

[Co(NH₃)₅(NO₃)](NO₃)₂ as an energetic coordination precursor for the preparation of Co₃O₄ nanoparticles at low temperature

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Abstract

In this paper, an energetic coordination compound namely pentamminenitratocobalt(III) nitrate, [Co(NH₃)₅(NO₃)](NO₃)₂, was used as a new precursor for the preparation of Co₃O₄ nanoparticles. The results showed that the complex is easily decomposed into the Co₃O₄ nanoparticles at low temperature (200 °C) without employing a surfactant or solvent and any complicated equipment. The product was characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). Optical and magnetic properties of the product were studied by UV-visible (UV-vis) spectroscopy and a vibrating sample magnetometer (VSM), respectively. FT-IR, XRD and EDS analyses confirmed the formation of highly pure spinel-type Co₃O₄ phase with cubic structure. TEM images showed that the Co₃O₄ nanoparticles are approximately in the range of 10 to 24 nm with a mean size of around 17 nm. The optical spectrum of the Co₃O₄ nanoparticles revealed the presence of two band gaps at 3.45 and 2.20 eV which are blue-shifted relative to reported values for the bulk sample. The magnetic measurement of the product showed a weak ferromagnetic order at room temperature.

Keywords: Co₃O₄ nanoparticles; Energetic complexes; Ferromagnetic order; Pentamminecobalt(III) complex; Thermolysis method; Transition metal oxides.

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INTRODUCTION

Nanostructured metal oxides have attracted great interest in recent years not only for their unique physical and chemical properties that significantly differ from those of corresponding bulk materials but also for wide range of their applications [1]. Among these oxides, spinel-type cobalt oxide (Co₃O₄), as a p-type semiconductor, has potential applications in gas sensors, heterogeneous catalysts, electrochemical devices, Li-ion batteries, magnetic materials and photocatalysts [2-11]. In recent years, the increasing interest has been focused on the synthesis of Co₃O₄ nanostructures with unique sizes and specific shapes because of the influences of particle size on their properties and applications. Various wet-chemical methods such as hydro-/solvothermal method, combustion method, microwave heating, sol-gel process, spray pyrolysis, sonochemical method, co-precipitation, ionic liquid-assisted method, polyol

method and a non-aqueous route have been reported to synthesize Co₃O₄ nanostructures [12-37]. Nevertheless, most of these methods involve complex processes, high calcination temperatures, and expensive and toxic precursors. In addition to these, they are either time consuming or require expensive instruments.

Over the past several years, the use of transition metal coordination compounds as precursors to prepare metal oxide nanostructures has received much attention. This simple method offers several unique advantages and significant merits over other methods, including easy workup, short reaction time, and the preparation of various inorganic nanomaterials with unique sizes, specific shapes and with narrow size distribution. Several coordination compounds have been used to synthesize Co₃O₄ nanostructures [38-43]. Recently, we have found that easily degradable and energetic coordination compounds composed of reducible

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ligands and oxidizing anions such as $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$, $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)](\text{NO}_3)_2$, $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ can be appropriate precursors to synthesize the metal oxides nanostructures at low temperature [44-46].

In the present work, we wish to report on the direct thermolysis of a well-known energetic pentamminecobalt(III) complex, $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ which has been resulted in Co_3O_4 nanoparticles at low temperature (200°C). The resulting product was characterized by differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), UV-visible spectroscopy, and magnetic measurement. The method is a fast, energy-efficient and environmentally friendly route to produce Co_3O_4 nanoparticles in only one step.

