

A facile thermal decomposition route to synthesise CoFe₂O₄ nanostructures

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The synthesis of CoFe₂O₄ nanoparticles has been achieved by a simple thermal decomposition method from an inorganic precursor, cobalt ferrous cinnamate hydrazinate (CoFe₂(cin)₃(N₂H₄)₃) which was obtained by a novel precipitation method from the corresponding metal salts, cinnamic acid and hydrazine hydrate. The precursor was characterized by hydrazine and metal analyses, infrared spectral analysis and thermo gravimetric analysis. Under appropriate annealing, CoFe₂(cin)₃(N₂H₄)₃ yielded CoFe₂O₄ nanoparticles, which were characterized for their size and structure using X-Ray diffraction (XRD), high resolution transmission electron microscopic (HRTEM), selected area electron diffraction (SAED) and scanning electron microscopic (SEM) techniques.

Keywords: CoFe₂O₄ nanoparticles; XRD; HRTEM; SAED; SEM

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1. Introduction

Spinel ferrites of nano scale are the most fascinating materials of this era, owing to their broad scope of applications in modern science and technology. They have interesting structural, magnetic and electrical properties [1]. Cobalt ferrite has been widely studied due to its excellent chemical stability, mechanical hardness, reasonable saturation magnetization and high magneto-crystalline anisotropy [2]. These properties make it a promising candidate for many applications, such as magnetic data storage, magnetic drug targeting, biosensors and magnetic refrigeration [3], ferrofluids and high-density information storage [4], spintronics [5], biomedicine [6], sensitive electrochemical sensor [7] and sustainable hydrogen production [8]. Recently, CoFe₂O₄ nanoparticles have been proven to be effective magnetic feeders and have found application as nanofluid for enhanced oil recovery [9].

Among the diverse methods employed for the synthesis of CoFe₂O₄ nanoparticles, such as hydrothermal technique [10], co-precipitation [11], micro-emulsion method [12], citrate-precursor

method [5], sol-gel method [13], etc., thermal decomposition of inorganic precursors is found to be interesting because of its simplicity, reproducibility and easy scale-up. This synthetic route does not require expensive chemicals. It is a low-energy reaction and can be carried out in a silica crucible in an open atmosphere. The purpose of this work is to prepare CoFe₂O₄ in nanoscale by the thermal decomposition of the inorganic precursor CoFe₂(cin)₃(N₂H₄)₃.

2. Experimental procedure

2.1. Preparation of cobalt ferrous cinnamate hydrazinate CoFe₂(cin)₃(N₂H₄)₃

The CoFe₂(cin)₃(N₂H₄)₃ compound was prepared by the addition of an aqueous solution (50 mL) of hydrazine hydrate (1 mL, 0.02 mol) and cinnamic acid (1.18 g, 0.0079 mol) to the corresponding aqueous solution (50 mL) of cobalt nitrate hexahydrate (0.58 g, 0.0018 mol) and ferrous sulphate heptahydrate (2.22 g, 0.0079 mol). The brown orange product, which had been formed immediately, was kept aside for an hour for digestion, then filtered and washed with water, alcohol, followed by diethylether and air dried.

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2.2. Preparation of cobalt ferrite nanoparticles

Cobalt ferrite nanoparticles were obtained from the autocatalytic decomposition of the precursor. In this method, the dried precursor was transferred to a silica crucible and heated to red hot condition in an ordinary atmosphere for about 45 minutes. The precursor started decomposing violently. The total decomposition of CoFe₂(cin)₃(N₂H₄)₃ led to the formation of CoFe₂O₄, which was quenched to room temperature, ground well and stored.

2.3. Characterization of the precursor

The hydrazine content in the precursor was determined by titration using KIO₃ as the titrant [14]. The percentage of cobalt and iron in the precursor was estimated by the standard methods given in the Vogel's textbook [14]. The infrared spectrum of the solid precursor sample was recorded by the KBr disc technique using a Shimadzu spectrophotometer. The simultaneous TG-DTA experiment was carried out in Universal V4.5A TA Instrument, in nitrogen atmosphere at the heating rate of 20 °C per minute using 5 – 10 mg of the sample. The temperature range was from an ambient to 700 °C.

