Interfacial Charge Transfer and Effective Termination of Electron Recombination Process in \((\text{ZnO})_{(1-x)/2}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x)/2}\)
Heterostructured Nanocomposite Material under Visible Light Irradiation

Saranya Ramachandran and Sivasamy Arumugam*®

Chemical Engineering Area, CSIR-Central Leather Research Institute, Adyar, Chennai 600 020, India

ABSTRACT: We have synthesized a novel heterostructured composite material-\((\text{ZnO})_{(1-x)/2}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x)/2}\)
wherein electron–hole recombination has been successfully inhibited by an interfacial charge-transfer mechanism across a semiconductor interface. As a result of this, the material possessed enhanced photoresponse under visible light irradiations. X-ray diffraction analysis shows the material to be highly nanocrystalline in nature. The band gap energy as calculated from the UV–vis–diffused reflectance spectroscopy was found to be 2.68 eV. Morphological studies by high-resolution scanning electron microscopy and high-resolution transmission electron microscopy analyses show the presence of distinct microrod-shaped \(\alpha\text{Bi}_2\text{O}_3\) and spherical ball-like clusters of ZnO and \(\text{Dy}_2\text{O}_3\) nanoparticles. X-ray photoelectron spectroscopy and energy-dispersive X-ray analyses confirm the presence of Bi, Zn, Dy, and O in the material. Atomic force microscopy (AFM) analysis revealed the high surface roughness and porosity of the prepared composite. Electron paramagnetic resonance analysis confirmed the in situ generation of \(\text{OH}^\cdot\) radicals under visible light irradiation. The photocatalytic efficiency of the \((\text{ZnO})_{(1-x)/2}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x)/2}\) composite material was evaluated by the photooxidation of Orange G (OG) dye molecules under visible light irradiation. The catalyst retained its original efficiency even after the 3rd cycle of its reuse thereby validating the economic feasibility of the system. By-product analysis by ESI-MS+ analysis proved the complete degradation of the OG molecules from the aqueous solution.

1. INTRODUCTION

Nanocrystalline semiconductor photocatalysts, such as TiO_2, ZnO, Bi_2O_3, CeO_2, ZrO_2, WO_3, \(\alpha\text{-Fe}_2\text{O}_3\), SnO_2, and so forth, have been gaining increasing attention because of their ability to use light energy to drive a variety of chemical oxidation reactions. These photocatalysts work on the principle of advanced oxidation process (AOP), wherein highly reactive \(\text{OH}^\cdot\) radicals are generated in situ when semiconductor photocatalysts are irradiated with light of a suitable wavelength. The wavelength of light employed depends on the band gap energy of the photocatalyst. The mechanism of AOP relies on the photoexcitation of the valence band electrons to the conduction band leaving behind positively charged holes in the valence band. These holes in the valence band react with water molecules adsorbed onto the catalyst surface, forming the \(\text{OH}^\cdot\) radicals. The \(\text{OH}^\cdot\) radicals are very strong oxidizing agents and are capable of oxidizing and completely mineralizing a wide range of toxic and recalcitrant organic compounds into carbon dioxide and water. However, one of the major limitations of using pristine semiconductor photocatalysts is the rapid recombination of the electron–hole pairs thereby hindering the generation of the \(\text{OH}^\cdot\) radicals. Thus, it is of utmost importance to increase the lifetime of the charge carriers to increase the efficiency of the photocatalyst.

Because of their similar band gap energies, ZnO has been employed as an efficient alternative photocatalyst to the more commonly used TiO_2. In addition to ZnO, Bi_2O_3 has also been receiving a lot of interest, as its band gap energy lies in the visible range. However, the photocatalytic efficiencies of the individual metal oxides are low because of the fast recombination of the photogenerated electron–hole pairs. The lifetime of the charge carriers can be increased by combining the pristine semiconductor metal oxides with other semiconductor metal oxides or rare earth oxides to form composite materials. In recent years, the development of ZnO/Bi_2O_3 composite materials has gained a lot of interest in the area of photocatalysis. Balachandran and Swaminathan synthesized heterostructured Bi_2O_3/ZnO by a hydrothermal
The synthesized ZnO/Bi2O3 composites showed higher photocatalytic activity than individual Bi2O3 or ZnO. Because of the similarities in their potentials, a heterojunction interface is formed when Bi2O3 and ZnO are combined. This allows the transfer of electrons from one particle to another, thereby improving the charge separation in the composite material. The photoresponse of the Bi2O3/ZnO composite has been further improved by combining it with noble metals such as Ag18 or with transition metal oxides such as NiO.19

In the present study, we have combined two semiconductor metal oxides (Bi2O3 and ZnO) with a rare earth oxide (Dy2O3) resulting in a hybrid heterostructured composite material of the following composition-(ZnO)(1−x)/2(Bi2O3)x,(Dy2O3)(1−x)/2 (ZBD). The material was found to possess enhanced photocatalytic activity in the UV and visible regions of the spectrum. Rare earth oxides such as Dy2O3 with their large band gap energies (4.2 eV) are insulating materials.20 They have been used as dopants or included in composite semiconductor photocatalysts, as they can increase charge separation by trapping the photoexcited conduction band electrons and preventing them from recombining with the valence band holes.13,20–22 Thus, in the synthesized composite material, the charge separation achieved by combining two semiconductor metal oxides will be further enhanced by the introduction of the rare earth oxide. The photocatalytic activity of the nanocomposite was evaluated by the degradation of a model pollutant-Orange G (OG) under visible light irradiation. OG is a monoazo dye used commonly as part of staining formulations in histology. It is also widely employed as a dyeing agent in the textile industry to dye wool and silk, and in paper, leather, and ink industries. However, OG has been reported to be a toxic pollutant20 which is an eye irritant and a potential mutagen and carcinogen. The molecular structure and chemical properties of the OG dye are given in Table S1 (Supporting Information).