EXPERIMENTAL

Materials and characterization techniques

All materials were purchased from Merck Company with high purity. The precursor complex, $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ was synthesized according to the literature method [47]. The thermal behavior of the precursor complex was studied using a Netzsch STA 409 DSC analyser at a heating rate of 5°C min^{-1} in air. The composition and phase purity of the Co_3O_4 nanoparticles were characterized by a Rigaku D/max C III X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were recorded in the 2θ range of 10° – 80° with a scanning step of 0.04° . To investigate chemical bonding of the products, infrared spectra were recorded on the diluted samples in KBr pellets using a Shimadzu 160 FT-IR spectrophotometer in the region 4000 – 400 cm^{-1} . The optical absorption spectrum was recorded on a Shimadzu 1650PC UV-vis spectrophotometer in the 200 – 700 nm wavelength range at room temperature. The samples for UV-vis studies were well dispersed in distilled water by sonication for 30 min to form a homogeneous suspension. Particle sizes were determined with a Zeiss EM900 transmission electron microscope operating at 50 kV and equipped with an energy dispersive X-ray spectroscopy. The TEM sample was prepared by dispersing the powder in ethanol by ultrasonic vibration. The magnetic properties of Co_3O_4 nanoparticles were measured using a vibrating sample magnetometer (VSM, Iran Meghnat Daghigh Kavir Company).

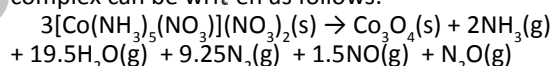
Preparation of Co_3O_4 nanoparticles

In order to prepare Co_3O_4 nanoparticles, an appropriate amount of the energetic $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex (2 g) was

powdered in a mortar and it was loaded into a porcelain crucible. The sample was then transferred into an electric furnace, heated at the rate of $10^\circ\text{C min}^{-1}$ from room temperature to 150°C in air atmosphere and was maintained at this temperature for 1 h. Similar experiments were performed for 2 g samples of the complex at the selected temperatures of 175, 200, 250°C . The obtained product at each temperature was cooled to room temperature and collected for the characterization.

RESULTS AND DISCUSSION

Initially, the thermal behavior of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex was investigated by DSC analysis. The DSC curve in Fig. 1 shows that the complex is decomposed in two main steps. The first step occurred at about 150°C , shows a small endothermic peak which can be explained by the loss of one or two molecules of NH_3 per molecule of complex. In second step, a sharp exothermic peak is observed in the range of 175 – 200°C which can be related to the explosive decomposition of the complex via a redox process taking place between the NH_3 ligands as reducing agents and the NO_3^- ions as oxidizing agents. This reaction resulted in the solid Co_3O_4 and gaseous products i.e. N_2 , NO , N_2O and H_2O [48]. According to the above results and literature [48], the preparation of Co_3O_4 from the energetic $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex can be written as follows:



The FT-IR spectra of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex and its decomposition products at different temperatures are shown in Fig. 2. For the starting complex in Fig. 2a, we can see the characteristic bands of the NH_3 ligands at

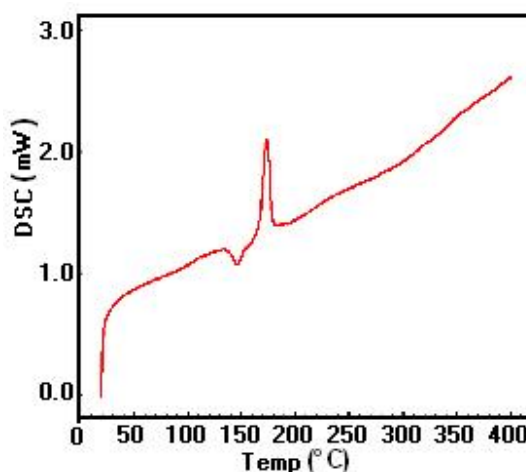


Fig. 1: DSC curve of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex

approximately 3500-3000, 1600-1500, 1020 cm^{-1} and the bands related to the NO_3 groups at 1450-1250 and 750 cm^{-1} [49]. For the sample decomposed at 150°C (Fig. 2b), most of the bands associated with the complex disappeared and two weak bands of the spinel-type Co_3O_4 structure at about 662 and 565 cm^{-1} are observed [50]. The former band is characteristic of the $\text{Co}^{\text{III}}\text{-O}$ vibration in an octahedral site, and the later one is attributable to the $\text{Co}^{\text{II}}\text{-O}$ vibration in a tetrahedral site of spinel-type Co_3O_4 lattice. As shown in Fig. 2c-e, the intensity of these two bands was

