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Preparation and characterization of cobalt oxide nanoparticles via solution combustion method

Mahesh D.Bedre[1], S.Basavaraja[2], D.Raghunandan[3], D.S.Balaji[1], A.Venkataraman[1]*
[1]Materials Chemistry Laboratory, Department of Materials Science, Gulbarga University, Gulbarga-585106, Karnataka, (INDIA)
[2]Veeco-India Nanotechnology Labarotory, Jawaharalal Nehru Cetre for Advanced Scientific Research, Bangalore-64, (INDIA)
[3]H.K.E's College of Pharmacy, Sedam Road, Gulbarga-585101, (INDIA)
E-mail : raman_chem@rediffmail.com
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ABSTRACT

The spherical shaped Co_3O_4 nanoparticles have interesting properties and potential applications in coatings, catalysis, sensors, anode materials in rechargeable batteries, solar energy absorbers, magnetism, etc. Inorganic nanoparticles with controlled size and shape are technologically important due to the strong correlation between these parameters and their properties. We have successfully prepared Co_3O_4 using a solution combustion method. The phase and purity of the synthesized product was examined by X-ray diffraction (XRD) pattern. Infrared spectroscopy studies were performed aiming to ascertain the metal oxygen bonding and nature of the synthesized cobalt oxide nanoparticles. SEM (Scanning electron microscope images show that the nanoparticles are nearly spherical in morphology and are in the range of 100 to 200 nm. Magnetic property and thermal behavior of the synthesized Co_3O_4 nanoparticles were studied by magnetic hysteresis loop tracer.

KEYWORDS

Cobalt oxide (Co_3O_4);
Solution combustion;
Structure and morphology;
SEM;
FTIR.

INTRODUCTION

In recent years, synthesis of nanoparticles has been intensively investigated. These materials have many special physical and chemical properties and potential applications owing to their unique particle sizes and surface effects[1-3]. In the past decades, many different techniques have been developed for preparation of nanoparticles. However, most research was focused on the preparation of noble metal and semiconductor metal oxide nanoparticles. Work on the preparation of nanocrystals of transitional metals and their oxides have been reported in the literature. Recently, the preparation, characterization, and application of some transitional metal oxide nanocrystals, such as cobalt oxide nanocrystals, have attracted due to their importance in technological applications based on their magnetic or catalytic properties[4-6]. Among various cobalt oxides, Co_3O_4 is an important ceramic oxide used for electrochemical, magnetic, solid-state sensors[7] heterogeneous catalysts, heterogeneous catalysts[8], electrochromic devices[9] and as absorbers of solar energy[10]. It was usually prepared by thermal decomposition of cobalt salts under an oxidizing atmosphere at temperatures between 250-900^{0}C[11-12]. In recent years, many methods such as sol-gel[13-15], spray pyrolysis[16],

chemical vapor deposition[17], chemical precursor routes[18-20], electrochemical and sonochemical synthesis[21-22] have been developed to obtain easily the crystalline Co_3O_4. However, a relatively high temperature is necessary in most of the above methods. In this paper, we present a simple route to prepare cobalt oxide (Co_3O_4) nanoparticles, using cobalt nitrate salt and PEG (polyethylene glycol) as the reactant. Combustion process is a relatively new technique, based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metal (usually nitrates) and some organic fuel, such as urea, citric acid, polymers, etc.[23-26]. The combustion process is due to an exothermic redox reaction between nitrate and the fuel. The large volume of gases produced during the reaction promotes the decomposition of over-inflated precursor gel and produces the nanoparticles. Some polymers, which contain polarity groups or atoms could complex metal ions and form a sol system without precipitation, to obtain a gel precursor. In this work, we choose polyethylene glycol (PEG) as the fuel to synthesize Co_3O_4 nanoparticles by combusting the cobalt salt. PEG solution has desired properties in water and contains many isolated hydroxyl functional groups, which not only can adsorb but can also complex with metal cations existing in the solution[27-29]. The PEG is a strong candidate for the formation of sol-gel system of metal. Moreover, Co_3O_4 is an excellent catalyzing material. A nanosized particle is a perfect catalyzing agent due to its huge surface area and activity. Hence, the preparation of nanosized Co_3O_4 particles is significant.

MATERIALS AND METHODS

All the chemicals were of AR grade and were used without further purification. Double distilled water was used for preparation of the required solutions.