2.4. Characterization of nanoparticles

The particle size of the synthesised nanoparticles was determined by high resolution transmission electron microscopy (HRTEM) operating on Jeol Jem 2100 advanced analytical electron microscope. Scanning electron microscopy (SEM) was performed with a HITACHI model S-3000H by focusing on nanoparticles to study the morphology. To check phase formation and purity, XRD pattern was recorded using an X-Ray diffractometer (X'per PRO model) with CuK α radiation, at 40 keV in the 2 θ range of 10 – 80 degrees.

3. Results and discussion

3.1. Chemical formula determination of the precursor

Based on the observed percentage of hydrazine (13.09), cobalt (24.32) and iron (47.17), which are

found to match closely with the calculated values (13.64), (25.11) and (47.60) for hydrazine, cobalt and iron, respectively, the chemical formula CoFe₂(cin)₃(N₂H₄)₃ has been tentatively assigned to the precursor, cobalt ferrous cinnamate hydrazinate.

3.2. FT-IR analysis of the precursor

From the IR spectrum of CoFe₂(cin)₃(N₂H₄)₃, it was observed that the N–N stretching frequency was identified at 972 cm⁻¹, which unambiguously proved the bidentate bridging nature of the hydrazine ligand [15]. The asymmetric and symmetric stretching frequencies of the carboxylate ions were seen at 1639 and 1411 cm⁻¹, respectively with the $\Delta\nu(\nu_{asym} - \nu_{sym})$ separation of 228 cm⁻¹, which indicated the monodentate linkage of the carboxylate groups. The N–H stretching was observed at 3367 cm⁻¹. The IR data thus confirmed the formation of cobalt ferrous cinnamate hydrazinate.

3.3. Thermal analysis of the precursor

As can be observed in Fig. 1, the precursor loses weight in three particular steps. The first step is the removal of two of the hydrazine molecules between room temperature and 210 °C with a weight loss of 9 %. The corresponding peak in DSC is observed as an exotherm. The second step is dehydrazination of the remaining hydrazine molecule and one of the three carboxylate groups, which takes place between 210 and 400 °C. The weight loss from 400 to 610 °C is attributed to the third step involving the decarboxylation of the remaining two carboxylate moieties in the dehydrazinated precursor, which gives CoFe₂O₄ as the final residue.

3.4. Characterization of CoFe₂O₄ nanoparticles

3.4.1. XRD analysis

XRD pattern of CoFe₂O₄ nanoparticles is shown in Fig. 2. Six characteristic peaks can be indexed as the cubic structure CoFe₂O₄, which is in accordance with the reported data (JCPDS File No 22-1086). The peaks with 2 θ values of 30.52°, 35.85°, 43.38°, 53.97°, 57.29° and 62.92°

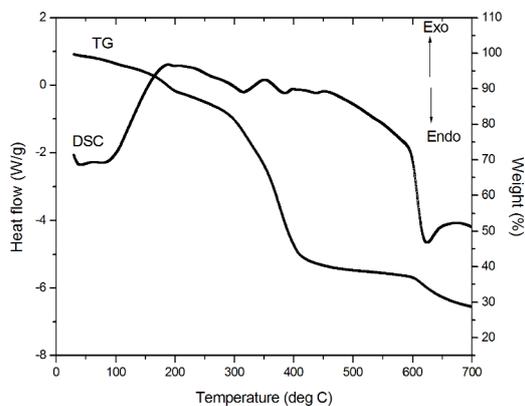


Fig. 1. TG-DSC curve of $\text{CoFe}_2(\text{cin})_3(\text{N}_2\text{H}_4)_3$.

correspond to the crystal planes (220), (311), (400), (422), (511) and (440) of crystalline CoFe_2O_4 , respectively. The average crystallite size, estimated using Debye-Scherrer formula, $D = k\lambda/(\beta \cos\theta)$, where, θ is Bragg diffraction angle, k is Blank's constant, λ is the source wavelength (0.154 nm), and β is the width of the XRD peak at half maximum height, is found to be around 12 nm. No characteristic peaks for other impurities are detected, confirming that the product obtained is phase pure.

