Facile Fabrication of a ZnO/Eu₂O₃/NiO-Based Ternary Heterostructure Nanophotocatalyst and Its Application for the Degradation of Methylene Blue

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ABSTRACT: The ZnO-based ternary heterostructure ZnO/Eu₂O₃/NiO nanoparticles are synthesized using waste curd as fuel by a simple one-pot combustion method. The as-synthesized heterostructure is characterized by using various spectroscopic and microscopic techniques including X-ray diffraction, UV-vis, FTIR, SEM, and TEM analyses. The photocatalytic activity of the ternary nanocomposite was tested for the photodegradation of methylene blue (MB) under solar light irradiation. The results have revealed that the ternary ZnO/Eu₂O₃/NiO photocatalyst exhibits excellent performance toward the photocatalytic degradation of the studied dye. Optimization studies revealed that the synthesized heterostructure exhibited a pH-dependent photocatalytic activity, and better results are obtained for specific concentrations of dye and catalysts. Among the different light sources employed during the study, the catalyst was found to possess the best degradation efficiency in visible light.

1. INTRODUCTION

Semiconductor-based photocatalytic degradation of hazardous dyes has attracted significant attention of researchers as a potential tool to solve the rapidly evolving problem of environmental pollution. Particularly, hazardous organic dyes used in textile industry are considered as dangerous environmental pollutants due to their strong persistent color and their ability to absorb dissolved oxygen from water bodies. These types of synthetic dyes seriously disturb the normal penetration of sunlight in rivers, which has significant effect on the aquatic organisms due to reduced photosynthetic activities. Besides, due to the strong stability, organic pollutants usually survive for longer time in the environment, which possibly makes them xenobiotic. Therefore, untreated textile effluent is potentially hazardous to both terrestrial and aquatic life by adversely affecting the natural ecosystem and causing long-term health effects. Hence, a variety of physicochemical and biological processes have been applied for the degradation of organic dyes, and additionally, various other methods have also been increasingly explored. Still, cost-effective removal of these dyes from effluents remains a major problem.

Recently, advanced oxidation processes have drawn considerable attention of researchers for the degradation of dyes from effluents. These processes are cost-effective, environmentally friendly, and possess strong ability to degrade a variety of complex dyes from wastewater. Typically, advanced oxidation processes are performed by irradiation using solar or ultraviolet light in the presence of photocatalysts. Further, in many cases, ultrasonication and H₂O₂ are also used to enhance the rate of degradation or adsorption of dyes on photocatalysts. Among various catalysts, semiconductor materials, such as Fe₂O₃, CdS, V₂O₅, ZnO, TiO₂, and so forth, have been prominently used as photocatalysts for the degradation of organic dyes. Particularly, ZnO-based photocatalysts have drawn considerable attention due to their extensive usage in the field of environmental remediation.

Zinc oxide (ZnO) offers excellent benefits including high chemical stability, excellent biocompatibility, unique electronic structure, and lower cost. However, the large band gap and fast recombination of photoinduced charge carriers have mainly inhibited the practical applications of ZnO. Therefore, to enhance the charge separation and to extend the response of ZnO toward the visible light, it is commonly modified by structural doping with both metallic and nonmetallic elements and also by the formation of heterojunctions with a second semiconductor component. Especially, the formation of a heterojunction offers promising opportunities to enhance the separation efficiency of photoinduced charge carriers. So far,
a variety of ZnO-based binary and ternary heterojunctions have been fabricated, such as 2D ZnO/ZnS binary heterostructures, ternary ZnO/Cu2O/Si nanowire arrays, ternary ZnO−ZnS−Gd2S3 nanostructural arrays, and so on.24−28

Therefore, for the purpose of photocatalytic degradation of organic dyes, rationally designed ZnO-based ternary heterojunctions offer great potential by facilitating the migration of electrons due to the presence of multicomponent photosystems.29 These systems effectively extend the lifetime of photogenerated charge carriers and enhance the scope of light absorption.23 Due to this, there is continued urge for the controlled fabrication of ternary heterojunctions. Typically, these types of systems are prepared by various physical and chemical methods including sol−gel, chemical vapor deposition, microwave heating, coprecipitation, and hydrothermal and solvothermal methods.30 Often, these techniques need high-tech instruments, long reaction times, and higher temperature; therefore, development of other facile methods is highly required. Contrarily, solution combustion is a facile technique, which is low cost, time and energy efficient, and easy to perform and scale up.31 In addition, eco-friendly starting materials can also be effectively applied in this technique.32 These benefits persuaded us to explore the synthesis of ZnO-based ternary heterojunctions using another photoactive metal oxide and lanthanide element.

Our group has been working toward the synthesis of various nanomaterials and its applications toward catalysis and removal of pollutants.33−35 In continuation of these efforts, we herein demonstrate the preparation of ZnO-based ternary ZnO/Eu2O3/NiO heterostructure nanoparticles (NPs) via a single-step combustion method. The as-prepared heterostructure NPs have been tested as a photocatalyst for the degradation of methylene blue (MB) under sunlight (cf. Scheme 1). The results indicate that the as-prepared ternary system demonstrated an improved photocatalytic activity. This work offers new insights into designing a multicomponent ZnO-based photocatalyst toward environmental remediation.

