

Article

High-Performance Photocatalytic Degradation—A ZnO Nanocomposite Co-Doped with Gd: A Systematic Study

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Abstract: This research aims to analyze the improvement in the photocatalytic properties of ZnO nanoparticles by incorporating Gd. In order to understand the influence of incorporating Gd into the ZnO matrix, the photocatalytic activity of the material is compared at various Gd concentrations. Different doping concentrations of Gd ranging from 0 to 0.075 are incorporated into ZnO and the synthesized ZnO-Gd nanocomposites are investigated using structural, morphological, and optical analyses using XRD, SEM, and UV-vis spectroscopy, respectively. The photocatalytic performance of the synthesized ZnO-Gd nanocomposites is determined via the degradation of organic contaminants under visible light. Regarding the latter, the results suggest that photocatalytic efficiency increases with increasing Gd doping levels up to an optimal doping concentration. The enhancement of the photocatalytic performance of Gd-doped ZnO is explained, along with the mechanism related to the availability of new pathways for charge carrier recombination. Among all of them, the 0.075 Gd-doped ZnO catalyst exhibits the highest photocatalytic activity which degrades 89% of MB dye after being irradiated with UV light for 120 min. However, pure ZnO degrades only 40% of MB dye within the same testing conditions. In closing, this work confirms the applicability of Gd-doped ZnO nanocomposites as photocatalysts in cleaning up the environment and in wastewater treatment.

Keywords: ZnO nanoparticles; photocatalysis; Mott–Schottky; band gap; sol–gel



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1. Introduction

Polluted water is any water that is harming the environment or has the potential to harm it and the effects of this pollution necessitate immediate action [1–3]. One of the leading causes of this pollution is the release of variable and hazardous organic pollutants, such as organic dyes and pharmaceutical waste effluent, in the wastewater stream [4,5]. These pollutants lead to deforestation, reduced clean and drinkable water, dire environmental consequences, gruesome sicknesses, and even genetic alterations in the long run [6,7]. Most of the conventional physical and chemical treatment methods, such as flocculation, coagulation, reverse osmosis, filtration, etc., are limited in the sense that they cannot remove the persistent dyes in water effectively [8,9]. Innovative solutions are needed to alter these dyes into non-hazardous byproducts, and photocatalysis appears to be a viable option for the remediation of this sort of wastewater [10–12]. Contaminant dyes have been degraded by photocatalytic processes using different semiconductor materials, such as Cu₂O, ZnO, TiO₂, and CuO [13–15]. Of all these materials, zinc oxide (ZnO) is preferred because it is

cheap, environmentally friendly, available, and possesses desirable physical and chemical characteristics [16,17].

Zinc oxide nanoparticles (NPs) are easily available wide-band-gap semiconductor materials that have potential applications in electronic, cosmetic, and biomedical industries and environmental remediation [18–21]. Besides their inherent characteristics, such as crystal structure, morphology, and bulk composition, defects also have critical roles in determining any of their properties. In general, defects in ZnO NPs are unfavorable from a crystallography point of view; however, defects can be useful for new applications, such as ferromagnetism, p-type conductivity, spintronics, optoelectronics, etc. [22,23]. In ZnO, various other structure defects such as zinc interstitial (Zni), oxygen interstitial (Oi), zinc vacancy (VZn), and oxygen vacancy (Vo) are also present [24,25]. These defects can change the physical nature of ZnO, for example, by converting diamagnetic ZnO into ferromagnetic, changing its photoluminescence properties, or tailoring the band gap [26,27]. The electron energy levels related to intrinsic defects in ZnO can affect the photoinduced transitions, thus affecting the probability of electron transition photoconductivity and the photocatalytic activity of ZnO NPs [28,29].

Numerous studies have shown that the photocatalytic properties of ZnO can be improved by doping with rare-earth elements (Ce, Eu, Sr, La, Gd, etc.) and transition metals (Mn, Ni, Cr, Cu, etc.), and by forming composites such as ZnO/ZnS, ZnO/SnO₂, ZnO/CuO, ZnO/Fe₂O₃, etc. [30–33]. Young-Hoon Kim et al. [34] and Danilenko et al. [35] have demonstrated the enhanced photocatalytic performance of ZnO by increasing the density of Vo, which is also supported by several publications. As the active sites of ZnO NPs are locally influenced by these defects, the effect of dopant types and doping levels on tuning ZnO's photocatalytic properties remains a challenging research area. Doping with rare earth ions has attracted significant interest due to the electronic transitions occurring within their 4f energy shells. Gd-doped ZnO NPs offer greater advantages and application potential due to their temperature-independent UV and visible luminescence, which is applicable in light-emitting displays, optical storage systems, drug delivery, and catalysis. Magnetic fields and temperature have been found to significantly impact Gd-doped ZnO. Another important property of Gd-doped ZnO is that, in addition to electron conductivity in ZnO, hole conductivity is also enhanced, as holes are more active in the 4f orbital of Gd than electrons. Gd-doped ZnO with varying dopant concentrations (Gd_xZn_{1-x}O, where $x = 0.00, 0.025, 0.05$, and 0.075) was synthesized using the sol–gel combustion method, and its efficiency in degrading MB under UV-light illumination was investigated. The process of doping has significant effects on the size, shape, and photocatalytic performance of ZnO NPs.