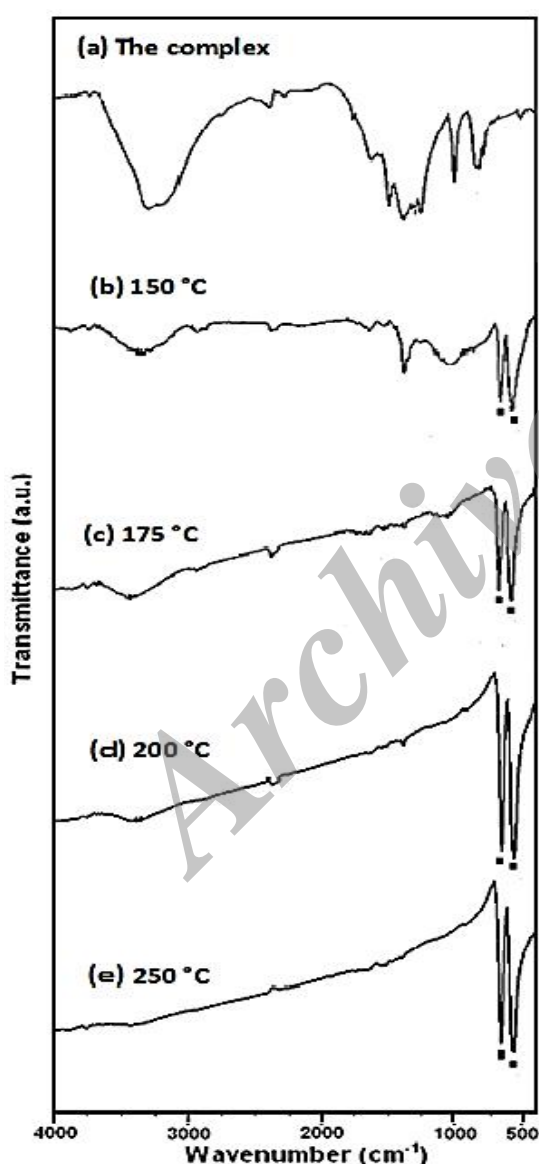


Fig. 2: FT-IR spectra of (a) the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex and its decomposition products at (b) 150 °C, (c) 175°C, (d) 200 °C, and (e) 250 °C

increased with the increase of the decomposition temperature from 150 to 175°C and, then to 200°C, but further increasing the temperature to 250°C did not change the intensity. This data confirms the complete decomposition of the complex to pure Co_3O_4 phase at 200°C.

The crystal structure and phase compositions of the decomposition products of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex at different temperatures were investigated by XRD, as shown in Fig. 3. The XRD pattern of sample decomposed at 150°C in Fig. 3a exhibits weak diffraction peaks with 2θ values at 19.50°, 31.37°, 37.02°, 39.10°, 44.97°, 55.84°, 59.58°, 65.44° and 77.65°. These diffraction peaks can be indexed to the crystalline cubic phase Co_3O_4 with lattice constant of $a = 8.076 \text{ \AA}$ and a space group of $\text{Fd}3\text{m}$, which are in agreement with the reported values (JCPDS Card No. 76-1802). This result confirms that the formation of the Co_3O_4 phase started at 150°C. As shown in Fig. 3b and 3c,

