

1 **Synthesis of Eu³⁺-doped ZnO/Bi₂O₃ heterojunction photocatalyst on graphene oxide sheets**
2 **for visible light-assisted degradation of 2,4-dimethyl phenol and bacteria killing**

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21 **Abstract**

22 We reported the immobilization of binary heterojunction $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ over the surface of
23 graphene oxide (GO) sheets by precipitation method to compose a visible light drive photocatalyst.

24 The ternary nanocomposites were characterized by different spectral technique like FESEM, FTIR,
25 XRD, XPS, EDX, HRTEM, UV-visible, PL, HPLC and LCMS analysis. The high specific surface
26 area of $106.0 \text{ m}^2\text{g}^{-1}$ of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ nanocomposites was ascertained by BET adsorption-
27 desorption isotherm. The nano-composite exhibit excellent photo-efficiency for the
28 photodegradation of 2, 4-dimethyl phenol (DMP) under visible region and was almost completely
29 mineralized in 100 min as compared to the bare and binary system. The mineralized products of
30 DMP were analyzed by HPLC and LCMS analysis. The kinetic model suggests the degradation
31 pathway obeys pseudo-first order kinetic. Their antibacterial property were assessed against *E. coli*
32 bacteria and nearly 90% of gram negative bacteria were killed by using ternary photocatalyst as
33 determined by CFU method. Also, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ nanocomposites possessed significant
34 recycle efficiency up to six consecutive cycles which is beneficial to minimize the tariff. The
35 improved photo-efficiency is due to the extension towards visible region, increase surface area,
36 and high charge separation in ternary heterojunction.

37 **Keywords:** Eu^{3+} doped ZnO; Bi_2O_3 ; Heterojunction formation; Enhanced photo-catalysis; 2,4-
38 dimethylphenol degradation; Antibacterial activity

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42 Introduction

43 Phenols and their derivative is a primary pollutant released by the various industries like
44 paint, textiles, paper, plastics, petroleum refining and pharmaceutical industries etc. [1]. The
45 existence of phenolic compounds in waste water need to be eliminated as it brings a lots of harmful
46 effects on human health and aquatic life. To address this, advanced oxidation processes (AOPs)
47 have found a valuable potential for the degradation of various pollutant in aqueous suspension [2].
48 Amongst, AOP's process employed for the organic pollutants degradation, visible light assisted
49 photocatalysis is of the most appropriate ones, owing to its several advantages like
50 inexpensiveness and effectiveness. Among the various semiconductors used for photocatalytic
51 processes, zinc oxide (ZnO) has emerged as a suitable catalyst for photocatalytic degradation and
52 mineralization of various organic and inorganic contaminants [3]. The excellence of ZnO is due to
53 its strong oxidizing power and low cost which makes it a favorable candidate to carry out
54 photocatalytic oxidation processes occurring in water media [4]. On exposure to solar light with
55 energy higher or equal to the band gap of ZnO semiconductor, generation of electron-hole pair
56 takes place. The generated electrons reacts with O_2 to form superoxide radicals ($O_2^{\bullet-}$) and
57 meanwhile, the holes reacts with H_2O or OH^- ions to produce hydroxyl radicals ($\bullet OH$) [5, 6].
58 Owing to strong oxidizing ability, $\bullet OH$ and $O_2^{\bullet-}$ degraded the pollutant and convert them into H_2O
59 and CO_2 [7]. However, ZnO is only active under UV light, and it also suffers from re-combination
60 of charge carrier produced during photocatalysis [8]. To overcome these drawbacks of ZnO and
61 similar semiconductors, till now, two main strategy have been employed: (i) doping with cationic,
62 anionic or rare earth elements and (ii) the construction of heterojunction with other semiconductors
63 [9–11]. These strategy aims to enhance the stability, photocatalytic efficacy and expand the
64 absorption of light in visible range. Nowadays, doping with a rare earth element, like Ln^{3+} ion, has

65 been revealed that can cause improvement in the ZnO photocatalytic activity [10]. Khataee *et al.*
66 prepared Eu³⁺ doped ZnO nanoparticles by using the sonochemical method and was exploited for
67 the photo-degradation of acid orange dye [10]. Similarly, Aneesh *et al.* prepared Eu³⁺ doped ZnO
68 nanoparticles with various amounts of Eu-dopant, in which the luminescence quenching of ZnO
69 nanoparticles was enhanced with increase in doping concentration of Eu [11].

70 On other hand, bismuth oxide (Bi₂O₃) is more advantageous and emerges as noble
71 photocatalyst with a band gap of ~1.75–2.8 eV active under visible light region [12, 13]. It is an
72 attractive compound with variety of application in electronics, fuel cells, ceramics, gas sensors and
73 catalyst etc. Earlier, Bi₂O₃ has already been utilized to boost the photocatalytic activity of metal
74 oxide semiconductor photocatalysts. For instance, Balachandran and Swaminathan prepared a
75 series of α -Bi₂O₃/ZnO nanocomposites with variable amounts of α -Bi₂O₃ (6.8–18.9 wt %) and used
76 them for photodegradation of acid red dye [14]. Similarly, Yang *et al.* reported the fabrication of
77 ZnO nano-fibers and β -Bi₂O₃ heterostructure and utilized it for Rhodamine B dye
78 photodegradation under both UV and visible light [15]. Due to low band gap and high rate of
79 recombination of bare Bi₂O₃ photocatalyst, limits its application to use as efficient photocatalyst.
80 Thus formation of heterojunction is an effective strategy for constructing visible light active
81 photocatalyst and also to mitigate the rate of electron-hole pair recombination. Coupling two
82 semiconductor with suitable energy gap and band edge potential to enhance the photoefficiency is
83 the sole criteria for forming heterojunction Here, the valence band edge and conduction band edges
84 of Bi₂O₃ make it suitable for the coupling with Eu³⁺-ZnO.

85 Recently, carbon material is acquiring lots of attention due to their versatile properties. The
86 various carbon derived material utilized so far as a supportive material for binary heterojunction
87 were graphene, graphene oxide, carbon nanotube, fullerene, activated carbon etc. Large specific

88 surface area, high electrical and thermal conductivity, and facile charge carrier mobility make
89 graphene oxide more advantageous to be utilized in combination with different binary and ternary
90 heterojunction for enhanced photo-efficiency [16]. In the present work, the follow-up of our
91 previous studies is continued in the field of graphene-based composites for photodegradation of
92 organic contaminants in aqueous suspension. Eu^{3+} doped ZnO was coupled with Bi_2O_3 which in
93 turn dispersed onto graphene oxide (GO) surface and the fabricated composite were then utilized
94 for photodegradation of DMP in water samples. Eu^{3+} -ZnO/ Bi_2O_3 /GO photocatalyst was
95 comprehensively characterized by FESEM, TEM, XRD, EDX, UV-visible techniques, along with
96 photoluminescence (PL) analysis. Due to the toxicity, carcinogenic nature, and resistance towards
97 degradation of DMP, it was photodegraded by utilizing Eu^{3+} -ZnO/ Bi_2O_3 /GO. Further, the
98 degradation kinetics followed by most plausible mechanism for the increased photocatalytic
99 efficiency of the ternary heterojunction was also proposed. Lastly, recycle efficiency of Eu^{3+} -
100 ZnO/ Bi_2O_3 /GO up to six catalytic cycle was also assessed for DMP degradation.

101 **2. Experimental**

102 **2.1. Fabrication of Eu^{3+} -ZnO/ Bi_2O_3 /GO**

103 Here, advanced Hummer method were executed to synthesize graphene oxide as per
104 previously reported work [16]. Eu^{3+} doped ZnO was prepared using the sonochemical method [17].
105 Typically, ZnCl_2 (1 g) and of $\text{C}_6\text{H}_9\text{EuO}_6 \cdot x\text{H}_2\text{O}$ (0.1 g) were dissolved in 100 mL of distilled water.
106 To this reaction mixture, NaOH (1M) was added to maintain pH 10 and the mixture was subjected
107 to ultrasonication for 1 h. The obtained white precipitates were rinsed with ethanol and deionized
108 water and dried at 80 °C in hot air oven. ZnO was prepared by the same procedure without addition
109 of $\text{C}_6\text{H}_9\text{EuO}_6 \cdot x\text{H}_2\text{O}$. In order to prepare Eu^{3+} -ZnO/ Bi_2O_3 /GO, GO (1 g) was dispersed in distilled
110 water (100 mL) with sonication for half an hour. To this suspension, 1.0 g $\text{Bi}(\text{NO}_3)_3$ and 30 mL

111 NH_4OH (1 M) were added with continuous stirring. In the next step, 0.5 g $\text{Eu}^{3+}\text{-ZnO}$ was added
112 to the reaction solution followed by sonication for 1 h. Eventually, precipitates were separated
113 and washed with water, dried at $80\text{ }^\circ\text{C}$ to obtain $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$ composite. The same route
114 was exploited to prepare Bi_2O_3 with no addition of GO and $\text{Eu}^{3+}\text{-ZnO}$ during the course of the
115 reaction. GO was used as support for $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ nanoparticles with even dispersal of $\text{Eu}^{3+}\text{-}$
116 $\text{ZnO/Bi}_2\text{O}_3$ and low agglomeration over its surface.

