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Magnetically separable copper substituted cobalt–zinc nano-ferrite photocatalyst with enhanced photocatalytic activity

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ABSTRACT

A series of nano crystalline copper substituted cobalt zinc ferrites, $Co_{0.6}Zn_{0.4}Cu_xFe_{2-x}O_4$ ($x=0.2$, 0.4, 0.6, 0.8 and 1.0) with cubic spinel crystal structure were synthesized by sol–gel auto combustion method. The X-ray diffraction analysis confirmed the formation of cubic phase with *Fd-3m* space group of all the prepared nano-ferrites. The lattice parameter was found to increase with increase in copper substitution. This may be attributed to larger ionic radius of copper as compared to that of iron. The electrical studies revealed that all prepared ferrites are semiconducting in nature. The saturation magnetization was found to be maximum at $x=0.4$, obeying Neel's two sub-lattice model and decreased thereafter due to spin canting effect. The photo catalytic degradation of methyl orange (MO) dye by $Co_{0.6}Zn_{0.4}Cu_xFe_{2-x}O_4$ ($x=0.2$, 0.4, 0.6, 0.8 and 1.0) ferrite was studied under visible irradiation. Significant enhancement in photo degradation of MO can be ascribed to the B-site occupancy of copper ion. This catalyst is also well separable from water media by applying external magnetic field, thus it can act as a promising catalyst for the remediation of textile wastewater.

1. Introduction

Environmental problems associated with perilous wastes and toxic water-pollutants have attracted much attention because of water scarcity and public health. Organic dyes, a constituent that is widely used in textile, paper, food and cosmetic industries are one of the major groups of pollutants in wastewater. Some of these dyes are transformed to intermediates which cause harmful effects on the aquatic life even at very low concentration [1]. These dyes can undergo anaerobic discolorations which are carcinogenic in nature, cause allergies problem [2,3]. Hence it is very important to safeguard the environment from such contaminants. Different methods have been used for color removal from the textile effluents such as adsorption, precipitation, air stripping, flocculation, reverse osmosis, and ultra-filtration [4].

Photo-catalysts such as ferrites are one of the most efficient materials for the removal of dye from the industrial effluents because of their excellent performance in the pollutant degradation. Many research groups have reported the photo-degradation of organic pollutants with the use of ferrite nanoparticles [5–9]. Fu et al. [5] reported the degradation of methylene blue (MB), Rhodamine B (RhB), methyl orange (MO), active black BL-G and active red RGB under visible-light irradiation with combination of $CoFe_2O_4$ nanoparticles and graphene. Nano-crystalline $CoFe_2O_4$ embedded one dimensional ZnO prepared by sono-chemical

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route have been used for the photo-catalytic degradation of phenolphthalein under UV irradiation and observed enhancement of the photocatalytic activity of the sample is due to the formation of a hetero-junction at the interface of $CoFe_2O_4$ and ZnO [6].Controlled synthesis of monodisperse $CoFe_2O_4$ nanoparticles by the phase transfer method and their catalytic activity on MB discoloration with H_2O_2 have been studied by Feng et al. [7] and the authors concluded that the $CoFe_2O_4$ nanoparticles show excellent catalytic performance in the oxidation of MB dye. The removal of RhB by $Co_xFe_{3-x}O_4$ magnetic nanoparticles activated Oxone was performed by Su et al. [8]. Photo-catalytic activity of $CoFe_2O_4$–Fe_3O_4 magnetic nano-composites (MNCs) synthesized by hydrothermal process was studied by Mishra et al. [9] and they reported that the MNCs degrade 93% of MO in 5 h of UV irradiation. Fan et al. [10] studied the photo-catalytic degradation of MB under visible light irritation with cobalt doped zinc ferrite ($Zn_{1-x}Co_xFe_2O_4$) and concluded that the $Zn_{0.8}Co_{0.2}$-Fe_2O_4composition had the highest photo-catalytic activity.

To the best of our knowledge, marvelous work has been reported on cobalt ferrite but till now there is no report about visible-light-induced photocatalyst based on copper substituted cobalt–zinc nanoferrites. In the present paper, we study the influence of Cu substitution on structural, magnetic and electrical properties of $Co_{0.6}Zn_{0.4}Cu_xFe_{2-x}O_4$ nano-ferrite and their photo-catalytic efficiency for the degradation of Methyl Orange (MO) dye.

