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Graphene oxide–metal oxide nanocomposites: fabrication, characterization and removal of cationic rhodamine B dye†

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The fabrication and characterization of graphene oxide (GO) nanosheets and their reaction with Fe_3O_4 and ZrO_2 metal oxides to form two nanocomposites, namely graphene oxide–iron oxide ($\text{GO-Fe}_3\text{O}_4$) and graphene oxide–iron oxide–zirconium oxide ($\text{GO-Fe}_3\text{O}_4@\text{ZrO}_2$), have been examined. The fabricated nanocomposites were examined using different techniques, e.g. transmission electron microscopy, X-ray diffraction, zeta potential measurement and Fourier transform infrared spectroscopy. Compared to GO, the newly fabricated $\text{GO-Fe}_3\text{O}_4$ and $\text{GO-Fe}_3\text{O}_4@\text{ZrO}_2$ nanocomposites have the advantage of smaller band gaps, which result in increased adsorption capacity and photocatalytic effects. The results also showed the great effect of the examined GO–metal oxide nanocomposites on the decomposition of cationic rhodamine B dye, as indicated by steady-state absorption and fluorescence, time correlated single photon counting and nanosecond laser photolysis techniques. The antibacterial activity of the fabricated GO and GO–metal oxides has been studied against Gram-positive and Gram-negative bacteria.

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1. Introduction

Water pollution has been a vital environmental issue for the last few decades.^{1,2} Industrial organic dyes and heavy metals are considered to be the most important sources of water pollution.^{1,2} For this purpose, membrane technologies based on nanomaterials have been extensively examined for water purification and desalination over the last few decades. Among the utilized nanomaterials in water treatment, graphene oxide (GO), with its fascinating 2D carbon framework with a honeycomb-like structure, has attracted much attention in the last decade for its unique specific surface area, high charge carrier mobility and electron conductivity.^{3–5}

Recently, there has been great interest in fabricating and utilizing novel graphene oxide–metal oxide nanocomposites for environmental remediation by the degradation and elimination of toxic organic contaminants and heavy metals, and for antibacterial applications.^{6–8} Compared with graphene oxide, graphene oxide–metal oxide nanocomposites show a unique structural morphology and photochemical properties which render them good candidates for water treatment projects.^{9–11}

Among the utilized metal oxides, zero valent iron (ZVI) has been widely used for separating water from harmful heavy metals^{12,13} and organic species.^{14–22} The fabricated graphene oxide–iron oxide nanocomposites showed high efficiency in the removal of tiny concentrations of chromium ions from water and industrial waste water.^{23–28} In addition, the zirconium oxide (ZrO_2) nanoparticles showed unique electrochemical properties when combined with graphene oxide.^{29–36} Compared with the widely used TiO_2 , zirconium oxide (ZrO_2) is less expensive and insoluble in water. According to the preparation method, ZrO_2 exhibited a band gap ranging from 3 to 5 eV. Such a wide band gap renders ZrO_2 a promising photocatalyst for the production of hydrogen in water decomposition.³⁷

Taking these unique properties into consideration, we report herein the fabrication and characterization of GO, graphene oxide–iron oxide ($\text{GO-Fe}_3\text{O}_4$) and graphene oxide–iron oxide–zirconium oxide ($\text{GO-Fe}_3\text{O}_4@\text{ZrO}_2$). This combination of graphene oxide with $\text{Fe}_3\text{O}_4\text{-ZrO}_2$ metal oxide and its application in the degradation of organic species is rare in the literature. Photocatalytic studies of the examined nanocomposites on the degradation of cationic rhodamine B dye (RhB) have been examined in detail using TEM, XRD, FTIR, steady-state absorption and fluorescence and nanosecond laser flash photolysis techniques.

2. Experimental section

2.1. Chemicals and materials

All of the chemicals and reagents were from Aldrich Chemicals and used without any further purification.

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2.2. Characterization techniques

UV-vis absorption and fluorescence measurements were taken using a Shimadzu UV-2450 spectrophotometer and a Shimadzu RF-5301PC spectrofluorometer, respectively. Picosecond time-resolved fluorescence lifetimes were recorded on a Fluo300 (PicoQuant, Germany). Lifetimes were evaluated using FluoFit software, which was attached to the equipment. Nanosecond transient absorption studies were recorded using a nanosecond laser flash photolysis technique (LP980, Edinburgh Instruments, UK). The instrument was connected with a tunable laser source (NT342B-10, Ekspla). Fourier transform infrared (FT-IR) spectra were obtained using a JASCO spectrometer 4100, using a KBr pellet technique. The X-ray diffraction (XRD) measurements were conducted using a Shimadzu 6000 model with Cu K α ($\lambda = 1.5418 \text{ \AA}$) as the incident radiation. Transmission electron microscopy (TEM) images were taken using a JEOL 2010 microscope operating under a maximum acceleration voltage of 200 kV. Zeta potential results were obtained using a Brookhaven zeta potential/particle size analyzer.

