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Experimental and Computational Investigation of Structural, Optical, Magnetic and Photocatalytic Properties of Zn Doped NiFe₂O₄ Nanoparticles

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Abstract

Zn-doped NiFe₂O₄ nanoparticles were synthesized via a simple co-precipitation method to investigate the effects of Zn incorporation on the structural, optical, and magnetic and photocatalytic properties of nickel ferrite. Zn-doped NiFe₂O₄ nanoparticles retain the cubical spinel structure but exhibit the lattice expansion, reduced optical band gap and decreased magnetization, as confirmed experimentally and supported by Density Functional Theory (DFT) calculations. Photocatalytic degradation of methylene blue (MB) under solar irradiation revealed that 2% Zn-doped NiFe₂O₄ achieved optimal performance, degrading 92% of MB within 150 minutes. This enhancement is attributed to the higher adsorption of MB dye, improved visible-light absorption, suppressed energy band gap, and band gap modification by the incorporation of Zn in NiFe₂O₄ nanostructures. These findings identify 2% Zn-doped NiFe₂O₄ as an efficient and sustainable material for visible-light-driven wastewater remediation.

Keywords: Photocatalysts, methylene blue, zinc-nickel ferrite, bandgap tuning, DFT studies.

1. Introduction:

Preservation and protection of natural resources are the main focus for researchers these days as industrial pollutants contaminate natural resources. Pesticides and organic dyes are also present in contaminated water. Irritation of skin, breathing problems and other health issues like cancer and nausea are related to these dyes. Methylene Blue (MB), which is an organic pollutant and belongs to cationic azo family and is cost friendly utilized in ink industries and in medication. MB is a toxic and non-biodegradable dye which poses severe risk for aquatic life as well as humans. Therefore, there is an urgent need to treat industrial waste water effluent (containing dyes like MB) before they are through into the rivers. [1, 2]

Conventionally, there are some methods i.e., adsorption, coagulation and other biological processes that have been used to remove these compounds, but they are insufficient to completely remove and break these into non-toxic compounds. Recently, photocatalytic process (advanced oxidation process) has gained a lot of attention, being an efficient, green and sustainable approach for wastewater treatment. Photocatalytic processes use electromagnetic radiation to activate semiconductor catalyst, generate reactive oxygen species to convert the toxic dyes to non-toxic molecules [3, 4].

Till now many photocatalysts have been studied and their catalytic performance has been evaluated. Among them the transition metal ferrites semiconductors with the general formula MFe_2O_4 ($M = Ni, Co, Zn, \text{etc.}$) have received considerable attentions due to their physicochemical properties i.e., chemical stability, narrow band gaps and excellent magnetic properties [5]. Specifically, nickel ferrite ($NiFe_2O_4$) has been widely explored because of its cost-effectiveness, tunable electronic structure and band gap in visible region. However, pristine ferrites often suffer from rapid electron–hole recombination, which limits their catalytic efficiency [6, 7].

To overcome these limitations, cationic substitution at the $\text{Ni}^{+2}/\text{Fe}^{+3}$ sites has been reported as an effective strategy to tailor the crystal structure, optimize the band gap, and improve charge separation dynamics. In this context, Zinc (Zn^{+2}) is an excellent dopant candidate due to its different ionic radius and valance state, which directly alter the cationic distribution in the host matrix. The redistribution and rearrangement of tetrahedral and octahedral sites not only influence the structural and electronic properties but also influence the magnetic behavior of the NiFe_2O_4 [8]

While the structural, optical and magnetic properties of Zn doped NiFe_2O_4 has been extensively studied [8-14] however focusing on the photocatalytic dye degradation application of Pristine NiFe_2O_4 varies widely but is often limited. For instance, Jia et al. and Biswas et al. has reported 85% of MB degradation in 360 minutes and 90% of MB degradation in 120 minutes by Pristine NiFe_2O_4 respectively [15, 16]. There are some other studies indicates the significantly lower efficiencies i.e., 52%, [17] 25% [18] and 59% [19] by Pristine NiFe_2O_4 . Consequently, they focused on constructing heterojunction and nanocomposites i.e., $\text{NiFe}_2\text{O}_4/\text{CuO}$ [17], $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_4$ [18], and $\text{NiFe}_2\text{O}_4/\text{NiO}$ [19] to achieve superior photocatalytic performance.

Regarding Zn-Ni based ferrites and other complex system, the existing reports preliminary explores the catalytic performance of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.3}\text{Zn}_{7-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ at $x=0.35$ nano ferrite, which have successfully degraded 90 and 34% of MB dyes respectively [20, 21] . However, these studies do not isolate the role of Zn incorporation in NiFe_2O_4 matrix. Mohammadzadeh Kakhki, Roya, et al. has reported the 45% MB Degradation in 180 mints, which was successfully improved by Co doping [22].

With the best of our knowledge there no dedicated report on the systematic photocatalytic investigation on the low-level Zn doped NiFe_2O_4 synthesized by cost effective chemical co-precipitation method. This work presents the very first comprehensive study that correlate the Zn

dopant concentration effect with the on the photocatalytic performance of NiFe_2O_4 under direct sunlight. Ours investigation along with the theoretical mechanistic insights show that 2% Zn is the optimal doping to achieve the highest catalytic performance. We attribute this superior performance to its highest dye adsorption capacity, tuned band gap toward visible light, electronic band modification and optimized kinetic parameters, all of which were elucidated by a combination of experimental analysis and theoretical insights.

2. Experimental procedure:

2.1 Materials and method

A simple, cost effective and facile chemical co-precipitation method was employed for the synthesis of nanoparticles. The materials that are used for the synthesis of undoped and Zn doped are given here; nickel (II) chloride [NiCl_2] 98%, iron (III) chloride hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] 99.5%, zinc (II) chloride [ZnCl_2] 99.5%, sodium hydroxide [NaOH] and Methylene blue. All the purchased chemicals were highly graded and were used without any further treatment. deionized water [H_2O] was used as a solvent throughout the synthesis process.

2.2 Synthesis of Zn doped NiFe_2O_4

In the synthesis of undoped by chemical co-precipitation method, the stoichiometric molar ration of 1:2 of NiCl_2 to FeCl_3 was dissolved in beaker A having 20 mL of deionized water under continuous magnetic stirring. In another beaker B, a homogeneous alkaline solution was prepared by dissolving NaOH in 50mL of deionized water. Once the homogeneous solution was prepared the NaOH from Beaker B was added drop wise to the Beaker A until the pH of the solution was raised to 12. The mixture was continuously stirred at 80 °C for 30 minutes to let the nucleation process complete. After few minutes, the precipitates were cooled down naturally at room temperature. The precipitates were washed thrice with distilled water by centrifugation at 2500

rpm for 3 minutes. The obtained product was dried in an electric oven at 100 °C for 12 hours and grounded into fine powder by mortal pestle. The fine powder was annealed at 700 °C for 4 hours in a muffle furnace to enhance crystallinity. Finally, the powder was stored in vials and was used for further characterizations as well as photocatalytic activity.

The 2% and 4% Zn doped NiFe_2O_4 were obtained in a similar method just by adding a stoichiometric amount of ZnCl_2 in the initial precursor. The obtained 2% and 4% Zn doped NiFe_2O_4 were stored and were used for further characterizations as well as photocatalytic activity. The schematic diagram of the synthesis of undoped and Zn doped NiFe_2O_4 nanostructures are shown in figure 1.

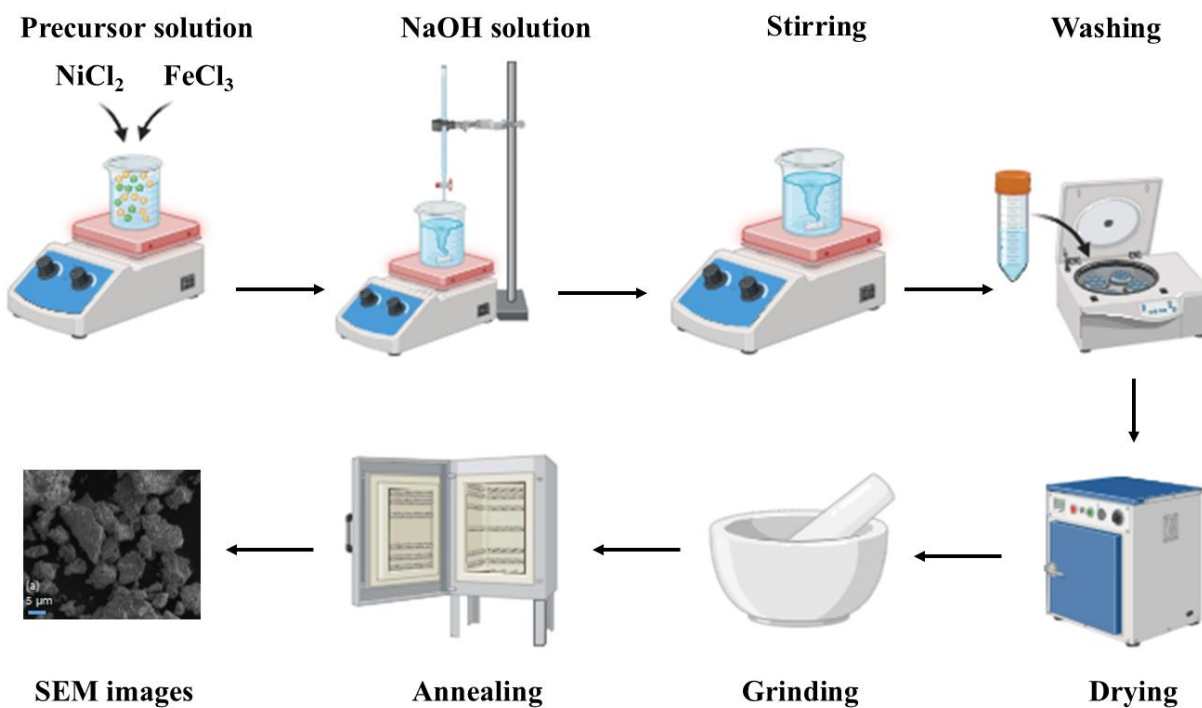


Fig. 1 Schematic illustration for synthesis of undoped and Zn doped NiFe_2O_4 nanoparticles.

2.3 Photocatalytic experiments

The photocatalytic activity of the synthesized nanoparticles was evaluated by monitoring the degradation of methylene blue (MB) dye under solar irradiation. Initially, a 10 mg/L MB aqueous solution was prepared as the optimized concentration for all experiments. For each photocatalytic test, 50 mg of the photocatalyst was dispersed in 120 mL of the MB solution in a glass beaker. The suspension was stirred in the dark for 30 minutes to establish adsorption-desorption equilibrium between the dye molecules and the surface of the photocatalyst. The absorbance spectra of the solution were immediately recorded by using a UV-Vis spectrophotometer in the range 500 to 800 nm. The absorbance of MB at its characteristic absorption peak at ~664 nm was considered for calculation purposes. At this point the % adsorption and adsorption capacity 'qe' was evaluated for each photocatalysts by following formulas [23];

$$\% \text{ Adsorption} = \left(1 - \frac{A_{A.D.}}{A_0} \right) \times 100$$

$$qe = \frac{(A_0 - A_{A.D.}) \cdot V \cdot C_0}{m \cdot A_0}$$

here $A_{A.D.}$ and A_0 represent the absorbance of the dye solution at adsorption-desorption equilibrium and the initial concentration of dye solution respectively. Other factor m, V and C_0 represent the mass of catalyst added, volume of the dye solution and initial dye concentration respectively.

following absorption-adsorption equilibration, the suspension was exposed to natural sunlight under continuous stirring. At each 30-minute intervals, 4 mL aliquots were withdrawn from the reaction mixture, centrifuged to remove any suspended catalyst particles, and the absorbance of the supernatant was immediately recorded using a UV-Vis spectrophotometer at the

characteristic absorption peak of MB (~664 nm). Finally, the photocatalytic performance was evaluated by calculating the % degradation using the equation:

$$\% \text{ dye degradation} = \left(1 - \frac{A}{A_0}\right) \times 100$$

All photocatalytic experiments were conducted under identical experimental conditions to ensure consistency and reliability.

