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Spinel $Ni_xZn_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$) nano-photocatalysts: Synthesis, characterization and photocatalytic degradation of methylene blue dye

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ABSTRACT

Spinel $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.0$ to 1.0) nanoparticles were successfully synthesized by a simple microwave combustion method (MCM) using metal nitrates as raw materials and glycine as the fuel. The structural, morphological and opto-magnetic properties of the spinel $Ni_xZn_{1-x}Fe_2O_4$ ferrites were determined by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray (EDX) spectroscopy, high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) pattern, UV–Visible diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy and vibrating sample magnetometer (VSM). Powder XRD, and EDX analysis was confirmed the formation of pure phase of spinel ferrites. HR-SEM and HR-TEM analysis was confirmed the formation of sphere like-particle morphology of the samples with smaller agglomeration. VSM analysis clearly showed the superparamagnetic and ferromagnetic nature of the samples. The M_s value is 3.851 emu/g for undoped $ZnFe_2O_4$ sample and it increased with increase in Ni content. Photo-catalytic degradation (PCD) of methylene blue (MB) dye using the samples were carried out and observed good PCD results.

1. Introduction

Recently, nanostructured spinel ferrite materials possess unique electro-magnetic, optical and catalytic properties with extensive range of applications in multidisciplinary areas [1–5]. Spinel ferrites are semiconductor materials with a general formula AB_2O_4 ($A = Mn^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}, etc.: $B = Fe^{3+}$) exhibit excellent opto-magnetic, electrical and catalytic properties. Among them spinel zinc ferrite ($ZnFe_2O_4$) is an essential material in the areas of gas sensor [4], catalyst [5], photo-catalyst [6] etc. It is already reported that $ZnFe_2O_4$ is a normal spinel structure with Zn^{2+} ions situated at the tetrahedral (A) sites, whereas Fe^{3+} ions at the octahedral (B) sites [2].

Moreover, metal cations such as Mn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, etc. were doped into the spinel $ZnFe_2O_4$ nanostructures, they improved the structural, morphological, magneto-optical and photocatalytic activity, due to their significant morphology and higher surface area with smaller particle size. However, Ni-Zn ferrite has attracted a vast of interest, because of its promising electromagnetic properties such as high resistivity, high permeability, and low dielectric loss in high frequency device applications. Also used in many areas such as biosensors, drug delivery, catalysts, pigments etc [7–10].

Various methods such as solvothermal, co-precipitation, hydrothermal, citrate precursor, sol–gel and polyol methods [11–17] etc. have been used for the preparation of Ni-Zn ferrite nanoparticles. However, the above said methods meets some weakness such as, high-energy consuming, need of complicated equipment, requirement of a strong base, higher processing temperature and also require rather long reaction time to complete the crystallization of final products [18]. Recently, microwave irradiation method has gained much importance for the preparation of such functional nano ferrites [19,20]. In this method, microwaves interacts the

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reactant molecules at the molecular level leads to a homogeneous heating, which results in the formation of ferrite nanoparticles within few minutes and leads to a higher efficiency [19,20].

Nowadays, spinel type magnetic nanomaterials have been extensively used in interdisciplinary areas and environmental applications, because of their outstanding catalytic activity, chemical stability, non-toxicity, and also reusability without loss in its catalytic activity. Due to the magnetic nature, spinel type nanomaterials have been easily separable and reusable catalysts. Hankare et al. [21] reported spinel $ZnFe_2O_4$ nano-catalysts for the PCD of methyl red and thymol blue. Manikandan et al. reported spinel ferrites photo-catalysts prepared by microwave irradiation method for the photocatalytic degradation (PCD) of methylene blue (MB) and 4-chloro phenol (4-CP); they found that the photocatalytic activity is increased with decrease in the crystallite size. Also, they reported the catalytic oxidation of benzyl alcohol into benzaldehyde using spinel ferrite nano-catalysts and found that the catalytic activity is increased with increase in the dopant cations [22–25]. Chung et al. [26] reported the PCD of methylene blue using TiO_2-$NiFe_2O_4$ and SiO_2-$NiFe_2O_4$ prepared by spray pyrolysis method. Fu et al. [27] reported $ZnFe_2O_4$-graphene photocatalyst for the PCD of MB. Xiong et al. [28] reported CdS-MFe_2O_4 nanocomposites for the PCD of rhodamine B and MB under visible-light irradiation.

However, there is no literature is available for the degradation of methylene blue dye under visible-light irradiation using Ni-doped $ZnFe_2O_4$ nano-photocatalysts prepared by microwave irradiation method using glycine as the fuel. Therefore, we have synthesized spinel $Ni_xZn_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) nanoparticles by microwave combustion method using glycine as the fuel. Also, spinel $Ni_xZn_{1-x}Fe_2O_4$ nanoparticles is highly remarkable and attractive to study as photocatalysts for PCD of azo dyes such as methylene blue, methyl orange, blue rhodamine B, methyl red and thymol blue, etc.