2. Experimental

2.1. Synthesis of cobalt–zinc nanoferrite

Nanoparticles of $Co_{0.6}Zn_{0.4}Cu_xFe_{2-x}O_4$ were synthesized by employing sol–gel auto combustion method [11,12]. The detailed process is represented in Fig. 1. The stoichiometric amount of precursors including citric acid ($C_6H_8O_7$), $Fe(NO_3)_3\cdot 9H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$ were used to prepared the nanoferrites. The metal salts were added in the molar ratio (Co:Zn:Cu:Fe = 0.6:0.4:x:2 − x) to get the desired product. At the first step, all the metal nitrates and citric acid were dissolved separately in the minimum amount of distilled water. Then all the metal nitrate solutions were mixed followed by the addition of the citric acid. An appropriate amount of ammonia solution was added to the solution to adjust the pH value to about 6. The mixed solution was stirred using a magnetic agitator at 80 °C. During evaporation, the solution became viscous and finally converted into a very viscous brown gel. The decomposition reaction continued till the whole citrate complex was consumed. The auto-ignition was completed within a minute, yielding the brown colored ashes. After that, all the samples were annealed at 400 °C, 600 °C, 800 °C and 1000 °C in a muffle furnace for 2 h.

2.2. Photo-catalytic activity evaluation

Photo-catalytic activity of all the magnetic nanoparticles was evaluated by measuring the degradation of MO in the aqueous solution under visible light irradiation. A 400 W mercury lamp was employed as light source. For each experiment, 0.1 g of photo-catalyst was dispersed in 100 ml of 30 mg/l of the MO aqueous solution. Prior to the irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure the adsorption–desorption equilibrium of MO aqueous solution with the photo-catalyst. The solution was exposed to visible light under stirring after addition of 2 ml of 30% H_2O_2. At given time intervals, 3 ml of aliquots were withdrawn and centrifuged to remove ferrite particles. The concentration of MO in aqueous solution was determined with the help of UV–vis spectrophotometer.

2.3. Physical measurements

Fourier Transform Infrared (FT-IR) spectra were recorded on Perkin Elmer RX-1 FT-IR spectrophotometer using KBr pellets in the range 1000–400 cm^{-1}. Crystal structure of all the samples were examined by Powder X-Ray Diffraction (XRD) patterns at room temperature (Bruker D8 Advance diffractometer), using Cu-$K\alpha_1$ radiation. The transmission electron microscopy (TEM) study was performed using a Hitachi (H7500) Transmission Electron microscope, operated at 120 kV. The electrical properties were measured using two-probe instrument in the range of 313–373 K. The magnetic properties were measured at room temperature by a Vibrating Sample Magnetometer (VSM) (155, PAR) up to a magnetic field of $\pm$15 kOe. Photo-irradiation was carried out using 400 W Hg lamp. The concentration of MO during the degradation was monitored by UV–vis spectrophotometer JASCO, V-530.

3. Results and discussion

3.1. Characterization of ferrites

3.1.1. FT-IR characterization

The FT-IR transmission spectra of ferrites expected to exhibit two characteristic peaks below 1000 cm^{-1} corresponding to the tetrahedral and octahedral stretching vibrations of the ferrite. The difference in the position of the bands for the various compositions was expected because of the difference in the distances for the octahedral and tetrahedral ions. However, only one peak was observed in the range of 571 cm^{-1} which was attributed to the intrinsic stretching vibrations of the tetrahedral M–O bond. The band corresponding to the octahedral stretching was not observed. This may be due to the reason that sometimes the band due to octahedral M–O stretching is observed slightly below 400 cm^{-1}. Since the given FT-IR spectra ranged between 400 cm^{-1} and 1000 cm^{-1}, any peaks below 400 cm^{-1} could not be observed. A sharp peak at 720 cm^{-1} corresponds to that of nujol.

3.1.2. Transmission electron microscopy (TEM) studies

The Transmission electron micrographs of all the ferrite samples were recorded by ultrasonically agitating the ferrite samples. Fig. 2 shows the typical TEM micrograph of $Co_{0.6}Zn_{0.4}Cu_{0.4}Fe_{1.6}O_4$ annealed at 1000 °C. The ferrite particles were of nano-dimensions ~25 nm and had