2.4 Material Characterization:

XRD (D8 Advance Bruker) with CuK α source having wavelength of 1.54056 Å was used for structural analysis and to check phase purity while morphological study was carried out using SEM. FTIR was performed using instrument FTIR (Bruker Alpha) for identification of attached functional groups. Magnetic properties were investigated using VSM. For calculation of bandgap, UV visible absorption spectroscopy was performed using instrument (SHIMADZU, UV-2450) and photocatalytic properties were also studied using SHIMADZU, UV-2450.

2.5 Computational method

All DFT [24] calculations were carried out using the QUANTUM ESPRESSO (QE) package [25], which employs a plane-wave basis set. The calculations used a combination of plane waves and ultrasoft pseudopotentials. Exchange–correlation effects were treated within the Generalized Gradient Approximation (GGA) [26]. The electronic wave functions were expanded on a plane-wave basis with kinetic energy and charge density cutoffs of 70 Ry and 300 Ry, respectively. Brillouin zone integrations were performed using Monkhorst–Pack k-point meshes [27]. A 12×12×12 k-mesh was employed for structural optimization, while a denser 16×16×16 grid was used for non-self-consistent field calculations to evaluate the electronic properties. Convergence with respect to all computational parameters was carefully checked, and the

Hellmann–Feynman forces on each atom were reduced below 0.004 eV/Å in all structural relaxations. To assess the thermodynamic stability of these compounds, the enthalpy of formation (ΔH) was calculated using the following expression:

$$\Delta H = E_{\text{tot}}(\text{Ni}_8\text{Fe}_{16}\text{O}_{32}) - 8E_{\text{tot}}(\text{Ni}) - 16E_{\text{tot}}(\text{Fe}) - 32E_{\text{tot}}(\text{O})/56$$

where $E_{\text{tot}}(\text{Ni}_8\text{Fe}_{16}\text{O}_{32})$ represents the total ground-state energy of the $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ compound, and $E_{\text{tot}}(\text{Ni})$, $E_{\text{tot}}(\text{Fe})$ and $E_{\text{tot}}(\text{O})$ denote the total energy of Ni, Fe and O atom in isolated atomic phase, respectively.

The GGA-PBE functional was selected for its effective balance between computational efficiency and reasonable accuracy concerning structural and electronic properties. This makes it a popular choice for complex oxide systems, such as Ni–Fe–O. GGA-PBE reliably predicts lattice parameters, formation energies, and qualitative trends in band structures, which are crucial for studying modifications induced by dopants in large supercells, such as $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ and its Zn-substituted variants. Despite its limitations, GGA-PBE is adequate for capturing relative trends, including changes in the density of states, spin polarization, and the impacts of Zn doping—particularly when the goal is to compare compounds using the same methodological approach. In systems where correlation effects are moderate, as seen in Ni–Fe–O spinels, GGA-PBE still provides reliable qualitative insights into electronic and magnetic behavior while maintaining a manageable computational cost compared to more advanced functionals, such as GGA+U or hybrid methods. Therefore, GGA-PBE was chosen as a practical and widely validated option that effectively balances accuracy and efficiency for investigating the properties of transition-metal oxides and the effects of doping.

3. Results and discussion:

3.1 Structural Investigation:

The crystal structure, phase purity and doping of prepared powder samples were investigated using X-ray diffraction (XRD) technique. The recorded patterns of all the samples are shown in Fig. 2 exhibited, well defined highly instanced and sharp peaks identifying the highly crystalline nature of prepared samples. The diffraction peaks at angle of 30.2° , 35.6° , 37.2° , 43.2° , 53.8° , 57.3° , 62.9° and 74.6° were indexed as (220), (311), (222), (400), (422), (511) (440) and (533) planes respectively, corresponds to the face centered cubic spinel structure of NiFe_2O_4 (PDF card# 86-2267) [28, 29]. A minor peak has been observed at 34.3° , which is attributed to the trace amount of iron oxyhydroxide phase [30].

With the addition of 2 and 4% Zn, we did not observe any additional peak related to Zn based compound, instead we observed a little shift in the pattern and change in the intensity as shown in figure 3. It is well known that by the addition of dopant having different radius will lead to the shift in the XRD pattern. The observed shift toward lower angle is the direct consequences of success doping of atom with larger ionic radius which is consistent with the previous literature [9]. We concluded the successful formation of highly crystalline single-phase cubic spinel structure of undoped and Zn doped NiFe_2O_4 .

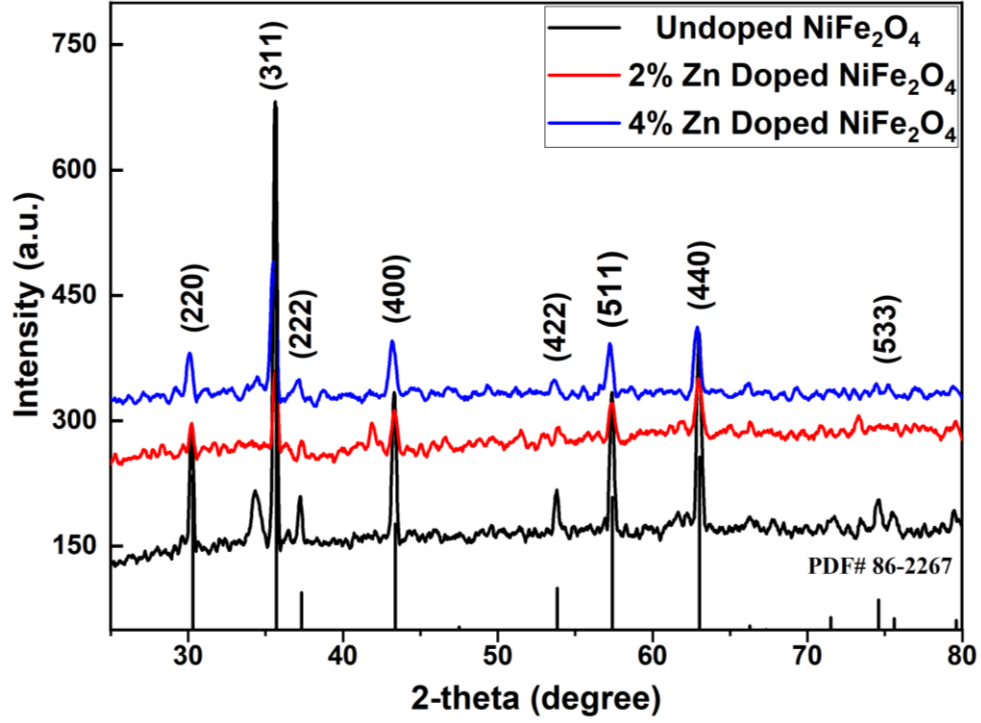


Fig. 2 XRD spectra of undoped and Zn doped NiFe_2O_4 nanoparticles

We calculate the average crystallite size was calculated using Debye Sherrer's equation presented as Eq [31].

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where, λ is wavelength of x-rays in nm, β is full width half maxima (FWHM) in radians while θ is the angle at which diffraction peak observed. The calculated average crystallite size for all samples in nm is shown in figure 3 and tabulated in Table 1. Average crystallite size found to be decreased with increasing dopant concentration i.e. Zn concentration in NiFe_2O_4 . Moreover, broadening of peaks in XRD spectra also indicates decrease in crystallite size. For undoped NiFe_2O_4 , the average crystallite size was found to be 26 nm while for 2% and 4% Zn doped NiFe_2O_4 found to be 25nm and 21 nm, respectively. This decrease in the crystallite size would

provide more surface area and active surface sites for the MB dye adsorption which will be more beneficial for the catalytic activity.

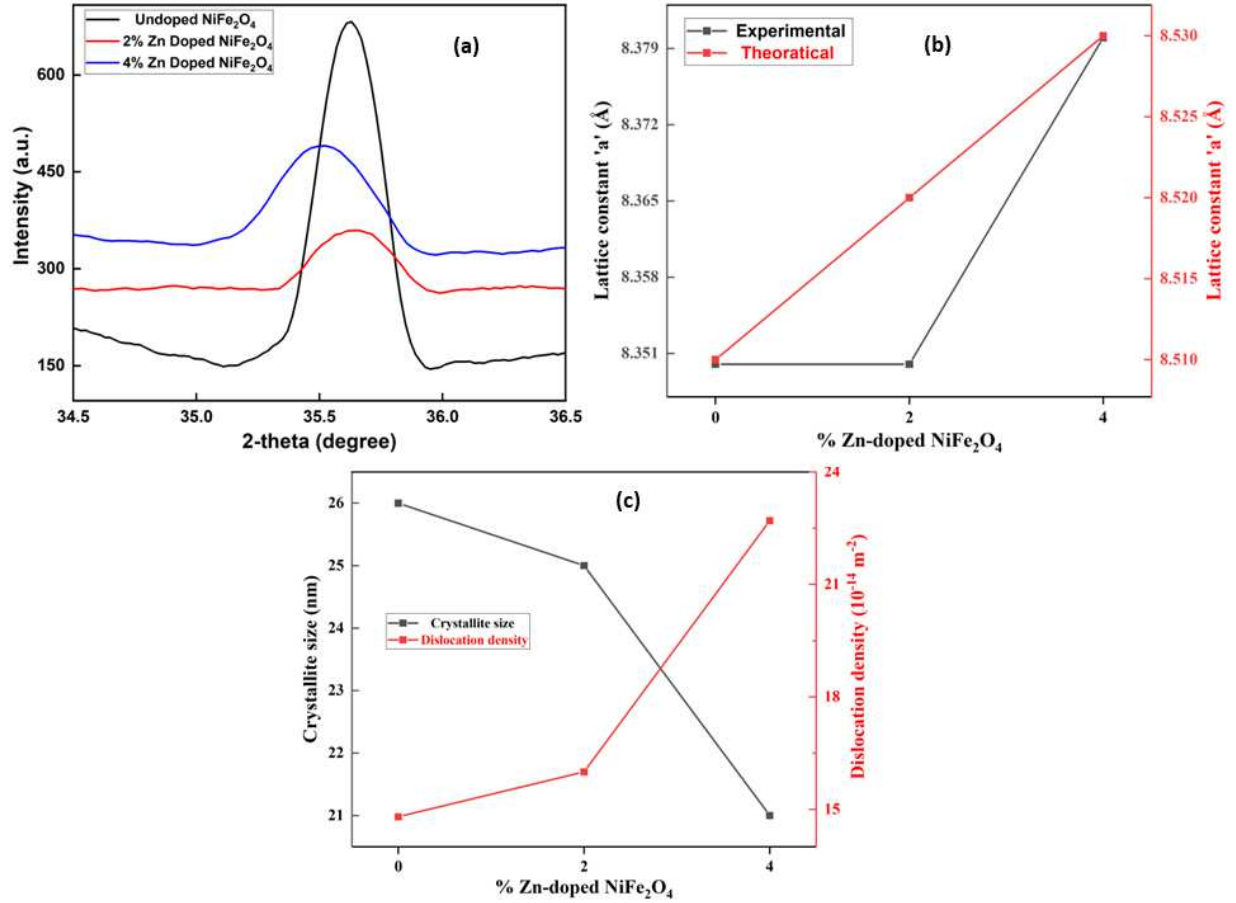


Fig. 3 a) Extended XRD pattern of undoped and Zn doped NiFe_2O_4 b) experimentally and theoretically calculated Lattice constant 'a' c) crystallite size and dislocation density variation with various Zn doping concentrations in NiFe_2O_4 .

In Ni ferrite, Fe^{3+} ions possess greater affinity to occupy tetrahedral site as compared to octahedral site, consequently Fe^{3+} ions and Ni^{2+} occupy their favored sites in crystal structure. When Zn^{2+} as a substitute is introduced in NiFe_2O_4 it typically prefers tetrahedral site while the

presence of Fe^{3+} compel Zn^{2+} to occupy octahedral site. In Zn-Ni ferrite, zinc ions occupy position in crystal different from where they normally occupy. This behavior produce smaller crystals [32].

Table 1. Average crystallite size, lattice constant, volume unit cell and dislocation density for undoped and Zn doped NiFe_2O_4 nanoparticles.