2. MECHANISM FOR PHOTORESPONSE UNDER VISIBLE LIGHT IRRADIATION

The enhanced photocatalytic activity of the prepared ZBD composite can be explained by the following mechanism. The energy levels at the interface of the ZnO and Bi2O3 in the photocatalyst have been reported to be similar to that of the Bi2O3/BaTiO3 system. When irradiated with light, electrons from the valance band of ZnO and Bi2O3 get excited to their respective conduction bands. No such excitation occurs in Dy2O3 owing to its insulating properties. The photoexcited conduction band electrons of ZnO undergo vectorial transfer to the conduction band of Bi2O3. 14,23 From the conduction band of Bi2O3, the electrons are trapped by the empty conduction band orbitals in Dy2O3.21 The photogenerated holes in the valance band of Bi2O3 migrate to ZnO, resulting in charge separation in the catalytic system. This interfacial charge transfer at the semiconductor interface24 results in an accumulation of holes which react with water molecules to produce OH radicals. These radicals are responsible for the complete degradation of organic pollutants adsorbed on the surface of the catalyst. The electrons trapped in the vacant f orbitals of Dy2O3 react with dissolved molecular oxygen in the reaction solution and undergoes photoreduction resulting in the formation of superoxide radical anions. However, electron paramagnetic resonance (EPR) analysis (section 3.6) after irradiating the prepared photocatalyst with visible light detects only the formation of OH radicals. This indicates the in situ-generated OH radicals to be the significant radical species involved in the photocatalytic oxidation of organic molecules by the ZBD nanocomposite material. The mechanism for the effective interfacial charge separation that occurs in the prepared composite material is shown in Figure 1. Thus, the prepared ZBD composite material exhibits enhanced photocatalytic activity when compared with the pristine metal oxides.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Studies. X-ray diffraction (XRD) studies were carried out to study the crystalline nature of the prepared material, and the obtained pattern is shown in Figure 2a. The two most prominent peaks at 27.5° and 33° correspond to the (120) phase of monoclinic α bismuth oxide crystal lattice (JCPDS card no. 6-294) and (220) phase of the tetragonal β bismuth oxide crystal lattice (JCPDS card no. 27-50), respectively. The sharpness of the peaks indicates the high nanocrystallinity of the material. In addition to this, the smaller peaks at 35° can be related to the (031) plane of α bismuth oxide.25,26 The peak at 46.3° corresponds to the (102) phase of the hexagonal wurtzite structure of the ZnO crystal lattice (JCPDS 36-1451).27 The series of low intensity peaks between 50° and 60° can be attributed to various lattice planes of Bi2O3 and Dy2O3 (JCPDS 01-079-1722).28 The absence of any other strong diffraction peaks of ZnO and Dy2O3 is due to their lower concentration in the material. The average crystallite size was calculated using the Debye Scherrer equation as given below

\[ d = \frac{0.944}{\beta \cos \theta} \]  

where \( \lambda \) denotes the wavelength of radiation equal to 0.154 nm, \( \beta \) is the full width at half maximum, and \( \theta \) is the half diffraction angle. The average crystallite size was calculated to be 38.56 nm. This confirms the nanocrystalline nature of the material.

3.2. Fourier Transform Infrared Spectroscopy. The analysis of the functional groups present on the surface of the
material was carried out by Fourier transform infrared (FT-IR) spectroscopy. The spectrum was scanned in the range between 400 and 4000 cm$^{-1}$, and the graph is shown in Figure 2b. The broad peak at around 3500 cm$^{-1}$ is as a result of adsorbed water molecules on the surface of the catalyst. A close look at the region between 400 and 600 cm$^{-1}$ shows the presence of three peaks at 425, 472.8, and 526.10 cm$^{-1}$. These correspond to the metal–oxygen stretching vibrations in ZnO, Dy$_2$O$_3$, and Bi$_2$O$_3$ respectively. The peaks between 1350 and 1500 cm$^{-1}$ are a result of the symmetric stretching in C$\equiv$O and C–O$\equiv$C groups. This could be due to the presence of CO$_2$ molecules that are adsorbed on the surface of the photocatalyst. The FT-IR spectrum of the photocatalyst post photodegradation is given below the original spectrum. Comparison between the two spectra shows them both to be very similar. The peaks corresponding to the metal–oxygen stretching remain unaltered, confirming that the prepared catalyst does not undergo any changes during the course of the photodegradation reaction. The absence of any additional peaks in the post degradation spectrum reiterates that the dye molecules have been completely photodegraded by the photocatalyst and do not remain adsorbed onto its surface at the end of the reaction.

3.3. UV–Vis–Diffused Reflectance Spectroscopy. The band gap energy and optical properties of the ZBD photocatalytic materials were studied by the UV–vis–diffused reflectance spectroscopy (DRS) technique. The absorption spectrum of ZBD2 is depicted in Figure 2c, whereas the spectra of the composites prepared in three different ratios (ZBD1, ZBD3, and ZBD4) are shown in Figure S1 (Supporting Information). Figure 2c indicates the ZBD2 composite to show strong absorption in the region between 200 and 400 nm, indicating it to be highly active in the UV region. In addition to this, significant absorption is also seen in the visible region. This suggests the prepared ZBD semiconductor material to be a promising visible active photocatalyst in addition to its UV light activity. The peaks between 800 and 1400 nm are attributed to the transitions in the f orbitals of the rare earth metal dysprosium present in the material. The band gap energy was calculated by plotting $(\alpha h \nu)^2$ versus $h \nu$ and extrapolating the graph. The plot is shown in Figure 2d and the obtained values for the pristine metal oxides and the ZBD material in different mole ratios are shown in Table 1. From the values, it is evident that the $(\text{ZnO})_{(1-x)/2}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x)/2}$ material has the lowest band gap energy amongst all ratios and when compared with the pristine metal oxides. This accounts for the photocatalytic activity of the material under both UV and visible light irradiation.