2. RESULTS AND DISCUSSION

2.1. UV−Vis Spectrum. Figure 1 a shows the UV−vis absorption spectrum of the as-prepared ZnO/Eu2O3/NiO NPs scanned in the absorption range from 800 to 200 nm. The as-prepared ZnO/Eu2O3/NiO NPs absorption spectrum yields two absorption bands, one in the UV region at ∼242 nm, which can be ascribed to the transitions (LMCT) from O2−(2p) to Mn+ (3d),36,37 while another absorption edge is observed in the visible region at 350 to 370 nm, which can be assigned to 6A1 + 6A1 to 4T1 + 4T1 transition, termed as "double-excitation process."38−41 This suggests that the prepared sample is photolytically active in the UV region as well as in the visible region; moreover, it also indicates the
crystalline nature of the as-prepared oxides. Further, the band gap energy of NPs has been calculated from the UV−vis spectra (Figure 1b) using Tauc’s equation (eq 1) and is found to be 3.69 eV.36

\[(aν^2) = b(νE_g)^n\]  

(1)

where \(E_g\) is the band gap energy in eV, \(a\) is the absorbance value, \(ν\) is the frequency, \(b\) is Planck’s constant, \(h\) is a constant, and \(n\) is equal to 1/2 and 2 for a direct and indirect transition, respectively. A wide range of absorption of light helps in effective photocatalytic degradation and enhances the efficiency.

2.2. X-ray Diffraction. The prepared mixed metal oxides are subjected to X-ray diffraction (XRD), and the obtained diffractograms are shown in Figure 2. A comparative XRD of NiO, ZnO, and Eu2O3 is also included in this figure. The evaluation of the diffraction pattern obtained for ZnO/Eu2O3/NiO NPs provides evidence that the as-prepared heterostructures are crystalline in nature. The pattern obtained corresponds to the mixture comprising hexagonal and cubic structures of ZnO, NiO, and Eu2O3. NiO shows the powder diffraction pattern of NiO with cubic structures (JCPDS no: 2-1216) with a lattice parameter \(a = 4.172\ \text{Å}\) and with a space group \(Pm3m\) (no. 225). Cubic Eu2O3 NPs are shown with a heterostructure (JCPDS no 86-2476), a lattice parameter \(a = 10.859\ \text{Å}\), and a space group \(Ia3\) (no. 206). Moreover, Figure 2 also shows that diffraction pattern obtained for ZnO is similar to the reference XRD pattern of ZnO obtained from ICSD, which is hexagonal with the heterostructure (JCPDS no 1-1136) and lattice parameters \(a = 3.242\ \text{Å}\) and \(c = 5.176\ \text{Å}\), while the space group is \(P6_{3}mc\) (no. 186).

2.3. FTIR Spectrum. The FTIR spectrum of ZnO/Eu2O3/NiO NPs is displayed in Figure 3. The FTIR spectrum of a CuO NP shows broad absorption bands at 2800 and 4000 cm\(^{-1}\), mainly ascribed to OH− from the hydroxyl group, which is probably attributed to the adsorbed water on the surface of the nanocrystals and also to the C−O groups on the surface of the ZnO/Eu2O3/NiO NPs. A peak at 3614 cm\(^{-1}\) is characteristic to the formation of the \(\text{Eu}_2\text{O}_3\) phase. A peak at \(\sim1063\ \text{cm}^{-1}\) is due to C=O stretching of acetate. The characteristic peaks less than 1000 cm\(^{-1}\), that is, 567 and 621 cm\(^{-1}\), can be attributed to the \(\delta\text{O}\) and \(\delta\text{O}−\delta\text{M}\) stretching modes of vibrational frequencies of metals interlinked by common oxygen atoms, which are also observed in the FTIR spectrum of ZnO (Figure S2).

2.4. Microscopic Analysis. 2.4.1. SEM Analysis. The morphological features of the as-prepared heterostructure, that is, ZnO/Eu2O3/NiO, are obtained by field emission scanning electron microscopy (FESEM) analysis, and the achievement of the nanostructured heterostructure is confirmed by TEM analysis, and the results obtained are given in Figure 4. The low-magnification FESEM image shown in Figure 4a reveals that ZnO/Eu2O3/NiO is composed of clusters of particles as well as flakes. Figure 4b is the high-magnification FESEM image which shows that part of the material is in the form of flakes in which all the flakes are interconnected and form a net-like structure with large pores. Based on the previously reported literature, it can be assumed that the flake-like morphology could belong to the NiO component of the heterostructure, while the clusters could be the ZnO and Eu2O3 NPs in the heterostructure.

Elemental mappings of bulk ZnO/Eu2O3/NiO have been collected and displayed in Figure 5. It shows that the as-prepared heterostructure contains the desired elemental composition, and the elements are well dispersed throughout the composition, which can play a synergetic role in the enhancement of the catalytic performance. Moreover, the ED spectrum of ZnO/Eu2O3/NiO heterostructure is given in Figure S1, which designates that all the expected elements such as Zn, Mn, Eu, and O are present and the percentage of elemental compositions is displayed in the inset table, which is
in accordance with the stoichiometric amount taken for the preparation of ZnO/Eu₂O₃/NiO heterostructure NPs.

2.4.2. TEM Analysis. Figure 6 shows the TEM images of ZnO/Eu₂O₃/NiO. Figure 6a−c shows the low- and high-magnification images which demonstrate that the spherical particles are distributed all over the sample as well as some incidents of agglomerations can be observed. The sizes of the particles are in the range between 20 and 60 nm. The selected area electron diffraction pattern (Figure 6d) indicates the polycrystalline form of the material, and the reflection planes obtained are very much in alignment with the information deduced from the XRD pattern.