2.3. Photocatalytic activity

The photocatalytic activities of GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ nanocomposites were evaluated for the adsorption of dyes, such as rhodamine B, without light and their efficiency for the degradation of rhodamine B (RhB) dye under visible light irradiation (simulator of sunlight; 150 W Xenon lamp, $\lambda > 420 \text{ nm}$). $1 \times 10^{-4} \text{ M}$ RhB dye and 2 mg nanocomposite were dispersed in 10 ml H₂O. Measurements were performed every 5 min after exposure to visible light. This experiment was repeated using UV light at 256 nm. OH \cdot radicals were generated more during the reaction, which can result in the rapid degradation of RhB dye molecules.³⁸ The photo degradation of RhB by graphene oxide-metal oxide nanocomposites was analyzed using steady-state absorbance and fluorescence, time-resolved fluorescence and nanosecond laser photolysis techniques.

2.4. Synthesis of nanocomposites based on graphene oxide (GO)

2.4.1 Synthesis of the GO nanostructure. Water dispersions and solid graphite oxide were prepared from natural graphite powder using a modified Hummers and Offeman's method.^{39,40} In a typical reaction, 8 g graphite flakes (Sigma Aldrich), 8 g NH₄NO₃ and 368 ml 98% (w/w) H₂SO₄ were mixed under stirring in an ice bath for 1 h. Then, 40 g KMnO₄ was slowly added to the mixture in the ice bath until the solution became green. The beaker was placed in a water bath at 35 °C and the solution was stirred for about 1 h to form a thick paste. 640 ml high-purity water was then added to the formed paste and stirred at 90 °C for 1 h. The formed solution turned brown. With the slow addition of 48 ml H₂O₂ (30%), the color changed from dark brown to yellow. The solid was filtered, washed with 10% HCl aqueous solution (3.2 L) to remove metal ions and washed with water several times. The resulting graphene oxide was dried at 45 °C for 24 h. The crystalline structure of the GO powder was identified using an XRD technique. Refinement was carried out

from a starting model based on information given in the Inorganic Crystal Structure Database (ICSD). The morphology of the synthesized GO was examined using transmission electron microscopy (TEM, JEOL 2100) under a maximum acceleration voltage of 200 kV.

2.4.2 Synthesis of the GO-Fe₃O₄@ZrO₂ nanocomposite. 0.04 g GO sheets were dispersed in 100 ml water for around 30 minutes. Then, 100 ml of the prepared solution (ZrOCl₂·8H₂O, 0.064 M FeCl₂·4H₂O and 0.129 M FeCl₃·6H₂O) was added. To the resulting mixture, KOH solution in ethanol (1 M, 90 °C) was added dropwise under stirring for 1 hour at 100 °C. At the end, we obtained a black precipitate that was harvested using centrifugation and washed with both water and ethanol. The formed GO-Fe₃O₄@ZrO₂ nanocomposite was dried under vacuum at 45 °C.

2.4.3 Synthesis of the GO-Fe₃O₄ nanocomposite. 0.04 g GO sheets were dispersed in 100 ml water for 30 minutes using ultrasound and 100 ml aqueous solution (FeCl₂·4H₂O and FeCl₃·6H₂O) was then added. To this mixture, KOH in ethanol (1 M) was added dropwise under stirring for 1 h at 100 °C. The obtained black precipitate (GO-Fe₃O₄) was harvested using centrifugation and washed with water and ethanol. The GO-Fe₃O₄ nanocomposite was dried under vacuum at 45 °C.

3. Results and discussion

3.1. Characterization of GO, GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ nanocomposites

Fig. 1 and S1† show the XRD patterns of the fabricated GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ nanocomposites, in addition to those of pure graphite powder, GO, Fe₃O₄ and ZrO₂. The XRD pattern of GO exhibited a diffraction peak at 10.9°^{41,42} which is significantly larger than that found in the XRD pattern of pure graphite (26.0°). This can be rationalized by the presence of oxygenated functional groups on the carbon sheets of GO.^{43,44} XRD analysis of GO-Fe₃O₄ showed diffraction peaks at 29.6°, 35.3°, 43.5°, 56.5° and 63.5°⁴⁵ while GO-Fe₃O₄@ZrO₂ showed peaks at 44.0°, 64.2° and 77.3°, as observed from the database, and a single phase with a monoclinic structure was formed. The main crystallite sizes of the GO and metal oxide nanocomposites were calculated based on the Debye-Scherrer formula (eqn (1)).⁴⁶

$$D = K\lambda/\beta \cos \theta \quad (1)$$

where K is a constant representing the shape factor (~ 0.9), λ is the wavelength of the X-ray source (1.5405 Å), β is the full width at half maximum of the diffraction peak and θ is the angular position of the peak. The average crystallite sizes of GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ were determined to be 8 and 10 nm, respectively.

