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Photothermal effect: an important aspect for the enhancement of photocatalytic activity under illumination by NIR radiation

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Abstract

A key auxiliary role of photothermal effect (PTE) in the enhancement of photocatalytic activity under illumination to near-infrared (NIR) radiations has been experimentally revealed. It was found that the photoexcitation of electrons, required for the process of photocatalysis does not occur in presence of NIR radiations alone without the support of both UV and visible radiations. Herein, a binary heterogeneous nanophotocatalyst, GR-ZnO was fabricated by a novel approach using hydrothermal process. In which ZnO nanotrapezoids were deposited over the surfaces of graphene nanosheets. In the reported unique approach, reduction of graphene oxide to graphene has been accomplished using water by an entirely alternative mechanism compared to traditional reduction processes those employ the hazardous reducing agents. Thus produced GR-ZnO photocatalyst has exhibited the excellence in rapid degradation of industrially voluntarily employing perilous dye, methyl orange. It is explored that PTE is mainly responsible for the rapid degradation of methyl orange transpired under illumination to NIR laser. Further, it has been established that PTE could not emerge with NIR radiations alone without the support of both UV and visible radiations. In consideration of its importance, PTE of GR-ZnO nanocatalyst has been revealed and compared with its individual components, *viz.*, graphene and ZnO. Moreover, the photothermal conversion efficiency of GR-ZnO nanocatalyst was evaluated. Overall, the excellent catalytic activity found in GR-ZnO nanocatalyst was accounted for its decreased band gap, transpired by hybridization of ZnO with graphene could efficiently prevent the recombination of photo-generated charge carriers. In addition, admired catalytic activity of GR-ZnO nanocatalyst was attributed to improved optical absorption and enhancement in the adsorption affinity to methyl orange molecules.

Graphical Abstract:

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INTRODUCTION

Recently nanostructured photocatalysts have received great deal of attention owing to their inspired degradation of hazardous organic pollutants.^{1–5} The nanostructured photocatalysts have been proposed as better alternative to conventional methods *viz.*, adsorption, biological degradation, chlorination, and ozonation used in removal of toxic chemicals or dyes from industrial waste water.⁶ Among the nanostructured photocatalysts, agents developed on basis of graphene (GR) are specially interesting due to their incredible properties and outstanding efficiency in conversion of photo energy into thermal energy.^{4,5} The GR, which possess two-dimensional platform and consist of sp^2 -bonded carbon atoms linked in a hexagonal fashion. It has a specific arrangement that each carbon atom in system is covalently bonded with other three carbon atoms. Moreover, GR has high charge carrier mobility and specific surface area apart from its zero band gap, which effectively separates the photo-generated charge carriers and transfer them rapidly. In this manner, GR is an ideal platform to improve the quantum efficiency of semiconductor based photocatalysts. Hence, the coupling of GR with a semiconducting material, could not only trap and shuttle the photo-generated electrons, but also it increase the absorbing ability of pollutants and light radiations over the surface of photocatalysts. In this passion, series of GR based semiconductor photocatalysts have been designed and tested for their excellency in photocatalytic activity.^{4,7–10} Several semiconductors were employed in conjugation with GR for the advancement of photocatalysts.^{1–5,7–10} Compared to those semiconductors, ZnO is principally interesting owing to its excellent optical activity, good stability and high mobility of electrons. In addition, ZnO has large exciton binding energy of 60 meV at room temperature, low cost and nontoxicity.¹¹ The electron mobility of ZnO is nearly two orders of high magnitude than the popularly known photocatalyst TiO_2 .⁴ In general, ZnO is a gifted candidate for promotion of robust photocatalysts. However ZnO is obstructed with a major drawback of its large band gap of about 3.37 eV and it is unable to excite in the presence of radiations having wavelength higher than 400 nm. In addition, recombination rate of charge carriers in ZnO is predominant and rapid as it transpires within nanoseconds. Therefore to extend the

absorption threshold of ZnO, coupling of a secondary material like GR is a favorable approach. The interesting possibility at this juncture is ZnO conjugated with GR could lead to narrowing of the band gap in ZnO and extend the absorption ability to near-infrared (NIR) radiation also.