3.4. X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) analysis is carried out to find out the oxidation states of the various elements and to confirm their presence in the prepared ZBD2 material. The full survey spectrum shown in Figure 3a confirms the presence of Zn, Bi, Dy, and O. The C 1s peak at 284.4 eV is attributed to the adventitious carbon from the XPS instrument. The peak at 530 eV is due to the O 1s state present in the metal oxides (Figure 3b). The peaks at 1021.08 and 1044.4 eV are attributed

![Figure 2. (a) XRD pattern, (b) FT-IR spectrum before and after photodegradation, (c) UV–vis–DRS, and (d) band gap energy calculation of the prepared $(\text{ZnO})_{(1-x)/2}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x)/2}$ material.](image-url)

### Table 1. Band Gap Energies of the Composite Materials in Different Molar Ratios

| material                  | band gap energy $E_g$ (eV) |
|---------------------------|----------------------------|
| Bi$_2$O$_3$               | 2.7                        |
| ZnO                       | 3.22                       |
| Dy$_2$O$_3$               | 4.2                        |
| $(\text{ZnO})_{(1-x/2)}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x/2)}$ ZBD1 | 2.7                        |
| $(\text{ZnO})_{(1-x/2)}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x/2)}$ ZBD2 | 2.68                       |
| $(\text{ZnO})_{(1-x/2)}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x/2)}$ ZBD3 | 2.75                       |
| $(\text{ZnO})_{(1-x/2)}(\text{Bi}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_{(1-x/2)}$ ZBD4 | 2.9                        |
to the Zn 2p\textsubscript{3/2} and Zn 2p\textsubscript{1/2} states (Figure 3c). This also confirms that Zn is present in the 2\textsuperscript{+} state in the nanomaterials.\textsuperscript{32} The peaks at 158 and 163.2 eV are due to the Bi 4f\textsubscript{7/2} and Bi 4f\textsubscript{5/2} states, respectively (Figure 3d).\textsuperscript{33} The peak at 1295 eV is attributed to the Dy 3d\textsubscript{5/2} state (Figure 3e).\textsuperscript{34}

3.5. High-Resolution Scanning Electron Microscopy.

The surface morphology of the prepared ZBD2 material was investigated by high-resolution scanning electron microscopy (HRSEM) analysis. The HRSEM image is shown in Figure 4a. The image reveals the presence of distinct microrod-shaped αBi\textsubscript{2}O\textsubscript{3}. Ball-like clusters are formed by the spherical nanoparticles of ZnO and Dy\textsubscript{2}O\textsubscript{3}. The individual spherical particles are around 40 nm in diameter. The image shows both the rods and spheres to be unagglomerated. The presence of micropores between the balls would result in an increase in the surface area of the material. This would ensure increased contact between the surface of the catalyst and the dye molecules, resulting in enhanced photocatalytic activity of the prepared semiconductor nanomaterial. Energy-dispersive X-ray analysis (EDAX) further confirms the presence of Zn, Bi, Dy, and O in the material (Figure 4b). The individual field emission SEM (FESEM) images of neat Bi\textsubscript{2}O\textsubscript{3}, ZnO, and Dy\textsubscript{2}O\textsubscript{3}, also prepared by precipitation method, are given in Figure S2 (Supporting Information). These images reveal the microrod structure of Bi\textsubscript{2}O\textsubscript{3} and the spherical nanoparticles of ZnO and Dy\textsubscript{2}O\textsubscript{3}.

3.6. High-Resolution Transmission Electron Microscopy.

High-resolution transmission electron microscopy (HRTEM) analysis was used to further confirm the shape and arrangement of the individual particles. The HRTEM images are shown in Figure 4c,d. In this case also microrods of αBi\textsubscript{2}O\textsubscript{3} are seen to be distributed amongst the spherical ZnO and Dy\textsubscript{2}O\textsubscript{3} particles. The HRTEM analysis also confirms the unagglomerated nature of the individual particles. The SAED pattern shown in the inset of Figure 4d reveals the highly crystalline nature of the material.

3.7. Atomic Force Microscopy.

The surface roughness and porosity of the material was investigated by atomic force microscopy (AFM) analysis. A 5 \( \mu \)m \( \times \) 5 \( \mu \)m surface of the sample was analyzed and the 2D and 3D images are shown in Figure 5a.b. The AFM image illustrates the highly rough nature of the material. The average roughness factor of the catalysts’ surface was found to be 40.97 nm. The vertical cross section of the ZBD material (Figure 5c) shows the presence of numerous
peaks and troughs once again indicating the uneven nature of the surface. This would be an important factor that accounts for the enhanced photocatalytic efficiency of the material.

3.8. EPR Spectroscopic Studies. EPR studies were carried out to confirm the in situ generation of OH\(^+\) radicals in the reaction solution when the ZBD catalyst is irradiated with visible light. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) is a spin trapping agent and is used to trap the generated OH\(^+\) radicals so that they may be detected and analyzed. On analysis of the reaction solution after 20 min of visible light irradiation, a quartet with the intensity ratio of 1:2:2:1 is obtained. The corresponding spectrum is shown in Figure 5c. The peaks in the quartet appear at a spacing of 14 units which is characteristic of the DMPO-trapped OH\(^+\) radical. The EPR analysis thus substantiates the formation of OH\(^+\) radicals which are responsible for the degradation of the OG dye molecules under visible light irradiation.

3.9. Determination of Surface Area of the Prepared Photocatalysts. The surface area of the prepared photocatalysts was measured by Brunauer–Emmett–Teller (BET)
isotherm analysis. The N$_2$ adsorption and desorption isotherms of ZBD1, ZBD2, ZBD3, and ZBD4 are shown in Figure 6(i), (ii), (iii), and (iv), respectively. From the BET isotherm, their surface areas were measured to be 8.18, 46.78, 11.03, and 9.32 m$^2$/g. Thus, of the four prepared ratios, ZBD2 (5:2:2) is observed to possess the highest surface area. Its pore radius and pore volume were 10.9 nm and 0.1363 cm$^3$/g, respectively. The highest surface area of this particular ratio would ensure greater extent of adsorption dye molecules on the catalyst surface, thereby resulting in an enhanced photocatalytic activity of the material. This agrees well with the high photocatalytic activity of ZBD2 compared with the other ratios prepared.
superior surface properties of the ZBD2 photocatalyst is clearly observed from Table S2 (Supporting Information).