Fig. 2 shows the TEM images of the fabricated GO, GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ nanocomposites with different magnifications. From the images, GO appeared as nano-sheets, while GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ appeared as nano-spherical shapes. The samples were analyzed using EDX with uniform particle morphology (Fig. S2†). The average size of the observed



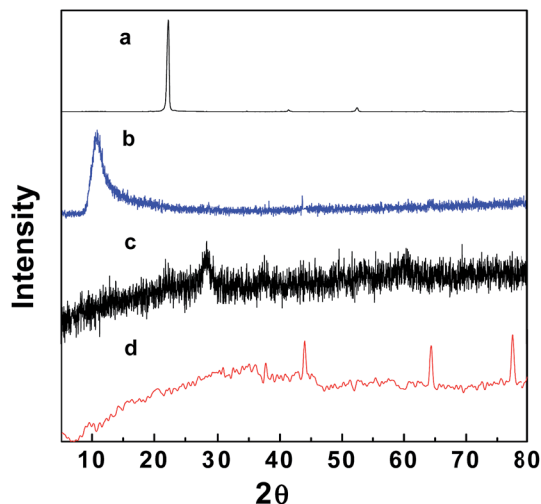


Fig. 1 XRD patterns of: (a) graphite, (b) graphene oxide, (c) GO-Fe₃O₄ and (d) GO-Fe₃O₄@ZrO₂.

metal oxides on the surface of graphene oxide was ~8 to 10 nm, which is in good agreement with that observed using XRD.

The absorption spectra of fabricated GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂ were recorded in water, as shown in Fig S3.† The absorption spectra exhibited an absorption peak with a maximum at ~228 nm, which was attributed to the $\pi \rightarrow \pi^*$ transitions of the aromatic C=C bonds.^{47,48} The absorption

bands at 390 and 360 nm correspond to GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, respectively. The band gap values of the nanocomposites were determined using eqn (2):^{49,50}

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where α is the absorption coefficient, ν is the frequency of light, h is Planck's constant, $h\nu$ is the photon energy, A is a proportionality constant, E_g is the band gap and $n = 1/2$ for the direct transitions.⁵¹ From the plot of $(\alpha h\nu)^2$ versus $h\nu$ (the insets of Fig. S3†), the band gaps for GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ were found to be 4.00, 3.20 and 3.66 eV, respectively.

A zeta potential technique has been used to predict the long term stability of the nanoparticles in solution and to understand the state of the nanoparticle surface. As shown in Fig. 3, the spectra show negatively charged particles for GO (−33), GO-Fe₃O₄@ZrO₂ (−41) and GO-Fe₃O₄ (−52). These negative values are related to the stability of the colloidal dispersions in water.

Fig. 4 shows a thermogravimetric analysis (TGA) diagram for GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ in the range of 25–700 °C. As seen from the TGA steps, the diagram shows that the decomposition steps of GO with changing temperature match the decomposition steps of GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, suggesting the successful loading of the metal oxides over the GO surface.

Fig. 5 shows the FTIR spectra of the GO, GO-Fe₃O₄-ZrO₂ and GO-Fe₃O₄ nanocomposites. The peaks observed at 508 cm^{−1} correspond to the characteristic stretching vibrations of the

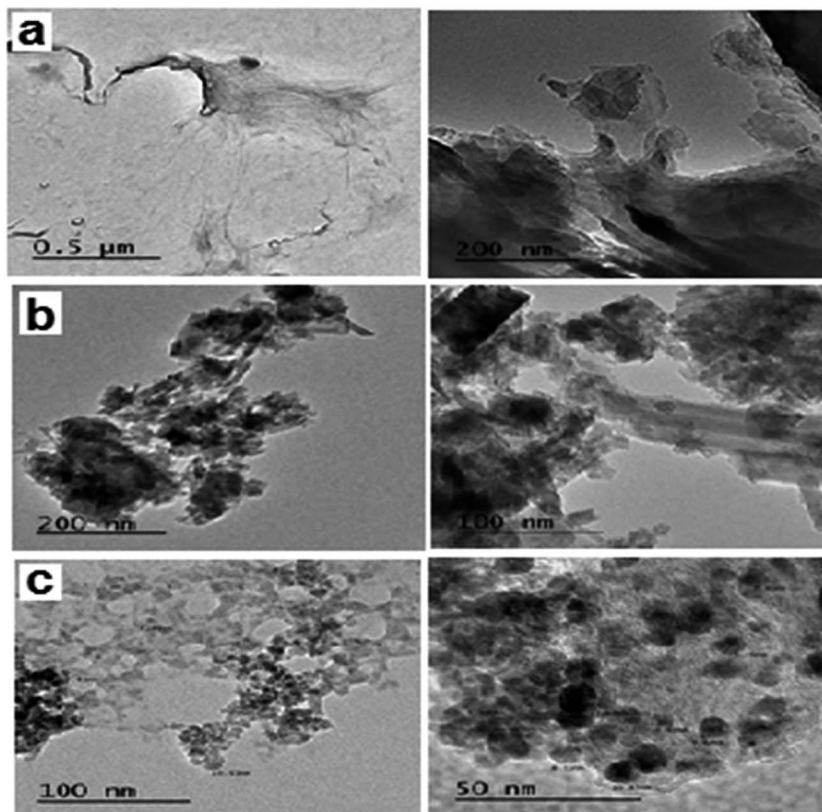


Fig. 2 TEM images of: (a) GO, (b) GO-Fe₃O₄@ZrO₂ and (c) GO-Fe₃O₄.