2.5. Photocatalytic Analysis. The theory of semiconductor photocatalysis says that the morphology, band gap, surface area, particle size, crystalline nature, and amount of hydroxyl ions on the surface of the photocatalyst determine its strength. The theory explains the formation of an electron and a hole on the surface of the semiconductor by the absorption of light, and the generated electrons and holes will take part in the reaction or they do recombine. If the external surface is provided for the charge carriers, they will relocate
where the electrons are caught by the semiconductor while the holes are trapped by hydroxyl radicals and form OH* and H\textsubscript{2}O\textsuperscript{*}. In the case of a ternary structure, more surface is available for relocation of charge carriers, and hence, the formed hydroxyl ions are utilized effectively to degrade MB.

As per the results obtained from UV–vis spectroscopy, it is evident that the heterostructure prepared is active in the UV–vis region as well as in the visible region. Moreover, the band gap calculated yielded $E_{g} = 3.79$ eV. In order to evaluate the photocatalytic performance of the heterostructure, that is, NiO/Eu\textsubscript{2}O\textsubscript{3}/ZnO, various experiments such as effect of light source, concentration of MB, load of catalyst, and pH are carried out and MB is taken as the standard pollutant for photocatalytic degradation in the study, and the variation of absorption peak intensity recorded at 663 nm ($\lambda_{max}$ of MB) is monitored to deduce the results obtained.

For the study, 100 cm\textsuperscript{3} of an aqueous solution of varying amounts of MB such as 5, 10, 15, and 20 ppm is taken for degradation experiments. The amount of as-prepared heterostructure is also varied, such as 5, 15, 30, and 45 mg of ZnO/Eu\textsubscript{2}O\textsubscript{3}/NiO. The solution is mixed with mixed metal oxide and aerated for 40 min while kept in the dark. The kinetics of the degradation is studied by periodically collecting 3 cm\textsuperscript{3} of the solution at intervals of 30 min, which is then subjected to centrifugation. From the absorbance spectra obtained by employing UV–vis spectroscopy, the initial ($C_i$) and final ($C_f$) dye concentrations in the system are confirmed and the % of degradation of the dye is determined by substituting the values obtained in eq 2.

$$\% \text{ of degradation} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

Moreover, when the photocatalytic activity of the as-prepared catalyst, that is, ZnO/Eu\textsubscript{2}O\textsubscript{3}/NiO, is compared with the individual components of the catalyst, that is, ZnO, Eu\textsubscript{2}O\textsubscript{3}, and NiO, it is observed that the degradation of MB obtained is 66, 40, and 72%, respectively, which is much lower than the 97% obtained from the use of the as-prepared catalyst, indicating the synergistic effect of all the three components of the catalyst on the degradation of MB. The graphical illustration of the degradation of MB using ZnO, Eu\textsubscript{2}O\textsubscript{3}, and NiO is given in Figure S2.

2.5.1. Effect of Light Source. Since the as-prepared heterostructure is photolytically active in both the UV region and in the visible region as confirmed from the UV–vis spectra, the first set of study is designed to confirm the light source that can yield the best performance of the as-prepared heterostructure. Hence, the photocatalytic degradation of MB employing ZnO/Eu\textsubscript{2}O\textsubscript{3}/NiO NPs is carried out in three different environments, that is, under sunlight, UV ray irradiation (wavelength 254 nm), and in the dark. From the results obtained, it is confirmed that the as-prepared mixed metal oxide is active under UV irradiation as well as in visible light, as realized by the UV–vis spectra obtained. However, in the case of the experiment carried out in the dark, the degradation of MB is found to be negligible. Moreover, when the degradation results obtained from the experiments carried out in sunlight and under UV ray irradiation are compared, the results revealed that degradation of MB is much more in sunlight than the degradation obtained in UV ray irradiation. In sunlight, the as-prepared mixed metal oxide NPs efficiently degrade 97% of MB, which is higher than the 72% degradation obtained under UV ray irradiation yielded in a reaction time of 150 min. Hence, it is confirmed that the photocatalyst ZnO/Eu\textsubscript{2}O\textsubscript{3}/NiO is most effective in sunlight, and all the further optimization experiments are carried out under sunlight. The degradation results obtained are illustrated in Figure 7.

![Figure 7. Variation of light source on the degradation of MB.](https://dx.doi.org/10.1021/acsomega.0c05170)

2.5.2. Effect of Amount of Catalyst. After the confirmation of the source of light for the efficient photocatalytic performance of the as-prepared heterostructure, the optimum amount of catalyst for the degradation of MB is evaluated by varying the catalyst in the range 5–40 mg under visible light. A 65% degradation of MB dye is observed when 5 mg of photocatalyst is used. The amount of catalyst is increased from 15 to 30 mg, and an increase in the degradation of MB from 82 to 97% is observed. However, when the amount of catalyst is increased further to 40 mg, then a decrease of degradation efficiency of the catalyst is observed and an 80% degradation of MB is obtained.

This reduction in the degradation of MB may be due to accumulation and sedimentation of the catalyst particles at higher concentrations, which in turn causes the increase in light scattering, which results in a decrease in the light path inside the solution; moreover, the higher concentration of the catalyst may also cause agglomeration of the photocatalyst, ensuing a decrease in the number of photocatalytic active sites. Hence, the optimum amount of photocatalyst for efficient degradation of MB is confirmed as 30 mg. The results obtained are graphically illustrated in Figure 8.