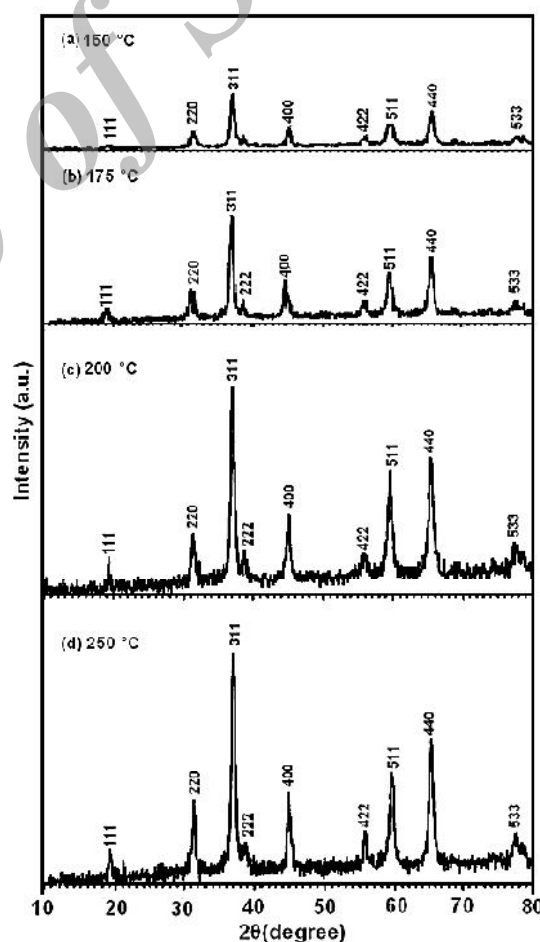


Fig. 3: The XRD patterns for the decomposition products of $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex at (b) 150°C, (c) 175 °C (d) 200°C and (e) 250°C .

the intensity of the characteristic peaks of the Co_3O_4 phase markedly increases as the decomposition temperature increases to 175°C and 200°C. XRD pattern of the sample decomposed at 250°C (Fig. 3d), shows only the peaks related to the Co_3O_4 without obvious changes.

Thus, 200°C is considered as an appropriate temperature for the complete decomposition of the precursor, as indicated by the FT-IR results. At this temperature, no peaks of other impurity phases have been detected, confirming that the final product is highly pure. The considerable broadening of the diffraction peaks demonstrates the nanometer character of the Co_3O_4 particles. The average size of the Co_3O_4 particles prepared at 200°C was estimated by the Debye–Scherrer equation [51]: $D_{\text{XRD}} = 0.9\lambda/(\beta\cos\theta)$ where D_{XRD} is the average crystalline size, λ is the wavelength of $\text{CuK}\alpha$, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg's angle. The average size of the Co_3O_4 nanoparticles calculated using the most intense peak (311) at $2\theta = 36.26^\circ$ is approximately 18 nm. This value is in accordance with TEM observations (discussed below).

The morphology and particle size of product obtained from the thermolysis of the $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ complex at 200°C were investigated by TEM. The TEM image of Co_3O_4 nanoparticles are shown in Fig. 4a. It can be seen

that nanoparticles have spherical morphology with a uniform size. Because of the small dimensions and high surface energy of the particles, it is easy for them to aggregate as seen in Fig. 4a. We also can find from this Fig that the morphology of the particles is almost homogeneous. Histogram revealing the size distribution of the Co_3O_4 nanoparticles is shown in Fig. 4b. From Fig. 4b, we obtained that the diameter sizes of the Co_3O_4 nanoparticles are approximately in the range of 10 to 24 nm with a narrow size distribution. The average particle size is 17 nm calculated from Fig. 4b, which is in agreement with the result calculated for the half-width of diffraction peaks using the Scherrer's formula, allowing for experimental error.

The elemental analysis of the Co_3O_4 nanoparticles was performed using the EDX on the SEM, as shown in Fig. 5. The peaks around 1.05, 6.95 and 7.95 keV are related to the binding energies of CoL , $\text{Co K}_{\alpha 1}$ and $\text{Co K}_{\alpha 2}$, respectively. Also, a peak near 0.50 keV corresponding oxygen is observed. The peak of C at 0.27 keV and peaks of Au at 2.20 and 9.75 keV are related to the SEM holding grid. The atomic percentages of Co and O were found to be 43.22% and 56.78%, respectively, which are near to the theoretical ratio (3:4) of the Co_3O_4 phase. The result indicates that the as-synthesized product is composed of high purity Co_3O_4 nanoparticles.

