Photocatalytic activity of Zn-doped Fe₂O₃ nanoparticles: a combined experimental and theoretical study

R SIVARANJANI, A THAYUMANAVAN and S SRIRAM*

Department of Physics, School of Electrical and Electronics Engineering, SASTRA Deemed University, Thanjavur 613401, India

*Author for correspondence (sukansriram@gmail.com)

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Abstract. Iron oxide (Fe₂O₃) nanoparticles were synthesized by a simple co-precipitation method. The effect of Zn concentration on Fe₂O₃ nanoparticles was investigated by structural and electronic properties. X-ray diffractograms indicate the formation of a hematite Fe₂O₃ structure. The calculated particle sizes for undoped-Fe₂O₃ and Zn-doped Fe₂O₃ are 31 and 15 nm, respectively. The photocatalytic test was performed against methylene blue to find the efficiency of the photocatalytic activity of the prepared nanoparticles. From the results, it is found that compared to undoped-Fe₂O₃, the efficiency of Zn-doped Fe₂O₃ increases considerably. To understand the mechanism behind the photocatalytic activity, a DFT-based calculation was performed to measure the band edge positions of the undoped and Zn-doped Fe₂O₃ nanostructures and the results are matched well with experimentally observed values.

Keywords. Fe₂O₃ nanoparticles; Zn doping; photocatalytic activity; DFT; bandgap and mobility.

1. Introduction

The contamination of the environment is majorly caused by the growth of industries. An important source of this contamination is organic dyes because they are non-biodegradable and toxic. Textile industry effluents contain a large number of organic dyes which are harmful to living species and the land's nearby industries. During the dyeing process, large amounts of effluents are released with high toxicity which make infertile the surrounding areas. To avoid this, many types of research studies are going on to find an efficient cost-wise and power consumption-wise methodology. Among many methods, the photocatalytic process [1] is one in which semiconductors are used to degrade many organic dyes. There are many semiconductors available for enhanced photocatalytic dye degradation. Among them, Fe₂O₃ photocatalysts have been successfully used to convert organic pollutants in water into the pollutant-free material through ultra-violet (UV) light [2]. It is a very attractive semiconductor photocatalyst due to its visible light active band gap of 1.9–2.1 eV [3]. It is highly resistive to photocorrosion. The application of Fe₂O₃ semiconductor is limited because of its higher charge carrier recombination rate. The photocatalytic activities of Fe₂O₃ doped with other suitable dopants lead to the efficient recombination of the photogenerated electron and hole pairs, which consequently improve the photocatalytic activity of Fe₂O₃. Many methods are used to produce Fe₂O₃ nanoparticles with various dopants [3–8]. Zn is one of the most suitable candidates for the Fe₂O₃ lattice, since it has valence properties similar to Fe. There are various reports available

in the literature based on the Fe₂O₃ nanoparticles for dye degradation [9–14]. However, only a few reports are available on Zn-doped Fe₂O₃ for dye degradation. Here, in the present work, the aim is to prepare the Zn-doped Fe₂O₃ nanoparticle as an efficient photocatalyst for organic dye degradation by a facile co-precipitation technique. Also, a theoretical calculation using density functional theory (DFT) is performed to gain an insight into the photocatalytic performance of the prepared nanoparticles based on the electronic band edges of the corresponding nanostructures.

2. Experimental

Undoped and Zn-doped Fe₂O₃ nanoparticles were synthesized by a simple and cost-effective soft chemical method. For the preparation of Fe₂O₃ nanoparticles, 0.1 M of ferric chloride was dissolved in 100 ml of deionized water with continuous stirring. After the homogeneous precursor formation, 0.1 N of NaOH was added drop by drop to maintain the pH value of the solution at 9. This mixture was heated at 85°C for 2 h with continuous stirring with a magnetic stirrer. Then, the solution was allowed to cool at room temperature and kept undisturbed for 24 h. A brownish precipitate was obtained, and it was filtered and washed using a mixture of water and ethanol in a ratio of 3:1. The obtained product was then dried at 110°C for 30 min. For the preparation of Zn-doped Fe₂O₃ nanoparticles, two different solutions with 10 and 20 at% of Zn concentration were prepared using zinc acetate as a

precursor for Zn with the same preparative conditions. Finally, all the prepared samples were annealed at 400°C for 2 h in a normal atmosphere and allowed to cool down to room temperature.

2.1 Characterization

The crystalline structure was determined by using an X-ray diffractogram (XRD) (PANalytical-PW 340/60X'pert PRO) with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). Surface micrographs are recorded using a transmission electron microscope (TEM) (JEOL-2010) with an operating voltage of 200 kV. The Fourier transform infrared (FTIR) spectra were recorded in the range of 4000–400 cm^{-1} using an FTIR spectrometer (Spectrum 100, Perkin Elmer, USA).