Sample	Average Crystallite Size (nm)	Lattice constant experimental (Å)	Lattice constant Theoretical (Å)	Volume (Å ³)	Dislocation Density ($\times 10^{14} \text{ m}^{-2}$)
Undoped NiFe_2O_4	26	8.35	8.51	582	14.8
2% Zn doped NiFe_2O_4	25	8.35	8.52	582	16
4% Zn doped NiFe_2O_4	21	8.38	8.53	588	22.7

Further in order to understand the effect of doping on the internal structure, we calculate the lattice parameter by following formula.

$$a = \left(\frac{\lambda}{2 \sin \theta} \right) (h^2 + k^2 + l^2)^{1/2}$$

Here we used the main characteristic peak with miller indices (311) to evaluate the lattice parameter. The comparison graph of lattice parameter calculated theoretically and experimentally are shown in figure 3. It is clear from the figure that lattice constant has increased with doping of Zn in NiFe_2O_4 . Increase in lattice constant might be due to greater ionic radii of Zn^{2+} (0.74 Å) as compared to Ni^{2+} (0.69 Å). Ni^{2+} preferred to occupy octahedral site while Zn^{2+} preferred for tetrahedral site. The replacement of large ionic atom with small ionic radii leads to the increase in the lattice parameter and unit cell volume is in accordance with the Vegard's law [33, 34].

Additionally, the theoretically calculated lattice parameter also follows the increasing trend further verifying the experimental results of doping as well as the increasing lattice parameters upon Zn doping. we also calculated the Dislocation density using Eq given below. Where, δ is dislocation density and D is average crystallite size in nm [35].

$$\delta = \frac{1}{D^2}$$

Dislocation density increases with increase in Zn dopant concentration in ferrites as shown in figure 3. It might be due to decrease in crystallite size leading to increase in boundary area of crystallites in particles. Alteration in lattice constant along with decrease in crystallite size introduce some sorts of distortions and oxygen vacancies in ferrites. Comparatively the 4% Zn doped NiFe_2O_4 has much higher dislocation values. increase in the distortion due to higher doping could have effects on the catalytic performance of our samples.

Overall, the structural analysis confirms the successful synthesis of highly crystalline single-phase cubic spinel structure of undoped and Zn doped NiFe_2O_4 . The incorporation of Zn leads to the systematic change in the crystallite size, lattice parameter, unit cell volume and dislocation density. The doped sample has modified and improved structural properties which would have direct effect on the photocatalytic performance.

3.2 Morphological characteristics:

After the detailed structural analysis, the morphology of undoped and Zn doped NiFe_2O_4 powder were examined with scanning electron microscopy (SEM) technique. The SEM

micrograph of all the prepared sample captured at the same scale of 5 μm are shown in figure 4.

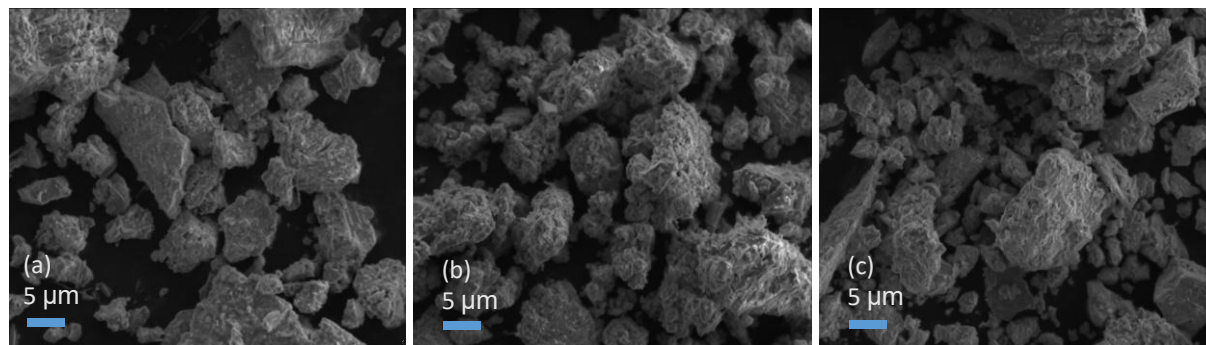


Fig. 4 (a) SEM image of (a) undoped NiFe_2O_4 , (b) 2% and (c) 4% Zn doped NiFe_2O_4 nanoparticles.

it can be seen from image that the irregular shape nanoparticles are formed, and agglomeration is also observed associated with large particles formation. This is according to the expectation as ferrite are magnetic in nature and have a tendency of agglomeration. However, in comparison to the undoped NiFe_2O_4 , the Zn-doped NiFe_2O_4 samples are more spherical in shape. Indicating the strong influence of doping on morphology as well. It can be clearly seen that number of small sized particles increase with increase in Zn doping in pure NiFe_2O_4 nanoparticles, it might be due to reduced agglomeration associated with huge influence of non-magnetic Zn doping in magnetic NiFe_2O_4 nanoparticles. Additionally, there might be a hypothesis that addition of doping would have influenced the nucleation process and as a result increased the number of nucleation centers. However, the ionic mismatching, difference in the electronegativity and surface energy could also be influencing factors. We assume that all these factors have synergistically played an important role and tuned the surface morphology of the undoped NiFe_2O_4 , the Zn-doped NiFe_2O_4 nanomaterials.

3.3 Vibrational analysis:

FTIR spectroscopy was employed to identification of chemical bonds, vibrational mode and for the identification of functional groups attached on the surface of undoped and Zn doped

NiFe₂O₄ nanomaterials. FTIR spectra of all prepared samples were carried out in wavenumber range of 500-4000 cm⁻¹ and presented in Fig. 5. Major frequency bands in the region of lower wavenumber attributed to metal-oxygen stretching modes, corresponds to the characteristic's peaks of spinel ferrites. The first vibrational mode at 555 cm⁻¹ is attributed to metal oxygen stretching mode at octahedral site referred as ν_2 while the second vibrational mode at 864 cm⁻¹ is attributed to Fe-O stretching mode at tetrahedral site referred as ν_1 [15, 36]. The presence of these band is the fingerprint of the formation of NiFe₂O₄ as corroborated well with the results of XRD analysis.

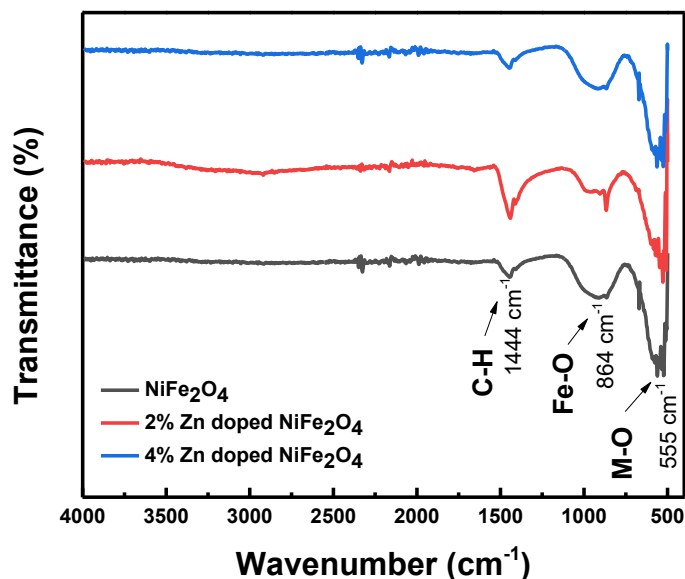


Fig. 5 FTIR spectra of undoped and Zn doped NiFe₂O₄ nanoparticles.

However, with the Zn doping, peak shift and change in the peak intensity have been observed. Indicating the modification in the vibrational properties of NiFe₂O₄ because of successful Zn doping at octahedral sites. This substitution alters the local bonding environment and affects the metal-oxygen bond strength due to the different ionic radius of Zn²⁺ (0.74 Å) compared to Ni²⁺ (0.69 Å). The cationic redistribution of Zn, Ni and Fe on tetrahedral and octahedral sites shift the bands positions [37]. The variation in bonds length (as observed in the

lattice variation) at tetrahedral and octahedral sites affects the frequency inversely, therefore, shift of bands toward lower wavenumber can also be attributed to increase in bonds length at both sites with addition of Zn. The change in the intensity peaks with doping could also been a signature of increased in the structural disorder (defects). The higher wavelength region, the weak bands corresponds to the O–H bending and stretching or vibrational mode of C-H, which is very common due to high surface area, hydrophilic nature or due to environment [38].

The FTIR analysis concludes and support the results obtained from structural analysis about the formation of the spinel ferrite structure and provides strong evidence of Zn incorporation into the NiFe_2O_4 lattice. Further, it indicates the alteration and modification of metal–oxygen bonding environment without introducing any secondary phases.

3.4 Optical studies:

Appropriate bandgap of material is mainly needed to use it as photocatalyst. In order to evaluate the optical band gap, UV visible absorption spectroscopy has been employed. The absorption spectra were recorded in the wavelength range 300-400 nm as shown in figure 6. All the samples show strong absorption in the visible region which increases with doping. This indicates that the samples can be used for the visible light activated photocatalytic activities. Absorbance is normally affected by grain size, lattice parameters, impurity centers and surface roughness is also a considerable factor in this regards [39].

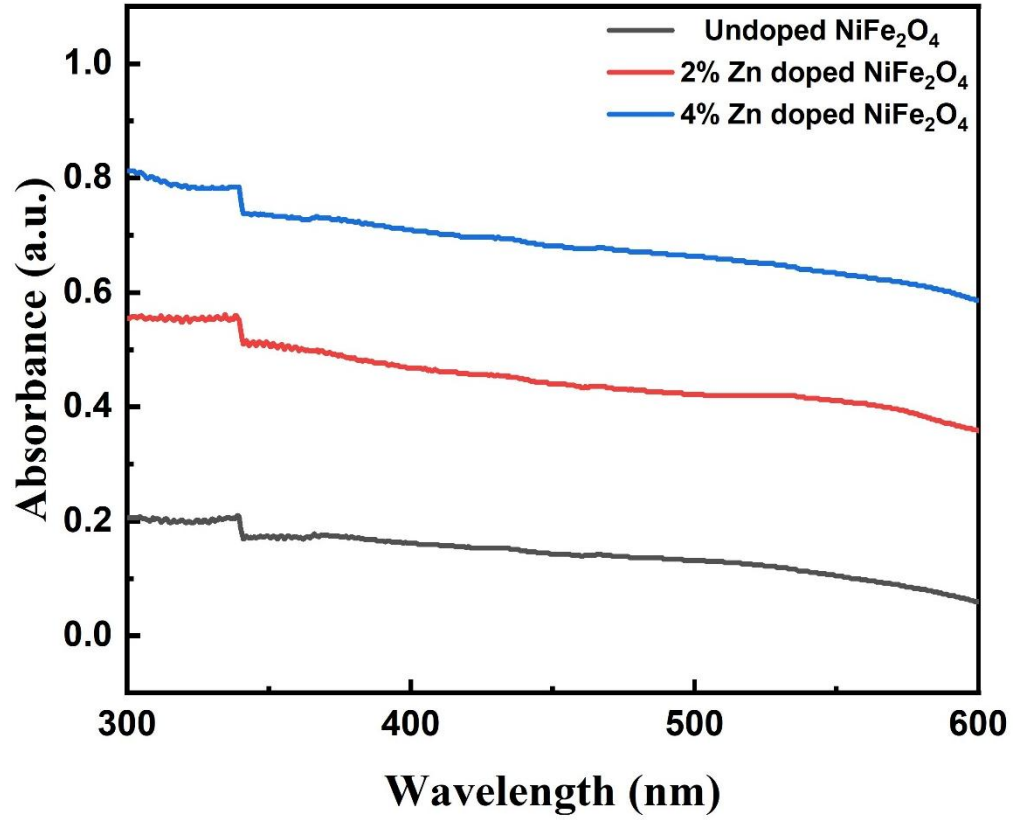


Fig. 6 UV-visible absorption spectra of undoped and Zn doped NiFe₂O₄ nanoparticles.

To evaluate the optical band gap, the Tauc's plots were constructed by plotting $(\alpha h\nu)^2$ verses photon energy ($h\nu$) as shown in figure. The linear extrapolation of each curve to the x-axis represents the optical band gap energies which are also shown in figure 7.

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where α is absorption coefficient, A is constant, $h\nu$ is energy of light and n is constant depending on transition of electron [40].

