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Synthesis of zinc substituted cobalt ferrites via reverse micelle technique involving in situ template formation: A study on their structural, magnetic, optical and catalytic properties

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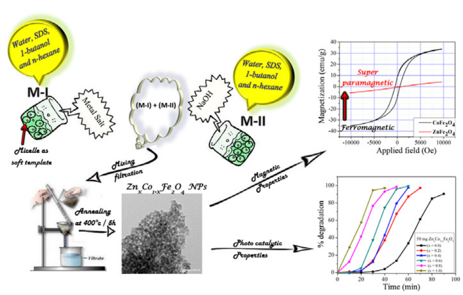
HIGHLIGHTS

- Controlled dimensions of Zn–Co ferrite nanoparticles by micro-emulsion technique.
- Spherical shape with uniform size distribution of ~5 nm was achieved.
- Significant shift from ferromagnetic to superparamagnetic with Zn^{2+} ion doping.
- Improved photocatalytic activity with Zn^{2+} ion doping.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano-crystalline particles of visible light responsive Zn–Co ferrites having formula $Zn_xCo_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were successfully synthesized via reverse micelle technique. Sodium dodecyl sulfate was used as a surfactant/templating agent. The ferrite formation was confirmed using powder X-Ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy. The spherical shape of the ferrite particles was established by High Resolution Transmission Electron Microscope (HR-TEM) analysis. From the magnetic studies, the ferromagnetic nature of $CoFe_2O_4$ was known. However, the nano-particles exhibited a transition from ferromagnetic to super-paramagnetic upon increasing the zinc concentration. In addition, the photo-Fenton activity of ferrites was also studied by carrying out degradation of Rhodamine B (RhB) dye under visible light irradiation. The catalytic activity increased with increase in zinc ion concentration.

1. Introduction

Homogeneous size distribution and regular shape of materials improve their applicability in various fields of science and technology. In order to control the particle growth and to reduce the energy losses associated with bulk powders; various research groups have proposed different technique to synthesize nano-sized particles, like hydrothermal method, ball milling, co-precipitation and reverse microemulsion method [1–7]. Out of these, reverse microemulsion method allows the fabrication of nano-crystals of almost homogeneous particle size, shape with well-defined boundaries and narrow size distribution. Reverse micelle method

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consists of mixing the two microemulsion system, one containing the metal salt precursors and the other having precipitating agent. The droplets of microemulsion behave as a nano-reactor, in which both the reactants come in contact with each other due the droplet collision and coalesce. Hence, nanometric size precipitates were formed in confined dimensions of the droplet [8]. The size of the micelle and hence, the final product, depends upon the water to surfactant molar ratio [9]. As the water to surfactant ratio is increased, particle size of the product increases [10].

A simple micro-emulsion synthesis route was applied by Pillai and Shah [11] to synthesize magnetic nano-particles of cobalt ferrite using water-in-oil emulsions consisting of water, cetyltrimethyl ammonium bromide (CTAB) as surfactant, n-butanol as co-surfactant and n-octane as oil phase. Obtained nano-particles were less than 50 nm in size and had high coercivity and saturation magnetization. Uskokovic et al. [12] reported the important role of precipitating agent and pH in process of synthesizing nano-sized Ni–Zn ferrite particles. Average particle size was found to be in the range of 20–30 nm for powders synthesized between precipitating pH values ranging in 8–10. Similarly, Kosak et al. [13] prepared zinc doped manganese ferrite and explained the role of co-surfactant for the expansion of the microemulsions stability region and made it possible to obtain more nano-particles as well. The particle size was in range of 4–9 nm with spherical shape. Thus, it can be concluded that the reaction conditions involved in the reverse micelle technique such as nature of surfactant, water to surfactant ratio, pH of solution, etc. strongly influence the particle size of ferrites, which in turn affects their properties.

The properties of ferrites are also influenced by their composition. Among various ferrites, cobalt ferrite is of utmost importance because of its unique and versatile properties. Further, the substitution of a non-magnetic ion/diamagnetic ion brings about interesting changes in its properties. For instance, zinc substitution in to the cobalt ferrite lattice tremendously influences the properties of cobalt ferrite. This is because zinc ions seek to the tetrahedral sites of the ferrite sub lattice, thereby resulting in a decreased magnetic moment. Fan et al. [14] reported the enhanced photo catalytic activity of cobalt doped zinc ferrite nanoparticles of 11–14 nm size for the degradation of methylene blue in 8 h. Sharma et al. [15] synthesized the MFe_2O_4 ($M = Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}$) spinel ferrite using sol–gel method having particle size of around 25–30 nm. The photo-Fenton activities of spinel ferrite were studied and it was found that zinc ferrite nanoparticles decolorize the textile dye in 45 min in comparison to the cobalt ferrite, where degradation occurs in 120 min.