2.2 Evaluation of MB degradation

The photocatalytic activities of the prepared nanoparticles were evaluated against the methylene blue (MB) dye in aqueous media under visible light radiation using an Xe arc lamp (300 W). Fifty milligrams of the prepared nanoparticles were dissolved in 100 ml MB aqueous solution ($1 \times 10^{-5} \text{ mol l}^{-1}$) separately and stirred in the dark atmosphere until the adsorption–desorption equilibrium is reached. Under the ambient atmospheric conditions, the mixture was exposed to visible light. At every 15 min interval, the reaction solutions were centrifuged and filtered to remove the photocatalyst. The photocatalytic reaction was monitored by recording the absorption spectrum of the MB ($\lambda = 664 \text{ nm}$) dye in the reaction solution for every 15 min using a UV–Vis spectrophotometer (Systronics 2003).

2.3 Computational details

DFT calculations were performed to theoretically validate the photocatalytic activity of the prepared nanoparticles by using the SIESTA package [15]. Generalized gradient approximation with Perdew–Burke–Ernzerhof [16] parameterization was used to estimate the exact exchange–correlation energy. The Troullier–Martins scheme-based pseudopotential was used to replace the interaction of core ions and valence electrons. A $3 \times 3 \times 3$ Monkhorst–Pack grid was used for Brillouin zone sampling. The plane wave cut-off in a three-dimensional space was set at 400 eV. The structures were optimized to ground state energy by employing the conjugate-gradient method.

3. Results and discussion

3.1 Structural studies

The phase composition and the crystalline structure of the prepared nanopowders are analysed by XRD. The obtained patterns are depicted in figure 1. From the diffractograms,

Figure 1. XRD patterns of (a) Fe_2O_3 , (b) Zn 10 at% doped- Fe_2O_3 and (c) Zn 20 at% doped- Fe_2O_3 .

it can be seen that wide and intense peaks are observed with mixed phases. The peaks are matched with an $\alpha\text{-Fe}_2\text{O}_3$ (hematite) (JCPDS card no. 89-0599) phase and the peak positions are identified as (012), (104), (110), (113), (024), (116), (214), (300) and (131) planes, respectively. However, a peak around 26° does not match with the hematite phase, and it is identified and assigned to the Fe_3O_4 (211) plane. The preferential growth of the nanoparticles is identified in the (110) plane. In the case of Zn-doped (at 10%) Fe_2O_3 , many peaks present in the undoped- Fe_2O_3 are diminished, and the crystalline structure is disturbed. This may be due to the placement of interstitial dopant atoms (Zn) inside the Fe_2O_3 lattice. It is also noticed that a secondary phase corresponding to the ZnO (110) plane confirms the presence of Zn in the base material. When the percentage of Zn increased to 20%, the crystallinity of the material dropped further, indicating that more strain is induced in the Fe_2O_3 lattice.

The crystallite sizes of the prepared Fe_2O_3 and Zn-doped Fe_2O_3 nanoparticles were determined by using Scherrer's formula [17]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

Figure 2. TEM images of the prepared Fe_2O_3 nanoparticles (a) at 10 nm level and (b) atomic plane view.

where λ is the $\text{CuK}\alpha$ radiation, β the full-width at half maximum value and θ the angle of diffraction. The calculated crystallite sizes are 31.25, 15.39 and 15.08 nm for Fe_2O_3 , $\text{Fe}_2\text{O}_3\text{-Zn@10\%}$ and $\text{Fe}_2\text{O}_3\text{-Zn@20\%}$, respectively. This indicates that when the Zn atom is doped with the Fe_2O_3 lattice, strain is induced, and hence the crystalline structure is disturbed. This is confirmed by the XRD spectra. The dislocation density is a measure of finding the defects inside the crystal, which can be determined by using the following formula [18]:

$$\delta = \frac{1}{D^2}. \quad (2)$$

The calculated dislocation densities of bare and Zn-doped Fe_2O_3 are 0.12×10^{15} , 0.42×10^{15} and 0.43×10^{15} lines m^{-2} , respectively. They indicate that on the addition of Zn to Fe_2O_3 , the degree of crystallization becomes very poor when compared with undoped- Fe_2O_3 .

3.2 Microstructural analysis

The TEM of Zn-doped Fe_2O_3 nanoparticles is shown in figure 2. From the figure, it can be seen that the prepared particles are spherical in nature. It is also noted that the grains are evenly distributed, and this may be attributed to the small size of the nanoparticles with high surface energy. The lattice fringes (figure 2b) at the level of 0.2 nm indicated the (116) plane with a 'd' value spacing of 0.16 nm.