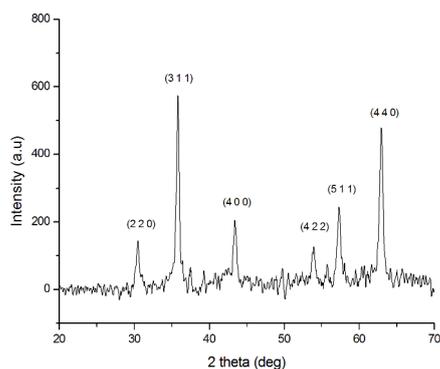
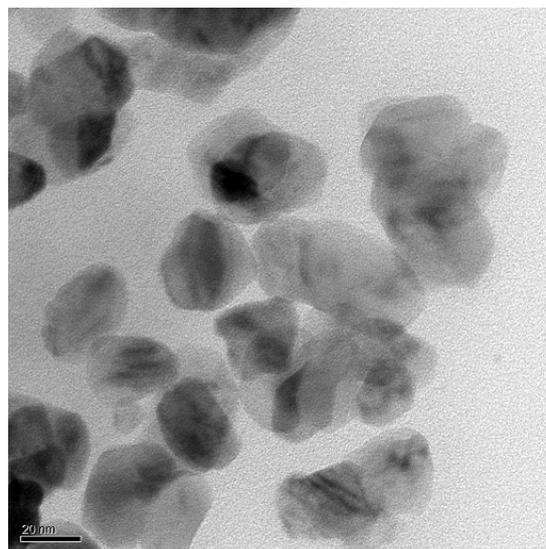


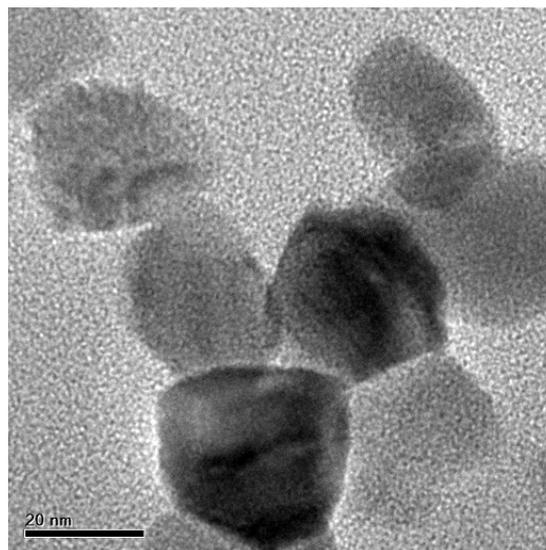
Fig. 2. XRD pattern of CoFe_2O_4 nanoparticles.

3.4.2. HRTEM analysis

HRTEM micrographs of CoFe_2O_4 are shown in Fig. 3, which show the particle size distribution of CoFe_2O_4 nanoparticles. It is evident that the



(a)



(b)

Fig. 3. HRTEM image of CoFe_2O_4 nanoparticles.

nanoparticles are of polydispersed spherical shape. The presence of some bigger particles should be attributed to the aggregation or overlapping of some small particles. The average grain size observed from the micrograph is about 12 – 13 nm, which is in agreement with the calculation using Scherrer's equation. Fig. 4 shows the selected area electron diffraction (SAED) pattern indicating sharp diffraction rings, which reveal the polycrystalline nature of the nanoparticles.

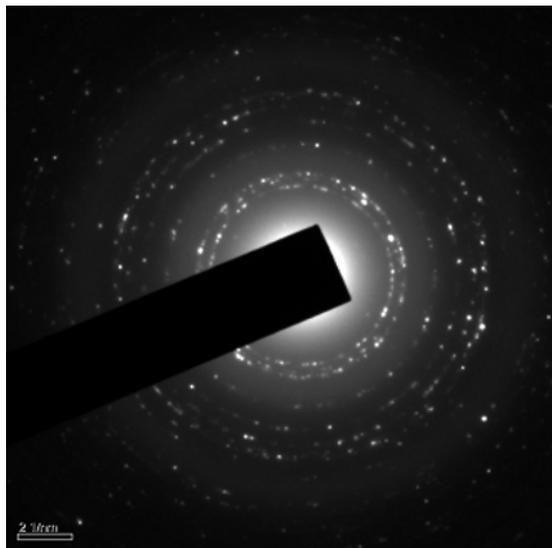


Fig. 4. SAED pattern of CoFe_2O_4 nanoparticles.