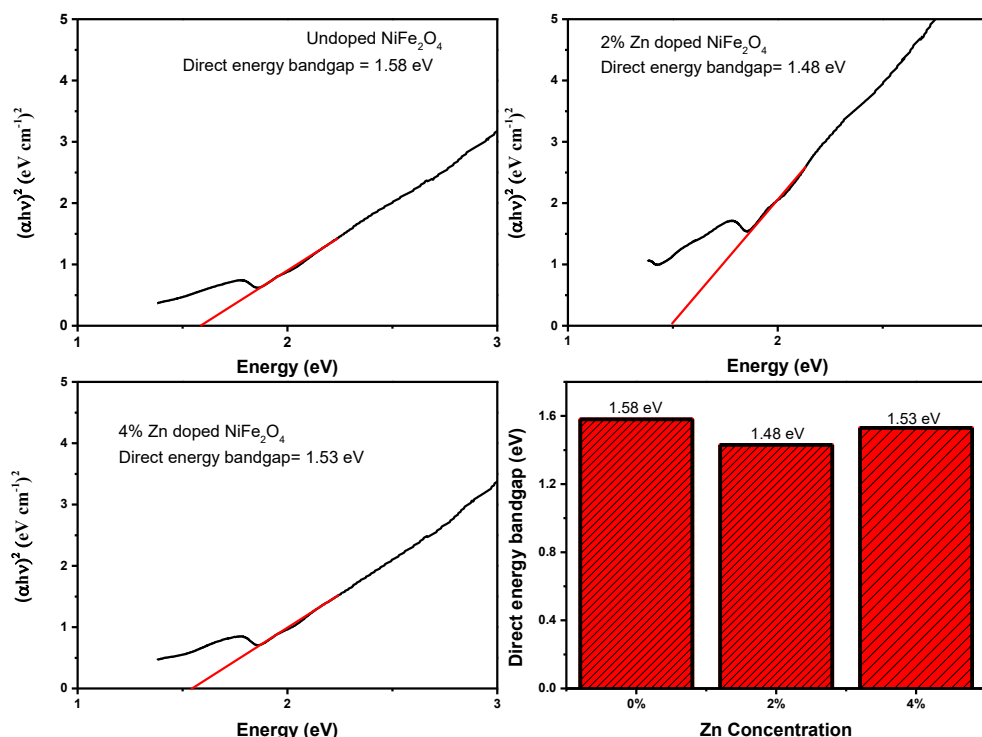


Fig. 7 Tauc plot for bandgap calculation and histogram representation of bandgap values of undoped and Zn doped NiFe_2O_4 nanoparticles.

The tauc plot revealed that the direct optical band gap of all the samples lies near the visible region and has effectively been used for the visible light activated photocatalytic activities. Interestingly, it also reveals that electronic structural modification by Zn doping. We observed that the optical band gap of undoped NiFe_2O_4 , decreased with Zn doping. this might be due to the creation of additional energy level within the optical band gap structure [41]. We assume these tunable band gap of NiFe_2O_4 could be effective for photocatalytic applications.

3.5 Magnetic properties:

The magnetic properties of undoped and Zn-doped NiFe_2O_4 nanoparticles were investigated using vibrating sample magnetometry (VSM) at room temperature, and the results are presented in Figure 8 as well as in Table 2. All samples exhibit soft ferrimagnetic behavior, as indicated by the characteristic hysteresis loops. Key magnetic parameters for the analysis are

saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) which reveal a non-linear dependency on Zn doping concentration. The undoped NiFe_2O_4 nanostructures exhibited a saturation magnetization (M_s) of 54.9 emu/g a remanent magnetization of 7.42 emu/g and coercivity of 61.74 Oe, which is typical spinal ferrites due to the super exchange interactions between Fe^{+3} ion at the octahedra (B) and tetrahedral (A) sites further are consistent with the soft ferrimagnetic nature. Only 2% Zn doping, the M_s decreases to 43.6 emu/g, M_r reduces to 5.21 emu/g and H_c slightly decreases to 58.4 Oe. This reduction is attributed to the dilution of magnetic interaction because of the substitution of a non-magnetic Zn^{+2} ions. This substitution leads to the disrupt the interaction and weakening in the net magnetic moments [42, 43].

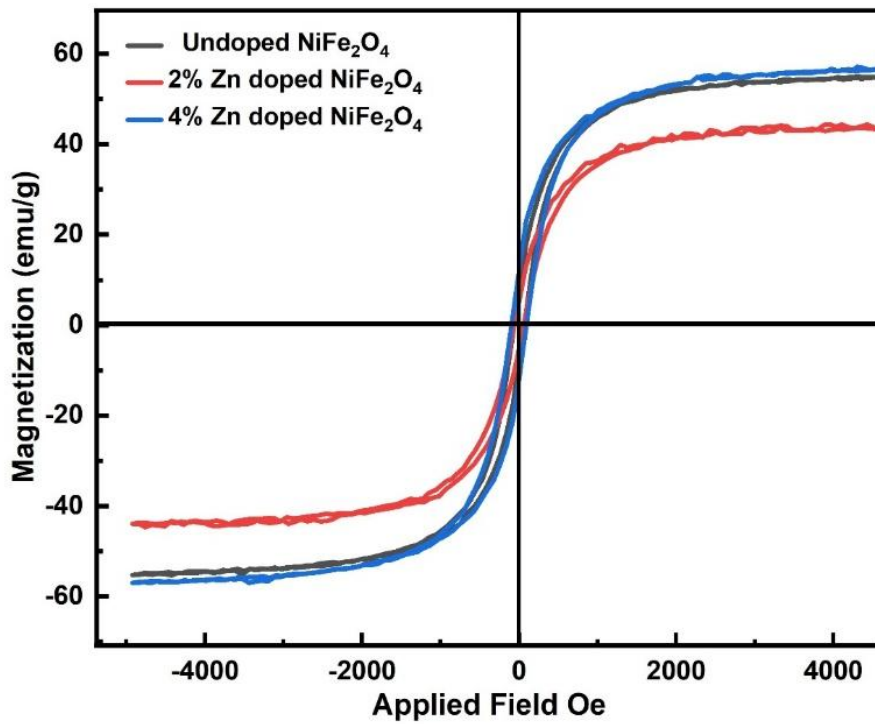


Fig. 8 Hysteresis loop for undoped and Zn doped NiFe_2O_4 nanoparticles.

Surprisingly, on further increasing the doping to 4% in NiFe_2O_4 , an unexpected enhancement in the magnetic parameters has been observed. the M_s increased to 56.6 emu/g, M_r rose to 12 emu/g,

and H_c significantly enhanced to 95.34 Oe, which clearly indicates a significant influence of doping to the magnetic behavior of the material. We assume that this surprisingly behavior is because of some complex mechanism happened at the atomic level by the redistribution of cations at higher doping level leading to the change in the magnetic dipole alignment [44].

Table 2. M_s , M_r and H_c values for undoped and Zn doped $NiFe_2O_4$ nanoparticles.

Composition	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	E_g
Undoped $NiFe_2O_4$	54.9	7.42	61.74	1.58 eV
2% Zn doped $NiFe_2O_4$	43.6	5.21	58.40	1.48 eV
4% Zn doped $NiFe_2O_4$	56.6	12	95.34	1.53 eV

Overall, we conclude that the Zn (non-magnetic) doping in the $NiFe_2O_4$ has strongly influenced the magnetic properties, at lower concentration it behaves as a soft magnetic, but at higher concentration it exhibits enhanced magnetic parameters. And these could be useful for many applications [45].

3.6 Computational Results:

We studied the structural, electronic, and magnetic properties of pure $Ni_8Fe_{16}O_{32}$ and Zn-doped $Ni_{8-x}Zn_xFe_{16}O_{32}$ ($x = 1, 2$) by first-principles using density functional theory (DFT). The corresponding results are shown in figures 9-12 and summarized in table 3. Figure 9(a–c) shows the ball-and-stick models used in our calculations, and. The structural optimization was performed using GGA for both pure $Ni_8Fe_{16}O_{32}$ and Zn-doped $Ni_{8-x}Zn_xFe_{16}O_{32}$ ($x = 0, 1, 2$). Several approaches can be employed to examine the stability of these compounds. In particular, the negative values of the formation enthalpy (ΔH) confirm that both pure and Zn-doped $Ni_8Fe_{16}O_{32}$ can be synthesized experimentally. The lattice constant values increase with increasing Zn concentration, while the total ground-state energy becomes more negative, indicating enhanced

thermodynamic stability upon Zn substitution. Furthermore, the calculated Fermi energy (E_F) increases gradually with Zn doping, suggesting modifications in the electronic structure. The calculated total and absolute magnetizations are also consistent with the effect of substitutional Zn doping. These results confirm the feasibility of stabilizing $\text{Ni}_{8-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{32}$ compounds, highlighting their potential for practical applications.

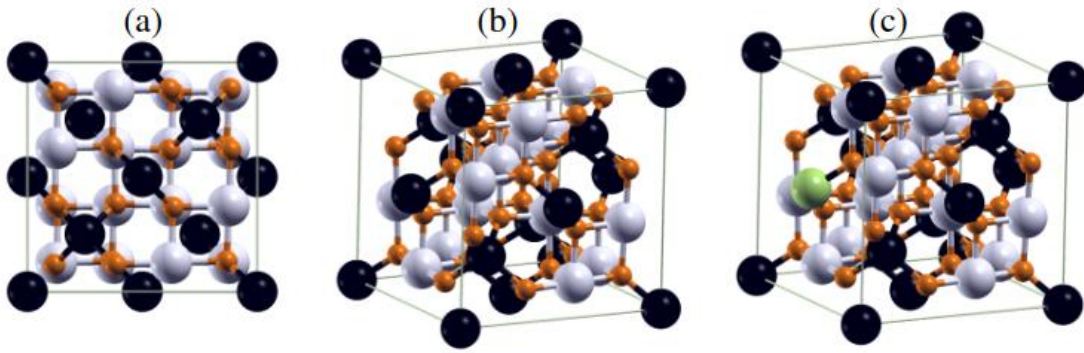


Figure 9: Ball-and-stick model of the $\text{Ni}_{8-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{32}$ crystal structure: (a) top view of the pure compound, (b) tilted side view, and (c) Zn substituted at the Ni site. The black, white, and orange spheres represent Ni, Fe, and O atoms.

The electronic properties of pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ and Zn-doped $\text{Ni}_{8-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{32}$ ($x = 1, 2$) compounds were analyzed to gain insights into their intrinsic behavior and potential applications. The electronic band structures, together with the total and partial densities of states, were calculated for both the pure and doped systems. Figure 10(a–c) shows the spin-polarized band structures, where the black and red curves represent the spin-up and spin-down channels, respectively. Several spin-up bands cross the Fermi level (0 eV), while the spin-down channel exhibits a finite bandgap, consistent with the values reported in Table 3.

Zinc (Zn) was selected as the dopant because it is a non-magnetic $3d^{10}$ cation (Zn^{2+}) with an ionic radius similar to that of nickel (Ni^{2+}). This similarity allows Zn to substitute for Ni sites without causing significant distortion to the Ni–Fe–O lattice structure. Consequently, Zn is ideal for investigating how the controlled disruption of the Ni-centered magnetic network influences the

half-metallic and ferrimagnetic properties of $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$. Since Zn does not introduce additional magnetic moments, its impact on the system is primarily electronic and structural. This enables a clear evaluation of how diluting the B-site modifies band edges, spin polarization, and the density of states near the Fermi level. Low doping concentrations ($x = 1$ and 2 , which approximately correspond to approximately 2% and 4%) were chosen to remain within the dilute substitution regime, where both lattice symmetry and ferrimagnetic ordering are maintained. In this range the structural perturbation is minimal, ensuring thermodynamic stability. The intrinsic half-metallicity is preserved, as excessive disorder from the dopant does not occur. Electronic modifications, such as changes in the density of states (DOS) at the Fermi level or slight variations in the minority-spin gap, can be directly attributed to the Zn substitution rather than to global lattice distortion. Therefore, small concentrations of Zn facilitate systematic tuning of electronic and magnetic behaviors while preserving the fundamental half-metallic framework, making them theoretically suitable for investigating dopant-dependent optimization in spintronics.