117 **2.2. Apparatus**

118 Transmission electron microscopy (TEM) pictures was captured on a randomly selected
119 area at voltage of 200 kV, using FP/5022-Tecnaï G2 20 S-TWIN (USA) instrument. A Nava Nano
120 SEM-45 (USA) instrument was applied for recording the scanning electron microscopy (SEM)
121 micrographs. A Perkin-Elmer Spectrometer (Spectrum RX-1) with KBr pellet was used for
122 recording the FTIR spectra ranges from $4000\text{-}400\text{ cm}^{-1}$. A Panalytical's X'Pert Prodiffractometer
123 with $\text{CuK-}\alpha\text{-1}$ (45 kV/100 mA) source was used for recording X-ray diffraction (XRD) patterns.
124 To estimate the optical absorption performance, using BaSO_4 as the reference, a diffuse reflectance
125 spectrophotometer (UV 3600, Shimadzu) was employed. A Coulter SA3100 instrument was
126 exploited for determination of the BET surface area of the sample by the aid of Nitrogen
127 adsorption-desorption isotherms. A FLS-920 instrument (Edinburgh) was employed for recording
128 the photoluminescence (PL) spectra. A digital lux-meter (750 lx) was used for the measurement
129 of light intensity. For the analysis of degradation product during mineralization, a test were
130 performed on a Water HPLC instrument (Austria) utilizing a C_{18} column ($5\mu\text{m}$, 25cm length and
131 7mm diameter) and taking a 1:39:60 ratio of acetic acid: methanol: water as eluent with a flow rate
132 of 0.5 mL min^{-1} . The LCMS information was obtained for analyzing degradation products using
133 JEOL GCMATE II GC-MS with a high-resolution data system.

134 **2.3. Photocatalytic activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$ for DMP degradation**

135 The photocatalytic experiment were conducted in a self-developed photoreactor. Details of
136 photoreactor are given in our previous work [18]. The estimation of chemical oxygen demand
137 analysis was done using the reflux technique [19]. CO_2 was estimated by titration of the reaction
138 mixture with NaOH solution [20]. The DMP removal percentage was computed using Eq. (1).

$$139 \quad \% \text{ removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

140 Where, C_t and C_0 are the instant and initial concentrations/COD of DMP, respectively.

141 **3. Results and discussion**

142 **3.1. Morphology and structure characterization of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$**

143 The FESEM images of GO and $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$ are laid out in Fig. 1 a-d. The
144 graphene oxide exfoliation can be observed in Fig.1 a. Fig. 1b shows the thin, wrinkled, non-
145 uniform and highly porous GO surface. The porous surface of GO facilitates the adsorption of
146 organic pollutants present in the aqueous phase. In Fig. 1c, dispersion of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$
147 photocatalyst onto GO surface can be clearly depicted. As can be seen in high magnification
148 FESEM image, the agglomerates of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ are of different size and shape (Fig.1d).
149 HRTEM analysis further ascertained the deposition of $\text{Eu}^{3+}\text{-ZnO}$ and Bi_2O_3 on porous GO sheets
150 (Fig.2a and b). The lattice fringes at 0.33 nm, 0.28 and 0.26 nm was ascribed to (120), (001) and
151 (002) plane of Bi_2O_3 , ZnO and GO respectively [21-22]. Selected area electron diffraction (SAED)
152 analysis confirmed the polycrystalline nature of the prepared photocatalyst (Fig. 2c). Fig. 2d
153 explains the interplanar spacing between the two layers of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$ is 0.28 nm which

154 indicate the successful incorporation of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ over graphene oxide sheet comparable
155 with previously reported works [22].

156 The XRD spectrum of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ is exhibit in Fig. 3a. The diffraction peaks
157 labeled with ♥ at $2\theta = 26.6^\circ, 49.9^\circ,$ and 48° were assigned to {120}, {200} and {433} planes of
158 Bi_2O_3 , respectively [13]. The diffraction peak of GO, denoted with ♦ at $2\theta = 26.2^\circ$, was due to
159 {002} plane of GO [2]. The XRD peaks leveled with ● at $31^\circ, 34^\circ, 37^\circ, 47.6^\circ, 56^\circ, 63^\circ, 65^\circ,$ and
160 70° were assigned to {100}, {002}, {101}, {102}, {110}, {103}, {102} and {112} planes present
161 in $\text{Eu}^{3+}\text{-ZnO}$ [10]. FTIR spectrum of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ is shown in Fig. 3b. The band at 525
162 was due to Zn-O stretching vibration [23]. The peaks at 1405, 1650 and 1020 cm^{-1} were due to
163 C-H (bending vibration), C=O and C-O-C stretching vibrations, respectively [24]. The peak at 862
164 cm^{-1} was due to Bi-O stretching vibration present in Bi_2O_3 [13]. The peak at 3435 was assigned to
165 O-H stretching of adsorbed water molecules [25]. The atomic percentage of Zn, Bi, Eu, C and O
166 is 6.7, 4.5, 0.54, and 55.70, 32.97 as depicted by EDX analysis (Fig. S1). The analysis of these
167 results confirmed the formation of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$.

168 To confirm the structural changes in GO after oxidation a Raman spectra of GO were
169 recorded between 500 and 2500 cm^{-1} as given in supplementary Fig. S2. The intensity of D and G
170 band in the spectra clearly explain the formation of GO from graphite using Hummer's method.
171 The D band determines the extent of disorder due to sp^3 hybridized carbon atom and G band
172 determines the graphitic mode due to sp^2 carbon atom. The Raman spectra of graphite has two
173 peak at 1366 cm^{-1} and 1598 cm^{-1} with I_D/I_G ratio 0.7. Whereas, the D and G band for GO is observed
174 at 1364 cm^{-1} and 1607 cm^{-1} with I_D/I_G ratio 1.03. Broad D band is due to the addition of defects
175 after oxidation. Further, the increase in I_D/I_G ratio from graphite to graphene oxide confirms the

176 incorporation of oxygen containing functional group. The observed peak is in good agreement the
177 existing literature [26].

178 The XPS analysis further support the FTIR spectra. Fig. 4 displayed XPS spectra of Eu^{3+} -
179 $\text{ZnO}/\text{Bi}_2\text{O}_3/\text{GO}$ nanocomposites. Different elements present in nanocomposites were analyzed
180 through XPS and provides information about chemical composition and oxidation states of
181 different elements. Through XPS analysis, presence of Europium (Eu), Zinc (Zn), Bismuth (Bi),
182 Oxygen (O) and Carbon (C) were confirmed in Eu^{3+} - $\text{ZnO}/\text{Bi}_2\text{O}_3/\text{GO}$ nanocomposites. The high
183 resolution spectra of C1s, O1s, Zn2p, Bi4f, and Eu3d core level could be observed in Fig. 4 (a-e).
184 The binding energies at 1165 eV and 1135 eV were accredited to $\text{Eu } 3d_{3/2}$ and $\text{Eu } 3d_{5/2}$ orbital (Fig.
185 4a) [27]. These energy peaks confirms the presence of Eu (III) in synthesized nanocomposites.
186 Zinc exhibited two sharp peaks at 1024 eV and 1043 eV binding energies which were assignable
187 to $\text{Zn-}2p_{3/2}$ and $\text{Zn-}2p_{1/2}$ in Zn^{2+} state of ZnO and shown in Fig. 4b [28]. XPS spectrum of Bi 4f
188 ($\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$) displayed in Fig. 4c possessed peaks at 158.6 and 164.5 eV [29]. Strong peak
189 established at 530.5 eV was associated to O 1s orbital of oxygen atom (Fig. 4d) [30]. XPS spectrum
190 of C1s showed sharp peaks at 283 and 288 eV were ascribed to sp^2 C-C bond and C-O bonds,
191 respectively (Fig. 4e) [31]. The spectra confirmed the successful formation of Eu^{3+} - $\text{ZnO}/\text{Bi}_2\text{O}_3/\text{GO}$
192 nanocomposites.