![Figure 8. Effect of catalyst amount for the efficient degradation of MB.](https://dx.doi.org/10.1021/acsomega.0c05170)
2.5.3. Effect of Concentration of MB. Further, the efficiency of the as-synthesized heterostructure, that is, ZnO/Eu2O3/NiO NPs, is evaluated for varying concentrations of MB in the range of 5–20 ppm under visible light with the amount of catalyst employed as 30 mg. From the results obtained, it is observed that the degradation of MB decreased from 96 to 65% when the concentration of MB is increased from 5 to 20 ppm. This may be attributed to the decreased absorption of light on the surface of photocatalyst with an increase in dye concentration, which leads to reduction in the generation of hydroxyl radicals, playing an important role in the degradation of MB present in the system. Therefore, it is essential to increase the suitable concentration of photocatalyst with increased dye concentration (Figure 9).

2.5.4. Effect of pH. It is well reported in the literature that the catalytic efficiency of a photocatalyst is directly related to the availability of hydroxyl radicals in the solution, which confirms that the rate of photocatalysis is usually more in alkaline solutions.

In order to understand the optimum pH for the efficient performance of the as-prepared mixed metal oxide, that is, ZnO/Eu2O3/NiO NPs, the pH of the MB solutions is varied from 6 to 10 pH. It is observed that when the reaction condition is pH 6, the degradation of MB obtained is 78%; however, when the pH is increased, then the degradation efficiency of the photocatalyst is highly improved and a 93 and 97% degradation of MB is obtained for pH 7 and pH 10, respectively. This can be attributed to the generation of higher rate hydroxyl radicals and due to the accumulation of hydroxyl radicals on the surface of the catalyst at higher pH (Figure 10).

2.5.5. Comparative Studies. A comparison of the photocatalytic activity of ZnO/Eu2O3/NiO for the degradation of MB with that of the previously reported ZnO-based photocatalytic systems is presented in Table 1. It is evident that the ternary ZnO/Eu2O3/NiO photocatalyst in the present study showed superior photocatalytic activity than several other catalysts reported in the literature.

2.6. Photocatalytic Mechanism. Based on the above experimental findings, a possible mechanism for the enhanced photocatalytic efficacy of ZnO/Eu2O3/NiO photocatalyst upon visible light irradiation is proposed and schematically illustrated in Scheme 2. Under visible irradiation, the ZnO/Eu2O3/NiO photocatalyst can be readily excited, and electron−hole pairs are generated on its surface. Moreover, due to the presence of Eu3+ in the photocatalyst, most probably sublevels beneath the conductive band are introduced and hence enhance the visible light response.66−68 Hence, the excited electrons and holes could be efficiently separated, overturning the potential of charge carrier reunion; consequently, •OH active radicals are generated from the electrons in the CB over a two-electron oxidation path,69,70 which directly decomposes the organic pollutant, MB dyes. As a result, the photoinduced •OH and h+ active radicals are responsible for the degradation, and the plausible mechanism is summed up as follows:

\[
\begin{align*}
\text{ZnO/Eu}_2\text{O}_3/\text{NiO} + h\nu (E > E_g) & \rightarrow \text{ZnO/Eu}_2\text{O}_3/\text{NiO} (c_{\text{CB}} + h^+_\text{CB}) \\
\text{ZnO/Eu}_2\text{O}_3/\text{NiO} (c_{\text{CB}}) + O_2 & \rightarrow O_4^- \\
\text{ZnO/Eu}_2\text{O}_3/\text{NiO} (c_{\text{CB}}) + O_2 + 2H^+ & \rightarrow H_2O_2 \\
H_2O_2 + O_4^- & \rightarrow •OH + OH^- + O_2 \\
•OH + MB & \rightarrow \text{Degraded products (major)} \\
O_2^- + MB & \rightarrow \text{Degraded products (minor)} \\
\text{ZnO/Eu}_2\text{O}_3/\text{NiO} (h^-_{\text{VB}}) + MB & \rightarrow \text{Degraded products}
\end{align*}
\]

3. EXPERIMENTAL METHODS

3.1. Synthesis of ZnO/Eu2O3/NiO. Stoichiometrically calculated amounts of zinc nitrate, nickel acetate, and europium nitrate, that is, 48.5 wt % Zn(NO3)2, 6H2O, 48.5 wt % Ni(CH3CO)2, and 3 wt % Eu(NO3)3·5H2O, are dissolved in 10 cm3 of distilled water and 6 cm3 perished curd is added to it under constant stirring for about 20 min. Subsequently, the thoroughly mixed mixture is kept in a muffle furnace at 400 °C. After 10 min, a blackish green powder is obtained, which is calcined at the same temperature for 3 h.

3.2. Characterization. The as-synthesized heterostructures are characterized by XRD, UV−vis, FTIR, FESEM, and TEM. The XRD characterization is carried out using a Bruker diffractometer [Cu Ka (λ = 1.5406 Å) X-ray source]. The
spectral characterization is carried out using a PerkinElmer UV−vis spectrometer and a Bruker IFS 66 v/S spectrometer for UV−vis and FTIR spectral analysis, respectively. The microscopic analysis such as SEM is carried out to understand the surface morphology, and particle size analysis is carried out by FESEM. TEM images are recorded with a transmission electron microscope, JEOL JEM2100 PLUS, operating at a 200 kV accelerating voltage.