2. Result and Discussion

2.1. XRD Analysis

Figure 1 shows the XRD profiles of the synthesized Zn_{1-x}Gd_xO samples ($x = 0, 0.025, 0.05$, and 0.075). Herein, we identified the hexagonal phase structure for the samples: pure ZnO and ZnO doped with different concentrations of Gd. It is also called the hexagonal phase and is set in the space group of P6₃mc. This structure has been found to consist of a series of Zn–O columns with tetrahedral coordination that repeat along a c-axis. For ZnO doped with Gd, the phase structure investigated will be hexagonal, as with pure ZnO, but with some Zn ions replaced by Gd ions. This has been categorized as a substitutional doping mechanism. When Gd ions are incorporated into the ZnO lattice, the lattice strain and defects such as vacancies or interstitials can be generated, altering the physical and chemical properties of the material. Rietveld refinement is a simple technique of studying the crystal structures of materials, such as ZnO and ZnO-Gd. In this case, the program models the crystal structure, compares it with the X-ray diffraction pattern observed, and calculates the changes in lattice parameters, atomic positions, and thermal vibrations. Rietveld refinement of the XRD data allows estimates of the phase purity, crystallite size, and lattice strain of the material needed to assess the impact of doping on the crystal

structure to be obtained. Consequently, the structure properties of the synthesized pure ZnO and ZnO doped with Gd are expected to have a hexagonal phase structure, and, based on this structure, the Rietveld refinement analysis can be employed to compare the crystal structure. The incorporation of rare earth ions ($\text{Gd}^{3+}/\text{Gd}^{2+}$) into the ZnO lattice resulted in a subtle shift towards lower 2θ angles in the XRD pattern, observed primarily in the dominant (101) diffraction peak. The larger size of introduced rare earth ions compared to Zn^{2+} acts like a crowbar, stretching the ZnO crystal lattice (unit cell expansion) and disrupting its perfect order (reduced crystallinity). This effect manifests as broader peaks in the X-ray data, similar to findings by Suneel Kumar et al. [34].

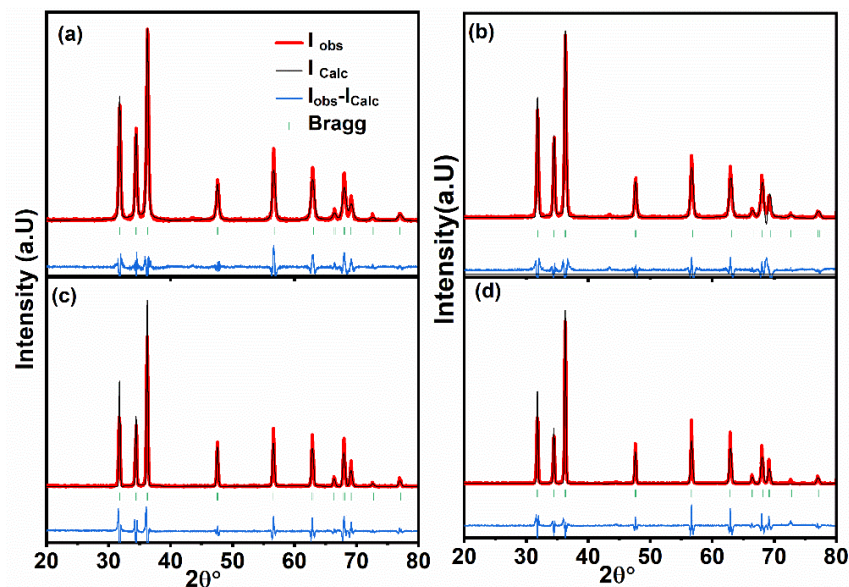


Figure 1. XRD patterns of (a) ZnO, (b) 0.025 Gd-doped ZnO, (c) 0.05 Gd-doped ZnO, and (d) 0.075 Gd-doped ZnO.

2.2. FTIR Analysis

The FTIR spectroscopy route was utilized to verify the existence of functional groups in both pristine and ZnO doped with Gd, as depicted in Figure 2a,b. The FTIR peak observed at around 443 cm^{-1} in pure ZnO is assigned to the lattice metal–oxygen bond (Zn–O), as shown in Figure 2b. Upon the analysis of FTIR, the peak detected at around 2924 cm^{-1} is associated with symmetric and asymmetric stretching vibrations of CH_2 adsorbed on the surface [36]. The widened peak observed in the range of $3100\text{--}3658\text{ cm}^{-1}$ signifies the stretching vibration of the O–H hydroxyl group due to surface-adsorbed water. In contrast to pristine nanoparticles, the ZnO doped with 5% Gd displays a broadening of the peak at the 417 cm^{-1} band position, indicating lattice distortion at the bond of Zn–O due to the presence of Gd dopant ions. Moreover, the introduction of Gd doping causes a shift in the FTIR spectrum towards higher wave numbers, signifying changes in bond length resulting from the substitution of Zn through Gd^{3+} ions. There are two extra peaks detected in the spectrum at 1388 and 1519 cm^{-1} , confirming the presence of Gd.