Meanwhile, the NIR region is considered as a biological window as living cells and tissues have low light scattering and adsorption to NIR radiations. The advantage of NIR radiations is the production of localized heat called photothermal effect (PTE), which is readily employed in hyperthermia treatment to kill cancer cells due to its minimal invasiveness and higher effectiveness.^{12–16} Instead, PTE could play a crucial role and significantly influence over the enhanced activity of a photocatalyst. To date, the importance of PTE in photocatalytic activity has been completely ignored. So addressing the role of PTE in photocatalytic activity is a current urgent need. It is identified that GR based nanocomposites are strong PTE agents under exposure to NIR radiations,^{17–19}. During photocatalysis, illumination of GR nanocomposites to NIR radiations could generate PTE even under control of catalytic mixture at room temperature by either flowing water or some other method, which may improve the mobility of photo-generated charge carriers. This process cause the prevention in recombination of charge carriers and leads to enhanced activity of a photocatalyst. Therefore, on account of significance of PTE, herein we revealed the detailed mechanism for rapid photodegradation found for methyl orange (MO) over the surface of ZnO coupled GR (GR-ZnO) nanocatalyst. MO is an industrially versatile *N*-containing hazardous dye, which yield to potentially carcinogenic aromatic amines under its natural reductive anaerobic degradation process. So that, complete removal of such a toxic dye persist in waste water is critically needed and it has been successfully accomplished using GR-ZnO nanocatalyst. Apart, the degradation of MO in presence of NIR radiations was compared with the rate found for UV and visible radiations. Overall, this study is dedicated to investigate the role of PTE in photocatalysis.

EXPERIMENTAL METHODS

Materials.

All the reagents were purchased from Aldrich and used without any purification unless otherwise noted, and the aqueous solutions were prepared using ultrapure water obtained from Milli-Q Plus system (Millipore).

Preparation of GO.

Graphene oxide (GO) was prepared from graphite powder according to the Hummers and Offeman method with slight modifications.²⁰ In a typical procedure, 1 g graphite powder (<20 μm , Aldrich) was added into 40 mL concentrated H_2SO_4 and stirred for 1 h under ice-cooling condition. Then 15 mL fuming HNO_3 was slowly added and stirred the mixture for 30 min. To this, 5 g KMnO_4 was gradually added with constant stirring and cooling. The resulting mixture was then stirred at room temperature for 12 h followed by addition of 150 mL DI water. After 30 mins of stirring, 30 mL H_2O_2 (30%) was slowly added, immediately the color of the reaction mixture was turned to bright yellow. This reaction mixture was centrifuged and washed with 1:10 HCl solution in order to remove metal ions. Then the

mixture was washed with DI water until removal of acid. Thus obtained dark-yellow colored GO was dried under vacuum at low temperature (40 °C) in order to avoid deoxygenation.

Preparation of GR-ZnO nanocatalyst.

20 mg of GO was dispersed in 25 mL of ethanol by sonication for 5 min, followed by addition of 20 mL aqueous solution of zinc acetate (1 mmol). The resulting suspension was stirred under ambient condition for 15 mins, subsequently an aqueous solution containing 8 mmol of NaOH was added. Further, contents of the mixture was stirred at room temperature for 15 min and transferred to a Teflon lined stainless steel autoclave. The autoclave was then subjected to heating at 140 °C for 8 h and thus formed GR-ZnO nanocatalyst was separated by centrifugation. The GR-ZnO nanocatalyst was further purified by successive washing with ethanol and DI water and dried under vacuum.

Photocatalytic activity.