Table 3. The DFT-calculated structural properties are given in units of Å. The total energy of the ground state is reported in Ry, while the Fermi energy, enthalpy, and bandgap for spin-up (pseudo-gap) and spin-down are given in eV. The calculated total magnetization and absolute magnetization are expressed in Bohr magnetons (μ_B/cell).

Sample	Lattice constant theoretical (Å)	Lattice constant experimental (Å)	E_{Total} (Ry)	E_F (eV)	ΔH (eV/atom)	M_s (μ_B/Cell)	M_{Absolute} (μ_B/Cell)	Ni -O	Fe -O	Zn -O	E_{gap} (Spin-up)	E_{gap} (Spin-down)	E_g Experimental (eV)
$\text{Ni}_7\text{Zn}_1\text{Fe}_{16}\text{O}_{32}$	8.51	8.35	-2598.27588736	8.8911	-6.23	63.88	85.01	1.96	2.06	-	1.75	0.95	1.58
$\text{Ni}_7\text{Zn}_2\text{Fe}_{16}\text{O}_{32}$	8.52	8.35	-2660.86522742	8.8612	-6.01	65.88	84.4	1.95	2.05	1.99	1.64	1.03	1.48

$\text{Ni}_6\text{Zn}_2\text{Fe}_{16}\text{O}_{32}$	8.53	8.38	-2723 .455230 9	8.82 19	-5.78	67.89	83.9	1.9 4	2.0 5	2.0 1	1.51	1.07	1.53
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This confirms the half-metallic nature of all three compounds, where the spin-up channel is metallic and the spin-down channel is semiconducting. The multiple band crossings at different k-points in the spin-up states further highlight their metallic character. Figure 2(b) presents the spin-polarized electronic band structure for Zn-doped $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ compound. Compared with the pure compound, band dispersion near the Γ -M path shows flattening, which may lead to heavier hole effective masses and reduced carrier mobility for spin down electron, although the system remains half-metallic [46].

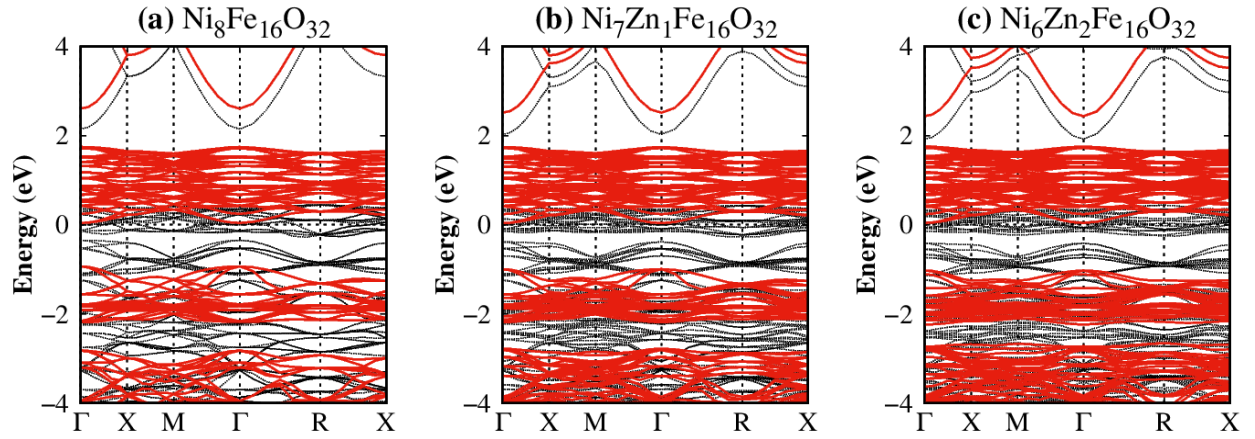


Figure 10: Electronic band structure of (a) Pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ compound (b) Zn doped at Ni-site (c) Two Zn doped at Ni-sites, The horizontal dashed line indicates Fermi energy level.

Figure 11(a–c) presents the calculated total density of states (TDOS) for pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$, $\text{Ni}_7\text{Zn}_1\text{Fe}_{16}\text{O}_{32}$, and $\text{Ni}_6\text{Zn}_2\text{Fe}_{16}\text{O}_{32}$. In all cases, the spin-up channel shows a relatively high density of states at the Fermi level, indicating metallic behavior, whereas the spin-down channel exhibits a finite bandgap, confirming the half-metallic nature of these compounds. For the single-Zn-

substituted system [Figure 11(b)], the half-metallicity is preserved, with a slight reduction in the pseudo-gap in the conduction band. Upon further Zn substitution [Figure 11(c)], the spin-down bandgap increases, approaching values within the visible spectrum. Additionally, higher Zn concentration leads to an increase in the TDOS at the Fermi level in the spin-up channel, which enhances the electronic conductivity, an effect desirable for photocatalytic applications.

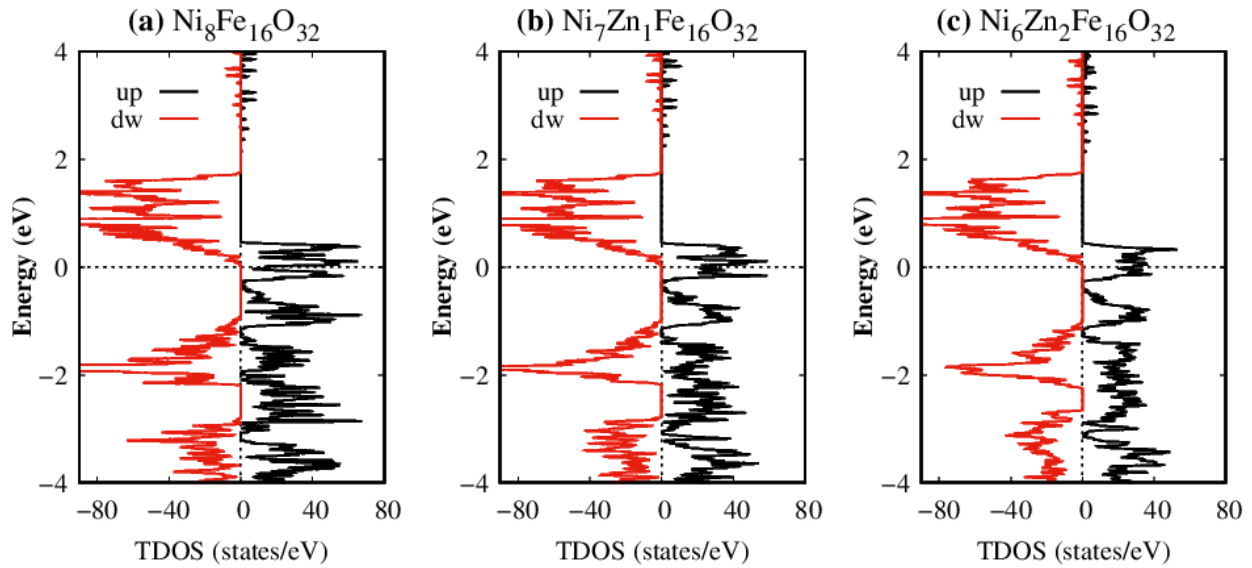


Figure 11. The calculated total density of state (TDOS) (a) Pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ compound (b) Zn doped at Ni-site (c) Two Zn doped at Ni-sites, The horizontal dashed line indicates Fermi energy level

Figures 12(a–c) display the spin-polarized partial density of states (PDOS) for pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ and Zn-doped $\text{Ni}_{8-x}\text{Zn}_x\text{Fe}_{16}\text{O}_{32}$ ($x = 1, 2$), confirming the half-metallic nature of these compounds. In all cases, the states at the Fermi level are primarily derived from Ni d -orbitals, indicating their key role in the metallic spin-up channel. In the spin-down channel, the valence band maximum (VBM) is mainly dominated by Ni d -states, with minor contributions from Fe d - and O p -orbitals. The conduction band minimum (CBM), on the other hand, originates predominantly from Fe d -states, accompanied by a subsidiary contribution from O p -states. The PDOS of the Zn-doped systems.

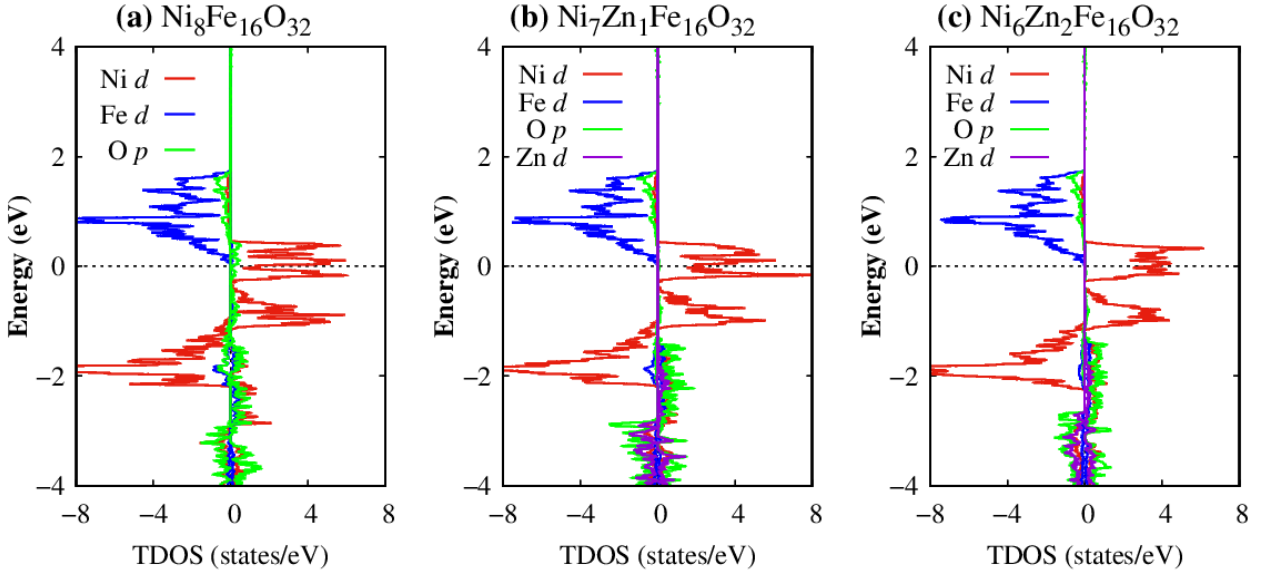


Figure 12. The calculated partial density of state (PDOS) (a) Pure $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ compound (b) Zn doped at Ni-site (c) Two Zn doped at Ni-sites, The horizontal dashed line indicates Fermi energy level.

[Figures 12(b–c)] follows a similar trend, where the Ni d -orbitals dominate the valence region and the Fe d -orbitals dominate the conduction region, confirming that substitutional Zn doping preserves the fundamental electronic structure of the parent compound.

In our computational studies, the optimized structures confirm the thermodynamic stability of all systems, as evidenced by their negative formation enthalpies. The substitution of Zn at Ni sites leads to a small increase in lattice constants and modifies the total ground-state energy, reflecting enhanced stability with higher Zn content which is consistent with our experimental results. Band structure and DOS results confirm the half-metallic nature of these compounds, with metallic behavior in the spin-up channel and semiconducting character in the spin-down channel. The electronic states near the Fermi level are mainly governed by Ni d -orbitals, while Fe d - and O p -orbitals contribute at the band edges. Zn doping increases the density of states at the Fermi level and slightly alters the spin-down bandgap, which may improve conductivity and tune magnetic responses. Overall, both pure and Zn-doped $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$ exhibit robust half-metallicity, making them attractive materials for future spintronic and magnetoelectronic applications.

The d-orbitals of nickel (Ni) and iron (Fe) play a crucial role in determining the electronic structure and magnetic behavior of $\text{Ni}_8\text{Fe}_{16}\text{O}_{32}$, as well as its zinc (Zn)-doped variants. The d-orbitals of both Ni and Fe contribute significantly to the electronic states both above and below the Fermi level. The partially filled 3d states of the Ni d-orbitals create a metallic spin-up channel, which is responsible for the material's half-metallic character. Additionally, the strong exchange splitting of the Ni d-orbitals helps stabilize spin polarization, making nickel a key element in governing the material's conductivity and magnetic response. In contrast, the d-orbitals of Fe atom primarily contribute to the spin-down (semiconducting) channel, shaping the minority-spin bandgap. The antiferromagnetic interaction between the Ni and Fe moments establishes the overall ferrimagnetic ordering. Furthermore, the Ni d-states and Fe d-states define the valence and conduction band edges in the spin-down channel, influencing the size of the spin-down bandgap and thereby affecting the degree of half-metallicity. So, to conclude Ni d-orbitals are responsible for metallic and spin-polarized conduction, while the d-states of Ni and Fe define the minority-spin bandgap and their magnetic coupling. The interplay between these elements results in the robust half-metallic ferrimagnetism observed in both pure and Zn-doped structures.