3.10. Photocatalytic Studies. The photocatalytic activity of the prepared composite materials in different ratios and the neat metal oxides was tested for the degradation of a model organic pollutant-OG, under visible light irradiation. The results for the degradation of 10 mg/L dye solutions with 1 g/L catalyst loading for all materials is shown in Figure 7a. From the results, it is clear that neat Dy2O3, ZnO, and Bi2O3 show only 13, 50, and 65% dye degradation, respectively. Among the four different ratios of the ZBD material, ZBD2 exhibited maximum dye degradation of more than 90%. The improved photocatalytic efficiency of the ZBD2 is due to the better charge separation that is achieved in the composite material. These results are also in agreement with the ultraviolet diffuse reflectance spectrometer (UV-vis-DRS) analysis wherein ZBD2 was found to possess the lowest band gap energy (2.68 eV) among all of the ratios. This would ensure the superior photoresponse of the material in the UV and visible regions of the spectrum. Thus, all further photocatalytic experiments were carried out with the ZBD2 material as a photocatalyst. In the absence of a photocatalyst, 12% dye removal was observed. This is attributed to the photolysis of the OG dye molecules by the irradiated visible light.

Comparison in the photocatalytic efficiency was made with ZnO/Dy2O3 and ZnO/Bi2O3 nanocomposites and with standard Degussa P25. Test reactions for the degradation of OG dye under visible light irradiation were carried out and the results are shown in Figure S3 (Supporting Information). In all cases, 10 mg/L OG solutions were degraded with 1 g/L catalyst loading. It is evident that after 6 h of visible light irradiation, Degussa P25 resulted only in 62.7% OG degradation. The ZnO/Dy2O3 and ZnO/Bi2O3 nanocomposites exhibited slightly higher degradation efficiencies resulting in 72.4 and 78.8% OG degradation, respectively. The ZBD2 material exhibited the highest photocatalytic efficiency wherein 95% dye degradation was achieved. Thus, comparison shows that the prepared ZBD2 composite material possesses maximum photocatalytic efficiency.

3.11. Preliminary Reactions. Preliminary reactions on the effect of aqueous pH, catalyst loading, and initial dye concentration were studied to optimize the various experimental parameters.

3.11.1. Effect of Aqueous pH. Aqueous pH is an important parameter in the treatment of industrial wastewater. Thus, it is essential to study the photocatalytic efficiency of the prepared ZBD2 material across the entire range of pH under visible light irradiation. The pH of the OG solutions was varied between 2 and 12 with the help of 0.1 N HCl and 0.1 N NaOH solutions. A catalyst loading of 1.5 g/L and initial dye concentration of 10 mg/L were employed for the photodegradation reactions, and the obtained results are shown in Figure 7b. It is evident that after 6 h of visible light irradiation, more than 90% degradation is achieved at all values of pH with maximum degradation occurring between pH 7 and 8. The marginal decrease in the photocatalytic efficiency of the material in the acidic and basic ranges could be due to the presence of excess H+ and OH− ions in the solution. These ions would get adsorbed onto the surface of the catalyst and hinder the organic moieties from reaching the catalyst surface. Also, under extreme acidic conditions, the excess H+ ions could act as radical scavengers thereby reducing the number of hydroxyl radicals available for dye oxidation. Thus, for the sake of cost and convenience, neutral pH was chosen for all further photocatalytic reactions. This is further supported by the zero-point charge of the catalyst which was found to be 7.54 (inset of Figure 7b).

3.11.2. Effect of Catalyst Dosage. The effect of catalyst dosage was studied to determine the optimum amount of catalyst required for efficient dye degradation under visible light irradiation. The catalyst dosage was varied from 0.5 to 2.5 g/L while the solution pH and initial dye concentration were fixed at 7 and 10 mg/L. The results obtained at the end of an irradiation time of 6 h are shown in Figure 7c. From the figure, it is observed that an initial increase in the catalyst loading from 0.5 to 1.5 g/L leads to an increase in the extent of degradation. This is because of the increase in total active surface area which would increase the amount of light absorbed thereby increasing the availability of active sites on the catalyst surface. A dosage of 1.5 g/L results in 95.15% OG degradation. Beyond this, however, an increase in catalyst loading results only in a marginal increase in % dye degradation. Beyond the optimum dosage, the dispersed catalyst particles in the reaction solution would block the light rays and result in increased light scattering. Thus, 1.5 g/L was fixed as the ideal catalyst dosage for the photocatalytic dye degradation reactions.

3.11.3. Effect of Initial OG Concentration. The effect of initial dye concentration on the photocatalytic efficiency of the ZBD material was studied and the results are shown in Figure 7d. In this case, the solution pH (neutral) and catalyst dosage (1.5 g/L) were kept constant while the initial OG concentration was varied from 5 to 50 mg/L. The obtained results show that as the initial dye concentrations increased from 5 to 50 mg/L, the % degradation decreased from more than 95% to around 55% after 6 h of visible light irradiation. This decrease could be because of decreased light penetration in the solutions of high dye concentrations. This would decrease the number of photons reaching the catalyst surface which would in turn lower the production of hydroxyl radicals. The photodegradation efficiency is directly related to the formation of hydroxyl radical which is a critical species in the degradation process.