2.3. UV-Vis Spectrum

The optical characteristics of the nanoparticles produced were examined using UV-vis spectroscopy. The spectrum of the UV absorption of both the pristine and Gd-doped ZnO preparations is depicted in Figure 3a. Analysis of the UV-vis spectrum indicates that the intensity of the absorption cut-off peak diminishes with higher concentrations of Gd, indicative of reduced crystallinity. Pure ZnO exhibits an absorption wavelength at around 94 nm , corresponding to a band gap of 3.15 eV . In comparison, 2.5, 5, and 7.5% Gd-doped ZnO display a redshift, with cut-off wavelengths around 400 and 403 nm and energy gaps of 3.1 eV and 3.07 eV , correspondingly. The decrease in the band gap of Gd-doped ZnO

is ascribed to the formation of narrow (medium) energy levels involving the ZnO band gap energy levels [14]. The shift towards longer wavelengths in the absorption peak of 2.5, 5, and 7.5% Gd-doped ZnO is ascribed to alterations in the defect structure within the lattice crystal and the formation of oxygen vacancies within the ZnO system of the crystal. However, ZnO doped with 0.05 Gd exhibits a blue shift relative to pristine zinc oxide through an absorption peak at around 390 nm and an energy gap of around 3.17 eV, as shown in Figure 3b. The augmented energy gap observed in ZnO doped with 0.05 Gd suggests a reduction in crystallite size compared to pristine zinc oxide [16]. The findings suggest that the heightened band gap in ZnO doped with 0.05 Gd is a consequence of the quantum confinement effect. Typically, as the crystallite size rises, the direct energy gap energy of nanostructured materials also grows, and noticeable changes in the morphology of the nanoparticles are observed in comparison to pure ZnO.

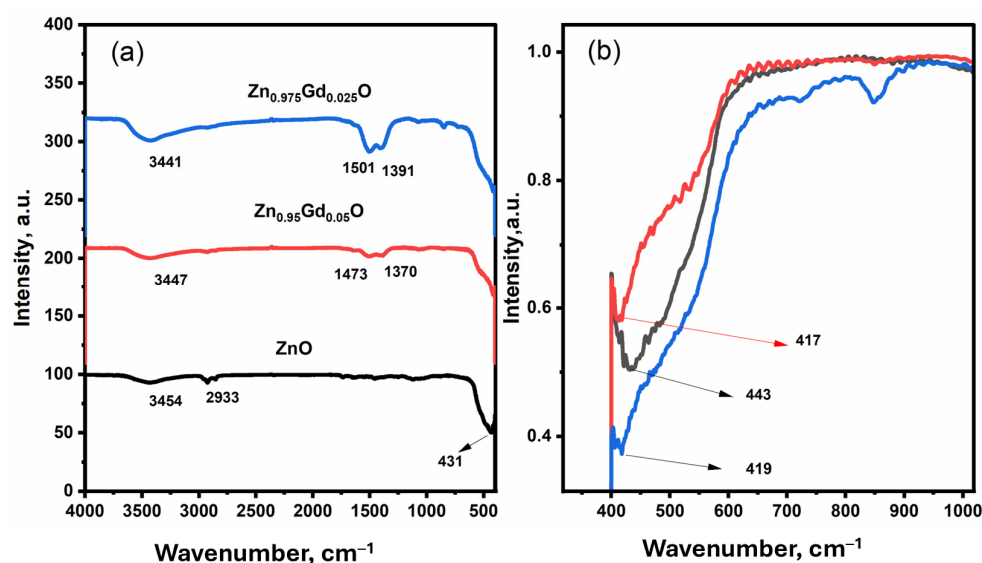


Figure 2. FTIR spectroscopy of (a) ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO and (b) selected peaks at around 417, 419, 443 cm^{−1} for ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO.

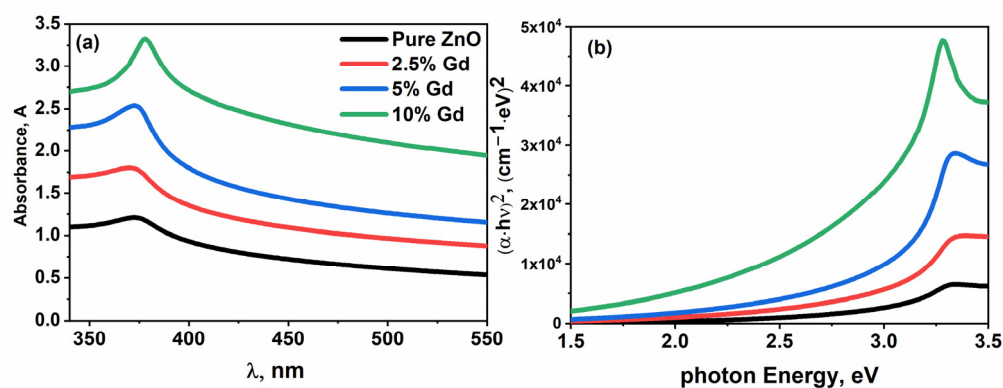


Figure 3. UV-vis spectroscopy (a,b) energy gap calculated of ZnO, 0.025 Gd-doped ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO.

Variations in the nanoparticle energy gap energy depend on various factors such as preparation conditions, shape, grain size, and alterations in lattice parameters within the crystal structure. While bulk ZnO possesses a direct energy gap of around 3.14 eV, in nanostructured zinc oxide, electronic states become discrete at the level of individual molecules and atoms. Consequently, the red shift of the energy gap and electronic transitions is restricted when electronic populations occupy discrete states, leading to a notable blue shift with an increase in the energy gap. The observed increase in the band gap of ZnO

doped with 0.05 Gd is primarily attributed to the quantum confinement effect, where the forbidden bandwidth enlarges as crystal size decreases. At the nanoscale, ZnO crystals exhibit high densities in the UV region and maximum transparency in the visible region due to electronic transitions from O2p to Zn3d orbitals. The introduction of Gd into ZnO alters the optical band gap, largely due to surface defects or oxygen vacancies within the ZnO crystal system. These vacancies or defects decrease crystal size, effectively widening the forbidden band gap. UV studies reveal that ZnO doped with 0.05 Gd exhibits increased photon absorption efficiency compared to pristine ZnO during photocatalysis.