4. CONCLUSIONS

In conclusion, we report the successful synthesis of ternary heterojunction ZnO/Eu₂O₃/NiO mixed metal oxides by a simple combustion route. The characterization of the as-prepared material revealed the crystalline nature and nanosize formation of ZnO/Eu₂O₃/NiO heterostructure. The as-prepared material is tested as a photocatalyst for the degradation of MB dye, a harmful industrial effluent. The photocatalyst displayed excellent degradation efficiency under visible light, and the kinetics of the catalyst revealed that up to 97% of degradation of MB can be obtained within 150 min under sunlight. Hence, further studies into the kinetics and fine-tuning of the economic and eco-friendly catalyst are in progress and shall be reported in future.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05670. ED spectrum of ZnO/Eu₂O₃/NiO with elements and their composition (PDF)

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**Notes**

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![Table 1. Comparison of Photocatalytic Activity of ZnO/Eu₂O₃/Mn₃O₄ for MB Degradation with Previously Reported Photocatalysts Containing ZnO NPs](https://pubs.acs.org/journal/acsodf)

| catalyst          | MB concentration | light source | catalyst amount | time (min) | degradation (%) | ref.   |
|-------------------|------------------|--------------|-----------------|------------|----------------|-------|
| ZnO/Eu₂O₃/NiO     | 5 ppm            | sunlight     | 30 mg           | 150        | 98             | herein |
| S−ZnO NPs        | 20 μM            | sunlight     | 30 mg           | 45         | 61.5           | 53    |
| N/La−ZnO         | 15 ppm           | sunlight     | 50 mg           | 60         | 97             | 54    |
| ZnO−SiO₂         | 9 ppm            | sunlight     | 10 mg           | 90         | 97.8           | 55    |
| ZnO NWs          | 10 ppm           | sunlight     | 100 mg/L        | 4320       | 100            | 56    |
| WO₃/ZnO@rGO      | 5 ppm            | vis. 200 W   | 10 mg           | 90         | 94.1           | 57    |
| Ag−ZnO/GO        | 15 ppm           | Xe 20 W × 5  | 20 mg           | 180        | 85             | 58    |
| TiO₂/ZnO/rGO     | 0.3 ppm          | Xe 300 W     | 0.1 g/L         | 120        | 92             | 59    |
| Mn−ZnO           | 10 ppm           | UV lamp      | 24 mg           | 60         | 60             | 60    |
| rGO−ZnO          | 5 × 10⁻⁴ mol/L   | vis. light   | 100 mg/L        | 120        | 90             | 61    |
| ZnO−CdO          | 3 × 10⁻⁵ mol/L   | Xe 250 W     | 360             | 97.8       | 62             |       |
| ZnO NPs          | 15 ppm           | Hg lamp 10 W | 100 mg          | 120        | 90             | 63    |
| Ag/ZnO           | 2 × 10⁻³ M       | Xe 100 W     | 100 mg          | 120        | 76             | 64    |
| ZnO/AC           | 2 × 10⁻⁵ M       | Hg lamp 30 W | 25 mg           | 45         | 92.2           | 65    |

**Scheme 2. Plausible Photocatalytic Reaction Mechanism for the Photodegradation of MB in the Presence of ZnO/Eu₂O₃/NiO NPs under Visible Light Irradiation**
REFERENCES

