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Synthesis and optical properties of cubic Co_3O_4 nanoparticles via thermal treatment of a trinuclear cobalt complex

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ABSTRACT

Cubic cobalt oxide nanoparticles with the formula of Co_3O_4 were synthesized via thermal treatment in air, using $[Co^{II}\{(\mu\text{-L})(\mu\text{-OAc})Co^{III}(NCS)\}_2]$; [$H_2L$=salen=1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene]; as precursor. Effect of calcination temperature and citric acid, as emulsifier, was investigated on the phase formation and particle size distribution of the products. Calcination of the precursor at 600 °C in the presence of citric acid results in the formation of Co_3O_4 nanoparticles with the average crystallite size of ~13 nm. The presence of citric acid provides conditions for the formation of more pure Co_3O_4 crystalline phase with smaller particles. The as-prepared nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), particle size analyzer (PSA), transmission electron microscopy (TEM), UV–vis and Photoluminescence (PL) spectroscopies. The optical property studies indicate that the absorption peaks of Co_3O_4 nanoparticles, prepared in the presence of citric acid, shift towards short wavelengths. This blueshift is related to the quantum size effect.

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1. Introduction

Cobalt oxide nanoparticles are important both for technological applications as well as for physics studies. Cobalt oxide is formed in five different oxidation states, out of which, Co_3O_4 is the most stable phase and is a p-type semiconductor [1]. In recent years, Co_3O_4 has attracted extensive interest due to its potential applications as heterogeneous catalysis [2], lithium rechargeable batteries [3], magnetic materials [4], and CO sensors [5]. Several researchers investigated the optical properties of Co_3O_4 nanoparticles [6–9]. The corresponding values for the band gaps in the bulk are reported to be 1.48 and 2.19 eV [1]. The observed blueshift in the band gap was explained as originating in the finite size effects of the nanoparticles [7]. There are several reports based on the UV–vis absorption studies [6–9]. However, the photoluminescence behavior of Co_3O_4 nanoparticles has been seldom reported.

It is now commonly understood that the behaviors of nanophase materials strongly depend on the shape and size of the particles, which is thus a key factor to their ultimate performance and applications [10,11]. Therefore, finding a suitable synthetic route for the formation of nanoparticles is vitally important. Nanoparticles of Co_3O_4 have been prepared by various methods like thermal decomposition of cobalt precursors under oxidizing condition [12], chemical spray pyrolysis [13], chemical vapor deposition [14], using organic surfactants [15], the traditional sol–gel method [16], surfactant free method [17] and precipitation–oxidation method [18]. Among the numerous methods developed for synthesizing metal oxide ultrafine powders, thermal treatment of metalorganic molecular precursor has been regarded as one of the most convenient and practical techniques [19]. It not only enables to avoid special instruments, complicated processes and severe preparation conditions, but also provides good control over purity, composition, homogeneity, phase and microstructure of the products [20].

Choosing a proper metalorganic molecular precursor, coupled with a rational thermolysis processes, causes to crystalline nanoparticles [21]. This study reports a facile synthesis and characterization of ultrafine cubic Co_3O_4 nanoparticles with control on morphology and crystallinity via thermal treatment of a solid metalorganic molecular precursor; $[Co^{II}\{(\mu\text{-L})(\mu\text{-OAc})Co^{III}(NCS)\}_2]$; [$H_2L$=salen=1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene]. Effect of the citric acid as emulsifier on the phase formation and crystallinity of the product is considered. The optical properties of as-prepared Co_3O_4 nanoparticles were also studied.

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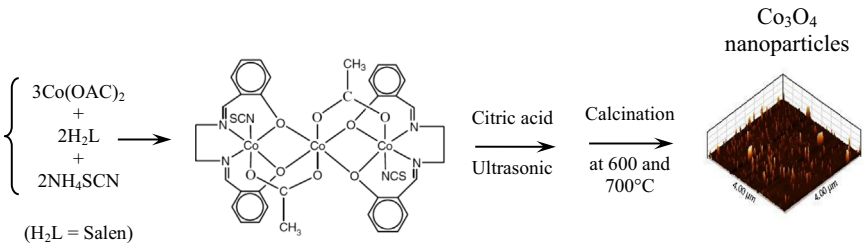

Scheme 1. Synthesis procedure for Co_3O_4 nanoparticles.

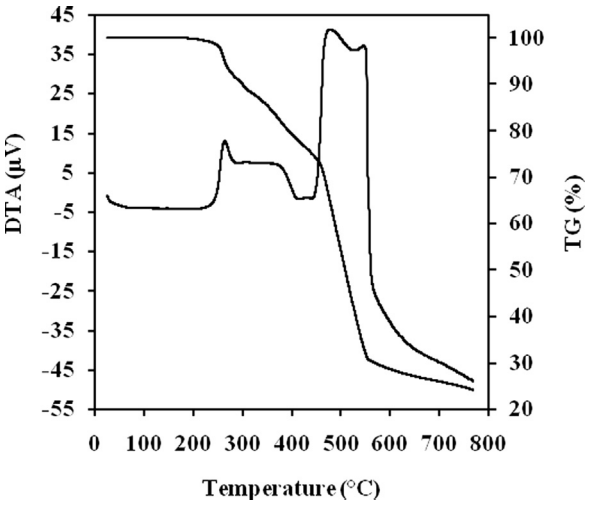

Fig. 1. TG/DTA of $[Co^{II}\{(\mu\text{-L})(\mu\text{-OAc})Co^{III}(NCS)\}_2]$ complex.