3.12. Kinetic Studies. The kinetics of photocatalytic degradation of OG was studied with different initial dye concentrations (5, 10, 15, 20, and 25 mg/L) using the prepared ZBD material as a photocatalyst. The previously optimized catalyst dosage of 1.5 g/L was employed. In each case, the progress of the reaction was monitored by withdrawing aliquots of the reaction solution at regular intervals of time and measuring the absorbance of the solutions. The plot of percentage degradation versus time is shown in Figure S4a (Supporting Information). From the figure, it is clear that as the initial dye concentration increases, the time taken for completion of the reaction also increases. OG solution (5 mg/L) undergoes 97.84% degradation at the end of 120 min of visible light irradiation, whereas 25 mg/L OG solution undergoes 95.8% degradation at the end of 660 min of visible light irradiation. In all the cases, more than 95% dye degradation is achieved. The completion of the reactions is also confirmed by the reduction in the chemical oxygen demand (COD) of the reaction solutions during the course of the reaction. The corresponding results are shown in Figure S4b (Supporting Information). The COD value of the 5 mg/L OG solution decreases from 480 to 32 mg/L, whereas 50 mg/L decreases from 832 to 96 mg/L under visible light irradiation. Thus, 93% COD removal is achieved for the 5 mg/L OG solution and 88% for the 25 mg/L OG solution. The COD
levels of the solution decrease to less than around 100 mg/L in all cases which confirms the efficient degradation of the OG dye molecules under visible light irradiation in the presence of the prepared ZBD material as a photocatalyst.

The obtained kinetic data were fitted to the pseudo-first-order rate equation as given below

\[ \ln(C_o/C_e) = kt \]  

where \( C_o \) and \( C_e \) are the initial and final dye concentrations at time \( t \) and \( k \) is the pseudo-first-order rate constant. From the experimental data, a graph of \( \ln(C_o/C_e) \) versus time was plotted as shown in Figure 8a. The rate constants for each of the initial dye concentrations were determined, and the obtained values are shown in Table S3 (Supporting Information). From the table it is clear that as the initial dye concentration increases from 5 to 25 mg/L, the rate constant decreased from \( 4.23 \times 10^{-2} \) to \( 0.55 \times 10^{-2} \) min\(^{-1} \). In all cases, the \( R^2 \) values are close to unity proves the goodness of the fit. This clearly shows that the photocatalytic dye degradation reactions follow pseudo-first-order kinetics.

3.13. Effect of Electrolytes. Apart from organic pollutants, industrial effluents also contained electrolytes such as NaCl, KCl, Na\(_2\)CO\(_3\), MgSO\(_4\), and so forth. Thus, it is important to study the effect of these electrolytes on the photocatalytic efficiency of the prepared ZBD2 material. The previously standardized pH and catalyst dosage were maintained. Dye solutions (10 mg/L) were photocatalytically degraded in the presence of varying amounts (0−7%) of the electrolyte solutions. The results (Figure 8b) show that the presence of the electrolytes retards the dye degradation. This could be because the anions in solution scavenge the OH radicals that are produced on visible light irradiation.\(^{37}\) As a result of this, the extent of dye degradation is lowered.

3.14. UV−Visible Absorbance Spectrum. Figure 9a shows the full UV-visible absorbance spectrum of the OG solutions at different stages of its photocatalytic degradation under visible light irradiation using the ZBD2 material as a photocatalyst. The spectrum of the dye solution at the commencement of the reaction shows absorption maximum at 483.5 nm. The chromophoric azo group in the dye molecule is responsible for this absorption. As the reaction proceeds, a decrease in the intensity of this absorption maximum is observed. This is due to the cleavage of the azo bond during the course of the photocatalytic dye degradation which is also responsible for the decrease in color intensity of the solution. At the end of the reaction, the peak at 483.5 nm has completely disappeared which shows the complete breakdown of the azo group. This eliminates any possibility of unreacted dye molecules in the solution at the end of the irradiation time.

3.15. Reusability. Keeping in mind the cost of the raw materials and their environmental effect, recycling of the photocatalyst must be considered to make the whole photocatalytic system more practical. In this regard, the photocatalytic efficiency of the used ZBD2 material was tested for the degradation of OG solutions under visible light irradiation for up to three cycles. At the end of each cycle the catalyst was filtered, washed, and reused. The obtained results are shown in Figure 9b. In each cycle, the progress of the reaction was monitored by measuring the absorbance of the reaction solutions withdrawn at regular intervals of time. The percentage of degradation at the end of the three cycles was
This illustrates that the ZBD catalyst retains its original efficiency even after the 3rd cycle of reuse.

3.16. ESI-MS+ Analysis. The possible intermediates that are formed during the photocatalytic degradation of OG under visible light irradiation using ZBD2 as a photocatalyst have been identified using the ESI-MS+ analysis. The ESI-MS+ spectrum of the neat and photocatalytically degraded OG dye solution is shown in Figure S5 (Supporting Information). The absence of the peak corresponding to the OG molecular ion at m/z 453 indicates that the OG dye molecules have been completely degraded from the aqueous solution. During the degradation process, intermediates of lower molecular weight (m/z-301.19, 236.2, 167.14, 101.06, 79.08, and 71.04) are formed. On the basis of the obtained m/z values, a plausible mechanism for the photocatalytic degradation has been proposed and is shown in Scheme 1.

The reaction proceeds by the random attack of OH+ radicals that are generated in the reaction solution on the OG dye molecules. The proposed pathway suggests the initial cleavage of the chromophoric group, resulting in the formation of substituted aromatic compounds. This cleavage is responsible for the decrease in the color intensity of the solution during the course of the reaction. Further reaction results in the opening of the aromatic ring to form conjugated branched alcohols. The obtained linear molecules finally undergo mineralization to give carbon dioxide and water. These results prove the effective photocatalytic degradation of the OG dye molecules.