193 The UV-visible spectroscopy was utilized to assess the UV-visible light activity of Eu^{3+} -
194 $\text{ZnO}/\text{Bi}_2\text{O}_3/\text{GO}$ (Fig. 5a). ZnO had an absorption maximum at 368 nm with dominated absorption
195 in the UV region [11, 15], which shows ultraviolet photo-response of ZnO. However, the
196 absorption maximum showed a red shift and was observed at 410 nm in Eu^{3+} doped ZnO. Bi_2O_3
197 had an absorption edge at 438 nm [11, 14, 15]. In case of Eu^{3+} - $\text{ZnO}/\text{Bi}_2\text{O}_3/\text{GO}$, the absorption

198 edge was shifted to the visible region involving a red shift in absorption maximum. Tauc's plots
199 were plotted to find the band-gap energy of prepared photocatalyst using equation 2 [32].

$$200 \quad \alpha h\nu = A(h\nu - E_g)^{n/2} \quad (2)$$

201 Where, index (n) can have 1, 2, 3, and 4 value for allowed direct and indirect electronic
202 transitions, and forbidden direct and indirect ones, respectively. Also, $h\nu$ is photon energy in Tauc
203 equation and α symbol shows absorption coefficient. The band gaps of ZnO, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$
204 and Bi_2O_3 are 3.36, 3.01, and 1.8 eV, respectively (Fig. 5b). The charge separation mechanism in
205 photocatalytic reaction was predicted by the photoluminescence analysis. ZnO had an emission
206 peak at 375 nm (Fig. 5c). The emission peaks intensity lowered in both $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ and $\text{Eu}^{3+}\text{-}$
207 $\text{ZnO/Bi}_2\text{O}_3/\text{GO}$. The decreased intensity of PL emission peak in $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ displayed
208 deferred rate of recombination as compared to $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$ and ZnO, respectively. This
209 attribute to the electron engulfing nature of graphene oxide sheets towards charge carriers [2]. Fig.
210 5d shows nitrogen adsorption-desorption isotherms of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$. The composite obeys
211 type IV isotherm with specific area of $106.0 \text{ m}^2/\text{g}$. This high specific surface area is highly suitable
212 for adsorption assisted photocatalytic degradation of the pollutant.

213 **3.2. Photocatalytic activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ for DMP degradation**

214 The photocatalytic activity of the composite was explored for the removal of DMP by the
215 aid of LED radiation. Fig. 6a exhibits photodegradation of DMP against the irradiation time period.
216 The simple light irradiation had no influence on the removal of DMP. The removal efficiencies of
217 99 %, 72 %, 51 %, 50 %, and 34 % were observed for $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$, $\text{Eu}^{3+}\text{-}$
218 ZnO, ZnO and GO. Thus, the efficiencies of the exanimate materials followed the order $\text{Eu}^{3+}\text{-}$
219 $\text{ZnO/Bi}_2\text{O}_3/\text{GO} > \text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3 > \text{Eu}^{3+}\text{-ZnO} > \text{Bi}_2\text{O}_3 > \text{GO}$. The DMP removal experiments were
220 also conducted under the dark condition to evaluate the percentages removed by adsorption

221 process. Throughout the adsorption process alone, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$, $\text{Eu}^{3+}\text{-}$
 222 ZnO , ZnO , and GO had the respective efficiencies of 34, 8, 6, 9, and 32 % for DMP removal
 223 (Fig. 6b). The efficiency of the adsorbents followed the trend $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO} > \text{GO} > \text{Eu}^{3+}\text{-}$
 224 $\text{ZnO/Bi}_2\text{O}_3 > \text{Eu}^{3+}\text{-ZnO} > \text{Bi}_2\text{O}_3$. The obtained result showed that $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ had the
 225 highest photocatalysis activity as well as the adsorption capability. The GO coupling with $\text{Eu}^{3+}\text{-}$
 226 $\text{ZnO/Bi}_2\text{O}_3$ increased the photo-catalytic degradation of DMP. This was because of notable
 227 adsorption of DMP onto graphene oxide sheets [16]. The kinetics of degradation were studied by
 228 Eq. (3) [33].

$$229 \quad -\frac{dC}{dt} = kt \quad (3)$$

230 Where, k is the rate constant, and C is DMP concentration at time t. This relation can be
 231 integrated between the limits of (0, C_0) and (t, C), from which one can have Eq. (4):

$$232 \quad -\ln\left(\frac{C}{C_0}\right) = kt \quad (4)$$

233 The graph between $-\ln(C/C_0)$ against time was used to find the value of rate constant. $\text{Eu}^{3+}\text{-}$
 234 $\text{ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO}$, Bi_2O_3 , and GO had the rate constant of 0.087, 0.050, 0.041, and 0.019,
 235 respectively. The R^2 values obtained were in the range 0.95-0.99 which indicated that pseudo-first
 236 order kinetic model was obeyed during the degradation processes. Both photocatalytic and
 237 adsorption experiments indicated that photocatalysis of DMP was significantly affected by
 238 adsorption process. So, further experiments were undertaken to find out the effect of adsorption
 239 on DMP degradation.

240 **3.3. Effect of adsorption on the photo-catalytic activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$**

241 Fig. 7 shows the effectiveness of the photocatalytic degradation of DMP, using the
242 composites, and compare their efficacy with adsorption ability alone, which is responsible for
243 removal process. Fig.7 displays DMP removal under three reaction parameter. The first half of the
244 graph display, adsorption of DMP without exposing towards light. The second half of the graph
245 indicate simultaneous adsorption and photocatalysis (i.e. A+P process) where, 98 %, 72 %, and
246 32% of DMP was removed using $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$, and GO, respectively.
247 However, conducting photocatalytic process after adsorption (i.e. A-P process) the removal
248 percentage of DMP in 3 h is 50 %, 68 %, and 34 % for $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3$, and
249 GO, respectively. The order for various catalytic processes was revealed as: $\text{A+P} > \text{A-P} > \text{DA}$.
250 During the A-P process, excessive adsorption of DMP on the surface of photocatalyst blocks
251 penetration of light and decreases the total photoactive volume of the photocatalytic systems. The
252 decreased photoactive volume causes a defatation of catalytic activity. By using the newly
253 prepared composite, the concurrent adsorption and photocatalysis processes are the most efficient
254 strategy for degrading DMP under visible light.

255 **3.4. Mineralization study and recycling performance of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$**

256 The complete mineralization of DMP was assessed by determining COD estimation and CO_2
257 formation during photodegradation (Fig. 8a and b). COD was assessed using $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$
258 assisted A+P process, while 65% and 64% removal were observed in the case of $\text{Eu}^{3+}\text{-ZnO}$ and
259 ZnO , respectively. Also, 78, 55, 20, and 2 mg/L of CO_2 were estimated during mineralization
260 of DMP using $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$, $\text{Eu}^{3+}\text{-ZnO}$, Bi_2O_3 , and GO photocatalyst, respectively. Both
261 COD and CO_2 estimations are in agreement with each other. This confirms the complete
262 mineralization of DMP into CO_2 and H_2O .

263 To explore the intermediate formed during the degradation of DMP, the HPLC analysis were
264 estimated at different time intervals of 0h, 2h, 4h, 6h, 8h,10, respectively. After exposure to visible
265 light, the decrease in intensity of peak at retention time nearly at 12 min was noticed for DMP as
266 displayed in Fig 8c. Further, a group of new peaks (circled in Fig. 8c) appeared in between 2 to 4
267 minutes which subsequently vanished after certain time interval. The appearance of these peaks
268 can be ascribed to the intermediates, developed during the mineralization process. In LCMS, peaks
269 at 122, 150, 182, 108, 94, 88 116, and 46 shown in Fig. 9d were ascribed to 2,4-DMP, 2-hydroxy-5-
270 formylbenzaldehyde, 4-hydroxyisophthalic acid, benzoquinone, phenol, oxalic acid, Maleic acid,
271 and formic acid, respectively.

272 **3.5. Band diagram and possible degradation mechanism**

273 In order to understand the basic mechanism of enhanced photocatalysis in Eu^{3+} -ZnO/ Bi_2O_3 /
274 GO , band positions of conduction band (CB) and valance band (VB) were determined exploiting
275 Eq. (5) and (6) [34, 35]:

$$276 E_{VB} = \chi - E^e + 0.5 E_g \quad (5)$$

$$277 E_{CB} = E_{VB} - E_g \quad (6)$$

278 Where, E_g represents the band gap of photocatalyst, E^e is equal to a constant value of 4.5
279 eV i.e. energy of free electron, and χ is electronegativity of semiconductor. The E_g and χ for Eu^{3+} -
280 ZnO were 3.15 and 5.79 eV while for Bi_2O_3 it was found to be 1.8 and 5.59 eV, respectively [36-
281 38]. The locations of VB and CB in Eu^{3+} -ZnO were 2.8 and -0.35 eV, respectively [36]. The
282 position of VB and CB in Bi_2O_3 was found to be 1.30 and -0.54 eV, respectively [38].The band
283 position of Eu^{3+} -ZnO and Bi_2O_3 was suited for formation of type II heterojunction with staggered
284 band position. The scavenging examinations were conducted by utilizing isopropyl alcohol (IPA),

285 benzoquinone (BZQ), ammonium oxalate (AO), and Cr(VI) ion as hydroxyl radicals (OH^\bullet),
286 superoxide radicals ($\text{O}_2^{\bullet-}$), holes (h^+_{VB}) and electrons (e^-_{CB}) scavengers, respectively [39]. The
287 removal efficiencies of 20, 54, 92, and 95 % were recorded in IPA, BZQ, Cr(VI), and AO,
288 respectively as shown in (Fig. S3). The presence of Cr(VI) and AO had no remarkable influence
289 on photocatalytic activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$. During the scavenging experiment, whereas,
290 OH^\bullet and $\text{O}_2^{\bullet-}$ radicals showed the highest oxidizing strength for the degradation of DMP. The
291 mechanism through which the new photocatalyst can mineralize DMP can be explained as follows
292 (Fig. 9). Under visible light, holes, and electrons were produced in valance and conduction band
293 of ZnO and Bi_2O_3 semiconductor, respectively. The migration of charge carrier takes place from
294 the VB of $\text{Eu}^{3+}\text{-ZnO}$ to VB of Bi_2O_3 in accordance with the position of its band potential. The band
295 position of $\text{Eu}^{3+}\text{-ZnO}$ and Bi_2O_3 was suited for formation of type II heterojunction with staggered
296 band position. At the same time, photo-excited electrons migrate from CB of Bi_2O_3 to CB of $\text{Eu}^{3+}\text{-}$
297 ZnO [40]. Due to this transfer, the recombining rate of photo-generated electron-hole pairs was
298 diminished to a greater extent. The reaction of CB electrons of ZnO with adsorbed molecular O_2
299 led to production of superoxide ($\text{O}_2^{\bullet-}$) radicals on the surface. The hole in VB of Bi_2O_3 reacts with
300 the H_2O molecule to produce hydroxyl radicals. The hydroxyl radicals and superoxide ultimately
301 oxidized DMP into CO_2 and H_2O . Based on the obtained results, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ emerged
302 as a potential photo-catalyst for degradation of DMP present in water.