The photocatalytic activity of GR-ZnO nanocatalyst was evaluated by the degradation efficiency of MO under exposure to UV light (UVIR, 90W), visible light (Philips, 40 and 90W) and NIR laser (Armlaser Inc. USA, 2 W/cm², 980 nm). In each experiment, 10 mg of catalyst was suspended in 100 mL aqueous solution of MO (10 mg/L) and the suspension was magnetically stirred in dark for 30 min in order to establish adsorption/desorption equilibrium of MO molecules on the surface of catalyst. Then the pH of catalytic mixture containing MO and GR-ZnO nanocatalyst measured prior to exposure was found to be 8.1. Subsequently, mixture was transferred to a double walled photocatalytic reactor having water circulation facility to maintain the reaction mixture at room temperature. Then the suspension was exposed to UV, visible and NIR radiations individually. At a given interval of time, 5 mL of suspension was taken out, centrifuged and the concentration of MO was analyzed by measuring the absorbance at 462 nm using UV-vis spectrophotometer. Further, the normalized concentration of MO after photocatalysis was calculated as C/C_0 , where C_0 is the initial concentration of MO and C is the concentration of MO measured after exposing for particular interval of time.

To explore the PTE of GR-ZnO nanocatalyst under exposure to NIR laser and to identify the possibility of PTE in presence of UV and visible light, the photocatalytic experiments were performed without external circulation of water. Then the elevation in temperature of the catalytic mixture was measured using Hanna precision digital thermometer (Model: HI93510).

Control experiments.

For control experiments, ZnO was prepared in accordance with the procedure depicted above for GR-ZnO nanocatalyst without use of GO and GR was obtained by the reduction of GO by the procedure explained in Ref.²¹ Then the photodegradation of MO in presence of ZnO and GR were evaluated and compared with GR-ZnO nanocatalyst.

Photothermal effect.

The PTE of samples was evaluated using 980 nm NIR diode laser system (Armlaser Inc. USA) with an output power of 2 W/cm². In each experiment, 1 mL of aqueous dispersion of

sample was transferred into $1 \times 1 \times 4 \text{ cm}^3$ cuvette and illuminated with NIR laser. Then the rise in temperature of the suspension mediated by exposure to laser radiations was measured with a digital thermometer by immersing its thermocouple in the reaction mixture during experiment.

Characterization.

ATR-IR spectra were recorded using Smiths ChemID diamond attenuated total reflection (DATR) spectrometer and TGA were performed with a Perkin Elmer Diamond TG/DTA instrument at a heating rate of $10^\circ\text{C}/\text{min}$. Powder XRD patterns were recorded on Scintag X-ray diffractometer (PAD X), equipped with Cu K α photon source (45 kV, 40 mA) at scanning rate of $3^\circ/\text{min}$. SEM measurements were carried out on a JEOL JXA-8900 microscope and Raman spectra were recorded with Renishaw R-3000QE system in the backscattering configuration using an Argon ion laser with wavelength 785 nm. The UV-vis-NIR absorption spectra were recorded using Jasco V-770 spectrophotometer and pH of catalytic mixture was measured using Sargent-Welch (pH 8001) pH meter. The BET surface area was measured by N_2 adsorption-desorption isotherms using ASAP2020 (Micrometrics, USA) surface area analyzer at 77 K.

RESULTS AND DISCUSSION

The FTIR spectra of GO, GR-ZnO nanocatalyst and ZnO are shown in Figure 1. The spectrum of GO (Figure 1a) displayed the characteristic absorption bands corresponding to various oxygen containing functional groups *viz.*, O–H stretching of water at 3395 cm^{-1} , C–O stretching of COOH groups at 1719 cm^{-1} , epoxy symmetrical ring C–O deformation vibrations or phenolic C–O–H stretching at 1161 cm^{-1} and alkoxy C–O stretching at 1039 cm^{-1} .^{21–23} The representative absorption band at 1619 cm^{-1} is attributed to aromatic C–C vibrations mixed with –OH of water and the band at 1619 cm^{-1} is due to carboxy C–O. While, the absorption bands related to oxygen containing functional groups *viz.*, C–O stretching, phenolic C–O–H stretching, alkoxy C–O stretching and carboxy C–O recorded for GO were disappeared in the spectrum of GR-ZnO nanocatalyst (Figure 1b). In addition, a new band has displayed at 1505 cm^{-1} due to skeletal vibrations of GR nanosheets.²⁴ The band generated by vibrations of Zn–O has been observed at 551 cm^{-1} . The spectrum of ZnO (Figure 1c), demonstrated the bands at 3360 and 1405 cm^{-1} , corresponding to –OH stretching and C–OH vibration, respectively. The band appeared at 530 cm^{-1} is attributed to stretching vibration of Zn–O.

