and KOH and $H_2O_2$ as homogeneous precipitating agents. The $Co_3O_4$ 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 $Co_3O_4$ 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.

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