2.4. Morphological Properties

Figure 4 demonstrates the scanning electron microscopy (SEM) photos of synthesized $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$, and 0.075) samples. SEM is a helpful method that can be used to investigate the morphology and microstructure of materials, in particular $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$, and 0.075). These characterizations using SEM give information on the particle size, shape, and distribution of the material, which may be altered by the doping concentration of Gd. Using SEM images, the as-prepared pure ZnO ($x = 0$) consists of hexagonal platelets or rods that have smooth surfaces and almost similar sizes. The platelets or rods are generally of the order of several microns in length and a few hundred nanometers in breadth; they adhere remarkably closely together and are arranged randomly. A high percentage of Gd added into the ZnO lattice brings about a change in the morphology and microstructure of the material. At low doping concentrations ($x = 0.025, 0.05$) in the SEM images, the dopant may elicit hexagonal platelet or rod-like morphology similar to that of ZnO, but with a smaller particle size and distorted forms. The particle size is anticipated to decrease with increasing Gd concentration because the lattice strain and defects created by the dopant ions lead to a reduction in particle size. The surface of the particles may also change toward being rougher and/or more porous, reflecting the development of defects and/or secondary phases. However, at higher doping concentrations ($x = 0.075$), SEM images may possess a higher degree of structural complexity with the presence of agglomerates, clusters, or secondary phases. This will probably coalesce into larger and more random-shaped particles, and there may be less distinct hexagonal platelet or rod-like shapes. These X-ray diffractions may be due to the limited solubility of Gd in ZnO, suggesting the possible existence of Gd-rich regions or compounds.

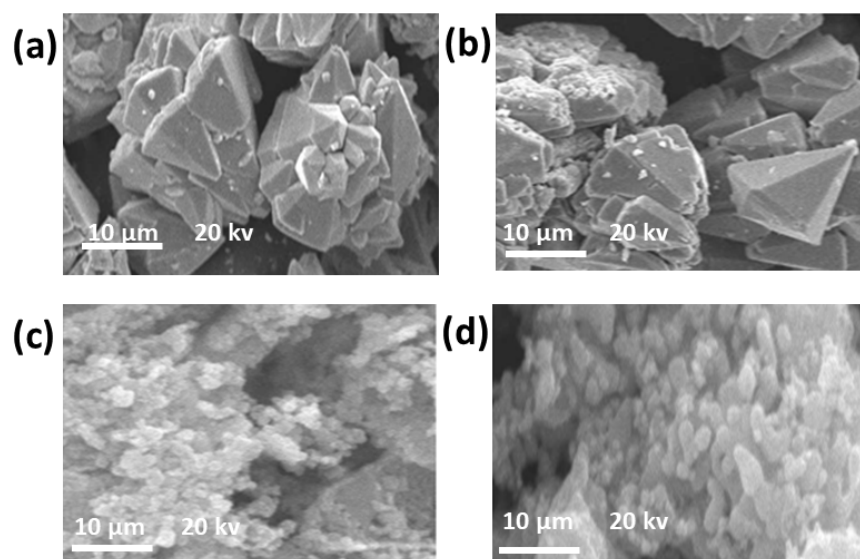


Figure 4. SEM photos of (a) ZnO, (b) 0.025 Gd-doped ZnO, (c) 0.05 Gd-doped ZnO, (d) 0.075 Gd-doped ZnO.

2.5. Photocatalytic Activity of $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$ and 0.075)

The photodegradation of MB under UV light was investigated for the following $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ samples: ZnO , $\text{Zn}_{0.975}\text{Gd}_{0.025}\text{O}$, $\text{Zn}_{0.95}\text{Gd}_{0.05}\text{O}$, and $\text{Zn}_{0.925}\text{Gd}_{0.075}\text{O}$. In a normal experiment, 0.025 g of zinc oxide, gadolinium oxide, or $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$, and 0.075) was mixed with 10 ppm of MB dye solution with a volume of 50 mL. Finally, the sample was filtered and centrifuged for 10 min at 5000 r.p.m, after which the sample was measured using UV-vis spectroscopy. Then, 30 min dark pre-illumination was carried out to achieve adsorption equilibrium between $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ (where $x = 0, 0.025, 0.05$, and 0.075) photocatalyst and MB solution. These MB molecules, which were adsorbed onto the $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ surface (with $x = 0, 0.025, 0.05$, and 0.075), interacted with the electron-hole pairs activated by UV light. A closed dark reactor with a 10 cm gap between the UV lamp and the MB- $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ (where $x = 0, 0.025, 0.05$, and 0.075) beaker was used. Consequently, the percent photodegradation of the MB solution was determined by measuring its absorbance at 665 nm. The photodegradation/removal efficiency was calculated using the following equation:

$$\text{Removal\%} = \frac{(C_i - C_f)}{C_i} \times 100$$

Following the completion of the photocatalytic degradation process, the starting and final MB concentrations (C_i and C_f) were calculated.