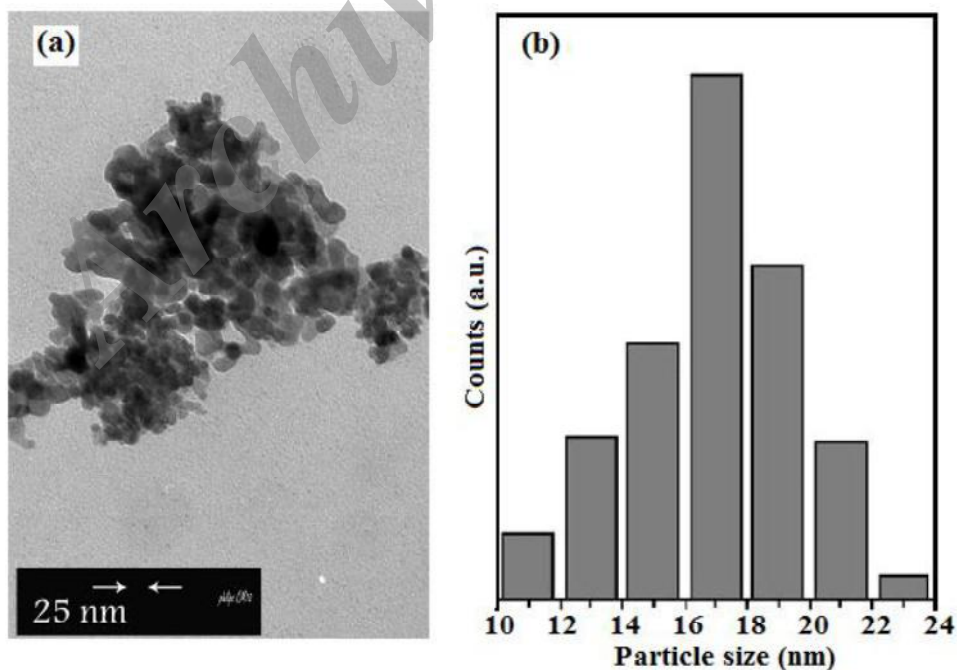


Fig. 4: (a) TEM image of the Co_3O_4 nanoparticles, and (b) Histogram showing the diameter distribution of the Co_3O_4 nanoparticles

The optical absorption properties of the as-prepared Co_3O_4 nanoparticles were investigated at room temperature by UV-vis spectroscopy. As can be seen in Fig. 6, two absorption bands appear in the wavelength ranges of 200–375 and 385–625 nm. These bands can be assigned to the $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ and the $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ charge transfer processes, respectively [52]. According to the following equation for a semiconductor [24]: $(\alpha h\nu)^2 = K(h\nu - E_g)$, where α is the absorption coefficient, K is a constant, $h\nu$ is the discrete photo energy (in eV), and E_g is the band gap energy, and the energy intercept of a plot of $(\alpha h\nu)^2$ vs $h\nu$ yields E_g for a direct transition (see the inset of Fig 6). The band gaps of the obtained Co_3O_4 nanoparticles are calculated to be 3.45 and 2.20 eV which are blue-shifted relative to reported values for the bulk sample (2.19 and 1.48 eV, respectively) [33,53]. The increase in the band gaps of the Co_3O_4 nanoparticles may ascribe to the small size effects of nanoparticles.

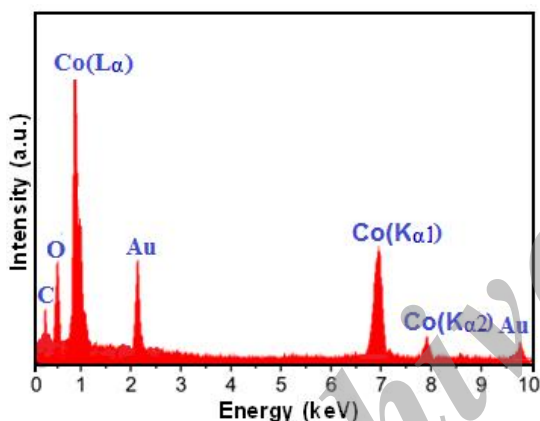


Fig. 5: EDX spectrum of the Co_3O_4 nanoparticles prepared at 200 °C.