(1) Natarajan, S.; Bajaj, H. C.; Tayade, R. J. Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. J. Environ. Sci. 2018, 65, 201–222.
(2) Bharagava, R. N.; Chowdhary, P. Emerging and Eco-Friendly Approaches for Waste Management, 1 ed.; Springer: Singapore, 2019; p 435.
(3) Pereira, L.; Alves, M. Dyes—environmental impact and remediation. In Environmental Protection Strategies for Sustainable Development; Springer: Dordrecht, 2012; pp 111–162.
(4) Malik, A.; Grohmann, E.; Akhtar, R. Environmental Deterioration and Human Health; Springer: Dordrecht, 2014.
(5) Khan, S.; Malik, A. Environmental and health effects of textile industry wastewater. In Environmental Deterioration and Human Health; Springer: Dordrecht, 2014; pp 55–71.
(6) Rovira, J.; Domingo, J. L. Human health risks due to exposure to inorganic and organic chemicals from textiles: A review. Environ. Res. 2019, 168, 62–69.
(7) Paždior, K.; Bilinska, L.; Ledakowicz, S. A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment. Chem. Eng. J. 2019, 376, 120597.
(8) Chiu, Y.-H.; Chang, T.-F.; Chen, C.-Y.; Sone, M.; Hsu, Y.-J. Mechanistic insights into photodegradation of organic dyes using heterostructure photocatalysts. Catalysts 2019, 9, 430.
(9) Hannachi, Y.; Hallid, A. Preparation and characterization of novel bi-functionalized serogel for removal of methylene blue and lead ions from aqueous solution in batch and fixed-bed modes: RSM optimization, kinetic and equilibrium studies. J. Saudi Chem. Soc. 2020, 24, 505.
(10) Wu, L.; Zhang, X.; Anthony Thorpe, J.; Li, L.; Si, Y. Mussel-inspired polydopamine functionalized recyclable coconut shell derived carbon nanocomposites for efficient adsorption of methylene blue. J. Saudi Chem. Soc. 2020, 24, 642–649.
(11) Paiman, S. H.; Rahman, M. A.; Uchikoshi, T.; Abdullah, N.; Othman, M. H. D.; Jaafar, J.; Ábas, K. H.; Ismail, A. F. Functionalization effect of Fe-type MOF for methylene blue adsorption. J. Saudi Chem. Soc. 2020, 24, 896.
(12) Pandey, A.; Kalal, S.; Ameta, C.; Ameta, R.; Kumar, S.; Punjabi, P. B. Synthesis, characterization and application of naïve and nano-sized titanium dioxide as a photocatalyst for degradation of methylene blue. J. Saudi Chem. Soc. 2015, 19, 528–536.
(13) Lv, S.-W.; Liu, J.-M.; Wang, Z.-H.; Ma, H.; Li, C.-Y.; Zhao, N.; Wang, S. Recent advances on porous organic frameworks for the adsorptive removal of hazardous materials. J. Environ. Sci. 2019, 80, 169–185.
(14) Hassaan, M. A.; El Nemr, A.; Madkour, F. F. Testing the advanced oxidation processes on the degradation of Direct Blue 86 dye in wastewater. Egypt. J. Aquat. Res. 2017, 43, 11–19.
(15) Navarro, P.; Gabaldón, J. A.; Gómez-López, V. M. Degradation of an azo dye by a fast and innovative pulsed light/H2O2 advanced oxidation process. Dyes Pigments 2017, 136, 887–892.
(16) Di, T.; Xu, Q.; Ho, W.; Tang, H.; Xiang, Q.; Yu, J. Review on Metal Sulphide-based Z-scheme Photocatalysts. ChemCatChem 2019, 11, 1394–1411.
(17) Belver, C.; Bedía, J.; Gómez-Avilés, A.; Peñas-Garzón, M.; Rodríguez, J. J. Semiconductor Photocatalysis for water purification. Nanoscale Materials in Water Purification; Elsevier: Netherlands, 2019; pp 581–651.
(18) Mills, A.; Davies, R. H.; Worsley, D. Water purification by semiconductor photocatalysis. Chem. Soc. Rev. 1993, 22, 417–425.
(19) Lavand, A. B.; Malghé, Y. S. Visible light photocatalytic degradation of 2-chlorophenol using Cu/ZnO/Cds nanocomposite. J. Saudi Chem. Soc. 2015, 19, 471–478.
(20) Pirhasemi, M.; Habibi-Yangieh, A.; Rahim Pouran, S. Review on the criteria anticipated for the fabrication of highly efficient ZnO-based visible-light-driven photocatalysts. J. Ind. Eng. Chem. 2018, 62, 1–25.
(21) Wetchakun, K.; Wetchakun, N.; Sakulsermsuk, S. An overview of solar/visible light-driven heterogeneous photocatalysis for water purification: TiO2- and ZnO-based photocatalysts used in suspension photoreactors. J. Ind. Eng. Chem. 2019, 71, 19–49.
(22) Gu, X.; Li, C.; Yuan, S.; Ma, M.; Qiang, Y.; Zhu, J. ZnO based heterojunctions and their application in environmental photocatalysis. Nanotechnology 2016, 27, 402001.
(23) Kumar, S.; Kumar, A.; Kumar, A.; Krishnan, V. Nanoscale zinc oxide based heterojunctions as visible light active photocatalysts for hydrogen energy and environmental remediation. Cat. Rev. 2020, 62, 346–405.
(24) Yu, X.; Wei, P.; Li, Y. Enhanced sunlight photocatalytic performance of ZnO/ZnS binary heterostructure sheets. Mater. Lett. 2019, 240, 284–286.
(25) Wei, P.; Yu, X.; Li, Y. Preparation of Fe3O4/ZnO/ZnS Composites with Enhanced Photoproduction Under Solar Irradiation. J. Electron. Mater. 2019, 48, 4877–4885.
(26) Wei, P.; Li, Y.; Yu, X.; Huo, J. Enhanced photocatalytic property of Fe doped ZnO nanoparticles prepared by sol-gel. IOP Conference Series: Earth and Environmental Science; IOP Publishing, 2019; p 022131.
(27) Hsiao, P.-H.; Li, T.-C.; Chen, C.-Y. ZnO/Cu 2 O/Si Nanowire Arrays as Ternary Heterostructure-Based Photocatalysts with Enhanced Photodegradation Performances. Nanoscale Res. Lett. 2019, 14, 244.
(28) Ranjit, K. S.; Ranjit Kumar, D.; Ghoreishian, S. M.; Hu, Y. S.; Han, Y.-K.; Thangavelu, R. K. R. A rationally controlled ZnS interlayer on ultra-long ZnO–Gd2S3 core–shell nanorod arrays for promoting the visible photocatalytic degradation of antibiotics. Nanoscale 2020, 12, 14047.
(29) Wang, M.; Tan, G.; Ren, H.; Xia, A.; Liu, Y. Direct double Z-scheme Q-g-C3N4/Zn2SnO4N/ZnO ternary heterojunction photocatalyst with enhanced visible photocatalytic activity. Appl. Surf. Sci. 2019, 492, 690–702.
(30) Lee, K. M.; Lai, C. W.; Ngai, K. S.; Juan, J. C. Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. Water Res. 2016, 88, 428–448.
(31) Kumar, A.; Rout, L.; Achary, L. S. K.; Mohanty, S. K.; Dash, P. A combustion synthesis route for magnetically separable graphene oxide-CuCeFe2O4-ZnO nanocomposites with enhanced solar light-mediated photocatalytic activity. New J. Chem. 2017, 41, 10568–10583.
(32) Varma, A.; Mukaysan, A. S.; Rogachev, A. S.; Manukyan, K. V. Solution combustion synthesis of nanoscale materials. Chem. Rev. 2016, 116, 14493–14586.
(33) Saif, S.; Tahir, A.; Asim, T.; Chen, Y.; Adil, S. Polymeric Nanocomposites of Iron-Oxide Nanoparticles (IONPs) Synthesized Using Terminalia chebula Leaf Extract for Enhanced Adsorption of Arsenic(V) from Water. Colloids Interfaces 2019, 3, 17.
(34) Adil, S.; Assal, M.; Khan, M.; Al-Warthan, A.; Siddiqui, M. R. H. Nano Silver-Doped Manganese Oxide as Catalyst for Oxidation of Benzyl Alcohol and Its Derivatives: Synthesis, Characterisation, Thermal Study and Evaluation of Catalytic Properties. Oxid. Commun. 2013, 36, 778–791.
(35) Shaik, M. R.; Adil, S. F.; Kuniyil, M.; Sharif, M.; Alwarthan, A.; Siddiqui, M. R. H.; Ali, M. I.; Tahir, M. N.; Khan, M. Facile Sonochemical Preparation of Au-ZrO2 Nanocatalyst for the Catalytic Reduction of 4-Nitrophenol. Appl. Sci. 2020, 10, 503.
(36) Komal, K.; Kaur, H.; Kainth, M.; Meena, S. S.; Kang, T. S. Sustainable preparation of sunlight active α-Fe2O3 Nanoparticles using iron containing ionic liquids for photocatalytic applications. RSC Adv. 2019, 9, 41803–41810.
(37) Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids. Green Chem. 2007, 9, 449–454.
(38) He, Y. P.; Miao, Y. M.; Li, C. R.; Wang, S. Q.; Cao, L.; Xie, S. S.; Yang, G. Z.; Zou, B. S.; Burda, C. Size and structure effect on optical transitions of iron oxide nanocrystals. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 71, 125411.
(39) Hashimoto, T.; Yamada, T.; Yoko, T. Third-order nonlinear optical properties of sol-gel derived α-Fe2O3, γ-Fe2O3, and Fe3O4 thin films. J. Appl. Phys. 1996, 80, 3184–3190.