3.4.3. SEM analysis

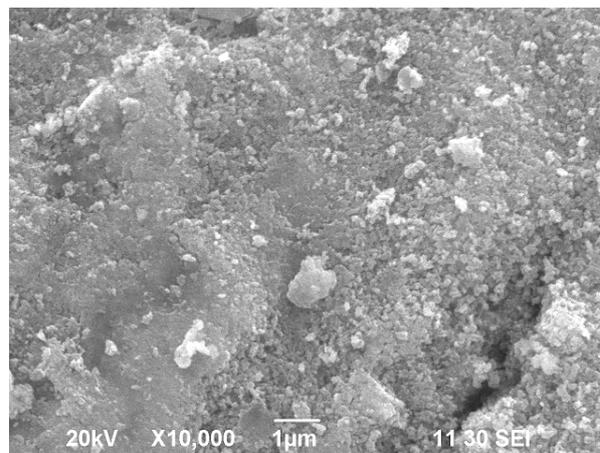
The morphology of CoFe_2O_4 was characterized by scanning electron microscope. The SEM pictures in Figs. 5a and 5b clearly show that the ferrite powder is mostly formed of nano-sized homogeneous grains with the presence of some agglomerated particles. EDX spectrum of CoFe_2O_4 nanoparticles is presented in Fig. 6, which furnishes the chemical compositional analysis of the nanoscale CoFe_2O_4 .

4. Conclusion

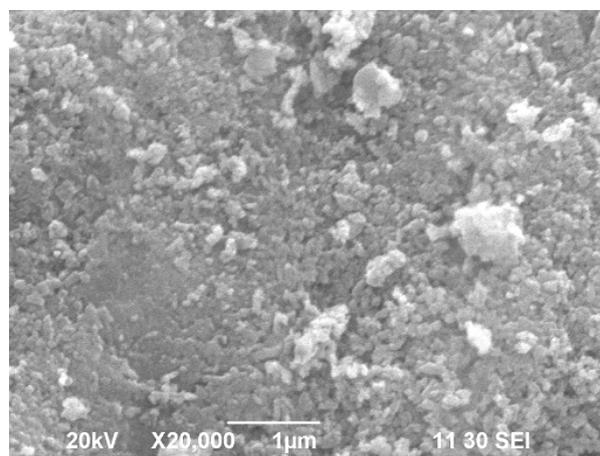
By using a facile thermal decomposition route, CoFe_2O_4 nanoparticles were successfully synthesized and characterized by XRD, HRTEM, SAED and SEM techniques. The average particle size of CoFe_2O_4 nanoparticles determined from XRD and HRTEM is about 12 nm. The present method is simplistic and commercially feasible. It is also efficient in terms of time and equipment. Hence, this method is an efficient and economical way to mass production of ultrafine cobalt ferrite powder.

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(a)



(b)

Fig. 5. a) SEM image of CoFe_2O_4 nanoparticles ($\times 10000$); b) SEM image of CoFe_2O_4 nanoparticles ($\times 20000$).

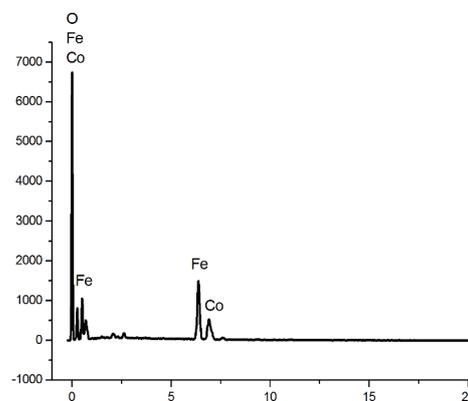


Fig. 6. EDX spectrum of CoFe_2O_4 nanoparticles.

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