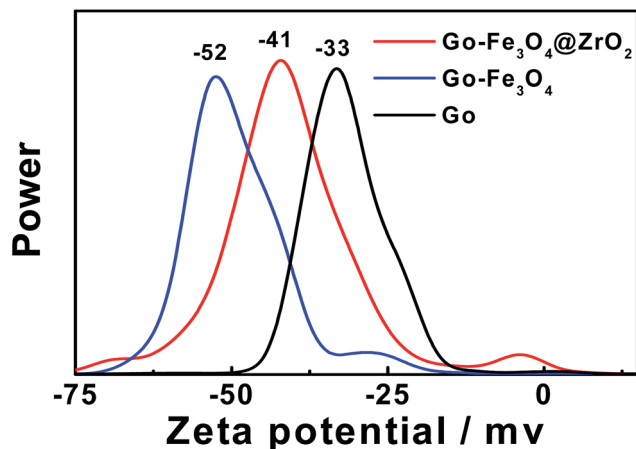


Fig. 3 The zeta potentials of GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ in water.

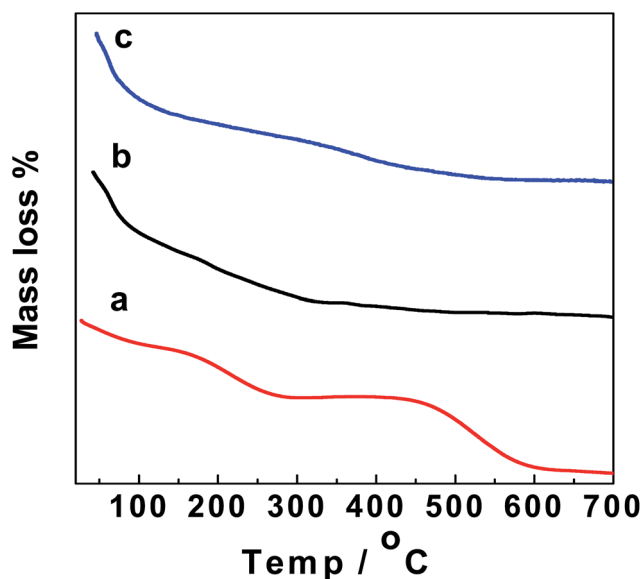


Fig. 4 TGA of: (a) GO, (b) GO-Fe₃O₄@ZrO₂ and (c) GO-Fe₃O₄.

C–O bond in GO nanoparticles.⁵² The characteristic peaks of GO vibration were recorded at 984 to 506 cm⁻¹. The broad absorption band observed at ~3455 cm⁻¹ corresponds to the stretching vibration of the O–H band of physically absorbed water.⁵³ The recorded peaks at 573 cm⁻¹ (for GO-Fe₃O₄@ZrO₂) and 587 cm⁻¹ (for GO-Fe₃O₄) correspond to the characteristic vibrations of the M–O bond.⁵⁴

3.2. Photocatalytic study of rhodamine B

3.2.1 Photocatalytic study of RhB under UV irradiation.

Fig. 6 and S4† show the absorption spectra of the photocatalytic degradation of RhB using GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ nanocomposites under UV irradiation at 256 nm. As shown, the characteristic absorption band of RhB dye was recorded at 554 nm. With increasing irradiation time, the absorption band of RhB at 554 nm is greatly decreased and red-shifted in the

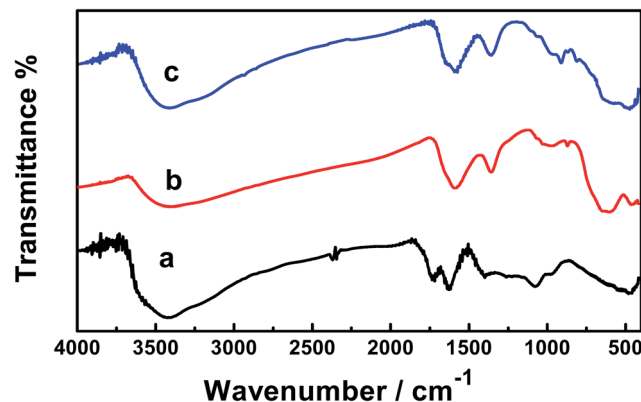


Fig. 5 FT-IR spectra of: (a) GO, (b) GO-Fe₃O₄ and (c) GO-Fe₃O₄@ZrO₂.

presence of GO nanocomposites. In a control experiment, the absorption band of RhB at 554 nm showed no significant changes under irradiation in the absence of GO nanocomposites (Fig. S5†).

