



## Original Research Paper

## Synthesis of spinel cobalt oxide nanoparticles using a modified polymeric precursor method



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## ABSTRACT

Metal oxide nanoparticles have been raising increasing interest. In this work, spinel cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nanoparticles of around 29 nm were synthesized using a modified polymeric precursor method. This method is based on the complexation of polyacrylate and cobalt ions in aqueous media by a chelation reaction, resulting in the synthesis of crystalline nanoparticles, confirmed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Some advantages of this technique are the fast, simple and efficient synthesis of nanoparticles after only 2 h of thermal decomposition at 480 °C and elimination of the aging step, which is an essential step in polymeric precursor-based methods such as sol–gel.

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## 1. Introduction

Spinel cobalt oxide ( $\text{Co}_3\text{O}_4$ ) is a material of scientific and technological interest because of its various properties, as well as the fact that it is a magnetic p-type semiconductor with two bandgaps of 2.0 eV and 1.46 eV [1], which interacts in the visible electromagnetic spectrum (absorption and emission) [2,3]. These characteristics make  $\text{Co}_3\text{O}_4$  suitable for several applications, such as magnetic storage devices [2], electrochemical catalysis and photocatalysis [3–5], improvement of electrode capacity and cycling stability in lithium-ion batteries [2,6,7], electrochemical sensors [4,6], precursors for solid-state synthesis [8], supercapacitors [9,10] and nanofluid coolants [11].

Cobalt presents two main oxidation states: +II and +III. These two valences enable cobalt to form the following oxides:  $\text{CoO}$ ,  $\text{Co}_2\text{O}_3$  (which exists in the hydrated form), and the more common spinel-type  $\text{Co}_3\text{O}_4$  (composed of cobalt in +II and +III valences,  $\text{CoO}\cdot\text{Co}_2\text{O}_3$ ) [12]. However, because of the polyvalent states of cobalt ion, control of the atmosphere is essential to produce the desired cobalt oxide, while the most suitable synthesis technique must be chosen and conditions controlled to obtain nanoparticles.

In view of the above, researchers have attempted to synthesize cobalt oxide nanoparticles by different methods, such as hydrothermal [1,2], soft chemical method [3,5,11], direct thermal decomposition [6,11], polymer-based synthesis [7,8,13], plasma

spray pyrolysis [9], solvothermal synthesis [14], microwave assisted synthesis [10,15], etc. Nonetheless, these techniques have disadvantages, such as long synthesis time, sometimes more than 20 h, and require the use of complex equipment or unusual reactants.

The polymeric precursor method has undergone modifications to make it faster. The complexation of polyacrylate and metal ions in water, followed by thermal decomposition, leads to the synthesis of several oxides with very fine primary particles, such as zirconia, alumina, yttrium, lead and barium titanates [16], and cerium [17]. Recently, Gunnewiek et al. [18] performed rapid synthesis of very fine chromium oxide nanoparticles. Although this technique is very useful and fast, few studies have focused on the use of an aqueous complexation of polyacrylate to synthesize metal oxide nanoparticles. This technique uses simple equipment, aqueous solutions and very common reactants such as ammonium polyacrylate, which is widely employed as a dispersant in ceramic suspensions.

In this study, a rapid, efficient and simple synthesis technique was used based on a modified polymeric precursor method. Pure spinel-type cobalt oxide nanoparticles were easily fast-synthesized in only 6–7 h. The technique consists in a water-based complexation reaction between polyacrylic anions and cobalt cations, which takes only ten minutes, followed by freeze drying and rapid thermal decomposition at a relatively low temperature, resulting in highly crystallized nanoparticles. In addition, the optimal condition of thermal decomposition temperature was determined and the nanoparticles were characterized.

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## 2. Experimental procedure

### 2.1. Polymeric complexation

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma–Aldrich, >98%) 0.5 M was prepared and stir-mixed into a solution of ammonium polyacrylate (molecular weight  $\sim 4500$ , Lamberti-Reotan LA) (15 wt.%, pH 8.0). The reaction was conducted at room temperature, mixing the cobalt nitrate and PA solutions (1:2-volume) under constant stirring. A purple metal-polymeric flocculated complex was formed (PA-Co) instantaneously. The PA-Co complex was washed and centrifuged three times to remove undesirable soluble ions. Both complex and washing water were very stable and their color did not change. The resinous complex was resuspended and freeze dried (Edwards Micro Modulyo), yielding a very fluffy powder in less than 3 h.

### 2.2. Thermal decomposition and characterization

The optimal temperature for thermal decomposition was determined by thermogravimetric analysis (TGA) and differential thermal calorimetry (DSC) (Netzsch STA 449 C), heated at  $5^\circ\text{C}/\text{min}$ , from room temperature to  $750^\circ\text{C}$ . The sample was then thermally decomposed at the same heating rate, with a soak of 120 min at the optimal temperature.