2. Experimental

2.1. Materials and methods

All the chemicals used in this study were of analytical grade obtained from Merck, India and were used as received without further purification. Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98%) and nickel nitrate ($Ni(NO_3)_2.6H_2O$) were used as precursors and glycine as a fuel for this method. The compositions were prepared with the addition of nickel by different molar ratios ($Ni_xZn_{1-x}Fe_2O_4$ with x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) to $ZnFe_2O_4$. For the preparation of pure and Ni-doped $ZnFe_2O_4$ using the microwave combustion technique, the precursor mixture in glycine was placed into a domestic microwave oven and exposed to the microwave energy in a 2.45 GHz multimode cavity at 850 W for 10 min. After the completion of the reaction, the solid powder was obtained and then it was washed with ethanol and dried at 70 °C for 1 h. The obtained powders were labeled as $ZnFe_2O_4$, $Ni_{0.2}Zn_{0.8}Fe_2O_4$, $Ni_{0.4}Zn_{0.6}Fe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$, $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and $NiFe_2O_4$ respectively and were used for further characterizations.

2.2. Characterization techniques

The structural characterization of $Ni_xZn_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) nanoparticles were performed using a Rigaku Ultima X-ray diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). Structural refinements using the Rietveld method was carried out using PDXL program; both refined lattice parameters and crystallite size of the obtained ferrites were reported. The surface functional groups were analyzed by Perkin Elmer FT-IR spectrometer. Morphological studies and energy dispersive X-ray analysis of $Ni_xZn_{1-x}Fe_2O_4$ nanoparticles have been performed with a Jeol JSM6360 high resolution scanning electron microscope (HR-SEM). The transmission electron micrographs were carried out by Philips-TEM (CM20). The surface area was derived from the N_2 adsorption–desorption isotherms using liquid nitrogen at 77 K by an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). The UV–Visible diffuse reflectance spectrum (DRS) was recorded at room temperature using Cary100 UV–Visible spectrophotometer to estimate their band gap energy. The photoluminescence (PL) properties were recorded using Varian Cary Eclipse Fluorescence Spectrophotometer. Magnetic measurements were carried out at room temperature using a PMC Micro-Mag 3900 model vibrating sample magnetometer (VSM) equipped with 1 T magnet.

2.3. Photocatalytic-degradation procedures

All photochemical reactions under identical conditions were carried out in a self-designed photocatalytic reactor. This model consists of eight medium pressure mercury vapor lamps (8 W) set in parallel and emitting 365 nm wavelength. It has a reaction chamber with specially designed reflectors made of highly polished aluminium and built in cooling fan at the bottom and black cover to prevent UV leakage. It is provided with the magnetic stirrer at the center. Open borosilicate glass tube of 40 cm height and 12.6 mm diameter was used as a reaction vessel. The irradiation was carried out using only six parallel medium pressure mercury lamps. The solution was aerated continuously by a pump to provide oxygen and for the complete mixing of solution.

3. Results and discussion

3.1. HR-SEM analysis

High resolution scanning electron microscopy (HR-SEM) was used to examine the surface morphology of the samples. Fig. 1a-c shows the HR-SEM micrographs of $ZnFe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$, $NiFe_2O_4$ samples, respectively, exhibited uniform, almost spherical shaped particle like morphology with loosely agglomerated particles.

3.2. HR-TEM analysis

Fig. 2a-c shows the high resolution transmission electron microscopy (HR-TEM) images of $ZnFe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$, $NiFe_2O_4$ samples, respectively, which consists of spherical shaped nanoparticles, which are good agreement and evidence of HR-SEM images. Also, the particle sizes of the sample ranging from 13 nm to 17 nm. Crystallite sizes, obtained from powder XRD analysis, are consistent with the sizes calculated from HR-TEM. Fig. 2d shows the selected-area electron diffraction (SAED) pattern of $Ni_{0.6}Zn_{0.4}Fe_2O_4$ sample, which confirms well crystalline nature of the final product. Also, show spotty ring pattern without any additional diffraction spots, which characteristics the well crystallites of the spinel ferrite structure [29].

3.3. EDX analysis

Fig. 3a-c shows the energy dispersive X-ray (EDX) results of $ZnFe_2O_4$, $Ni_{0.6}Zn_{0.4}Fe_2O_4$, $NiFe_2O_4$ samples, respectively. The peaks corresponding to the elements Fe, Zn and O were observed in undoped $ZnFe_2O_4$ (Fig. 3a) and the peaks of the elements Fe, Zn, Ni and O were observed in $Ni_{0.6}Zn_{0.4}Fe_2O_4$ sample (Fig. 3b). Also, the peaks corresponding to the elements Fe, Ni and O were observed in