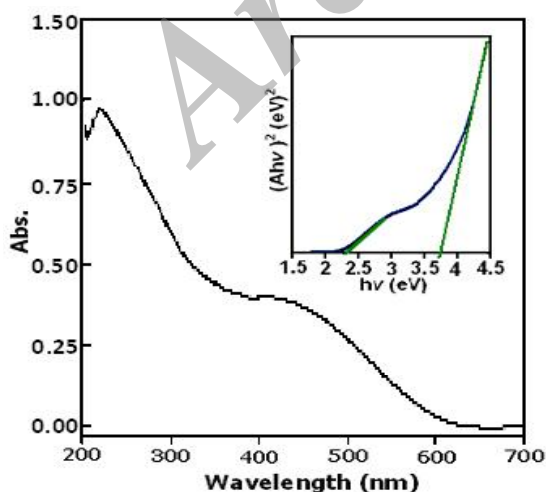


Fig. 5: EDX spectrum of the Co_3O_4 nanoparticles prepared at 200 °C.

The magnetic property of the Co_3O_4 nanoparticles was measured at room temperature. As shown in Fig. 7a, the magnetization is approximately linear with the field and it does not attain the saturation even at the applied field of 8 kOe. Fig. 7b indicates the expansion of magnetization near the lower applied field. We can see a fine hysteresis loop which is characteristic of weak ferromagnetic behaviour, although bulk Co_3O_4 has antiferromagnetic nature. This behavior may arise due to uncompensated surface spins and/or due to finite size effects of the Co_3O_4 nanoparticles [11, 54-56].

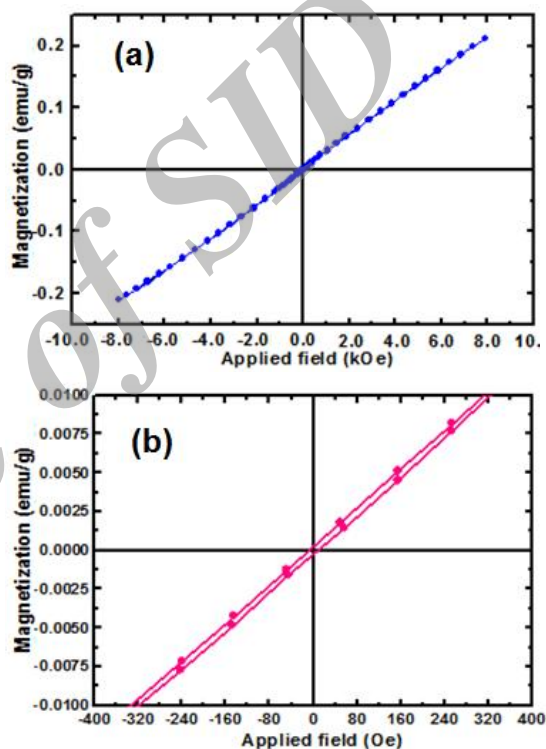


Fig. 7: (a) Magnetization curve as a function of applied magnetic field for Co_3O_4 nanoparticles at room temperature, and (b) the expansion of magnetization vs. field near the lower applied field

CONCLUSIONS

In conclusion, Co_3O_4 nanoparticles with an average particle size of 17 nm have been successfully prepared via thermal decomposition of the $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$ at 200 °C. Co_3O_4 nanoparticles are formed from this complex via a redox reaction between NH_3 ligands and the NO_3^- ions. This method yields sphere-like Co_3O_4 nanoparticles with a narrow size distribution and weak ferromagnetic behavior. The estimated optical absorption band gaps of the Co_3O_4 nanoparticles are relatively blue-shifted,

compared with the values for the bulk sample. This approach provides a one-step simple and inexpensive route for the preparation of Co_3O_4 nanoparticles with high purity in order to high-technology applications.

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