The results from the Density Functional Theory (DFT) calculations align with the experimental trends and provide a detailed microscopic explanation for them. Specifically, the calculated major spin (spin-up) pseudo gap, which represents the energy window in the conduction band, decreases with increasing zinc (Zn) substitution—from 1.75 eV to 1.64 eV with the first Zn substitution. This decrease corresponds with the experimental observation of the optical gap narrowing from 1.58 eV to 1.48 eV. This agreement suggests that the observed reduction is not merely an artifact but is attributed to genuine electronic-structure changes captured by DFT. Microscopically, the calculations reveal that Zn substitution disturbs the electronic states centered

around nickel (Ni)—specifically, the Ni 3d–O 2p hybridization. This disturbance shifts the Ni-derived band edges, bringing the majority-spin conduction and valence edges closer together, resulting in a reduced spin-up gap. Additionally, it increases the density of states (DOS) near the Fermi level, which is consistent with enhanced electronic delocalization that lowers the effective optical gap. Importantly, the overall half-metallic character remains intact; thus, the changes reflect a tuning of the band edges rather than a complete shift in electronic phase. A few caveats explain the remaining quantitative differences. Factors such as excitonic effects, finite temperature, defects, strain, and sample disorder can shift the measured optical gap by several tenths of an electron volt. DFT supports and elucidates the experimental narrowing of the bandgap by demonstrating the Zn-induced shifts in the Ni-derived band edges and the increased DOS at the Fermi level. Although the exact numerical values may differ due to methodological and experimental variations, the calculated changes in electronic structure provide a coherent atomic-level rationale for the observed narrowing from 1.58 eV to 1.48 eV.

3.7 Photocatalytic activity:

After the detailed theoretical and computational analysis, we used the prepared undoped NiFe_2O_4 and Zn doped NiFe_2O_4 nanoparticles as photocatalyst for the dye degradation of methylene blue. Methylene blue is a model dye that has been used for the photocatalytic evaluation of photocatalysts. The recorded absorption spectra of MB solution at different irradiation times for all the photocatalysts are shown in figure 13. Further the degradation efficiency was also evaluated by measuring the decrease in the intensity values at the characteristic peak (664 nm) of Methylene blue dye and are summarized in table.

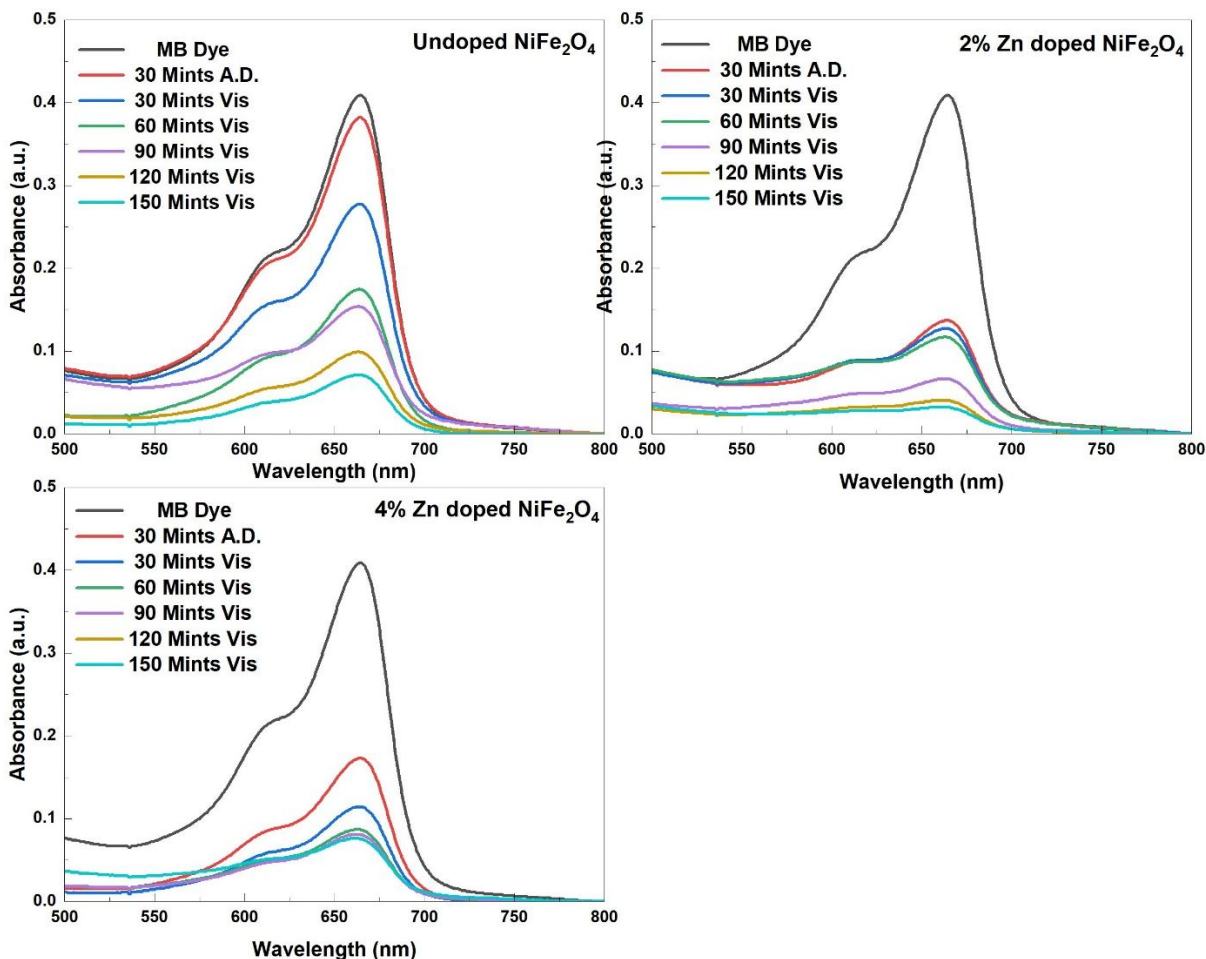


Fig. 13 Absorption spectra of MB with time in the presence of undoped and Zn doped NiFe_2O_4 nanoparticles Photocatalyst.

In the graph, all three samples show a gradual decrease in the absorbance values, which indicate that all the photocatalysts are active toward the photocatalytic degradation of MB dye. Before the illumination to visible light, we stirred the dye-catalyst colloidal solution under dark condition for 30 minutes to establish the adsorption–desorption equilibrium between the dye molecules and catalyst surface [47]. In this process dye molecules tend to absorb on the surface of catalysts, which is a necessary step for catalytic performance. In the next step the solution was irradiated to the visible light for 150 minutes. When incident light with energy greater than the optical band gap energy of the photocatalyst falls in photocatalyst, it produces electron-hole pairs.

These electron-hole pairs react with the O_2 and H_2O as a result produces reactive oxygen species (ROS), which are responsible for the degradation of MB dyes. A systematic diagram of this process is shown in figure [48-50]

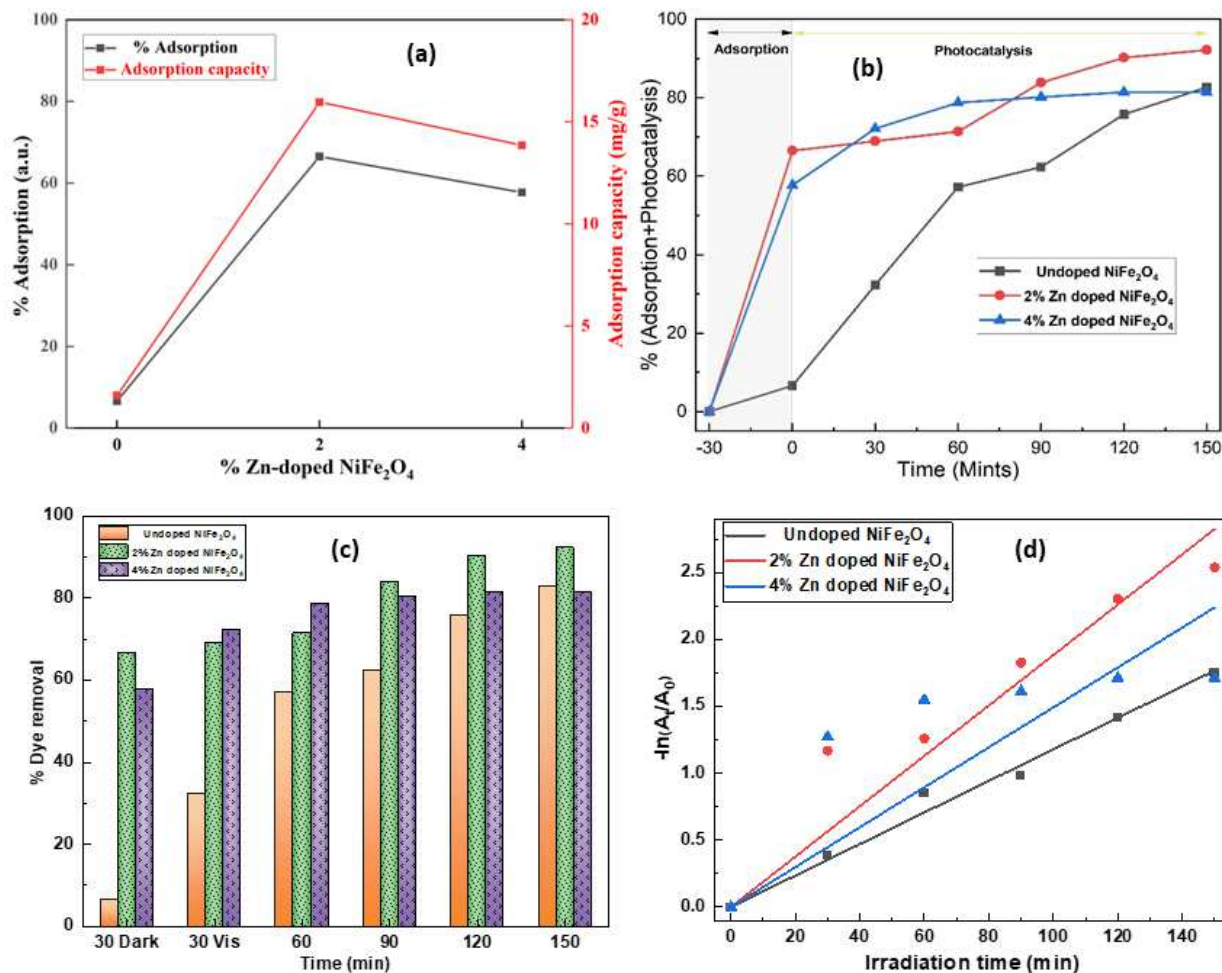


Fig. 14 % adsorption capacity graph (a), % degradation graph (b), bar graph (c) and rate constant plot (d) of Methylene Blue with time in the presence of for undoped and Zn doped $NiFe_2O_4$ nanoparticles Photocatalyst.

We have systematically investigated both Adsorption under dark and photocatalytic degradation for all the samples as shown in figures 14 and table 4. The calculated % adsorption values show that the Zn doped samples have much higher % adsorption values as compared to undoped samples. The undoped sample adsorbed only 6.6% but on the other hand 2% Zn-doped

ferrite has shown a remarkable higher, nearly ten-fold absorption efficiency (66.5%). Similarly, the further increase in Zn concentration, the 4% Zn doped NiFe₂O₄ nanoparticles shows nearly 58% of adsorption which is also incredibly higher than undoped NiFe₂O₄. For further deep understanding, we have evaluated the adsorption capacity 'q_e', which is purely the intrinsic property of catalysts and provide quantitative information about the amount of dye adsorption in a unit mass of catalysts. figure 14 (a) clearly shows that drastic higher amount of MB dye adsorption on the unit mass of catalyst. This pre-photocatalytic adsorption step is directly linked with the catalytic activity of samples. This enhancement is attributed to several doping-induced modifications. Firstly, surface charge modification due to its different valance state which has created more electrostatic attraction. Secondly, the modification in the crystal structure by increase in the dislocation density which has introduced more concentration of surface-active sites. Additionally, the decrease in the crystallites size has enhanced the surface-active sites. All of these synergistically results in this higher adsorption of doped catalyst [51].