Experimental techniques

In a typical procedure, an aqueous solution of cobalt nitrate was adopted as a starting material. 1 gm of cobalt nitrate and 1gm of PEG is dissolved in 10 ml of distilled water in two separate glass beakers of 100 ml capacity. Both the solutions were then mixed and kept approximately for half an hour at room temperature, till a red precursor solution was obtained. The precursor solution was then heated on a hot plate with vigorous agitation till the water of the solution completely evaporated and semisolid mass is obtained. Further this semisolid mass is heated to get a grey ash colored solid residue. The grey ashes obtained after combustion were calcined in an oven at 300^0C for 2 hrs to obtain the final product. The end product was triturated to obtain a fine powder which is subjected for further characterization.

Characterization techniques

The XRD pattern was obtained employing a JEOL JDX-8p spectrometer using CuKα radiation (λ = 1.54 Å). The X-ray generator was operated at 30 kV and 20 mA. The scanning range, 2θ was selected. The scanning speed of 1^0/min and a chart speed of 20 mm/min were used for the precise determination of the lattice parameters. High-purity silicon powder was used as an internal standard. The coherently diffracting crystallographic domain size (d_{XRD}) of the Co_3O_4 nanoparticles was calculated from X-ray diffraction line broadening after subtracting the contribution from the CuKα component (Rachinger correction) and correcting for the instrumental width. The integral line width was used in the Scherrer formula to calculate d_{XRD} of the (3 1 1) plane.

The scanning electron micrograph (SEM) images of the samples were obtained with a JSM-840A scanning electron microscope. The scanning electron microscope was operated at 12 kV. The FT-IR spectrum of Co_3O_4 nanoparticles was recorded on a Perkin-Elmer Spectrum One instrument in the range 4000-400 cm^{-1} at a resolution of 4 cm^{-1} by making KBr pellets. The preliminary magnetic measurement of the sample was recorded at room temperature on a Magneta, Magnetic hysteresis loop tracer.

RESULTS AND DISCUSSION

X-ray diffraction studies (XRD)

The phase and purity of the synthesized product was examined by X-ray diffraction (XRD) pattern. The X-ray diffraction pattern of Co_3O_4 sample is shown in figure1 is identified as the single phase Co_3O_4 with a suitably crystalline cubic structure (JCPDS file no.: 78-1970). The mean particle diameter was calculated from the XRD pattern according to the line width of the (3 1 1) plane refraction peak using the following Debye-Scherrer equation[30],

$$D = K\lambda / \beta_{1/2} \cos\theta$$

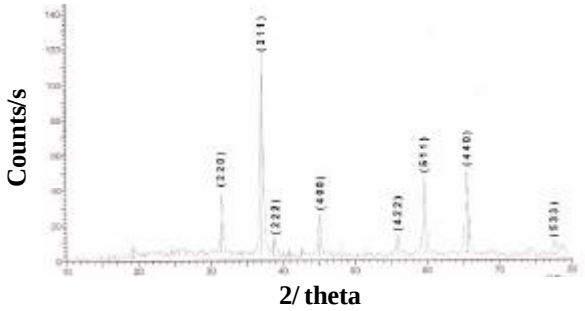

Figure 1: XRD spectra of Co_3O_4.