2.6. Photocatalytic Activity and Mechanism of the Reaction

We investigated the photocatalytic degradation of methylene blue (MB) dye in ZnO suspension using the photo-Fenton reaction and compared its efficiency with ZnO -doped Gd prepared through the co-precipitation route. ZnO is a promising candidate for photocatalysts used in practical and large-scale applications, as it can be produced at a low cost from non-toxic materials exhibiting a high level of activity. Nevertheless, the photocatalytic ability of ZnO can be enhanced by doping it with rare-earth metal similar to Gd. For this investigation, ZnO pristine and 0.025, 0.05, and 0.075 Gd ZnO photocatalysts were based on a sol-gel method. These catalysts were tested by degrading MB dye under UV light irradiation. Figure 5a–d shows the photocatalytic performance of pure and Gd-doped ZnO catalysts.

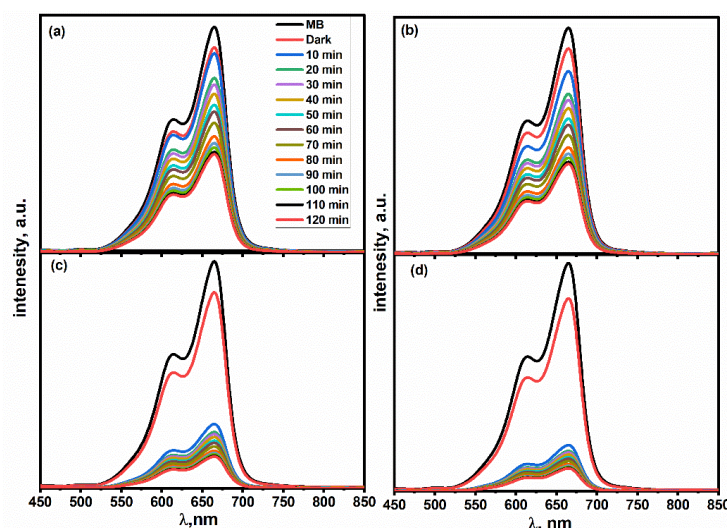


Figure 5. Photocatalytic degradation of (a) ZnO , (b) 0.025 Gd-doped ZnO , (c) 0.05 Gd-doped ZnO , and (d) 0.075 Gd-doped ZnO .

Among all, 0.075 Gd-doped ZnO catalyst exhibited the highest photocatalytic activity which degraded 89% of MB dye after being irradiated with UV light for 120 min, as

shown in Figure 6. However, pure ZnO degraded only 40% of MB dye within the same testing conditions. The increase in the photocatalytic activity of Gd-doped ZnO catalysts is associated with a defect band caused by introduced gadolinium ions, which serve as electron traps that can inhibit charge recombination [11]. To assess the photocatalytic efficiency of a catalyst, the kinetic rate constant turned out to be a useful parameter. In this study, a series of experiments for the degradation of methylene blue (MB) dye using pure ZnO and different Gd-doped ZnO photocatalysts (0, 0.025, 0.05, and 0.075 wt%) were investigated using the Langmuir–Hinshelwood kinetic model to calculate the kinetic rate constants. The kinetic rate constant for pure ZnO was determined to be 0.0065 min^{-1} and that for 0.025 Gd-doped ZnO was found to be 0.0068 min^{-1} . Nonetheless, the kinetic rate constant was found to rise with increasing Gd doping concentration, up to its maximum of 0.00723 min^{-1} using 0.075 Gd-doped ZnO, as demonstrated in Figure 7. As mentioned earlier, the increase in the kinetic rate constant with Gd doping may be explained by the better photocatalytic activity of Gd-doped ZnO. The Gd ions play the role of electron trap centers and the inhibition of electron–hole recombination leads to the formation of ROS. ROS are involved in the degradation of MB dye; the higher the concentration of ROS, the higher the rate of degradation. The kinetic rate constant of 0.075 Gd-doped ZnO-NPs is more than that of pure ZnO which shows that this catalyst has high efficiency in degrading the MB dye. The increase in the rate constant for kinetics also confirms that 0.075 Gd-doped ZnO possesses superior photocatalytic activity due to the inserted Gd ions, as demonstrated in Table 1.

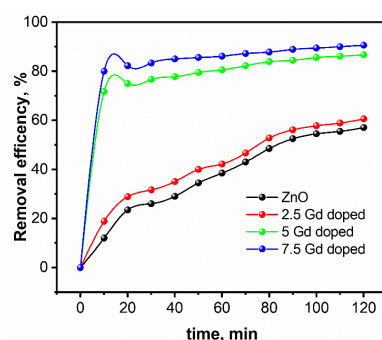


Figure 6. Removal efficiency of ZnO, 0.025 Gd-doped ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO.

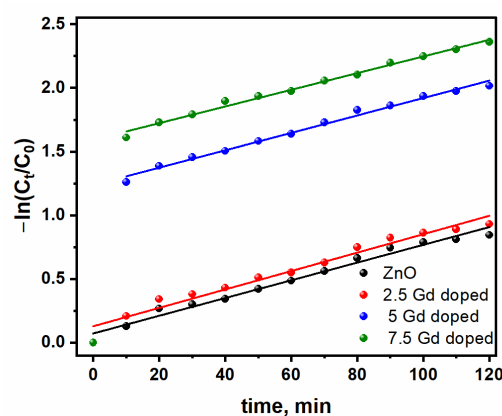


Figure 7. $-\ln C_t/C_0$ vs. time of ZnO, 0.025 Gd-doped ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO.