303 Recycling efficiency of the photocatalyst is very crucial for its long-term application in
304 water purification process. The photo-catalyst was separated after each cycle thorough
305 centrifugation process and utilized for the next photocatalytic cycle. After six catalytic cycles, the
306 photo-efficiency of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ was reduced from 98 to 89% (Fig. S4a). Furthermore,
307 XRD, EDX and FITR analysis of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ was performed (Fig. S4(b-d)). XRD, EDX

308 and FTIR spectra of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ did not show any significant change in the crystalline
309 structure of the ternary heterojunction even after six catalytic cycles. It indicates the long-term
310 stability of prepared photocatalyst for DMP degradation.

311 **3.6. Photocatalytic antibacterial activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$**

312 The photocatalytic antibacterial activity of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ was assessed using *E. coli*
313 as model bacterium under visible light. As shown in Fig 10a the percentage killing dramatically
314 increased to 90%, on exposure of photocatalyst towards the source of visible light for 60 min.
315 However, 10 % cell viability of *E. coli* were observed for 3 mg/ml of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ under
316 visible light Fig. 10b. The results clearly indicates the strong antibacterial activity of ternary
317 photocatalyst against gram negative strains. Generation of ROS (e^- , h^+ , $\text{O}_2^{\bullet-}$, OH^{\bullet}) during the
318 photocatalytic process plays a crucial role in photocatalytic antibacterial performance [41]. Thus,
319 to explore the role of generated ROS, scavenging experiments were performed to traps the ROS
320 as shown in Fig. 10c. Isopropyl alcohol, ammonium oxalate, Cr(VI), and benzoquinone were used
321 as scavengers for hydroxyl radical, holes, electron, and superoxide radical anion, respectively [42-
322 43]. It can be clearly depicted from Fig. 10c that hydroxyl radical and superoxide radical were the
323 chief oxidizing species responsible for antibacterial activity on 0.5mM optimized scavenging
324 concentration [16]. Addition of isopropanol and benzoquinone traps the OH^{\bullet} and $\text{O}_2^{\bullet-}$ from the
325 reaction system, thus found very small decrease in cell viability.

326 **4. Conclusion**

327 In summary, $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ a ternary heterojunction was successfully fabricated via
328 precipitation method. The photocatalytic efficiency of type-II heterojunction were evaluated against
329 DMP and antibacterial property were assessed against *E. coli* under visible light source. Doping
330 of ZnO with Eu^{3+} lowers the band gap of ZnO as compared to un-doped ZnO, further confirmed
331 by band gap analysis. In the ternary heterojunction Bi_2O_3 and graphene oxide sheets traps electron
332 from ZnO conduction band, thereby decreasing rate of recombination as validate by PL results.
333 Moreover, integration of $\text{Eu}^{3+}\text{-ZnO}$ with Bi_2O_3 extend the absorption towards visible region. With

334 the simultaneous adsorption and photodegradation (A+P) process, the novel ternary heterojunction
335 was capable of degrading 98 % of DMP in 100 min. Nearly, 78% of CO₂ removal were estimated
336 for DMP mineralization which further aid the mineralization process. The extent of mineralization
337 also established by HPLC and LCMS analysis. Similarly, nearly 90% of *E. coli* were killed when
338 the photocatalyst were exposed to visible light source for 60 min. The mineralization obeys
339 pseudo-first order model. Further, scavenging experiments reveals that OH[·] and O₂^{·-} were the
340 principal oxidizing species responsible for mineralization. Also, the nanocomposites were
341 recyclable up to six consecutive cycles this maintain the cost effectiveness of the photocatalyst.
342 Thus, Eu³⁺-ZnO/Bi₂O₃/GO nanocomposites can be easily applied for the detoxification of
343 pollutant present in water.

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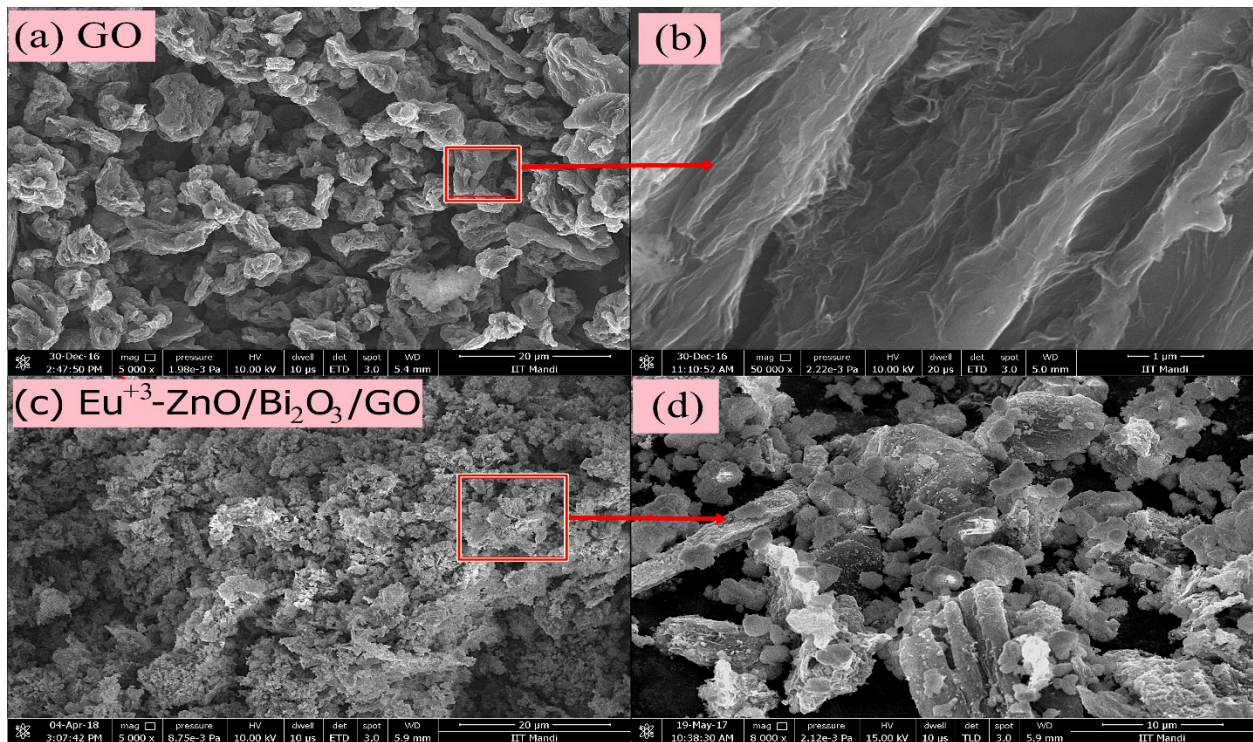


Fig. 1. FESEM images of (a) GO (b) magnified image of selected portion of (a), (c) Eu^{3+} -ZnO/ Bi_2O_3 /GO and (d) magnified image of selected portion of (c).