The observed rate constants for the photocatalytic degradation of RhB with GO nanocomposites were determined using eqn (3):

$$\ln(C/C_0) = -k_{\text{obs}}t \quad (3)$$

where C_0 (mg l⁻¹) is the initial dye concentration and k_{obs} depends on the initial dye concentration (C_0).^{55,56} From the linear plot of $\ln(C/C_0)$ with irradiation time, the degradation rates (k) of RhB in the presence of GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ were determined to be 0.0479, 0.0997 and 0.05328 min⁻¹, respectively. This finding indicates a higher rate constant in the case of the GO-Fe₃O₄@ZrO₂ nanocomposite compared to that of GO.

The efficiency of the photocatalytic degradation process was determined using eqn (4):

$$D (\%) = [A(\text{RhB})_0 - A(\text{RhB})_t] / A(\text{RhB})_0 \quad (4)$$

where $A(\text{RhB})_0$ and $A(\text{RhB})_t$ are the absorbance changes of RhB at 554 nm with time, in the dark and under light irradiation, respectively.^{57,58} Fig. 7 illustrates that 80% of the RhB dye was degraded in the presence of GO within around 90 minutes. This percentage was increased to 90% and 98% of RhB in the presence of Fe₃O₄ and Fe₃O₄@ZrO₂, respectively, suggesting the significant effect of the examined metal oxides (Fe₃O₄ and Fe₃O₄@ZrO₂) in increasing the photocatalytic degradation of RhB/GO composites. This high efficiency for RhB degradation by GO-Fe₃O₄@ZrO₂ (98%) is found to be considerably higher compared to that reported for TiO₂-rGO (81%).⁵⁹ The proposed mechanism for the photodegradation of cationic RhB dye using GO-metal oxide nanocomposites is shown in Scheme 1,⁶⁰⁻⁶³ where the surface of GO has the ability to receive electrons from the high conduction band (CB) of ZrO₂, which reacts with oxygen to produce superoxide anion radicals (O₂^{•-}) and OH[•] radicals, leading to the rapid oxidation of the organic molecules.



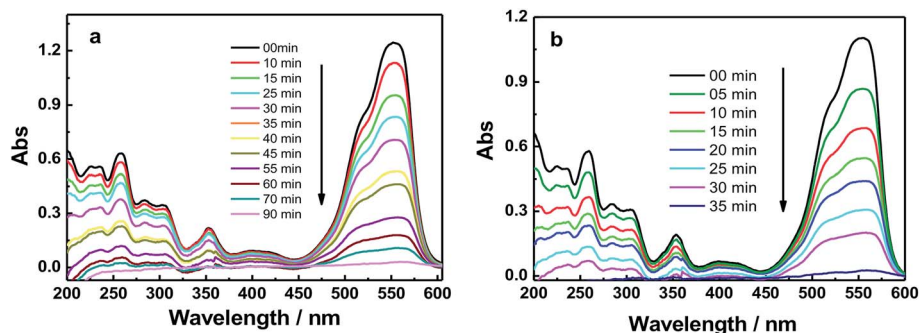


Fig. 6 UV-absorbance spectra of RhB in the presence of: (a) GO and (b) GO-Fe₃O₄@ZrO₂ in water at the indicated time intervals under UV irradiation at 256 nm.