3.3 FTIR spectrum analysis

The vibrational bands and the functional groups present in the prepared nanoparticles were analysed by taking the FTIR spectrum at room temperature. FTIR spectra of Fe_2O_3 and

Figure 3. FTIR spectra of Fe_2O_3 and Zn-doped Fe_2O_3 nanoparticles.

Zn-doped Fe_2O_3 are shown in figure 3. It is seen from the FTIR spectra of the prepared Fe_2O_3 nanoparticles, at 3422.14 cm^{-1} ,

Figure 4. Absorption spectra of (a) pristine ZnO, (b) 10% and (c) 20% Zn-doped Fe₂O₃ nanoparticles.

that a broad peak is observed, and it is attributed to the stretching mode of a hydroxyl group (O–H) present on the surface. A shoulder peak at 2922.14 cm^{-1} is regarded as $-\text{CH}_2-$ and $-\text{CH}_3-$ groups. Two peaks observed at 1626.31 and 1384.30 cm^{-1} are attributed to the asymmetric (C–O) and symmetric stretching (C–O) frequencies of the carbonyl groups, respectively. The absorption bands appearing at 576.86 cm^{-1} are attributed to the vibrations of Fe₂O₃ [19]. In the case of Zn-doped Fe₂O₃ nanopowders, the FTIR spectrum shows only the hydroxyl group (O–H) around 3400 cm^{-1} . However, the presence of the Fe–O stretching mode of Fe₂O₃ is maintained around 570 cm^{-1} . However, the Zn percentage is increased to 20 at% and an additional peak of around 440 cm^{-1} is increased, and this is attributed to the stretching of Zn–O [20]. This additional peak confirms the presence of Zn atoms in the Fe₂O₃ lattice.

3.4 Photocatalytic studies

The photocatalytic activity of Fe₂O₃ and Zn-doped Fe₂O₃ nanoparticles was evaluated for MB dye degradation under visible light illumination. The absorption spectra of the MB dye with undoped and Zn-doped Fe₂O₃ nanoparticles are shown in figure 4. From the spectra, it is seen that the

characteristic absorption of MB (at 663 nm) was decreased when increasing the irradiation time. It is also seen from the figure that when Zn was doped with Fe₂O₃, the characteristic peak of MB is broadened, indicating the incorporation of Zn on Fe₂O₃. The efficiency of the prepared nanoparticles for degrading the MB dye can be calculated using the following equation [21]:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100, \quad (3)$$

where C_0 , C_t , A_0 and A_t are the initial concentration, the concentration at any time, the initial absorption and the absorption at any time, respectively. Table 1 shows the calculated dye degradation efficiencies of the undoped and Zn-doped Fe₂O₃ samples. From the values in the table, it can be seen that the degradation efficiency increases with the increase in doping concentration of Zn. The degradation efficiencies of the prepared powders for the same amount of dye concentration have been reported in [22] for the ZnO photocatalyst functionalized by graphitic carbon nitride (gC₃N₄) and silver (Ag). The photocatalytic degradation of the MB dye can also be explained by plotting a first-order kinetic plot described by Langmuir–Hinshelwood [23]. Figure 5 shows the C/C_0 as a function of

Table 1. Dye degradation efficiencies of Fe₂O₃ nanoparticles.

Structure	Efficiency (%)
Fe ₂ O ₃	78.17
Fe ₂ O ₃ @Zn10%	82.35
Fe ₂ O ₃ @Zn20%	84.36

Figure 5. Photocatalytic degradation as a function of time for Fe₂O₃ nanoparticles.

light exposure time for the MB dye. The rate constant k is calculated by using the equation [22]:

$$k = \frac{\ln(C_0/C)}{t}, \quad (4)$$

where C_0 , C and t are the concentration of the dye solution before irradiation, after irradiation and time in minutes, respectively. The calculated rate constants for the samples Fe₂O₃ and Zn-doped Fe₂O₃ are 0.0170, 0.050548 and 0.06714 min⁻¹, respectively (figure 6).

The enhancement of the photocatalytic activity may be due to the decrease in the diffusion path length of the photogenerated electrons excited by UV-visible light irradiation and by the reduction of the crystallite size. In the case of the Zn-doped Fe₂O₃, the enhancement is due to the shift of the band edges of Fe₂O₃ by the incorporation of the Zn atoms in the Fe₂O₃ lattice. Due to this, the photon energy can easily shift the valence band (vb) electrons into the conduction band (cb). This enhances the photocatalytic activity of the prepared Zn-doped Fe₂O₃ nanoparticles.

The mechanism of the photocatalytic activity of Zn-doped Fe₂O₃ nanopowders is shown in figure 5.