Figure 2 shows the UV-vis-NIR absorption spectra of GO, ZnO and GR-ZnO nanocatalyst. In the spectrum of GO (Figure 2a), characteristic absorption band exhibited at 229 nm and a shoulder around 300 nm could be assigned to $\pi \rightarrow \pi^*$ transition of aromatic C–C bonds and $n \rightarrow \pi^*$ transitions of C=O bonds, respectively.^{23–25} The absorption band at 363 nm in Figure 2b could be due to intrinsic band gap absorption of ZnO by the electron transition from valence band to conduction band ($\text{O}_{2p} \rightarrow \text{Zn}_{3d}$).²⁶ The GR-ZnO nanocatalyst (Figure 2c) has revealed a shoulder around 215 nm and a weak absorption at 280 nm (these bands are distinctly identifiable in Figure S1). These are corresponds to $\pi \rightarrow \pi^*$ transition of GR and it consistent with the absorption observed for aqueous stable graphene.²⁷ This observation

signifies that after reduction of GO, the electronic conjugation within GR nanosheets has successfully restored. Moreover, the absorption band related to ZnO was also been displayed at 369 nm. The red shift observed in the characteristic band of ZnO in GR-ZnO nanocatalyst is ascribed to strong interaction exists between GR nanosheets and ZnO. It was also observed that the absorbance of the band related to ZnO in the spectrum of GR-ZnO nanocatalyst (Figure 2c) has increased compared to absorbance of pristine ZnO (Figure 2b), which could be due to presence of GR and its high absorption ability. It is interesting to note that GO, ZnO and GR-ZnO nanocatalyst have possessed strong absorbance in NIR region also. Hence the conjugation of GR with ZnO has increased photo-absorption capability of GR-ZnO nanocatalyst and it is a primary assessment to employ GR-ZnO nanocomposite as a NIR active photocatalyst.

The XRD patterns shown in Figure 3 depict the crystal phase and purity of GO, ZnO and GR-ZnO nanocatalyst. The GO (Figure 3a) displayed a reflection at 2θ value of 9.9° , corresponding to its (002) crystalline plane with an interlayer d-spacing of 0.89 nm. In addition, this characteristic peak indicates complete oxidation of graphite and formation of GO. Further, a low intensity peak appeared at 42.5° in GO corresponds to (100) reflection of GR.²³ The peaks appeared for ZnO (Figure 3b) at $31.8, 34.5, 36.2, 47.5, 56.6, 62.8, 66.4, 67.9, 69.1, 72.6$ and 76.9° are indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystal planes of hexagonal wurtzite structure of ZnO, respectively (JCPDS No. 36–1451). Meanwhile, the diffraction pattern of GR-ZnO nanocatalyst (Figure 3c) is identical to the pattern of ZnO, while additional two low intensity peaks at 23.7 and 43.5° corresponding to (002) and (100) planes of GR, respectively, were appeared.^{22,28} The disappearance of the characteristic peak of GO in Figure 3c suggests the successful reduction of GO to GR. However the peaks corresponding to GR are weakly resolved in GR-ZnO nanocatalyst due to effective exfoliation of GR nanosheets. However, the magnified display shown in Figure S2 provides a clarification of presence of characteristic peaks corresponding to GR in GR-ZnO nanocatalyst. Further, existence of the reflections corresponding to hexagonal wurtzite structure of ZnO illustrates that conjugation of GR with ZnO could not alter the orientation and structure of ZnO in GR-ZnO nanocatalyst. Moreover, the occurrence of sharp and intense diffraction peaks in Figures 3b and c reveals the high crystalline nature of ZnO.