4. CONCLUSION

The heterostructured composite material-(ZnO)x(Bi2O3)1−x(Dy2O3)x was prepared by a simple precipitation method. Effective charge separation was achieved at the semiconductor interface followed by trapping of the electrons in the vacant f orbitals of the rare earth oxide. The inhibition of the electron−hole recombination process rendered the material highly photoresponsive under visible light irradiation. The crystalline nature of the material was studied by XRD analysis. The band gap energy as calculated from the UV-vis-DRS spectrum 2.68 eV. Morphological studies by HRSEM and HRTEM analyses show the presence of distinct microrod-shaped αBi2O3 and spherical nanoparticles of ZnO and Dy2O3 that form ball-like clusters. The SAED pattern also confirms the crystallinity of the material. XPS and EDAX shows the high purity of the material and the presence of Bi, Zn, Dy, and O in the material. AFM analysis revealed the high surface roughness and porosity of the prepared composite. EPR
spectroscopy was employed to confirm the in situ generation of OH· radicals in the reaction solution. The prepared composite material was found to possess enhanced photocatalytic activity for the degradation of OG under visible light irradiation. Preliminary studies were carried out to optimize the solution pH, catalyst dosage, and initial dye concentration. The catalyst exhibited good activity across all values of pH. All further reactions were carried out at neutral pH for the sake of cost and convenience. An optimum catalyst dosage of 1.5 g/L was set for a dye solution of 10 mg/L concentration. Kinetic studies were carried out with various initial dye concentrations. The obtained data fitted well with the pseudo-first-order kinetic model. A decrease in the catalytic efficiency was detected in the presence of commonly occurring industrial electrolytes. The catalyst was observed to retain its original efficiency even after the 3rd cycle of its reuse thereby validating the economic feasibility of the system. The by-product analysis, carried out using ESI-MS⁺ analysis proved the complete degradation of the OG molecules from the aqueous solution.

5. MATERIALS AND METHOD

5.1. Chemicals Required. Zinc nitrate hexahydrate (Zn(NO3)2·6H2O, 99%), bismuth nitrate pentahydrate (Bi(NO3)3·5H2O, 99%), and dysprosium nitrate hexahydrate (Dy(NO3)3·6H2O 99%) were purchased from Sigma-Aldrich, India. O G (C36H10N4Na2O2S2), sodium chloride (NaCl, 99.5%) were acquired from S D Fine-Chemicals Ltd., Mumbai, India. Potassium chloride (KCl, 99%) and sodium carbonate (Na2CO3, 99.9%) were procured from Merck, India Ltd. Magnesium sulphate (MgSO4·7H2O, 99.5%), potassium dichromate (K2Cr2O7, 99.9%), and ferrous ammonium sulphate ((NH4)2SO4·FeSO4·6H2O, 99%) were obtained from Qualigens Fine Chemicals, India. Concentrated sulphuric acid AR (H2SO4, 98%) and sodium hydroxide (NaOH) were received from HiMedia Laboratories Private Ltd. Concentrated nitric acid (HNO3) was obtained in SRL Chemicals.

5.2. Synthesis of ZBD Composite Material. The ZBD composite material in different ratios was synthesized by the simple precipitation method wherein the nitrate salts were employed as the metal oxide precursors. A typical procedure is as follows. Zn(NO3)2·6H2O (0.59 g) and 1.39 g of Dy(NO3)3·6H2O were dissolved separately in 20 mL of double-distilled water. Bi(NO3)3·5H2O (4.85 g) was dissolved in 50 mL of dilute nitric acid. Here, the ZnO, Bi2O3, and Dy2O3 precursors have been taken in 2:5:2 molar ratios. An aqueous solution of NaOH was employed as the precipitating agent. The NaOH solution was added drop wise to the Bi(NO3)3·5H2O solution with vigorous stirring until a white precipitate was formed, and a pH value greater than 10 was reached. To this continuously stirred solution, either of the other two metal nitrate solutions and aqueous sodium hydroxide were added alternately in a similar manner, resulting in a solution of pH ≈ 12. Stirring was continued for 2 more hours, when the white precipitate turned pale yellow. The solution was then filtered and washed thoroughly with distilled water multiple times, followed by a final wash with ethanol. The obtained solid was then dried overnight at 80 °C and sintered in a muffle furnace at 550 °C for 2 h. The sintered powder was ground, stored in an airtight container and labeled as ZBD2.

The above procedure was carried out taking the three nitrate precursors in different ratios. Composites with the following overall compositions were obtained: (ZnO) (1−x)/(Bi2O3) x(Dy2O3) (1−x)/(Z n O) (1−x)/(Bi2O3) x(Dy2O3) y/(Z n O) (1−x)/(Bi2O3) y(Dy2O3) (1−x)/2 and (ZnO) (1−x)/(Bi2O3) y(Dy2O3) y/(Z n O) (1−x)/(Bi2O3) y(Dy2O3) (1−x)/2. Each of these composites was synthesized by a similar procedure described above. The composites were labeled as ZBD1-1:1, ZBD2-2:5:2, ZBD3-5:2:2, and ZBD4-2:2:5 respectively, where the value of x = 0.56. Among these, ZBD2 exhibited maximum photocatalytic activity. The percentages of ZnO, Bi2O3, and Dy2O3 in the ZBD2 photocatalyst are 22, 56, and 22%, respectively.

5.3. Characterization Techniques. The crystalline phases and crystallite size of the synthesized photocatalytic material were identified by the X-ray powder diffraction technique (PANalytical X-ray diffractometer, Germany) with Cu Kα radiation (λ = 1.5418 Å). The 2θ scan range was between 10° and 70° with an accelerating voltage of 40 kV and an emission current of 25 mA. Infrared transmission spectrum of the sample was obtained using a FT-IR spectrometer (PerkinElmer). The optical properties of the powder samples were studied using an UV–DRS (Shimadzu UV-2600, Japan) with a scan speed of 200 nm/s using BaSO4 as standard. The morphologies of the ZBD nanostructures were characterized by FESEM and HRTEM (JEOL 3010). Photocatalytic activity of the synthesized catalyst was studied for the photodegradation of OG using an annular slurry type visible photoreactor (Heber Scientific, Chennai, India) with a 500 W tungsten filament lamp. The absorbance of the degraded solution was measured using a UV–visible spectrophotometer and its COD was determined using a COD digester (Thermo Reactor HACH DRB 200).