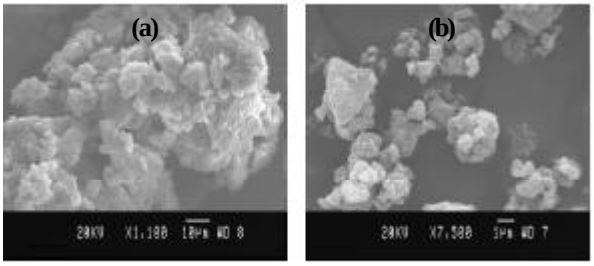

Figure 2.: SEM images of Co_3O_4 at low magnification and high magnification

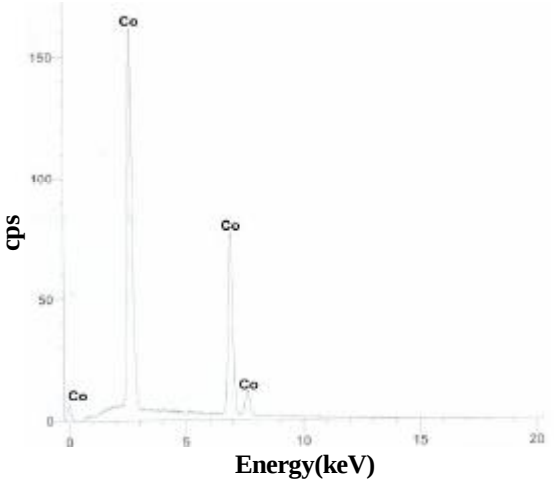

Figure 3: EDAX of Co_3O_4

The equation uses the reference peak width at angle θ, where λ is the X-ray wavelength (1.5418 Å), $\beta_{½}$ is the width of the XRD peak at half height and K is the shape factor, about 0.9 for spherical shaped particles. The average crystallite size calculated from peak width is about 50 nm, which is in accordance with the SEM results discussed later.

Fourier transform infrared spectroscopy (FT-IR) studies

Infrared spectroscopy studies were performed aiming to ascertain the metal oxygen bonding and nature of the synthesized cobalt oxide nanoparticles. FTIR spectra of the samples Co_3O_4 shows the absorption in the region 3380, 1640, 1085, 555 and 455 cm^{-1} as given in the TABLE 1. The peak at 3380 and 1640 cm^{-1} corresponds to water of hydration and the peak at 1085 cm^{-1} is due to the presence of some overtones. The peaks at ~550 and 450 cm^{-1} correspond to the metal-oxygen vibratonal modes. The peaks below 1000 cm^{-1} corresponds to the metal oxygen vibration modes. The metal oxygen frequency observed for the Co_3O_4 [31-32] is in accordance with literature value as given in TABLE 1.

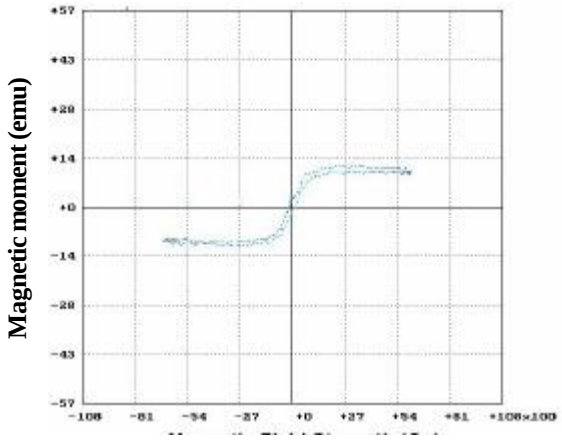

Figure 4: Magnetic Hystersis curve of the Co_3O_4 at room temperature

TABLE 1: IR band positions and fundamental vibrations

ν (cm^{-1})	Fundamental vibrations
550	ν (Co-O, T)
650	ν (Co-O)
1640	δ_{OH} (Co-OH, T)
3380	δ_{OH} (Co-OH, T)

The figure 2(a and b) shows the SEM images of the Co_3O_4 sample in low and high magnification respectively. In low magnification image, the agglomerated particles joined together one above the other to form cluster type structure in the range of 1 to 10 microns. However, in high magnification images shows nearly spherical nanoparticles of 100 to 200 nm are observed.

Energy dispersive X-ray microanalysis (EDAX)

The chemical identity and purity of the as synthesized Co_3O_4 were investigated with energy dispersive X-ray microanalysis (EDAX) and the pattern is shown in figure 3 clearly indicated the presence of only theo-

retical cobalt without any impurities indicating the purity of the sample.

Magnetic hysteresis

Magnetic measurements were performed on the cobalt oxide nanoparticles with the use of magnetic hysteresis loop tracer. Figure 4 shows the hysteresis loop for the cobalt oxide nanoparticles measured at room temperature (300 K), the saturation magnetization (M_s) obtained at room temperature was found to be 12.07 emu/g, remanent magnetization (M_r) was 2.13 emu/g and coercivity (H_c) was 140.50 Oe. This behavior suggests the magnetic nature of the sample.

CONCLUSIONS

Nanoparticles of Co_3O_4 has prepared by a solution combustion method. PEG could sequester with metal cation and formatted homogeneous solution. XRD and EDAX measurements confirmed the formation of pure and single-phase cobalt oxide (Co_3O_4) nanoparticles with the crystallite size of 50 nm calculated by Scherrer equation. The solution combustion method is simple and economical for the preparation of nanoparticles of metal oxides.

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