Impedance spectroscopy is a potent means for investigating the electrical characteristics of materials, such as semiconductors and photocatalysts. In this work, the impedance of pure ZnO, as well as 0, 0.025, 0.05, and 0.075 Gd-doped ZnO nanoparticles, was recorded at room temperature as a function of frequency. The impedance spectra were fitted with

the equivalent circuit model, and the charge transfer resistance (R_{ct}) was obtained. Pure ZnO has a higher impedance, which suggests a lower charge transfer rate along with high electron–hole pair recombination. On the other hand, it was observed that with an increased concentration of Gd doping, higher impedance values are obtained, which indicates an increase in the rate of charge transfer and a decrease in the probability of recombination between electron–hole pairs. The highest resistance against charge transfer between electrode and material is referred to as charge transfer resistance (R_{ct}). The impedance spectra were analyzed using the equivalent circuit model to extract R_{ct} values of pure ZnO, as well as 0, 0.025, 0.05, and 0.075 Gd-doped ZnO nanoparticles, as shown in Figure 8. The high R_{ct} value of pristine ZnO reflects a low charge transfer rate, together with the large recombination process of electron–hole pairs. In contrast, the R_{ct} value decreases remarkably with rising Gd doping levels, which can be attributed to faster charge transfer and lower electron–hole pair recombination, as exhibited in Figure 8.

Table 1. Rate constant values of ZnO, 0.025 Gd-doped ZnO, 0.05 Gd-doped ZnO, and 0.075 Gd-doped ZnO.

Samples	Rate Constant	R^2
ZnO	0.00654	98
2.5% Gd-doped ZnO	0.00683	96
5% Gd-doped ZnO	0.00696	99
7.5% Gd-doped ZnO	0.00723	99

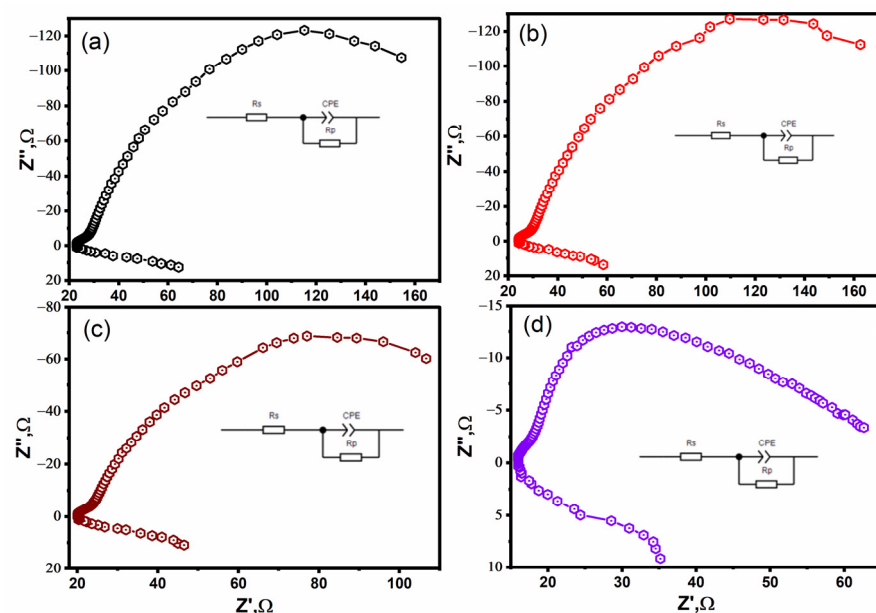


Figure 8. EIS of (a) ZnO (in set equivalent circuit), (b) 0.025 Gd-doped ZnO (in set equivalent circuit), (c) 0.05 Gd-doped ZnO (in set equivalent circuit), and (d) 0.075 Gd-doped ZnO (in set equivalent circuit).

Cole–Cole analysis, which is missing in previous studies but was carried out in this study, shows that the R_{ct} value decreases during the spectral analysis of the impedance semicircle and increases in the Gd doping concentration, therefore reducing the rate of recombination of electron–hole pairs and improving charge transfer. It can be inferred from these results that the electrical properties of ZnO nanoparticles can be improved through Gd doping to enhance its photocatalytic activity. Mott–Schottky analysis is a comparative technique largely employed in the investigations of electric semiconductor materials, including zinc oxide and its nanoparticles, as shown in Figure 9.