5.4. Photocatalytic Reactions. In a typical photocatalytic experiment 1.5 g/L of the photocatalyst was used to treat OG solutions of different concentrations in the slurry visible photoreactor. A calibration graph of the absorbance values of standard OG solutions was plotted. On completion of the reaction, the absorbance of the degraded solution was measured and compared with the calibration graph to determine the extent of dye degradation. Percentage degradation was calculated using the following relationship

\[
\% \text{ degradation} = \frac{C_0 - C_x}{C_0} \times 100
\]

where \( C_0 \) is the initial dye concentration and \( C_x \) is the dye concentration at the end of the reaction. The progress of the reaction was monitored by measuring the absorbance of the reaction solutions at the absorbance maximum of OG and by determining the reduction in COD of the solution.

**ASSOCIATED CONTENT**

5. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00549.

Molecular structure and chemical properties of OG dye; UV–visible absorption spectrum of (a) ZBD1, (b) ZBD3, and (c) ZBD4 nanocomposite materials; surface characteristics of the ZBD photocatalysts prepared in different ratios; FESEM images of neat (a) Bi2O3, (b) ZnO, and (c) Dy2O3; comparison of photocatalytic efficiencies; (a) kinetics and (b) reduction in COD for the degradation of OG under visible light irradiation; rate constant and coefficient of determination (R²) values for different initial dye concentrations; and ESI-MS⁺ spectrum for the OG dye photocatalytically degraded under visible light irradiation (PDF)
CORRESPONDING AUTHOR
E-mail: arumugamsivasamy@yahoo.co.in
Fax: +91-044-24911589, +91-044-24437401

ORCID

Sivasamy Arumugam: 0000-0003-2926-8791

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors would like to thank CSIR, New Delhi, for providing fellowship under the CSIR JRF scheme and INDUS MAGIC 12 FYP for providing research facilities to carry out this research work.