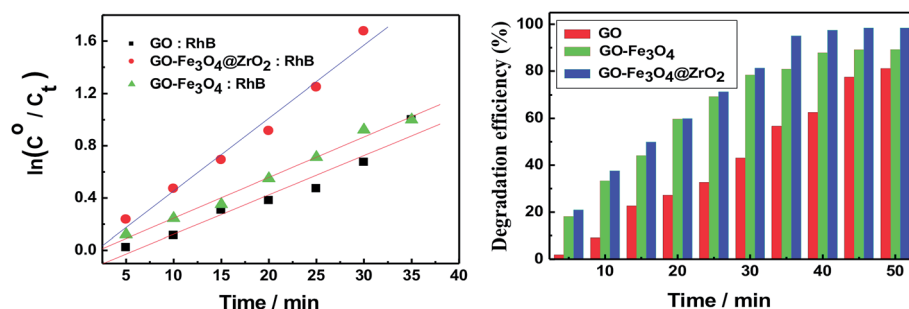


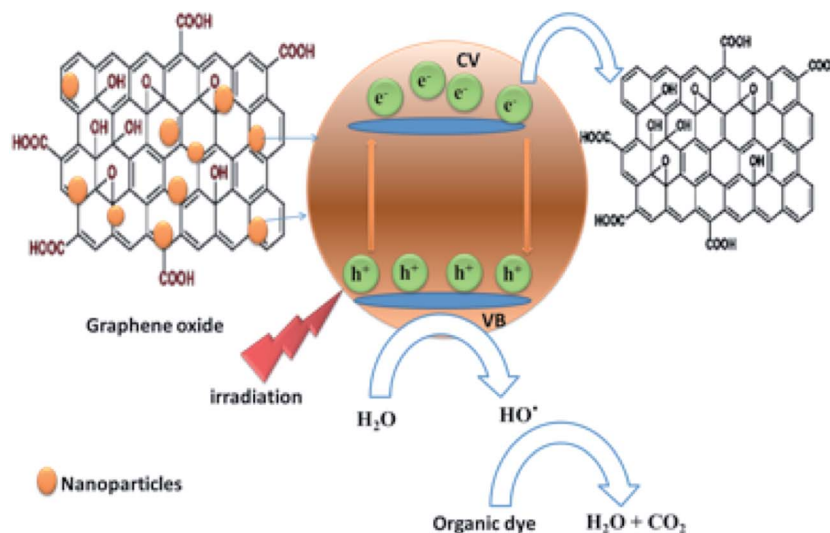
Fig. 7 (Left) Pseudo-first-order plots for the photodegradation of RhB with GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, with increasing irradiation time. (Right) The photo-degradation efficiency (%) of RhB with GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, with changing irradiation time ($\lambda = 256$ nm).

3.2.2 Photocatalytic study of RhB under a sunlight simulator. The photocatalytic degradation of RhB was examined with GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ nanocomposites under visible light irradiation (sunlight simulator, UXL-151D-O, Xe 150 W, $\lambda > 420$ nm). As shown in Fig. 8 and S6,[†] the results showed no photocatalytic activity from the GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ nanocomposites toward RhB. On the other hand,

GO showed a low efficiency that may be explained by the adsorption process of the dye over the GO surface.

3.3. Adsorption process of RhB on the surface of GO nanocomposites

Dye molecules were entrapped on the surface of GO and GO-nanocomposites in aqueous solution. From Fig. 9 and S7,[†]



Scheme 1 The proposed mechanism for the photodegradation of cationic dye by graphene oxide-metal oxide nanocomposites.



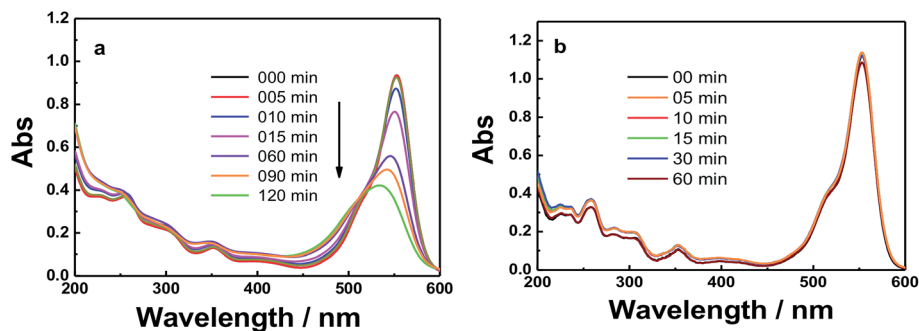


Fig. 8 Absorbance spectra of RhB dye in the presence of: (a) GO and (b) GO-Fe₃O₄@ZrO₂ at the indicated time intervals under irradiation.

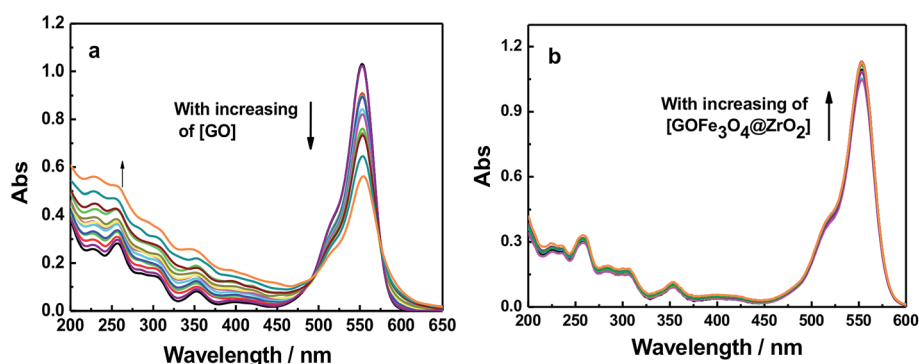


Fig. 9 Absorption spectra of RhB (1.7×10^{-5} M) with different concentrations of (a) GO and (b) GO-Fe₃O₄@ZrO₂ in water.

one can see that the absorption band of RhB at 550 nm decreased gradually with increasing amounts of GO (0.2 g l^{-1}). For GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂, different features were observed where the absorption band of RhB was considerably increased with increasing amounts of GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂. The fluorescence measurements showed the same trend as observed for the absorption studies. As seen in Fig. 10 and S8,[†] the fluorescence maximum band of RhB at 579 nm was significantly decreased in the presence of GO, but not in the presence of GO-Fe₃O₄ or GO-Fe₃O₄@ZrO₂. The adsorption process could be explained by the dye binding with GO through hydrogen bonding, and electrostatic interactions.^{64,65}