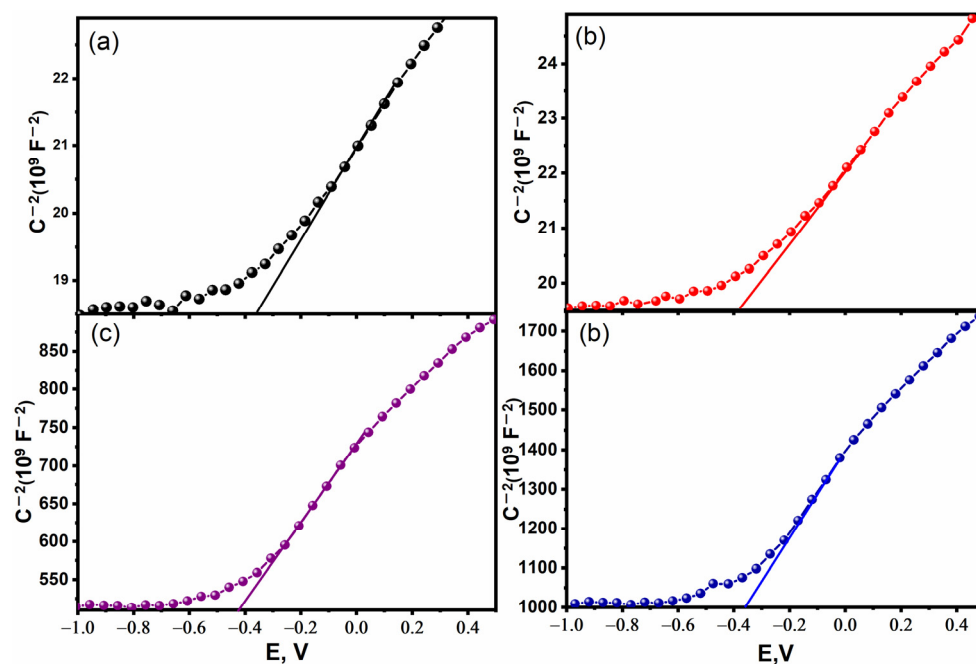


Figure 9. Mott-Schottky plot of (a) ZnO, (b) 0.025 Gd-doped ZnO, (c) 0.05 Gd-doped ZnO, and (d) 0.075 Gd-doped ZnO.

The Mott–Schottky analysis of pure ZnO and 0.025, 0.05, and 0.075 Gd-doped ZnO nanoparticles was carried out in order to find their flat-band potential (V_{fb}) and donor density (N_d) values. The Mott–Schottky plot is a graphical representation of the capacitance of the space charge region as a function of the applied voltage. In this work, Mott–Schottky plots were obtained by applying an oscillating voltage to the sample and measuring the capacitance at a frequency of 500 Hz. The Mott–Schottky plot depicts the variations of N_d while the intercept with the plot’s vertical axis depicts the N_{fb} . The Mott–Schottky plots obtained for 0, 0.025, 0.05, and 0.075 Gd-doped ZnO show a positive slope, indicating the expansion of p-type semiconductors. The values of the flat-band potential (V_{fb}) and density of donor ions (N_d) were calculated from the graphs of the Mott–Schottky plots. For pure ZnO, $V_{fb} = -0.31$ V/Ag/AgCl; however, V_{fb} drops as the Gd doping concentration increases.

The flat-band potential (V_{fb}) for undoped ZnO was determined to be -0.31 V versus Ag/AgCl; in contrast, the value of flat-band potential (V_{fb}) was found to increase with an increase in the concentration of Gd dopant. The flat-band potential (V_{fb}) values of 0.025 Gd/doped ZnO, 0.05 Gd/doped ZnO, and 0.075 Gd-doped samples were -0.33 , -0.37 , and -0.30 V, respectively. The increase in V_{fb} with an increase in Gd concentration can be attributed to the addition of Gd ions, which introduce a distorted structure in the lattice of ZnO and modify the electronic structure. The enhancement of donor density (N_d) with Gd concentration also supports the fact that Gd ions replace some ions in the lattice of ZnO, thus creating an electronic state within the band gap. This finding indicates that Gd dopants exhibit potential for improving the electrical conductivity of ZnO nanoparticles and their effectiveness as photocatalysts.

2.7. Photocatalyst Growth Mechanism

This proposed degradation mechanism for Gd co-doped ZnO is described in Figure 10 below. This is true when light with a wavelength equal to or greater than the bandgap energy of ZnO interacts with the material when electrons and holes are created. By doping the Gd, the generated electrons are effectively annihilated, hence reducing the recombination rate. These trapped electrons are then able to react with oxygen, forming superoxide radicals. At the same time, hydroxyl ions interact with holes forming hydroxyl radicals.

The generated $\text{OH}\bullet$ and $\text{O}_2\bullet^-$ radicals that are formed play a role in breaking the dye molecules. Gd co-doped ZnO exhibits a higher degradation rate compared to pure ZnO due to two primary factors: decreased recombination rate and the enhanced generation of $\text{OH}\bullet$ and $\text{O}_2\bullet^-$ radicals.

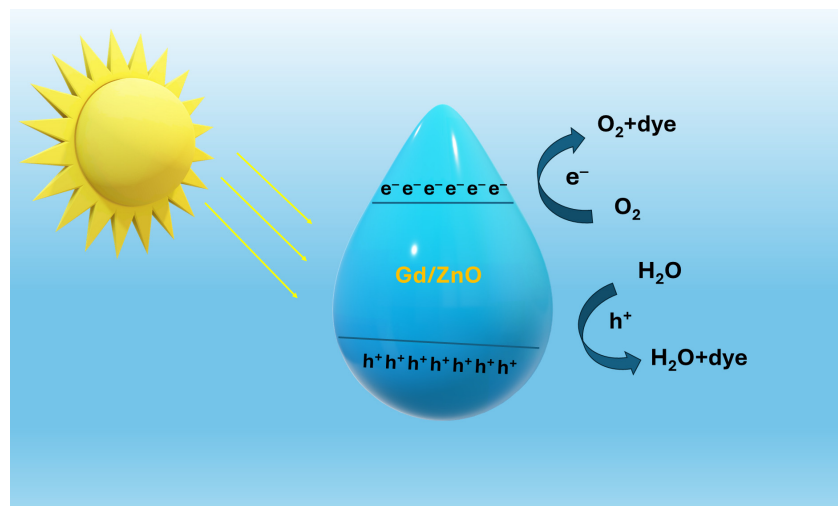


Figure 10. Photocatalytic reaction mechanism.