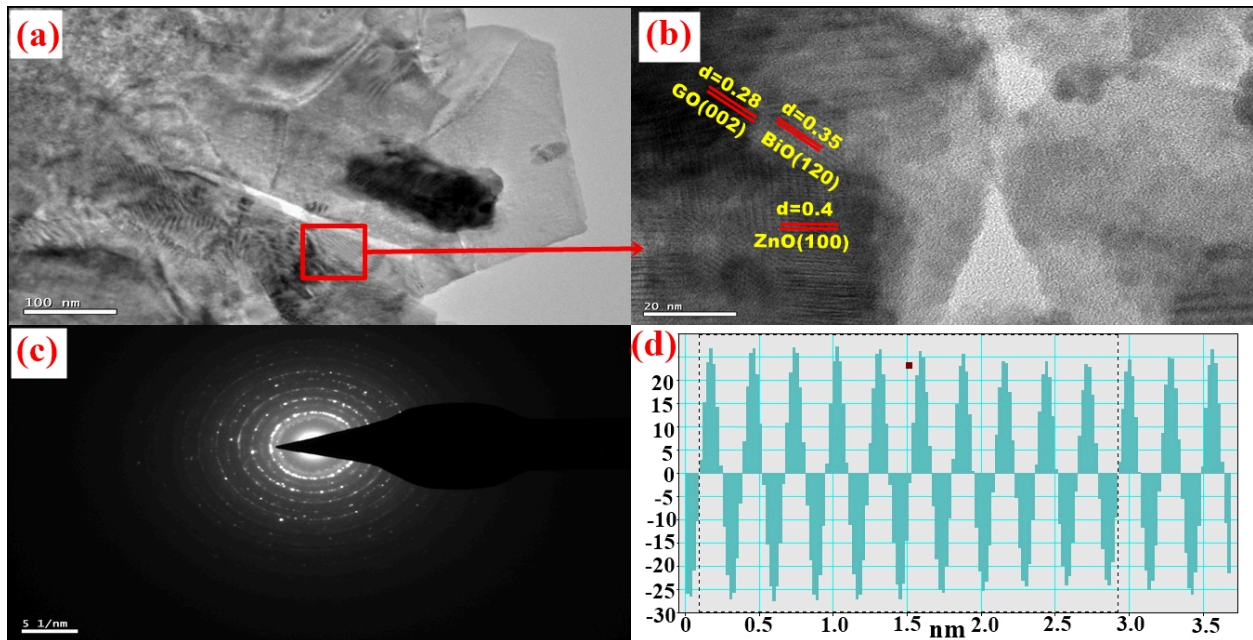


Fig. 2. (a) TEM images of Eu^{3+} -ZnO/ Bi_2O_3 /GO (b) magnified image of selected portion of (a), (c) SAED pattern of Eu^{3+} -ZnO/ Bi_2O_3 /GO and (d) planar spacing of the composite.

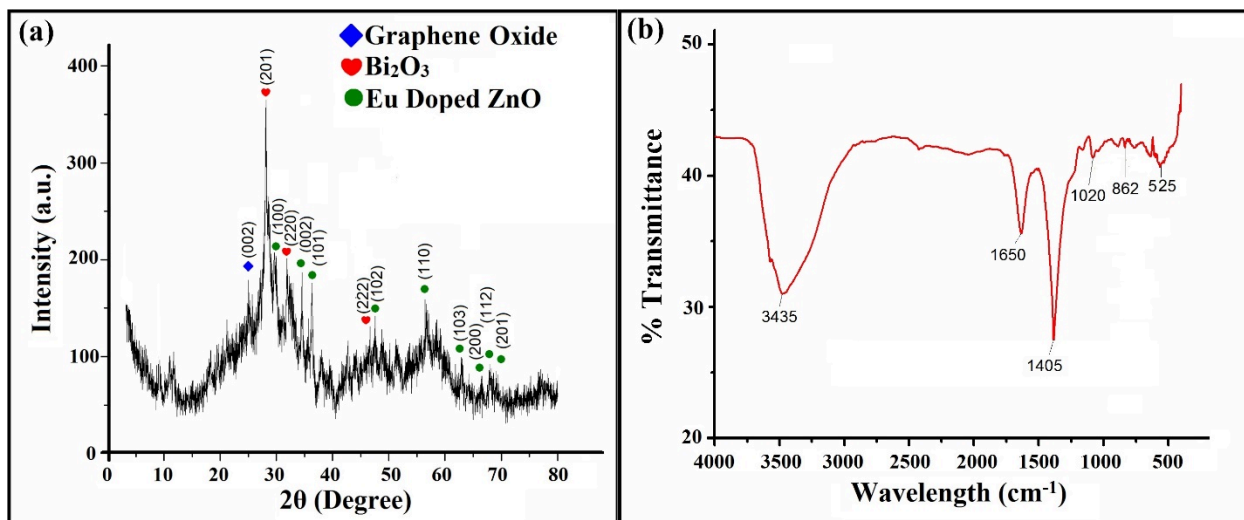


Fig. 3. XRD and FTIR spectra of Eu³⁺-ZnO/Bi₂O₃/GO nanocomposite.

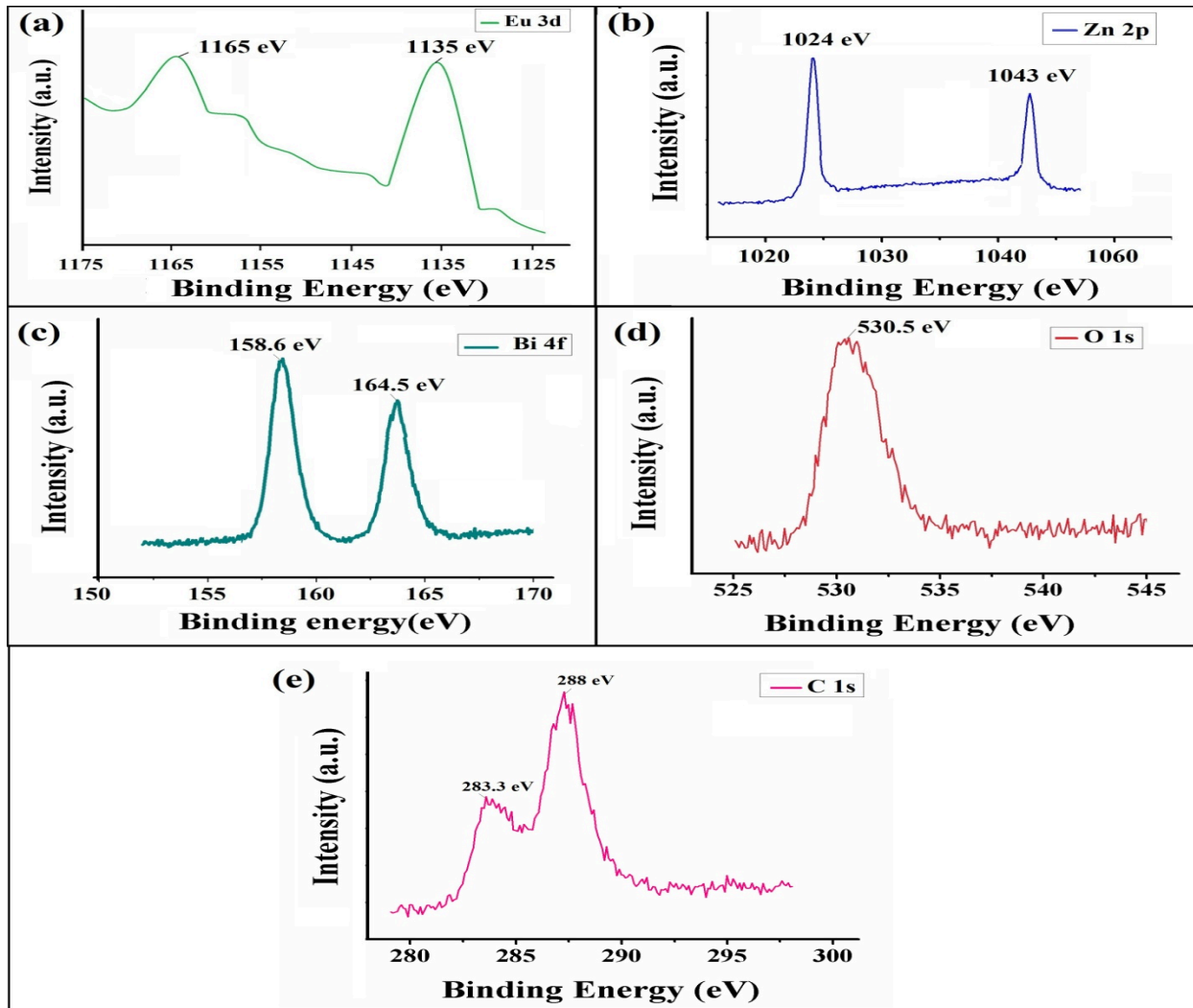


Fig. 4. XPS spectra of Eu³⁺-ZnO/Bi₂O₃/GO nanocomposite.