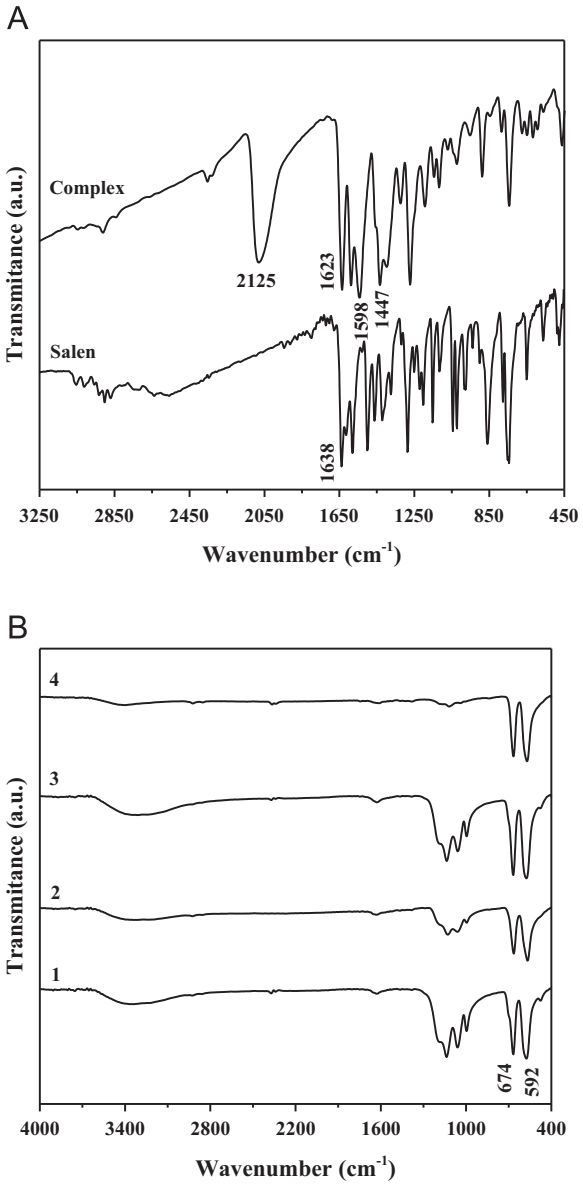

Fig. 2. FT-IR spectra of prepared samples.

2. Experimental

2.1. Synthesis of precursor complex

The precursor complex $[Co^{II}\{(\mu\text{-L})(\mu\text{-OAc})Co^{III}(NCS)\}_2]$; [$H_2L$=salen=1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] was prepared according to the procedure that is reported in Ref. [22] (Scheme 1). The salen, H_2L, was synthesized by the condensation of salicylaldehyde with ethylenediamine in methanol. A methanolic solution of $Co(OAc)_2 \cdot 6H_2O$ (15 mmol) was added to a yellow solution of H_2L (10 mmol) in methanol. The solution was stirred for 15 min. A methanolic solution of NH_4SCN (10 mmol) was added and was stirred for 60 min. The precipitate was filtrated and was washed with sufficient amount of hot methanol.

2.2. Preparation of Co_3O_4 nanoparticles

The prepared complex was completely powdered and calcined stepwise at 600 and 700 °C for 5 h by a heating rate of 10 °C/min from room temperature. In all synthesis, 3 g of precursor complex (0.0032 mol) was used. To investigate the role of citric acid as emulsifier on the phase formation, morphology and particle size of the products, precursor complex was added to a solution of citric acid in ethanol. Mole number of citric acid was selected to be equal of the mole number of precursor complex. The samples were sonicated, dried and calcined as before. Samples that were prepared in the absence of citric acid are denoted as 1 (calcined at 600 °C) and 2 (calcined at 700 °C). The ones that were prepared in the presence of citric acid are denoted as 3 (calcined at 600 °C) and 4 (calcined at 700 °C).

2.3. Materials characterization

All the chemicals were purchased from Merck and used as received without further purification. Thermogravimetric (TG) and differential thermal analysis (DTA) of the precursor complex were carried out using a thermal gravimetric/differential analyzer (BÄHR-Thermoanalyse GmbH Model STA 503). The sample was heated continuously with a heating rate of 10 °C/min from room temperature to 800 °C in a static air atmosphere. The FT-IR spectra of samples were collected using a Perkin-Elmer FT-IR spectrometer. X-ray diffraction patterns of the freshly calcined samples were recorded in a Bruker AXS diffractometer D8 ADVANCE with

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