Table 4. Calculated Photocatalytic parameters of undoped and Zn doped NiFe₂O₄ nanoparticles.

Sample	Undoped NiFe₂O₄	2% Zn doped NiFe₂O₄	4% Zn doped NiFe₂O₄
%Adsorption	6.6	66.5	57.7
Adsorption Capacity q_e	1.60	15.96	13.85
%Degradation	82.6	92.2	81.4
K Value (min⁻¹)	0.0117	0.0188	0.0149
R²	0.9958	0.9733	0.8827
T_{1/2} (ms)	58.8	36.8	46.5
E_g Experimental (eV)	1.58	1.48	1.53

Valance band potential (eV)	0.56	0.61	0.59
Valance band potential (eV)	2.14	2.09	2.12

Following the adsorption under solar light irradiations, the degradation efficiencies of all the samples have similar trend the 2% Zn-doped ferrites has achieved the highest photodegradation efficiency of 92% lagging behind the other undoped (82.6%) and 4% doped ferrites (81.4%) photocatalysts as shown in the graphs and bar graph (figure 14). This confirms that the adsorption has a critical role in the degradation of MB dye. But adsorption is not only factor, contributing to the degradation of dyes. Although the 4% Zn-doped ferrites have comparatively high adsorption capacity (q_e) but has lower photodegradation. Which indicate that the excessive Zn incorporation has introduced the structural defects and mid-gap states which accelerates the electron-hole recombination's and reduces the photocatalytic efficiency despite higher adsorption capacity.

These findings suggest that the adsorption of dye molecules on the surface of catalyst plays an important role in the overall degradation of methylene blue dye. The high adsorption pre-concentrates the dye molecules near the active sites, thereby increasing the probability of their reaction with photogenerated reactive oxygen species (ROS).

3.7.1 Kinetic studies of photocatalytic process

To further understand the degradation behavior, the kinetics data was analyzed by using the pseudo first order modeling fitting with expressing given below

$$\ln \frac{C_o}{C_t} = Kt$$

Here K appears to be the rate constant indicating the direct measure of the reaction speed and the linearity of the plots were validated by R² values. Further the half-life of degradation reaction was also calculated, and all the values are tabulated in table 4.

$$t_{1/2} = \frac{0.693}{K}$$

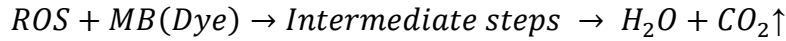
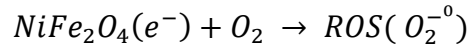
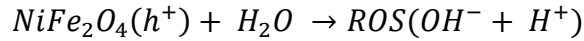
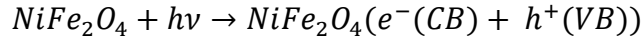
The 2% Zn-doped ferrites have much higher rate constant values of approximately 0.0188 min⁻¹ which is almost 1.6 times higher than the undoped ferrite catalyst have 0.0117 min⁻¹ value. The 4% Zn Doped-Ferrites show an intermediate value of rate constant. The calculated half-life of the degradation reaction which reflects the time required to degrade 50% of MB dye further follows and supports the same trend. The 2% Zn doped ferrites have shortest lifetime of 36.8 min as compared to the undoped (46.5 min) and 4% Zn doped Ferrites (58.8 min). A comparative analysis of our photocatalysts with other previously published reports on NiFe₂O₄ based photocatalysts are summarized in table 5. Table clearly highlights the faster rate constant of our 2% Zn doped NiFe₂O₄ than most of undoped and even Co-doped NiFe₂O₄ as well composite samples.

All of these observations confirm that the superior photocatalytic performance of 2% Zn doped ferrites as compared to other counterparts. This enhancement of degradation by the Zn doping could be due to the enhanced light absorbance capability, improved charge separation property and high availability of sites for the MB dyes on the surface of Photocatalysts [52]. Which synergistically leads to improved photocatalytic properties if 2% Zn-doped NiFe₂O₄ nanoparticles as compared to other nanostructures. These findings suggest that undoped NiFe₂O₄ nanostructure has a potential to degrade MB dye, but the Zn doping has significantly improved its catalytic performance. We suggest that 2% Zn doping into NiFe₂O₄ would be an optimal doping to offer an

ideal balance between structural, optical and electronic properties required for the higher photocatalytic degradation of organic dyes under sunlight irradiations [53].

3.7.1 Degradation mechanism

In general, the overall the photocatalytic mechanism can be described as following steps; the adsorption of dyes on catalysts under dark conditions, the creation of electron hole pairs, the migration of photoinduced electron-hole pairs to the surface of the catalysts, the creation of reactive Oxygen species (ROS) and the degradation of MB dyes by attacking the ROS as explained in the equation below and also illtreated in the figure 15 [23].



The reactive oxygen species (ROS) are the result of oxidation and reduction reaction which strongly depends on the conduction and valance band edge position. Hence, we evaluated the conduction and valance band potentials using the following relations.

$$E_{VB} = X - E_e - 0.5E_g$$

$$E_{CB} = E_{VB} + E_g$$

Here the X , E_g , E_{CV} and E_{VB} represent electronegativity, energy band gap, conduction band position and valance band position of photocatalysts. We used $X= 5.85$, $E_e= 4.5$ eV and E_g optical band gap of each photocatalyst to evaluated the Conduction band and valance band potentials as

given in table 4 and figure 15 [54]. It is very interesting to observe that Zn doping has not only tuned the optical band gap (decreased) but also altered the conduction as well as valance band potentials of NiFe_2O_4 . The conduction band of Undoped NiFe_2O_4 were located at 0.56 eV, but upon doping it slightly shifted to 0.61 and 0.59 eV for 2 and 4% Zn doping respectively. This electronic modification by uplifting of conduction band from 0.56 to 0.61 eV is the direct indication of the enhanced reduction ability of conduction elections in 2% Zn doped NiFe_2O_4 . The higher reduction reaction at the conduction band produces more superoxide radicals (ROS) which are directly degraded MB dye. On the other hand, in the valance band, a slight shift toward less positive potential has been observed. The valance band also changes from 2.14 to 2.09 eV with the 2% Zn doping. This has reduced electron-hole recombination processes and has eventually enhanced the catalytic degradation process by increasing the lifetime of charge carriers. Additionally, all the samples have enough oxidation potential to oxidize the water and produce reactive oxygen species for the degradation process [51].

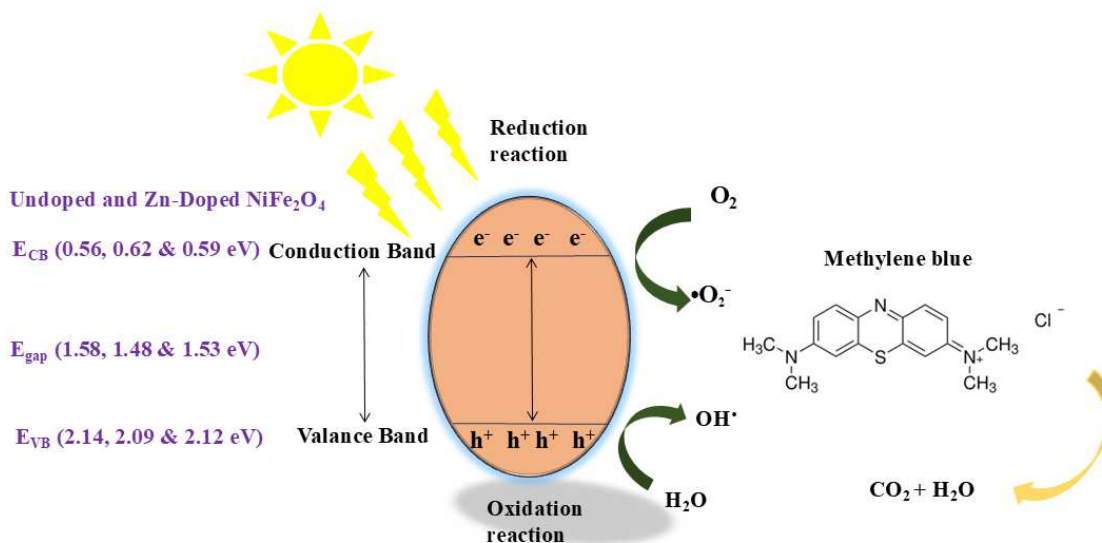


Fig. 15 schematic diagram of photocatalytic degradation of Methylene Blue the presence of for undoped and Zn doped NiFe_2O_4 nanoparticles Photocatalyst.

In short, the CB and VB synergistically produce sufficient ROS to degrade above 80% of MB dye. Comparatively, the 2% Zn doping in NiFe₂O₄ makes it most favorable electronic configuration compared to others. Its narrower energy band gap has enhanced visible light absorption to produce more electron-hole pairs, the slight uplifting has further enhanced its reducing capacity by producing more ROS and lastly its VB has enough oxidative ability to further support by producing ROS by oxidizing water with less recombination process. This all makes 2% Zn doped NiFe₂O₄ to have superior catalytic performance than others.

Table 5. Comparison of different reported photocatalyst with dye degrading efficiencies.

Photocatalyst	Organic dye	Removal capacity	K values (min ⁻¹)	References
NiFe ₂ O ₄	MB dye	85% after 360 minutes	-	[16]
NiFe ₂ O ₄	MB dye	52% after 105 minutes	0.0105	[17]
NiFe ₂ O ₄	MB dye	25% after 80 minutes	0.0035	[18]
NiFe ₂ O ₄	MB dye	59% after 120 minutes	-	[19]
NiFe ₂ O ₄	MB dye	90% after 120 minutes	0.0149	[15]
NiFe ₂ O ₄	MB dye	45% after 180 minutes	0.002	[22]
NiFe ₂ O ₄	MB dye	82.6% after 150 minutes	0.0117	Current Research
Ni _{0.5} Zn _{0.5} Fe ₂ O ₄	MB dye	26 % after 180 minutes.	-	[55]
4% Co doped NiFe ₂ O ₄	MB dye	100% after 180 minutes	0.01	[22]
NiFe ₂ O ₄ /GO	MB dye	90% after 150 minutes	-	[56]
4% Zn doped NiFe ₂ O ₄	MB dye	81% after 150 minutes	0.0188	Current Research
2% Zn doped NiFe ₂ O ₄	MB dye	92% after 150 minutes	0.0149	Current Research

5. Conclusions:

This study demonstrates the successful synthesis of Zn-doped NiFe₂O₄ nanoparticles via a facile co-precipitation method, presenting a systematic and thorough investigation into how low-level Zn⁺² doping alters the functional properties of NiFe₂O₄ for photocatalytic applications. The comprehensive characterizations, along with theoretical DFT calculations, confirms that the addition of Zn²⁺ into the NiFe₂O₄ spinel lattice induces controlled structural evolution, manifesting

as lattice expansion and a reduction in crystallite size along with the increase in the density of surface-active sites. The achievement of this work is to figure out the non-monotonic optimization window, with 2% Zn doping as the optimal concentration. The doping has specifically engineered the following properties in the host material: crystal structure, electronic structure, surface chemistry and energy band positions. The decrease in the optical band gap has maximized the visible light harvesting. The decrease in the crystallite size due to non-magnetic Zn doping has provided more surface-active species. The generation of highly electronegative surface leads to the exceptionally high MB dye adsorption capacity. The uplifting of conduction band has directly enhanced the reduction reaction and produces more electron hole pairs. As a results of all these modifications, the 2% Zn doped NiFe_2O_4 nanostructures exhibit the superior photocatalytic performance by degradation 92% of Mb dye in 150 minutes with highest recorded rate constant of 0.0188 min^{-1} , outperforming the other counter ferrites. The 4% doped sample shows the significant improvement in the adsorption capacity and light absorption but are counterbalanced by the detrimental increase in the dislocation density. These findings suggest that the prepared samples with modified optoelectronic properties can not only be used for wastewater treatment but can effectively be used for other spintronic as well as advanced ceramic applications.