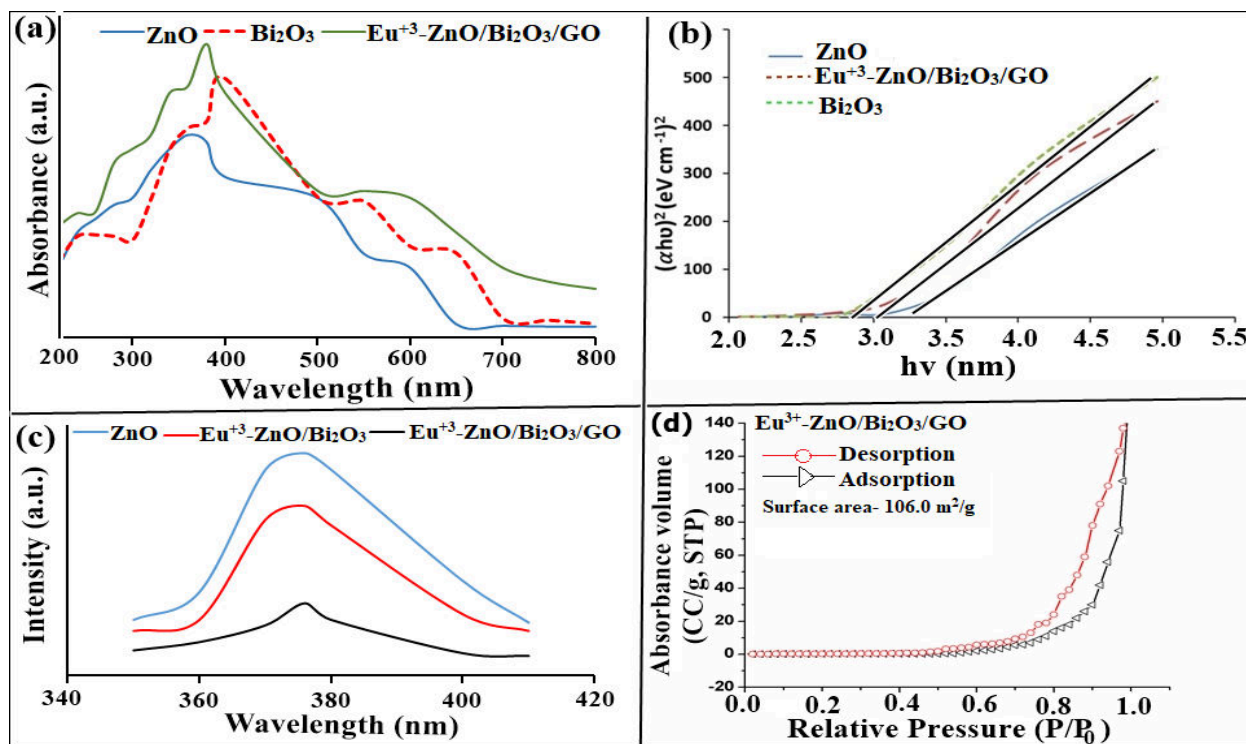


Fig. 5. (a) UV-visible analysis, (b) Band gap calculation, (c) photoluminescence analysis and (d) BET adsorption-desorption isotherms of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$.

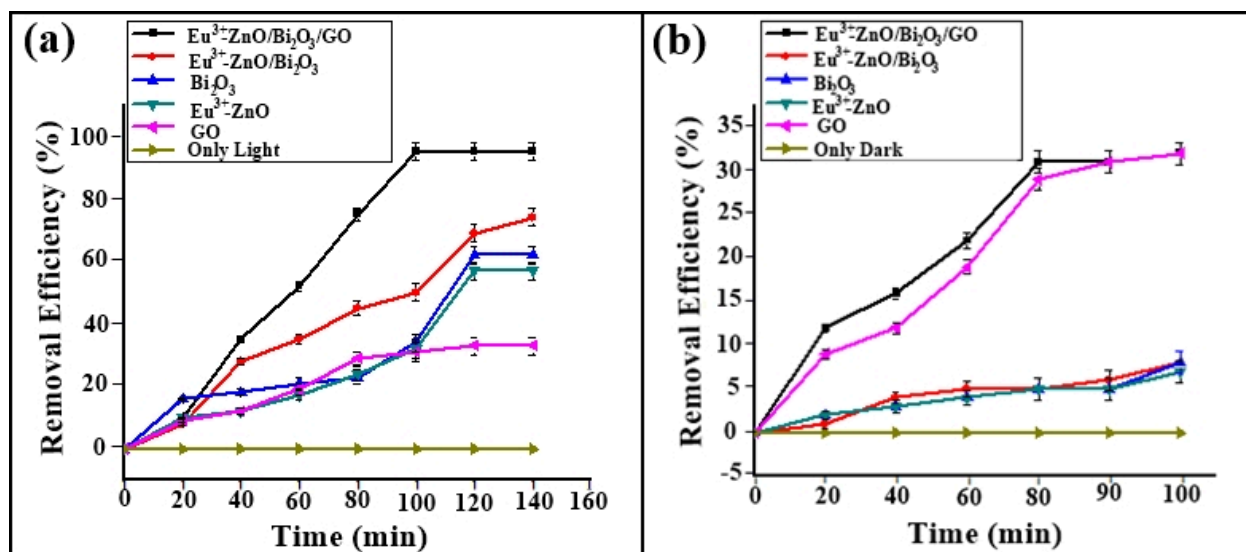


Fig. 6. (a) Photocatalytic degradation of DMP and (b) adsorptional removal of DMP using $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$ [Reaction conditions: initial reaction pH= 4.0; $[\text{DMP}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{photocatalyst}] = 50 \text{ mg}/100 \text{ mL}$; and intensity of light = 750 lx].

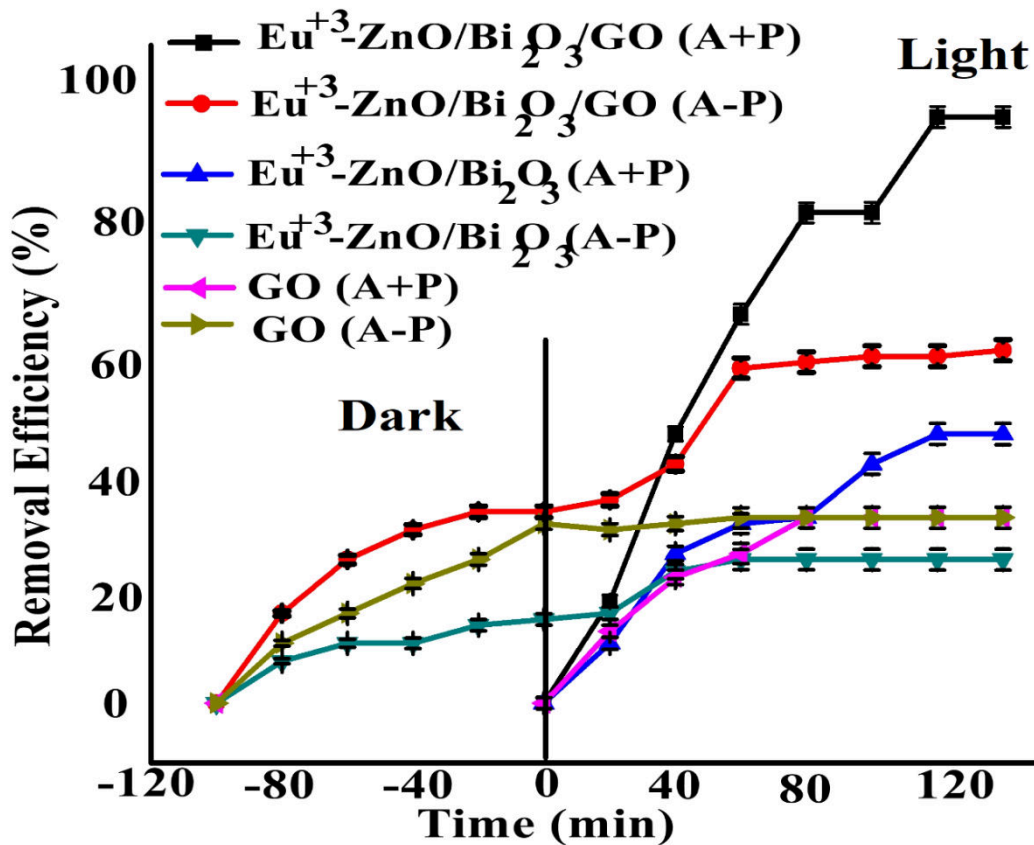


Fig. 7. Effect of adsorption on photodegradation of DMP using $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3/\text{GO}$. [Reaction conditions: initial reaction pH= 4.0; $[\text{DMP}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{photocatalyst}] = 50 \text{ mg}/100 \text{ mL}$; and intensity of light = 750 lx].