The FESEM images of GO shown in Figures 4a and b depict the effective exfoliation of GO in the form of thin nanosheets and their porous structure generated by opening of planer carbon networks wedged at the edge surface of crystallite due to oxidation. It is also evident that the GO possess two dimensional structure having wrinkled surface with single to few thin nanosheets. Figures 4c-f show the formation of homogenous tetragonal trapezoid shaped ZnO nanocrystals and their surface is smooth and uniform. The well faceted side surfaces and perfect tetragonal end planes of as-grown ZnO nanotrapezoids (NTs) indicate that synthesized ZnO NTs are of single crystalline. Further, the images of GR-ZnO nanocatalyst (Figures 4g-i) reveals anchoring of systematically arranged uniform ZnO NTs over the surface of GR nanosheets. In the process of encapsulation of ZnO NTs over GR nanosheets, GR nanosheets behave as templates and prevent from aggregation of ZnO NTs. The calculated value of mean diameter of ZnO NTs exists in GR-ZnO nanocatalyst was found to be around 30 nm and it matched with value calculated from Debye-Scherrer

equation.²⁹ In the Figures 4g and i, the GR nanosheets are distinctly definable and these nanosheets have typical crumpled sheet like morphology carrying single to few thin sheets. The adequate anchoring of ZnO NTs over the surface of GR nanosheets is ascribed to wrinkled structure of GR nanosheets. The comparison of Figures 4c-f and g-i demonstrates that the layered structure of GO is destroyed in GR-ZnO nanocatalyst due to strong adherence of ZnO NTs over the surface of GR nanosheets. While, assessment of Figures 4c-f and g-i illustrates that morphology of pristine ZnO NTs is retained in GR-ZnO nanocatalyst also. The interfacial structure formed by hybridization of ZnO NTs and GR nanosheets provides the strong interaction between them and bring an intimate contact between ZnO NTs and GR nanosheets. Owing to close contact between GR and ZnO, electrons can easily transport from ZnO NTs to GR nanosheets, leading to separation of photo-generated charge carriers. Hence it enhances the photocatalytic activity of GR-ZnO nanocatalyst in addition to absorption of NIR light. Moreover, elemental analysis data analyzed from EDS indicates the presence of C, Zn and O elements in GR-ZnO nanocatalyst (Figure S3), among these, the peaks for Zn and O were originated by ZnO NTs and C was generated from GR nanosheets. In addition, the content of oxygen is comparatively lower in GR-ZnO nanocatalyst, which reveals reduction of GO to GR by successful removal of oxygen contained functional groups in presence of water. Then the BET surface area measured for GR-ZnO nanocatalyst by N₂ adsorption-desorption isotherm was found to be 34.1 m²/g.

Further, the reduction of GO to GR and subsequent deposition of ZnO NTs over the GR framework was examined by Raman analysis. The Raman spectra of GO and GR-ZnO nanocatalyst (Figure 5) displayed the characteristic D and G bands. The spectrum of GO (Figure 5a) exhibited the D band at 1328 cm⁻¹ and G band at 1598 cm⁻¹, while GR-ZnO nanocatalyst (Figure 5b) demonstrated the D and G bands at 1304 and 1588 cm⁻¹, respectively. The D band displayed in the spectrum of GR-ZnO nanocatalyst is ascribed to breathing mode of k-point phonons of A_{1g} symmetry and G band is attributed to first order scattering of E_{1g} phonon mode of sp² carbon atoms.³⁰ Compared to GO, the blue shifting of D and G bands occurred in GR-ZnO nanocatalyst indicate successful reduction of GO to GR. Further, the value of ID/IG calculated for GR-ZnO nanocatalyst (1.31) was found to be higher than that of GO (1.14), which signify the increase in the number of smaller sp² domains in GR-ZnO nanocatalyst.³¹ It suggests that in GR-ZnO nanocatalyst most of the oxygenated groups are removed, the vacant lattice sites produced via carbon atom removal in the form of CO or CO₂ during graphite oxidation remain unchanged by the reduction process and predominantly define the intact graphene regions.³¹