(40) Sherman, D. M.; Waite, T. D. Electronic spectra of Fe3+ oxides and oxide hydrides in the near IR to near UV. Am. Mineral. 1985, 70, 1262–1269.

(41) Tsuda, N.; Nasu, K.; Fujimori, A.; Siratori, K. Electronic Conduction in Oxides; Springer Science & Business Media, 2013; Vol. 94.

(42) Sharma, V.; Prajapati, R. C. Synthesis of mixed metal oxide nanoparticles of SnO2 with SrO via sol–gel technology: their structural, optical, and electrical properties. J. Sol-Gel Sci. Technol. 2018, 87, 41–49.

(43) Padil, V. V. T.; Černík, M. Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. Int. J. Nanomed. 2013, 8, 889.

(44) Mohamed, W. S.; Abu-Dief, A. M. Synthesis, characterization and photocatalytic enhancement of Eu2O3-ZnO mixed oxide nanoparticles. J. Phys. Chem. Solids 2018, 116, 375–385.

(45) Julien, C.; Nazri, G. General overview of vibrational spectroscopy of layered transition-metal oxides. Materials Research Society Symposium Proceedings, Warrendale, PA; Materials Research Society, 1999; pp 79–90.

(46) Ma, L.; Pei, X.-Y.; Mo, D.-C.; Heng, Y.; Lyu, S.-S.; Fu, Y.-X. Facile fabrication of NiO flakes and reduced graphene oxide (NiO/RGO) composite as anode material for lithium-ion batteries. J. Mater. Sci.: Mater. Electron. 2019, 30, 5874–5880.

(47) Zhang, Z.; Ma, Y.; Bu, X.; Wu, Q.; Hang, Z.; Dong, Z.; Wu, X. Facile one-step synthesis of TiO2/Ag/SnO2 ternary heterostructures with enhanced visible light photocatalytic activity. Sci. Rep. 2018, 8, 10532.

(48) Pourrahmad, A.; Sohrabnezhad, S.; Kashefian, E. AgBr/nanoAlMCM-41 visible light photocatalyst for degradation of methylene blue dye. Spectrochim. Acta, Part A 2010, 77, 1108–1114.

(49) Salthivel, 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 TiO2. Sol. Energy Mater. Sol. Cells 2003, 77, 65–82.

(50) Ghaly, H. A.; El-Kalliny, A. S.; Gad-Allah, T. A.; Abd El-Sattar, N. E. A.; Souaya, E. R. Stable plasmonic Ag/AgCl-polyaniline photoactive composite for degradation of organic contaminants under solar light. RSC Adv. 2017, 7, 12726–12736.

(51) Manjunath, K.; Souza, V. S.; Ramakrishnappa, T.; Nagaraju, G.; Scholten, J. D.; Dupont, J. Heterojunction CuO-TiO2 nanocomposite synthesis for significant photocatalytic hydrogen production. Mater. Res. Express 2016, 3, 115904.

(52) Lingampalli, S. R.; Gautam, U. K.; Rao, C. N. R. Highly efficient photocatalytic hydrogen generation by solution-processed ZnO/PT/CdS, ZnO/PT/CdS1−xZnxS and ZnO/PT/CdS1−xSex hybrid nanocomposites. Energy Environ. Sci. 2013, 6, 3589–3594.