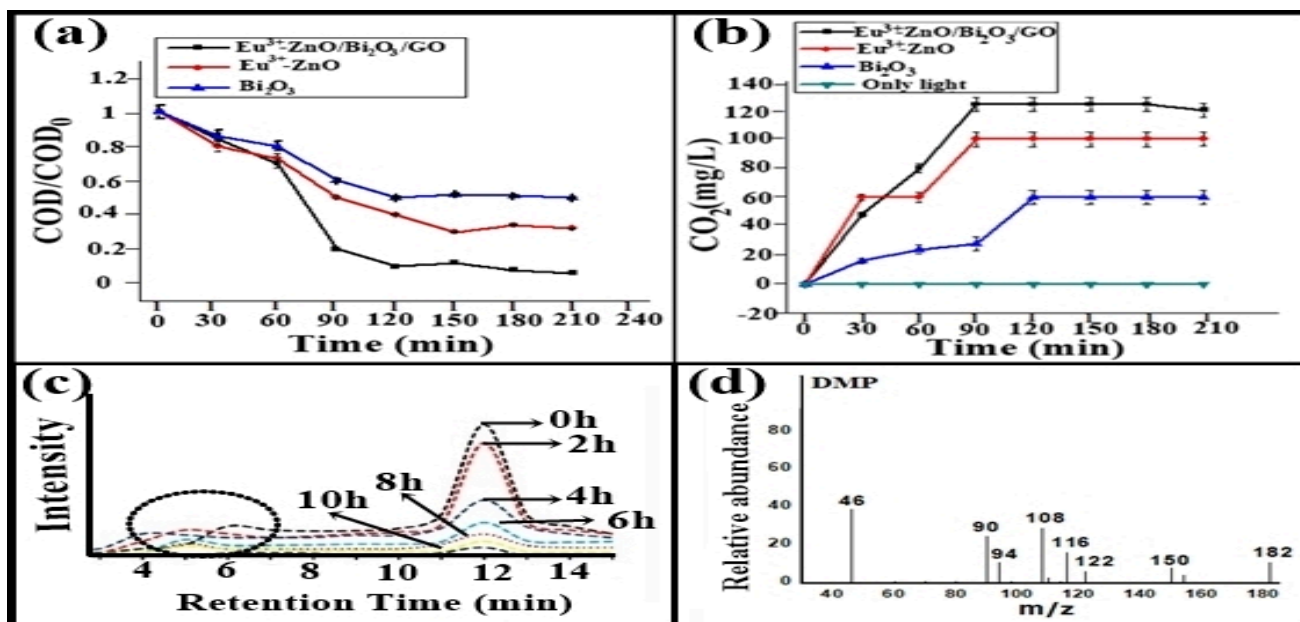


Fig. 8. (a) COD removal (b) CO₂ estimation, (c) HPLC and (d) LCMS analysis of Eu³⁺ ZnO/Bi₂O₃/GO [Reaction conditions: initial reaction pH= 4.0; [DMP] = 1 × 10⁻³ mol dm⁻³; [photocatalyst] = 50 mg/100 mL; and intensity of light = 750 lx].

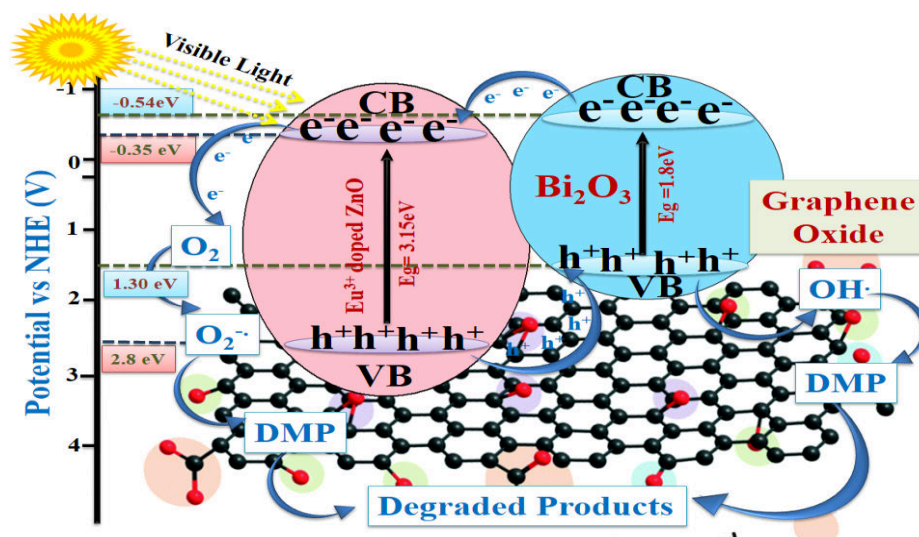


Fig. 9. Mechanistic view for enhanced photocatalytic degradation of DMP

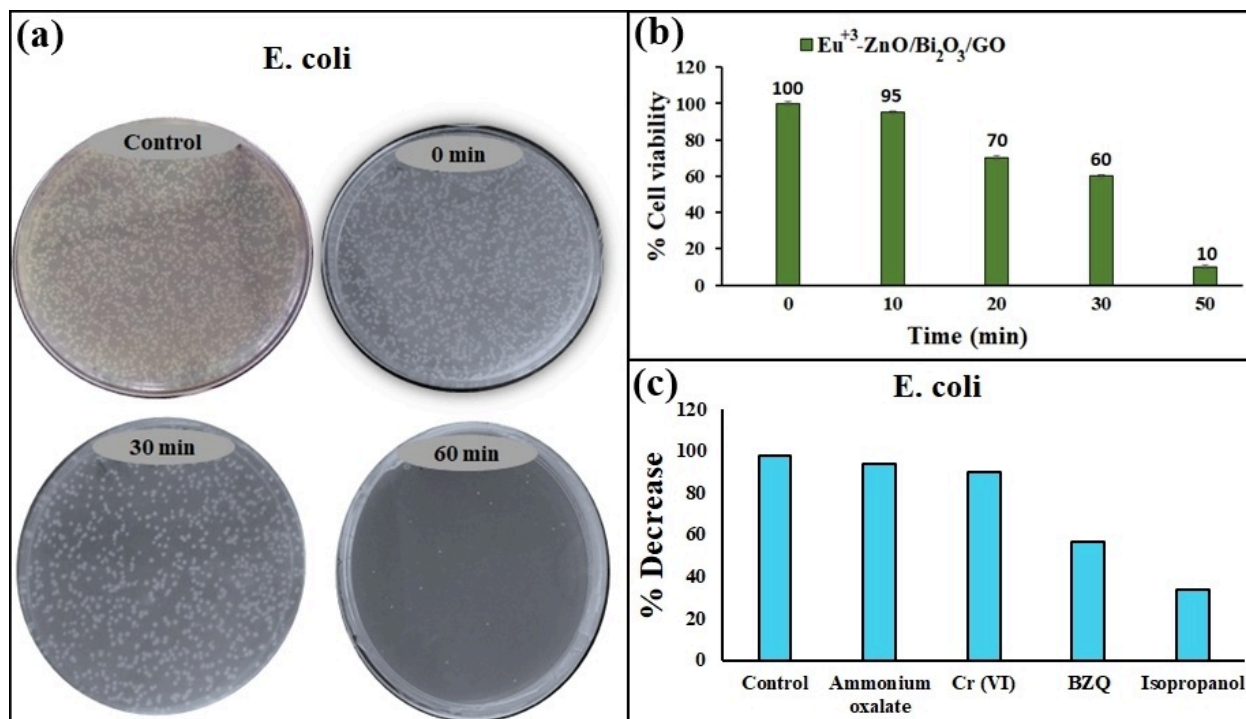


Fig. 10. (a) Antibacterial study of Eu³⁺-ZnO/Bi₂O₃/GO against *E. coli* by CFU method in the presence of visible light, (b) percentage cell viability under different time of light exposure of

Eu⁺³-ZnO/Bi₂O₃/GO, (c) Effect of radical scavengers on photocatalytic antibacterial activity of Eu⁺³-ZnO/Bi₂O₃/GO. [Reaction time = 1 h; light intensity = 750 lx; (c) Scavenger concentration: 0.5mM of isopropanol, benzoquinone, ammonium oxalate, Cr(VI) for 0.5 mg/ml of Eu⁺³-ZnO/Bi₂O₃/GO under solar light irradiation].

Supplementary Figures (SSSCIE_2020_148R2)

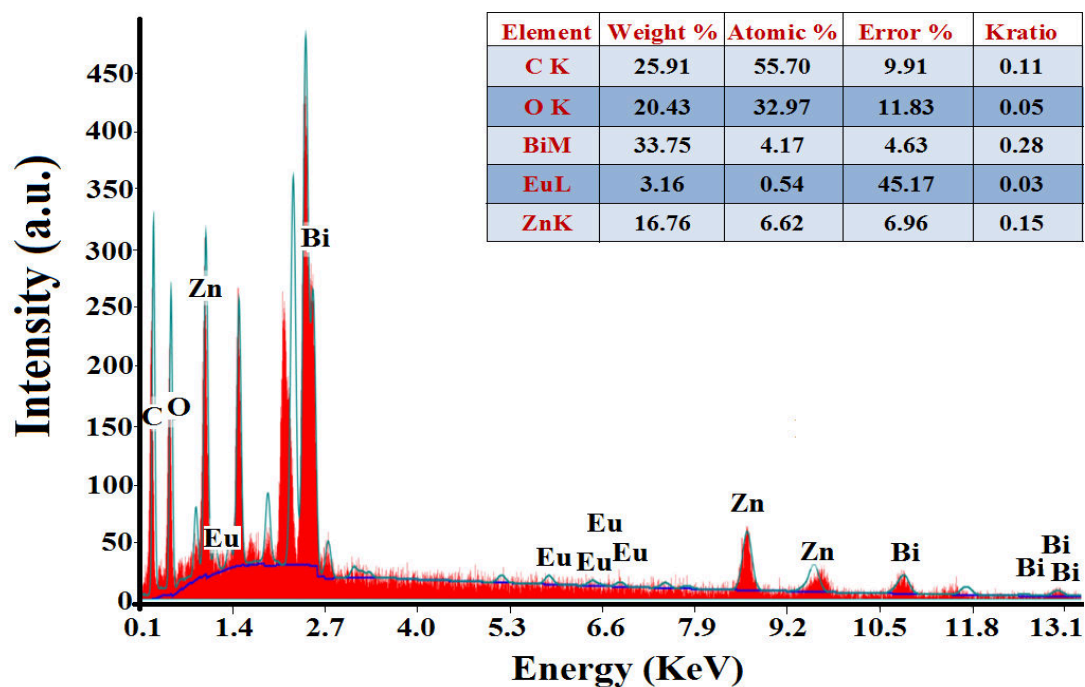


Fig. S1. EDX spectrum of $\text{Eu}^{3+}\text{-ZnO/Bi}_2\text{O}_3\text{/GO}$ nanocomposite.