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Data Availability Statement:

Data shall be available on request.

Competing interest:

The authors have no relevant financial or non-financial interests to disclose.

References:

1. Hoffmann, M.R., et al., *Environmental applications of semiconductor photocatalysis*. Chemical reviews, 1995. **95**(1): p. 69-96.
2. Ravelli, D., et al., *Photocatalysis. A multi-faceted concept for green chemistry*. Chemical Society Reviews, 2009. **38**(7): p. 1999-2011.
3. Rafiq, A., et al., *Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution*. Journal of Industrial and Engineering Chemistry, 2021. **97**: p. 111-128.
4. Vani, K., et al., *Impact of rare earth Tb³⁺ substitution in cobalt ferrites: Tuning structural, dielectric, magnetic properties and photocatalytic activity*. Ceramics International, 2025. **51**(1): p. 240-251.
5. Casbeer, E., V.K. Sharma, and X.-Z. Li, *Synthesis and photocatalytic activity of ferrites under visible light: a review*. Separation and Purification Technology, 2012. **87**: p. 1-14.
6. Matsushita, N., et al., *Ni-Zn ferrite films synthesized from aqueous solution usable for sheet-type conducted noise suppressors in GHz range*. Journal of electroceramics, 2006. **16**(4): p. 557-560.
7. Valenzuela, R., *Novel applications of ferrites*. Physics Research International, 2012. **2012**(1): p. 591839.
8. Kavas, H., et al., *Cation distribution and magnetic properties of Zn doped NiFe₂O₄ nanoparticles synthesized by PEG-assisted hydrothermal route*. Journal of Alloys and Compounds, 2009. **479**(1-2): p. 49-55.
9. Nazari, N., M. Golzan, and K. Mabhouti, *Study of Urbach energy and Kramers–Kronig on Mn and Zn doped NiFe₂O₄ ferrite nanopowder for the determination of structural and optical characteristics*. Scientific Reports, 2024. **14**(1): p. 6407.
10. Abushad, M., et al., *Synthesis and role of structural disorder on the optical, magnetic and dielectric properties of Zn doped NiFe₂O₄ nanoferrites*. Journal of Molecular Structure, 2022. **1253**: p. 132205.
11. Heiba, Z.K., et al., *Structure and optical properties of Zn and Mn co-doped nano-NiFe₂O₄*. Journal of Materials Science: Materials in Electronics, 2021. **32**(17): p. 22718-22729.
12. Sivaprakash, P., et al., *Influence of Zn²⁺ doping towards the structural, magnetic, and dielectric properties of NiFe₂O₄ composite*. Journal of Materials Science: Materials in Electronics, 2020. **31**(19): p. 16369-16378.
13. Anupama, M., et al., *Effect of Zn substitution on the structural and magnetic properties of nanocrystalline NiFe₂O₄ ferrites*. Ceramics International, 2018. **44**(5): p. 4946-4954.
14. Alghamdi, E.A. and R. Sai, *Adjusting the gas detection characteristics of NiFe₂O₄ spinel ferrite nanoparticles through the introduction of Zn doping*. Results in Physics, 2024. **59**: p. 107549.
15. Biswas, B., et al., *Investigation of structural, optical, and magnetic properties of NiFe₂O₄ for efficient photocatalytic degradation of organic pollutants through photo fenton reactions*. Heliyon, 2024. **10**(17).
16. Jia, Z., et al., *A new strategy for the preparation of porous zinc ferrite nanorods with subsequently light-driven photocatalytic activity*. Materials Letters, 2011. **65**(19-20): p. 3116-3119.
17. Riaz, R., et al., *NiFe₂O₄/CuO heterostructures optical, magnetic and photocatalytic properties: Methylene blue dye degradation under solar light irradiation*. Journal of Molecular Structure, 2024. **1309**: p. 138174.

18. Kamal, S., et al., *Synthesis of boron doped C₃N₄/NiFe₂O₄ nanocomposite: An enhanced visible light photocatalyst for the degradation of methylene blue*. Results in Physics, 2019. **12**: p. 1238-1244.
19. Rana, P.S., *Structural, optical, electrical, and photocatalytic application of NiFe₂O₄@ NiO nanocomposites for methylene blue dye*. Ceramics International, 2023. **49**(9): p. 13520-13530.
20. Elmekawy, A., et al., *Synthesis, characterization and correlation studies on the Ni–Zn–Mn ferrite as a photocatalyst*. The European Physical Journal Plus, 2024. **139**(8): p. 747.
21. Sagar, A., et al., *Structural, optical, and photocatalytic properties of Ni–Zn and Mg–Zn spinel ferrites*. Interactions, 2024. **245**(1): p. 86.
22. Mohammadzadeh Kakhki, R., et al., *Visible light photocatalytic degradation of textile waste water by Co doped NiFe₂O₄ nanocomposite*. Journal of Materials Science: Materials in Electronics, 2017. **28**(5): p. 4095-4101.
23. Azmat, S., et al., *Solar light triggered photocatalytic performance of WO₃ nanostructures; waste water treatment*. Materials Research Express, 2018. **5**(11): p. 115025.
24. Kohn, W. and L.J. Sham, *Self-consistent equations including exchange and correlation effects*. Physical review, 1965. **140**(4A): p. A1133.
25. Giannozzi, P., et al., *QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials*. Journal of physics: Condensed matter, 2009. **21**(39): p. 395502.
26. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*. Physical review letters, 1996. **77**(18): p. 3865.
27. Rappe, A.M., et al., *Erratum: Optimized pseudopotentials [phys. rev. b 41, 1227 (1990)]*. Physical Review B, 1991. **44**(23): p. 13175.
28. Adinaveen, T., et al., *Revolutionizing Textile Applications: Unveiling the Potential of NiFe₂O₄ Nanoparticles for Enhanced Performance*. Fibers and Polymers, 2024. **25**(1): p. 121-130.
29. Yuan, F., et al., *Controlled synthesis of tubular ferrite MFe₂O₄ (M= Fe, Co, Ni) microstructures with efficiently electrocatalytic activity for water splitting*. Electrochimica Acta, 2019. **324**: p. 134883.
30. Li, Y., et al., *Controlled fabrication and characterization of α -FeOOH nanorods*. Journal of Inorganic and Organometallic Polymers and Materials, 2022. **32**(4): p. 1400-1408.
31. Bernardino, E.G., et al., *Photocatalyst of manganese ferrite and reduced graphene oxide supported on activated carbon from cow bone for wastewater treatment*. Environmental Science and Pollution Research, 2024. **31**(3): p. 4779-4796.
32. Kurmude, D., et al., *Superparamagnetic behavior of zinc-substituted nickel ferrite nanoparticles and its effect on mossbauer and magnetic parameters*. Journal of Superconductivity and Novel Magnetism, 2014. **27**(8): p. 1889-1897.
33. Atif, M., et al., *Studies on the magnetic, magnetostrictive and electrical properties of sol–gel synthesized Zn doped nickel ferrite*. Journal of Alloys and Compounds, 2011. **509**(18): p. 5720-5724.
34. Zdorovets, M. and A. Kozlovskiy, *The effect of lithium doping on the ferroelectric properties of LST ceramics*. Ceramics International, 2020. **46**(10): p. 14548-14557.
35. Raza, A., et al., *Effect of Ni doping on the magnetic and photocatalytic properties of CoFe₂O₄ nanoparticles*. Journal of Materials Science: Materials in Electronics, 2024. **35**(25): p. 1703.
36. Mubasher, M.M., et al., *Barium doping effects on frequency-dependent dielectric properties of cobalt ferrite nanoparticles*. Materials Innovations, 2022. **2**(3): p. 1-10.
37. Savunthari, K.V. and S. Shanmugam, *Effect of co-doping of bismuth, copper and cerium in zinc ferrite on the photocatalytic degradation of bisphenol A*. Journal of the Taiwan Institute of Chemical Engineers, 2019. **101**: p. 105-118.

38. Andhare, D.D., et al., *Effect of Zn doping on structural, magnetic and optical properties of cobalt ferrite nanoparticles synthesized via. Co-precipitation method*. Physica B: Condensed Matter, 2020. **583**: p. 412051.
39. Lassoued, A., et al., *Synthesis, structural, optical and morphological characterization of hematite through the precipitation method: Effect of varying the nature of the base*. Journal of Molecular Structure, 2017. **1141**: p. 99-106.
40. Lassoued, A. and J. Li, *Magnetic and photocatalytic properties of Ni–Co ferrites*. Solid State Sciences, 2020. **104**: p. 106199.
41. Yadesa, D., J.N. Guyasa, and T.T. Beyene, *Effect of codoping zinc oxide nanoparticles with sulfur and nitrogen on its energy bandgap, antioxidant properties, and antibacterial activity*. Advances in Materials Science and Engineering, 2024. **2024**(1): p. 4275035.
42. Bercoff, P. and H. Bertorello, *Localized canting effect in Zn-substituted Ni ferrites*. Journal of magnetism and magnetic materials, 2000. **213**(1-2): p. 56-62.
43. Hernández-Gómez, P., et al., *An approach to the magnetic disaccommodation in Ti-substituted Ba–W hexaferrites*. Journal of Applied Physics, 2000. **87**(9): p. 6250-6252.
44. Heiba, Z.K. and M.B. Mohamed, *Effect of magnesium deficiency on magnetic properties tuning and cation redistributions of magnesium ferrite nanoparticles*. Journal of Materials Science: Materials in Electronics, 2019. **30**(1): p. 786-796.
45. Sláma, J., et al., *Magnetic properties of selected substituted spinel ferrites*. Journal of Magnetism and magnetic Materials, 2013. **326**: p. 251-256.
46. Meinert, M. and G. Reiss, *Electronic structure and optical band gap determination of NiFe₂O₄*. Journal of Physics: Condensed Matter, 2014. **26**(11): p. 115503.
47. Singh, C., et al., *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*. Materials Chemistry and Physics, 2015. **156**: p. 188-197.
48. Ali, S. and T. Ahmad, *Treasure trove for efficient hydrogen evolution through water splitting using diverse perovskite photocatalysts*. Materials Today Chemistry, 2023. **29**: p. 101387.
49. Ali, S.A. and T. Ahmad, *Chemical strategies in molybdenum based chalcogenides nanostructures for photocatalysis*. international journal of hydrogen energy, 2022. **47**(68): p. 29255-29283.
50. Rajabi, H.R., et al., *Fast sonochemically-assisted synthesis of pure and doped zinc sulfide quantum dots and their applicability in organic dye removal from aqueous media*. Journal of Photochemistry and Photobiology B: Biology, 2018. **181**: p. 98-105.
51. Azmat, S., et al., *A closer look at the interface of Cs₃Bi₂Br₉ lead free perovskite in photocatalytic process*. Journal of Physics and Chemistry of Solids, 2025. **199**: p. 112534.
52. Katoch, G., et al., *Sol-gel auto-combustion developed Nd and Dy co-doped Mg nanoferrites for photocatalytic water treatment, electrocatalytic water splitting and biological applications*. Journal of Water Process Engineering, 2023. **53**: p. 103726.
53. Harish, K., et al., *Optical and photocatalytic properties of solar light active Nd-substituted Ni ferrite catalysts: for environmental protection*. ACS Sustainable Chemistry & Engineering, 2013. **1**(9): p. 1143-1153.
54. Nguyen, L.T.T., et al., *Synthesis of magnetic NiFe₂O₄/gC₃N₄ heterojunction photocatalysts for boosting dye degradation performance under visible-light irradiation*. Nanoscale Advances, 2025. **7**(2): p. 536-548.
55. Ivanin, S., et al., *Studying the Photocatalytic Activity of a Nanosized Powder and Fibers Based on Nickel–Zinc Ferrite*. Russian Journal of Inorganic Chemistry, 2024. **69**(5): p. 683-689.
56. Bayantong, A.R.B., et al., *Nickel ferrite nanoenabled graphene oxide (NiFe₂O₄@ GO) as photoactive nanocomposites for water treatment*. Environmental Science and Pollution Research, 2021. **28**(5): p. 5472-5481.