Thus, suitable metal dopant, controlled particle size, shape with homogeneity in size distribution of ferrite nano-particles as well as the composition of the ferrite play a huge role in the enhancement of properties and catalytic activities. In addition, it would be interesting to study the role of zinc ion substitution in improving the catalytic behavior of other ferrites.

So, in our present work, our aim is to synthesize zinc doped cobalt ferrites by micro-emulsion method using sodium dodecyl sulfate (SDS)/1-butanol as soft template and to control the size distribution, particle morphology and shape of nano-particles. In addition, it is also aimed to investigate the photo-catalytic activity of the ferrites by generating an active Fenton's reagents for the photo-degradation of Rhodamine B (RhB) dye. The structure of obtained ferrite nano-particles was investigated by different techniques such as Powder X-ray Diffraction (XRD), High Resolution Transmission Electron Microscopy (HR-TEM), Energy Dispersive X-ray spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FT-IR). The magnetic and optical properties of nano composites were also studied.

2. Experimental

2.1. Materials

Cobalt chloride hexahydrate ($CoCl_2.6H_2O$, 97%), Zinc chloride ($ZnCl_2$, 98%), ferric chloride ($FeCl_3$, 99.5%), sodium dodecyl sulfate (SDS, 90%), sodium hydroxide (NaOH, 98%), sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2, 30% w/v) and Rhodamine B (99.7%) were purchased from Loba Chemicals and used without further purification. AR grade ethanol (C_2H_5OH 99.9%), n-butanol ($C_4H_{10}O$ 99.7%) and hexane (C_6H_{14} 99.7%) were purchased from Fisher Scientific. Deionized water was obtained using an ultra-filtration system (Milli-Q, Milipore) with a measured conductivity of 35 mho cm^{-1} at 25 °C.

2.2. Physical measurements

The powder X-Ray Diffraction (XRD) studies were carried out using Powder X-ray Diffractometer (PANanalytical) with Cu Kα radiation. The instrumental broadening, calculated from the (1 1 1) peak of Si sample was 0.7 Å. DIFFRAC-plus TOPAS, version 2.1 technical reference software was used to calculate the dimensional changes in the lattice parameter. HR-TEM images and EDX were recorded using FEI Technai G2 F20 operated at 200 keV with magnification of 6×10^6 times and resolution of 0.2 A°. The FT-IR spectra were recorded using FT-IR instrument (PERKIN ELMER) with KBr pellets between the range 4000–400 cm^{-1}. A pressure of 8 ton was applied to prepare the pellets. Optical properties were analyzed by UV–vis absorption (Analytikjena specord-205) spectrophotometer. The magnetic properties were measured at room temperature by a Vibrating Sample Magnetometer (VSM) (155, PAR) up to a magnetic field of ±10 kOe. Specific surface area was determined by N_2 adsorption method using single point surface area analyzer (SMARTSORB-93) after preheating the samples at 150 °C for 1 h. Photo-irradiation was carried out using 160 W Hg lamp having a flux density of 96,000 lux at the target surface. The distance between the light source and the target surface was 6 inches.

2.3. Synthesis of zinc doped cobalt ferrite by reverse micelle method

Zinc doped cobalt ferrites of the formula, $Zn_xCo_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were synthesized using reverse micelle method as shown in Fig. 1. In reverse micelle technique, two microemulsion systems were prepared by mixing water, SDS, 1-butanol and n-hexane in following weight ratio (89.82:3.03:5.568:1.637, w/w) [16]. A clear transparent solution was obtained in 10 min, which indicated the formation of stable micelle. Ferric chloride, zinc chloride and cobalt chloride were dissolved in first microemulsion system in required stoichiometric amounts and were sonicated for 30 min. In second microemulsion, 20 ml of 5 M NaOH was added. The two microemulsions were mixed together and subjected to rapid magnetic stirring for an hour. Hydroxides of zinc, cobalt and iron were precipitated within the nano reactors which were formed due reverse micelle process. The obtained brown precipitates were filtered, washed several times with distilled water and absolute ethanol. The final product was dried in oven at 110 °C. Further, the sample was annealed at 400 °C for 5 h.

2.4. Photo-Fenton activity

The photo-Fenton activity of $Zn_xCo_{1-x}Fe_2O_4$ nano-particles was evaluated by the degradation of aqueous solution of RhB under visible light irradiation. 50 mg of catalyst was added to

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