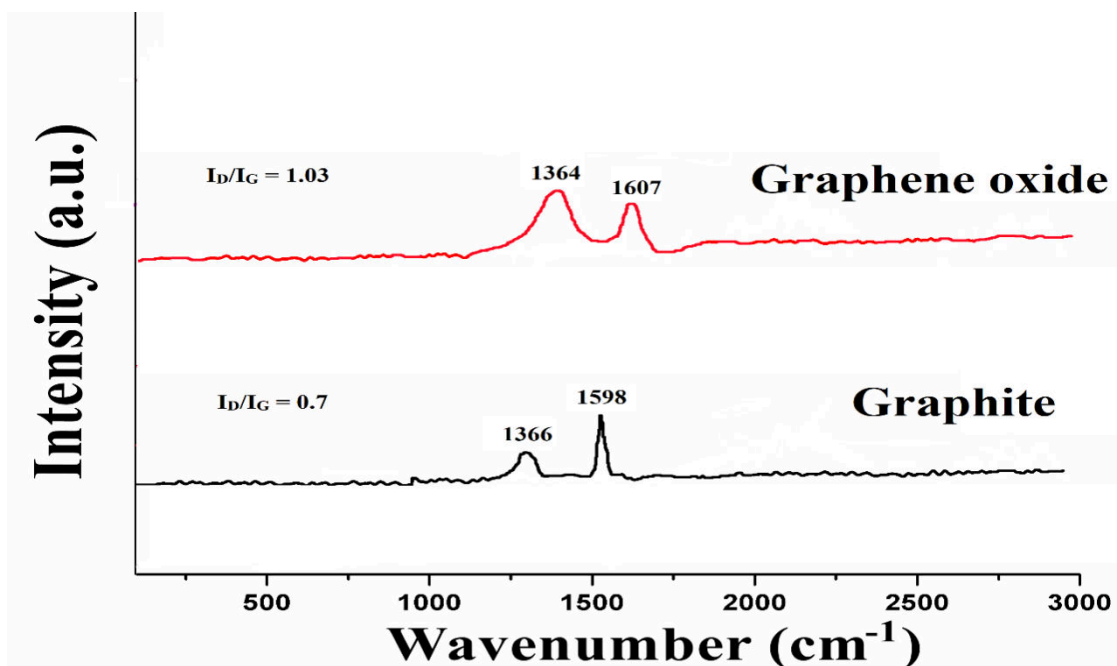


Fig. S2. Raman analysis of Graphite and graphene oxide.

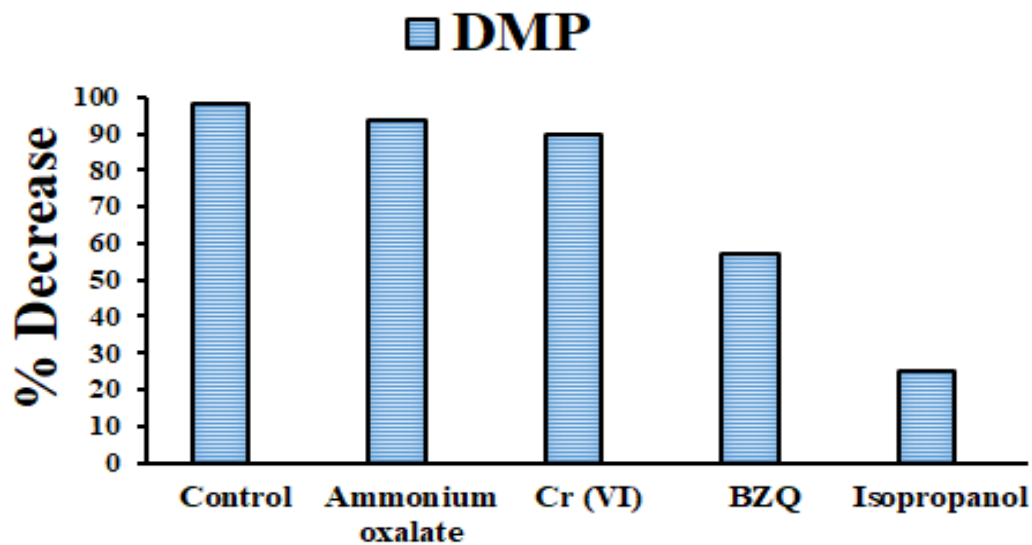


Fig. S3. Effect of radical scavengers on DMP degradation by using Eu^{3+} -ZnO/ Bi_2O_3 /GO.

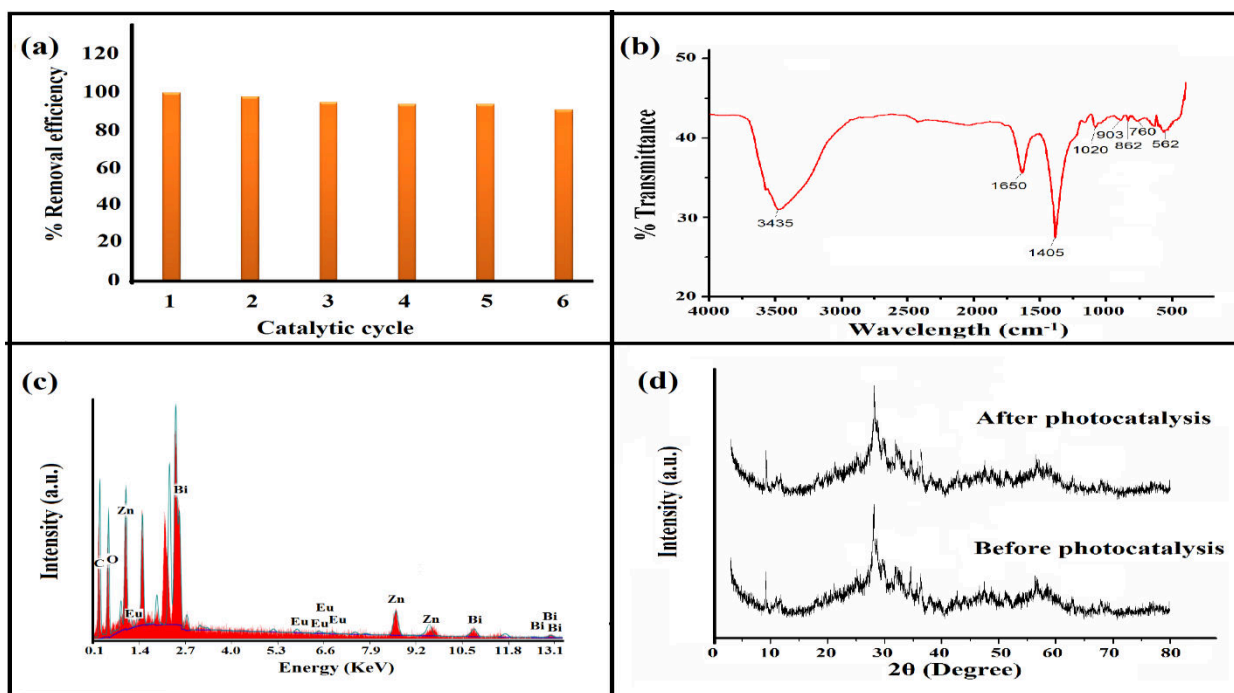


Fig. S4. (a) Recycle efficiency of Eu^{3+} -ZnO/ Bi_2O_3 /GO (b) FTIR spectra of Eu^{3+} -ZnO/ Bi_2O_3 /GO after photocatalysis (c) EDX analysis of Eu^{3+} -ZnO/ Bi_2O_3 /GO after photocatalysis and (d) XRD pattern of Eu^{3+} -ZnO/ Bi_2O_3 /GO before and after photocatalysis [Reaction conditions: initial reaction pH= 4.0; [DMP] = 1×10^{-3} mol dm^{-3} ; [photocatalyst] = 50 mg/100 mL; and intensity of light = 750 lx].

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Synthesis of Eu^{3+} doped ZnO heterojunction photocatalyst on graphene oxide sheets for visible light-assisted degradation of 2,4-dimethyl phenol and bacteria killing

Shandilya, Pooja

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