To assess the stability of the synthesized photocatalysts, a recycling experiment was conducted under UV-vis light irradiation, and the results are presented in Figure 11. Five consecutive cycles of MB dye degradation were performed using Gd/ZnO nanoparticles. After each cycle, the photocatalyst was recovered through ultracentrifugation, washed with acetone and deionized water, and dried at 60 °C for 1 h. To compensate for the approximately 17% weight loss during the recycling process, a small amount of fresh photocatalyst was added to the recovered sample for each subsequent cycle. The recycling experiment demonstrates the high stability of Gd/ZnO nanoparticles, making them a promising candidate for organic pollutant degradation.

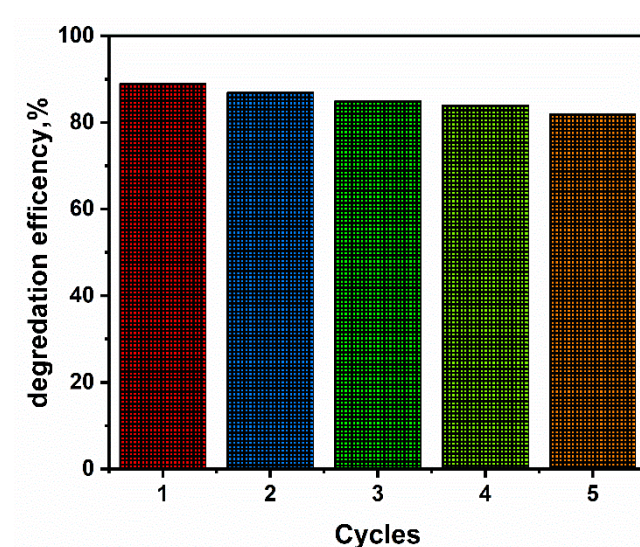


Figure 11. Recycle test of 0.075 Gd-doped ZnO.

3. Experimental Work

3.1. $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ Synthesis

All the required chemicals for our research study were identified by Loba Company, including zinc nitrate, citric acetate, samarium oxide, and isopropanol. As part of our

research study, $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$, and 0.075) nanoparticles were synthesized using the sol–gel combustion method. In this typical procedure, a precursor solution containing zinc nitrated, gadolinium oxide, and citric acid dissolved into isopropanol (50 mL) was prepared in a beaker. The citric acid solution was also stirred at room temperature until homogeneity without losing the stoichiometric ratios of citric acid to metal cation. The mixture was then heated on a magnetic stirrer up to approximately 80°C and stirred until it transformed into a gel. When heated further to the ignition point, the material burst into flames and resulted in large lightweight ash. The obtained material was heat-treated to a temperature of around 600°C and then milled to a very fine particle size. The gel combustion technique has benefits over other methods because of its easiness and cheapness, in addition to high rates of yield. Moreover, this approach aligns well with the principles of the circular economy, emphasizing effectiveness and sustainability.

3.2. Characterization

Phase- and micro-characterization studies of $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ ($x = 0, 0.025, 0.05$, and 0.075) nanoparticles were conducted using XRD, FTIR, and SEM analyses. FTIR analysis was carried out using a BRUKER Tensor 37 FTIR spectrophotometer, with a scan at wave number intervals of 4 m^{-1} to 40 m^{-1} . Electron microscopy was performed on the Jeol JFC 1100 E at a scale of 20,000 times and an accelerating voltage of 25 KV. The XRD patterns were obtained with the LAN Scientific diffractometer equipped with a monochromatized $\text{Cu-K}\alpha$ radiation source operating at 30 kV and 16 mA. The optical parameters of the synthesized $\text{Zn}_{1-x}\text{Gd}_x\text{O}$ were analyzed using a UV–visible spectrophotometer (JASCO, V 570) in the range of 200 to 1000 nm. The impedance and Mott–Schottky tests were studied using workstation Cortest Cs305. The photocatalysis experiment was conducted with a xenon lamp of 500 watts, with 25 mg of photocatalyst materials.

4. Conclusions

$\text{Zn}_{1-x}\text{Gd}_x\text{O}$ (0, 0.025, 0.05, and 0.075) was synthesized via the sol–gel combustion route. The XRD proved that all materials have the same structural phase (hexagonal phase) and do not appear as a new additional phase from other impurities. UV-vis spectrum analysis indicates that the intensity of the absorption cut-off peak diminishes with higher concentrations of Gd, indicative of reduced crystallinity. Pure ZnO exhibits an absorption wavelength at around $\sim 394\text{ nm}$, corresponding to a band gap of 3.15 eV. In comparison, 0.025, 0.05, and 0.075 Gd-doped ZnO display a redshift, with cut-off wavelengths around 400 and 403 nm and energy gaps of 3.1 eV and 3.07 eV, correspondingly. The decrease in the band gap of Gd-doped ZnO is ascribed to the formation of narrow (medium) energy levels involving the ZnO band gap energy levels. Using SEM images, the as-prepared pure ZnO ($x = 0$) consists of hexagonal platelets or rods that have smooth surfaces and almost similar sizes. The platelets or rods are generally of the order of several microns in length and a few hundred nanometers in breadth; they adhere remarkably closely together and are arranged randomly. A high percentage of Gd added into the ZnO lattice brings about a change in the morphology and microstructure of the material. Among them all, the 0.075 Gd-doped ZnO catalyst exhibits the highest photocatalytic activity, which degrades 89% of MB dye after being irradiated with UV light for 120 min. However, pure ZnO degrades only 40% of MB dye within the same testing conditions. It was observed that with increased concentrations of Gd doping, higher impedance values are obtained, which indicates an increase in the rate of charge transfer and a decrease in the probability of recombination between electron–hole pairs.

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