3.4. Laser studies of the photodegradation process of RhB by GO composites

Fluorescence lifetime measurements showed the same trend as observed for the fluorescence measurements (Fig. 11 and S9[†]). Upon exciting RhB with 470 nm laser light, the fluorescence decay-time profile of the singlet-excited state of RhB (¹RhB*) decayed with a monoexponential decay, from which the fluorescence lifetime of ¹RhB* was determined to be 1.7 ns. With increasing amounts of GO, the substantial quenching of the fluorescence lifetime was considerable and the decay could be fitted satisfactorily to a biexponential decay. The fast decaying component had a lifetime of 120 ps (58%), while the slow decaying component had a lifetime of 1.9 ns (42%). The lifetime

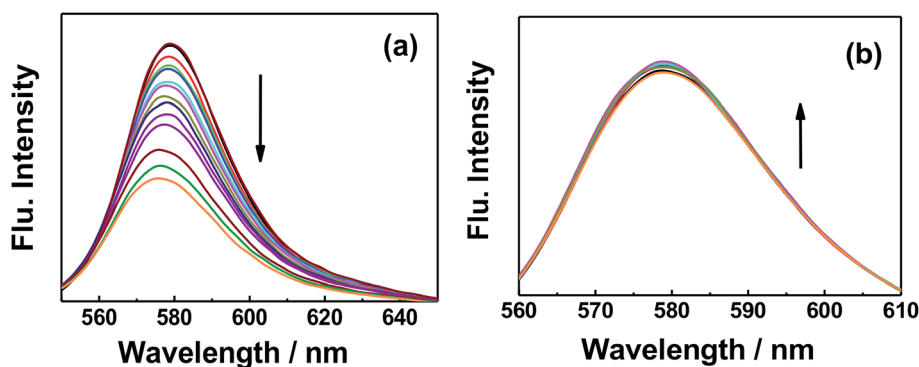


Fig. 10 Fluorescence changes of RhB (1.7×10^{-5} M) with the addition of different concentrations of (a) GO and (b) GO-Fe₃O₄@ZrO₂ in water.



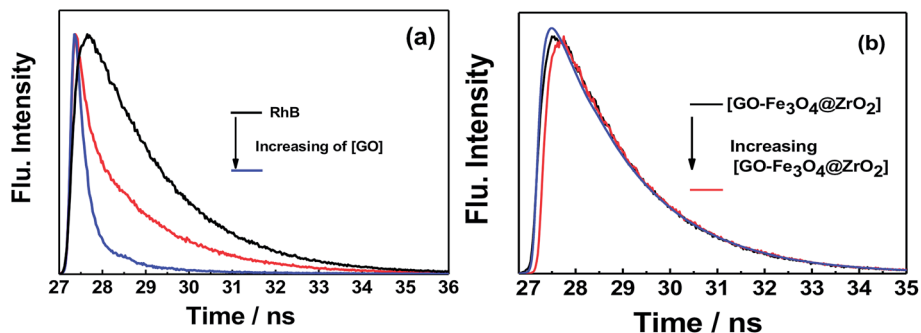


Fig. 11 Fluorescence decay profiles of the singlet-excited state of RhB in the presence of (a) GO and (b) GO-Fe₃O₄@ZrO₂ in water; $\lambda_{\text{ex}} = 420 \text{ nm}$; $\lambda_{\text{em}} = 580 \text{ nm}$.

of the slow decaying component is close to that of the free RhB. Based on the change in the recorded fluorescence lifetimes of RhB in the absence and presence of GO, the rate and efficiency of the quenching process were determined to be $7.74 \times 10^9 \text{ s}^{-1}$ and 93%, respectively.^{66–68} For GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂, it was observed that the fluorescence lifetime of ¹RhB* was kept almost the same with increasing concentrations of both GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂. These measurements are in good agreement with the steady-state fluorescence measurements. These measurements suggest a higher adsorption of RhB over the surface of GO, but not GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂.

Nanosecond transient absorption spectroscopy was used to obtain further insight into the excited state interactions of RhB with GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, to corroborate the observed interaction by both steady-state and time-resolved fluorescence techniques. To achieve this, RhB dye was probed with excitation at $\lambda = 550 \text{ nm}$ in an oxygen-free water solution. The nanosecond transient absorption spectrum of RhB in water was dominated by pronounced bleaching between 540 and 600 nm, which was due to the depletion of the singlet ground state (Fig. 12 and S10†). In the case of RhB-GO, it was observed that the singlet state of RhB recovered quickly with increasing