(53) Thambidurai, S.; Gowthaman, P.; Venkatachalam, M.; Suresh, S. Natural sunlight assisted photocatalytic degradation of methylene blue by spherical zinc oxide nanoparticles prepared by facile chemical co-precipitation method. Optik 2020, 207, 163865.

(54) Youssef, A. M.; Yakout, S. M. Superior sunlight photocatalytic of N/La codoped ZnO nanomaterials synthesized using different chelating agents. Opt. Mater. 2020, 107, 110072.

(55) Stanley, R.; Alphas Jebasingh, J.; Manisha Vidyavathy, S. Enhanced sunlight photocatalytic degradation of methylene blue by rod-like ZnO-SiO2 nanocomposite. Optik 2019, 180, 134–143.

(56) Mahana, A.; Guly, O. I.; Momin, S. C.; Lalmuanzeli, R.; Mehta, S. R. Sunlight-driven photocatalytic degradation of methylene blue using ZnO nanowires prepared through ultrasonication-assisted biological process using aqueous extract of Anaabara dolioi. Opt. Mater. 2020, 108, 110205.

(57) Chaudhary, K.; Shaheen, N.; Zulfiqar, S.; Sarwar, M. I.; Suleman, M.; Agboola, P. O.; Shakir, I.; Iars, M. F. Binary WO3-ZnO nanomaterials supported rGO ternary nanocomposite for visible light driven photocatalytic degradation of methylene blue. Synth. Met. 2020, 269, 116526.

(58) Tran Thi, V. H.; Pham, T. N.; Pham, T. T.; Le, M. C. Synergistic Adsorption and Photocatalytic Activity under Visible Irradiation Using Ag-ZnO/GO Nanoparticles Derived at Low Temperature. J. Chem. 2019, 2979517.

(59) Raghavan, N.; Thanag, A.; Venugopal, G. Enhanced photocatalytic degradation of methylene blue by reduced graphene-oxide/titanium dioxide/zinc oxide ternary nanocomposites. Mater. Sci. Semicond. Process. 2015, 30, 321–329.

(60) Barick, K. C.; Singh, S.; Aslam, M.; Bahadur, D. Porosity and photocatalytic studies of transition metal doped ZnO nanoclusters. Microporous Mesoporous Mater. 2010, 134, 195–202.

(61) Ferreira, H. W.; Silva, L. G. A.; Pereira, B. C. S.; Gouveia, R. F.; Andrade, C. T. Adsorption and visible-light photocatalytic performance of a graphene derivative for methylene blue degradation. Environ. Nanotechnol. Monit. Manag. 2020, 14, 100373.

(62) Saravanan, R.; Shankar, H.; Prakash, T.; Narayanan, V.; Stephen, A. ZnO/CdO composite nanorods for photocatalytic degradation of methylene blue under visible light. Mater. Chem. Phys. 2011, 125, 277–280.

(63) Soto-Robles, C.; Nava, O.; Cornejo, L.; Lugo-Medina, E.; Vilchis-Nestor, A.; Castro-Beltrán, A.; Luque, P. Biosynthesis, characterization and photocatalytic activity of ZnO nanoparticles using extracts of Justicia spicigera for the degradation of methylene blue. J. Mol. Struct. 2021, 1225, 129101.

(64) Messil, M. F. A.; Ahmed, M. A.; Soltan, A.; Anis, S. S. Synthesis and characterization of photocatalytic activity of Ag-ZnO/GO nanoparticles for photocatalytic degradation of methylene blue under UV and solar irradiation. J. Phys. Chem. Solids 2019, 135, 109086.

(65) Mydeen, S. S.; Kumar, R. R.; Sambathkumar, S.; Kottaisamy, M.; Vasantha, V. S. Facile Synthesis of ZnO/AC Nanocomposites using Prosopis Juliflora for Enhanced Photocatalytic Degradation of Methylene Blue and Antibacterial Activity. Optik 2020, 224, 165426.

(66) Qi, K.; Cheng, B.; Yu, J.; Ho, W. Review on the improvement of the photocatalytic and antibacterial activities of ZnO. J. Alloys Compd. 2017, 727, 792–820.

(67) Kumar, S. G.; Rao, K. S. R. K. Comparison of modification strategies towards enhanced charge carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO2,WO3 and ZnO). Appl. Surf. Sci. 2017, 391, 124–148.

(68) Zheng, Y.; Lin, J.; Wang, Q. Emissions and photocatalytic selectivity of SrWO4:La3+ (Eu3+, Tb3+, Sm3+ and Dy3+) prepared by a supersonic microwave co-assistance method. Photochem. Photobiol. Sci. 2012, 11, 1567–1574.

(69) Huang, K.; Hong, T.; Yan, X.; Huang, C.; Chen, J.; Chen, M.; Shi, W.; Liu, C. Hydrothermal synthesis of g-C3N4/CdWO4-nanocomposite and enhanced photocatalytic activity for tetracycline degradation under visible light. CrystEngComm 2016, 18, 6453–6463.

(70) Zhao, W.; Wang, Y.; Yang, Y.; Tang, J.; Yang, Y. Carbon spheres supported visible-light-driven CuO-BiVO4 heterojunction: Preparation, characterization, and photocatalytic properties. Appl. Catal., B 2012, 115–116, 90–99.