REFERENCES

1. Devillers, D. Semiconductor Photocatalysis: Still an Active Research Area Despite Barriers to Commercialization. European 2006, 17, 1–6.
2. Pearson, A.; Jani, H.; Kalantar-zadeh, K.; Bhargava, S. K.; Bansal, V. Gold Nanoparticle Decorated Keggin Ions/TiO2 Photocatalyst for Improved Solar Light Photocatalysis. Langmuir 2011, 27, 6661–6667.
3. Zhang, Z.; Shao, C.; Li, X.; Zhang, L.; Xue, H.; Wang, C.; Liu, Y. Electrospun nanofibers of ZnO–SnO2 heterojunction with high photocatalytic activity. J. Phys. Chem. C 2010, 114, 7920–7925.
4. Uddin, M. T.; Nicolas, Y.; Olivier, C.; Toupane, T.; Servant, L.; Muller, M. M.; Kleebe, H.-J.; Ziegler, J.; Jaegermann, W. Nanostructured SnO2–ZnO heterojunction photocatalysts showing enhanced photocatalytic activity for the degradation of organic dyes. Inorg. Chem. 2012, 51, 7764–7773.
5. Bi, D.; Xu, Y. Improved Photocatalytic Activity of WO3, through Clustered Fe2O3 for Organic Degradation in the Presence of H2O2. J. Environ. Sci. 2013, 25, 280–287.
6. Indrakanti, V. P.; Kubicki, J. D.; Schobert, H. H. Photoinduced activation of CO2 on Ti-based heterogeneous catalysts: current state, chemical physics-based insights and outlook. Energy Environ. Sci. 2009, 2, 745–748.
7. Li, D.; Haneda, H. Morphologies of zinc oxide particles and their effects on photocatalysis. Chemosphere 2003, 51, 129–137.
8. Yao, Y.; Li, G.; Ciston, S.; Lueptow, R. M.; Gray, K. A. Photoreactive TiO2 Carbon Nanotube composites: synthesis and reactivity. Environ. Sci. Technol. 2008, 42, 4952–4957.
9. Ma, H.; Cheng, X.; Ma, C.; Dong, X.; Zhang, X.; Xue, M.; Zhang, X.; Fu, Y. Synthesis, Characterization, and Photocatalytic Activity of N-Doped ZnO/ZnS Composites. Int. J. Photoenergy 2013, 2013, 625024.
10. Jiang, D.; Zhang, S.; Zhao, H. Photocatalytic degradation characteristics of different organic compounds at TiO2 nanoporous film electrodes with mixed anatase/rutile phases. J. Environ. Sci. Technol. 2007, 41, 303–308.
11. Kuo, H.-L.; Kuo, C.-Y.; Liu, C.-H.; Chao, J.-H.; Lin, C.-H. A highly active bi-crystalline photocatalyst consisting of TiO2 (B) nanotube and anatase particle for producing H2 gas from neat ethanol. Catal. Lett. 2007, 113, 7–12.
12. Yang, D.; Liu, H.; Zheng, Z.; Yuan, Y.; Zhao, J.-c.; Wacławek, E. R.; Ke, X.; Zhu, H. An efficient photocatalyst structure: TiO2(B) nanofibers with a shell of anatase nanocrystals. J. Am. Chem. Soc. 2009, 131, 17885–17893.
13. Reddy, J. K.; Srinivas, B.; Kumari, V. D.; Subrahmanyan, M. Sm2O3–Doped Bi2O3 photocatalyst prepared by hydrothermal synthesis. ChemCatChem 2009, 1, 492–496.
14. Balachandran, S.; Swaminathan, M. Facile fabrication of Bi2O3–ZnO photocatalyst and its enhanced photocatalytic activity. J. Phys. Chem. C 2012, 116, 26306–26312.
15. Park, S.; Jun, J.; Kim, H. W.; Lee, C. Preparation of one dimensional Bi2O3-core/ZnO-shell structures by thermal evaporation and atomic layer deposition. Solid State Commun. 2009, 149, 315–318.
16. Li, C.; Zhang, J.; Yang, J.; Wang, T.; Lv, X.; Tang, Z. Methods to improve the photocatalytic activity of immobilized ZnO/Bi2O3 composite. Appl. Catal., A 2011, 402, 80–86.
17. Mohanedi, M.; Hosseini, A.; Nazempour, N.; Rahimi, M.; Salavati, H. Synthesis of ZnO/Bi2O3 and SnO2/Bi2O3/BiO mixed oxides and their photocatalytic activity. Iran. Chem. Commun. 2015, 3, 374–387.
18. Balachandran, S.; Prakash, N.; Swaminathan, M. Heterostructured Ag–Bi2O3–ZnO as a bifunctional nanomaterial. RSC Adv. 2016, 6, 20247–20257.
19. Trusova, E. A.; Vokhmitcev, K. V. Obtaining of ZnO nanoparticles decorated with Bi2O3 and NiO by modified sol-gel technique. J. Am. Ceram. Soc. 2014, 97, 135–140.
20. Josephine, G. A. S.; Sivasamy, A. Nanocrystalline ZnO doped on lanthanide oxide Dy2O3: a novel and UV light active photocatalyst for environmental remediation. Environ. Sci. Technol. Lett. 2014, 1, 172–178.
21. Li, J. Z.; Zhong, J. B.; Zeng, J. F.; Feng, F. M.; He, J. J. Improved photocatalytic activity of dysprosium-doped Bi2O3 prepared by sol–gel method. Mater. Sci. Semicond. Process. 2013, 16, 379–384.
22. Korake, P. V.; Kadam, A. N.; Garadkar, K. M. Photocatalytic activity of Eu2+/doped ZnO nanorods synthesized via microwave assisted technique. J. Rare Earths 2014, 32, 306–313.
23. Lin, X.; Xing, J.; Wang, W.; Shan, Z.; Xu, F.; Huang, F. Photocatalytic activities of heterojunction semiconductors Bi2O3/ BaTiO3: a strategy for the design of efficient combined photocatalysts. J. Phys. Chem. C 2007, 111, 18288–18293.
24. Osako, K.; Matsuzaki, K.; Hosono, H.; Yin, G.; Atrash, D.; Sakai, E.; Susaki, T.; Miyachi, M. Examination of interfacial charge transfer in photocatalysis using patterned CuO thin film deposited on TiO2. Appl. Mater. 2015, 3, 104409–104414.
25. Jha, R. K.; Pasricha, R.; Ravi, V. Synthesis of bismuth oxide nanoparticles using bismuth nitrate and urea. Ceram. Int. 2005, 31, 495–497.
26. Hou, J.; Yang, C.; Wang, Z.; Zhou, W.; jiao, S.; Zhu, H. In situ synthesis of α-β phase heterojunction on Bi2O3 nanowires with exceptional visible-light photocatalytic performance. Appl. Catal., B 2013, 142, 504–511.
27. Zheng, M.; Wang, Z.-S.; Wu, J.-Q.; Wang, Q. Synthesis of nitrogen-doped ZnO nanocrystals with one-dimensional structure and their catalytic activity for ammonium perchlorate decomposition. J. Nanopart. Res. 2010, 12, 2211–2219.
28. Karthikeyan, B.; Suchand Sandeep, C. S.; Pandiyarajan, T.; Venkatesan, P.; Philip, R. Spectrally broadened excitonic absorption and enhanced optical nonlinearities in Dy3+/doped ZnO nanoparticles. Appl. Phys. A: Mater. Sci. Process. 2011, 102, 115–120.
29. Khan, S. H.; Suriyaprabha, R.; Pathak, B.; Fulekar, M. H. Photocatalytic degradation of organophosphate pesticides (Chlorpyriphos) using synthesized zinc oxide nanoparticle by membrane filtration reactor under UV irradiation. Front. Nanosci. Nanotechnol. 2015, 1, 23–27.
30. Trivedi, M. K.; Tallapragada, R. M.; Branton, A.; Trivedi, D.; Nayak, G.; Satiyal, O.; Jana, S. Evaluation of Atomic, Physical, and Thermal Properties of Bismuth Oxide Powder: An Impact of Biofield Effects on photocatalysis. Am. J. Nano Res. Appl. 2015, 3, 94–98.
31. Zhang, Y.; Zhang, K. L.; Jia, M. K.; Tang, H.; Sun, J. T.; Yuan, L. J. Synthesis, Characterization of a novel compound SnEr2O4. Chin. Chem. Lett. 2002, 13, 587–589.
32. Bhirud, A. P.; Sathe, D. D.; Waichal, R. P.; Nikam, L. K.; Kale, B. B. An eco-friendly, highly stable and efficient nanostructured p-type N-doped ZnO photocatalyst for environmentally benign solar hydrogen production. Green Chem. 2012, 14, 2790–2798.
33. Xu, J.-J.; Chen, M.-D.; Fu, D.-g. Preparation of bismuth oxide/titania composite particles and their photocatalytic activity to degradation of 4-chlorophenol. Trans. Nonferrous Met. Soc. China 2011, 21, 340–345.
34. Barreca, D.; Gasparotto, A.; Milanov, A.; Tondello, E.; Devi, A.; Fischer, R. A. Nanostructured Dy2O3 films: An XPS investigation. Surf. Sci. Spectra 2007, 14, 52–59.
(35) Wang, X.; Wu, P.; Huang, Z.; Zhu, N.; Wu, J.; Li, P.; Dang, Z. Solar photocatalytic degradation of methylene blue by mixed metal oxide catalysts derived from ZnAlTi layered double hydroxides. *Appl. Clay Sci.* 2014, 95, 95–103.

(36) Sakthivel, S.; Neppolian, B.; Shankar, M. V.; Arabindoo, B.; Palanichamy, M.; Murugesan, V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO$_2$. *Sol. Energy Mater. Sol. Cells* 2003, 77, 65–82.

(37) Yang, Y.; Wu, Q.; Guo, Y.; Hu, C.; Wang, E. Efficient degradation of dye pollutants on nanoporous polyoxotungstate–anatase composite under visible-light irradiation. *J. Mol. Catal. A: Chem.* 2005, 225, 203–212.