The material was subjected to X-ray diffractometry (Siemens D5005) to characterize its crystallinity, index the phase and identify the lattice parameters, using  $K\alpha$  radiation of copper ( $\lambda = 1.54 \text{ \AA}$ ). The  $2\theta$  range varied from  $20^\circ$  to  $80^\circ$ , and planes distances and cell parameters ( $a$  and volume) were calculated. The planar distances were calculated using Bragg's equation:

$$n\lambda = 2d_{hkl} * \sin \theta \quad (1)$$

The lattice parameter  $a$  and cell volume,  $V$ , were calculated as [19]:

$$1/d^2 = (h^2 + k^2 + l^2)/a^2 \quad (2)$$

$$V = a^3 \quad (3)$$

The average crystallite size,  $t$ , was estimated using Scherrer's equation (Eq. (4)), where  $B$  is the peak broadening at full width half maximum (FWHM), and  $\theta$  is the diffraction angle.

$$t = 0.9\lambda/B * \cos \theta \quad (4)$$

The as-synthesized powder was deagglomerated in a mortar, resulting in a very fine dark powder. For the surface area ( $S_{\text{BET}}$ ) analysis, the surface of powder was cleaned by treating it thermally at  $180^\circ\text{C}$  under vacuum for two hours. The  $S_{\text{BET}}$  was determined using the cold  $\text{N}_2$  adsorption/desorption technique (Micromeritics ASAP 2020), calculated by the Brunauer–Emmet–Teller (BET) equation. The average spherical particle size ( $d_{\text{BET}}$ ) was estimated from the Eq. (5), where  $\rho_{\text{th}}$  is the theoretical density for  $\text{Co}_3\text{O}_4$  ( $6.055 \text{ g/cm}^3$ ).

$$d_{\text{BET}} = 6/(S_{\text{BET}} * \rho_{\text{th}}) \quad (5)$$

Micrographs of the powder morphology were recorded with a scanning electron microscope (SEM, Philips XL30 FEG). The powder was dispersed ultrasonically in acetone and dripped onto the aluminum sample holder. After it dried, a very thin gold layer was sputtered onto the sample. Micrographs were also recorded by transmission electron microscopy (TEM), select area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2F20). The primary particle size was measured using an image analyzer program. Around 65 particles were counted in four TEM images of different regions of the same sample.

## 3. Results and discussion

Fig. 1(a) depicts the thermogravimetric analysis (line) and the first derivative ( $d(\text{TGA})/dt$ ) curve of the dry fluffy complex, showing weight loss as a function of temperature, while Fig. 1(b) depicts the DSC curve. Note the presence of four peaks on the derivative curve (Fig. 1(a)) corresponding to the following temperatures: a maximum peak at around  $50^\circ\text{C}$ , which corresponds to water adsorption, a peak with minimum at  $221^\circ\text{C}$ , followed by another at  $257^\circ\text{C}$ , and lastly a peak between  $380$  and  $459^\circ\text{C}$ .

The mass increase below  $50^\circ\text{C}$  is associated with water adsorption (a well defined peak on the DSC curve). This water loss occurs at about  $100^\circ\text{C}$ . An exothermic peak occurs at around  $180^\circ\text{C}$ , followed by another at approximately  $225^\circ\text{C}$ , with a mass loss of about 30%. We believe that the peaks at  $221$  and  $257^\circ\text{C}$  correspond to the initial decomposition and formation of intermediary phases, and that the final range (from  $380$  to  $459^\circ\text{C}$ ) corresponds to the formation of cobalt oxide. An analysis of the TGA curve indicates that mass loss above  $460^\circ\text{C}$  is very low. There are corresponding inflexions on the dTGA curve, indicating the onset of thermal decomposition reactions. The last reaction step occurs at  $370^\circ\text{C}$  (an inflexion on the dTGA curve and an endothermic peak on the DSC curve), ending at  $460^\circ\text{C}$ . The latter step is believed to be associated with the formation of cobalt oxide, and the decomposition temperature was set at  $480^\circ\text{C}$ , heating rate of  $5^\circ\text{C}/\text{min}$ , and a soak

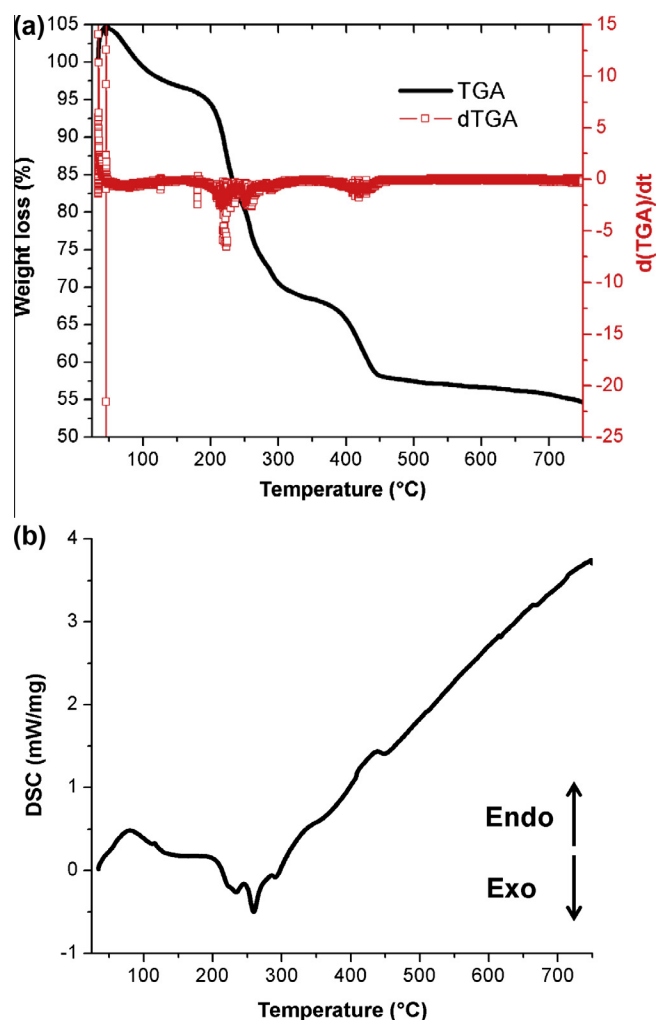


Fig. 1. (a) Thermogravimetric analysis and first derivative curve, and (b) DSC curve of the PA-Co complex.

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