Since there are two processes majorly involved in organic dye degradation (photocatalytic and photosensitization), it is necessary to identify which one is more influential among it. Generally, in the photosensitization process, the light

absorbed by the MB dye undergoes excitation. Then, the e⁻ from the excited dye is transferred to Fe₂O₃, and hence a series of consecutive reactions lead to the production of CO₂ and H₂O. On the other hand, due to the light irradiation, the transfer of an electron from the vb to the cb of Fe₂O₃ undergoes reduction and due to the holes in the vb result in oxidation reactions. However, the possible mechanism for the Fe₂O₃ photocatalytic activity is discussed in detail [24]. The photogenerated electrons and holes are created under the illumination of visible light and, on the one hand, the generated holes contribute to oxidation of the MB dye. However, the photogenerated electrons are reacted with H₂O₂ and form OH radicals, which consequently degrade the MB dye. Another possibility is the Fe³⁺ ions are forming Fe²⁺, and hence it reacts with H₂O₂ (Fenton's reagent reaction) [25] which in turn oxidize the MB dye and successful degradation. The addition of Zn to Fe₂O₃ further enhances photocatalytic activity, which may be attributed to the oxidation of Zn into Zn²⁺, which shows a synergetic effect with Fe²⁺ in OH radical production. This trend is increased with an increase in the Zn concentration. A simple form of Fenton's reaction is shown by the following equation:

3.5 Theoretical verification of photocatalytic activity

The photocatalytic activity of the prepared nanostructures can be verified theoretically by performing DFT simulations. Bahers *et al* [26] reported that the band gap and effective mass of a nanostructure play an important role in the determination of the photocatalytic activity. The calculated band gap structures of Fe₂O₃, Fe₂O₃@Zn10% and Fe₂O₃@Zn20% are 1.14, 0.8 and 0.6 eV, respectively. For better photocatalytic performance, the band gap of the material should be <2.2 eV [27]. However, the calculated band gaps are less than the experimental values since DFT underestimates the band gap [27]. This is due to the well-known reason for the unknown exact exchange-correlation energy. Nevertheless, it gives relatively to the experimentally observed results. The reduction of the band gap of Zn-doped Fe₂O₃ may be attributed to the overlapping of Zn '3d' orbitals with the Fe '3d' orbitals. Another important parameter to evaluate the photocatalytic activity is effective mass. For favourable photocatalysis, the mobility of the charge carriers should be very low, since it reduces the recombination rate and helps the charge carriers to reach the active sites. The mobility can be directly related to the effective mass of the charge carriers by the following relation [26]:

$$\mu = e \frac{\tau}{m^*}, \quad (5)$$

where τ is the collision time and m^* the effective mass. The effective masses of the three different structures were calculated using the parabolic curve fitting method. Table 2 shows

Figure 6. Photocatalytic mechanism of Fe_2O_3 nanoparticles.

Table 2. Calculated effective masses of Fe_2O_3 nanostructures.

Structure	Effective mass (m^*)
Fe_2O_3	$0.217m_e$
$\text{Fe}_2\text{O}_3@\text{Zn}10\%$	$0.312m_e$
$\text{Fe}_2\text{O}_3@\text{Zn}20\%$	$0.363m_e$

the calculated effective masses of Fe_2O_3 , $\text{Fe}_2\text{O}_3@\text{Zn}10\%$ and $\text{Fe}_2\text{O}_3@\text{Zn}20\%$ nanostructures. From the results, it is observed that the electron effective mass of Fe_2O_3 is lesser than that of the Zn-doped Fe_2O_3 structures. This results in the decrease of the diffusion coefficient and consequent reduction in mobility.

From the theoretical calculations, it is concluded that a decrease in the band gap and an increase in the effective mass enhance the photocatalytic activity of Zn-doped Fe_2O_3 structures when compared to the undoped- Fe_2O_3 structure.

4. Conclusion

Undoped and Zn-doped Fe_2O_3 nanoparticles were synthesized by a facile co-precipitation method. The XRD pattern revealed that undoped- Fe_2O_3 nanoparticles are crystalline. However, when Zn is added, the crystallinity decreases with reduction in the particle size. The average crystallite sizes of the undoped and Zn-doped Fe_2O_3 nanoparticles are found to be 31.25, 15.39 and 15.09, respectively. TEM images showed uniformity at the sublattice level. The photocatalytic test was performed for the prepared nanoparticles against the MB dye in aqueous solution. This revealed that the dye degradation efficiency of Fe_2O_3 could be increased by doping Zn atoms

in the lattice. A theoretical verification based on DFT calculations was performed to gain an insight into the performance of the corresponding nanostructures based on their band gap and effective mass. The observed experimental and theoretical results are in good agreement with each other.

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