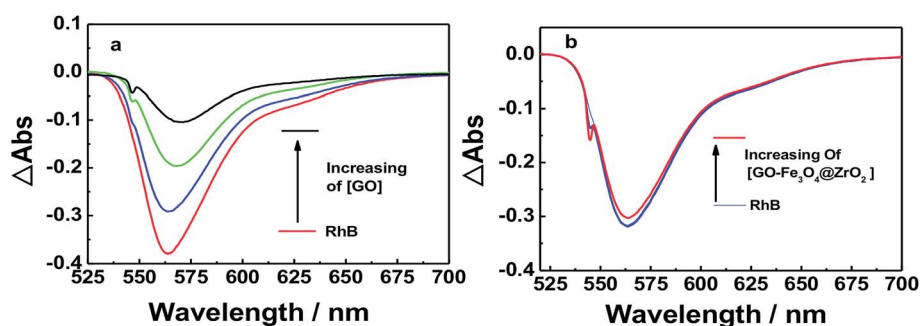


Fig. 12 Nanosecond transient absorption spectra of RhB dye in the presence of (a) GO and (b) GO-Fe₃O₄@ZrO₂ in an oxygen-free water solution; $\lambda_{\text{ex}} = 550 \text{ nm}$.

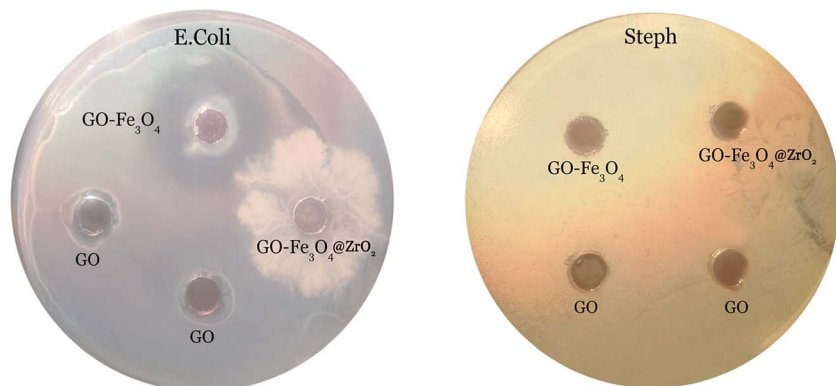


Fig. 13 Zone of inhibition tests against *E. Coli* and *Steph* strains in the presence of GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄, at a concentration of 0.5 mg ml^{-1} .



amounts of GO, confirming the quenching of the singlet state of RhB by the GO. In the case of RhB with GO-Fe₃O₄@ZrO₂, the intensity of the ground state bleaching remained almost unchanged with increasing amounts of GO-Fe₃O₄@ZrO₂, suggesting that there was no interaction between RhB and Fe₃O₄@ZrO₂.

3.5. Antibacterial activity of GO and nanocomposites

Antibacterial activity was tested against Gram-positive and Gram-negative bacteria using BHI agar plates and the agar diffusion method. The GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ samples were evaluated. The resulting antibacterial effect could be rationalized by the diffusion of GO, Fe₃O₄@ZrO₂ and GO-Fe₃O₄ over the agar surface, preventing bacterial growth in the specific area occupied by the nanocomposite. As seen from Fig. 13, we observed only a small zone of inhibition around GO, indicating limited bacterial toxicity against *E. coli*.⁶⁹ In contrast, the GO-Fe₃O₄ sample showed a significant inhibitory effect against *E. coli*. The presence of clear zones on the BHI agar surface proves that the GO-Fe₃O₄ composite was able to inhibit the growth of *E. coli*, whereas no antibacterial activity was detected for raw GO and GO-Fe₃O₄@ZrO₂ against *E. coli*. The GO, Fe₃O₄@ZrO₂ and GO-Fe₃O₄ samples showed no antibacterial activity against *Staph.* The experiment was conducted to characterize bacterial killing with concentration (0.5 mg ml⁻¹) and the cellular viability was measured after 24 h exposure time.

4. Conclusion

Novel nanocomposites of graphene oxide with iron oxide (GO-Fe₃O₄) and iron oxide-zirconium oxide (GO-Fe₃O₄@ZrO₂) were fabricated and characterized using XRD, TGA, FTIR, and TEM techniques. From the optical absorption measurements, the energy band gap values were found to be 4.00, 3.66, and 3.20 eV for GO, GO-Fe₃O₄ and GO-Fe₃O₄@ZrO₂, respectively. All of the steady-state absorption and fluorescence, time-resolved fluorescence and nanosecond transient absorption spectroscopy results confirmed that RhB is efficiently adsorbed over the surface of graphene oxide (~93%). Different features were observed in the presence of metal oxides (Fe₃O₄ and Fe₃O₄@ZrO₂) over the surface of graphene oxide. GO and Fe₃O₄@ZrO₂ had a small zone of inhibition against *E. coli* and in contrast, the GO-Fe₃O₄ sample showed a significant inhibitory effect against *E. coli*. GO, GO-Fe₃O₄@ZrO₂ and GO-Fe₃O₄ showed no antibacterial activity against *Staph.*

Conflicts of interest

The authors declare no conflict of interest.

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