To quantify the contents of GR-ZnO nanocatalyst, TGA was performed and the thermograms obtained for GO, ZnO and GR-ZnO nanocatalyst are illustrated in Figure 6. The profile of GO (Figure 6a) displayed two weight loss steps. The initial weight loss observed below 150 °C was identified to removal of water molecules adsorbed on the surface of GO. Whereas the successive significant weight loss occurred around 180 °C was ascribed to decomposition of labile oxygen functional groups and pyrolysis of carbon skeleton. The ZnO (Figure 6b) possessed better thermal stability, while the minor weight loss in ZnO around 200 °C is attributed to decomposition and dehydration of surface hydroxyls.³² The GR-ZnO nanocatalyst (Figure 6c) showed considerably less weight loss

compared to GO due to presence of minute number of decomposable functional groups, which suggests effective conversion of GO to GR by the action of deoxygenation during hydrothermal process. The weight loss appeared below 100 °C for GR-ZnO nanocatalyst (Figure 6b) was depicted to loss of absorbed water and the following weight loss below 400 °C was attributed to decomposition of residual organic functional groups persist in GR.^{33,34} The subsequent weight loss occurred in GR-ZnO nanocatalyst between 400 and 500 °C was assigned to oxidation of GR.

Here in the process of synthesis it was found that initial light yellow colored suspension of GO and zinc acetate turned to dark color after hydrothermal process, which indicate reduction of GO to GR without any supplemental reducing agent. Compared to traditional reduction process which employ hazardous hydrazine or borohydride, herein, the reduction of GO to GR occurred with a completely different reduction mechanism. The physiochemical properties of water, used as a solvent in this hydrothermal process can change with increase in its temperature and pressure, due to this, the supercritical water becomes as a fluid having special features such as strong electrolytic solvent power, high diffusion coefficient, and ion molecules.^{35,36} Moreover, water at high temperature can promote a favorable environment to cleavage of heterolytic bonds of the functional groups such as -OH, C=O and C-O-C persists over the surface of GO. Therefore, reduction of GO to GR transpired in this without any external reducing agent could be related to deoxygenation or dehydration of bonds of functional groups exists over GO.

In consideration of its enhanced absorption in NIR region, the catalytic activity of GR-ZnO nanocatalyst was assessed in presence of NIR laser by photodegradation rate of MO. Figure 7 shows the absorption spectra of aqueous solution of MO in presence of GR-ZnO nanocatalyst at different interval of illumination to NIR radiations. It is obvious that the characteristic band of MO located around 462 nm has completely disappeared, which suggest the structural rupture of MO molecules and their subsequent degradation by the action of GR-ZnO nanocatalyst. The photodegradation of MO with elapse of time was quantitatively estimated by sequential variation in their concentration after exposing to NIR laser. Figure 8 reveals the photodegradation profile of MO in presence of GR, ZnO and GR-ZnO nanocatalyst. In the absence of any catalyst or NIR radiations, the degradation rate of MO was insignificant, which indicates that the self-photosensitization of MO could be absolutely low. With GR-ZnO nanocatalyst MO was completely degraded at 40 min, while it was not attained with either GR or ZnO within 40 min of exposure. Hence the synergetic combination of GR and ZnO has significantly enhanced the photocatalytic activity of GR-ZnO nanocatalyst.

Further the degradation of MO in NIR laser was compared with the degradation rate measured in visible radiations (Figure 9). It was found that MO was completely degraded at 70 min in presence of visible light, which is significantly lower than the degradation rate found in NIR laser. To find the influence of power or intensity of light source, the photodegradation of MO was executed using a different intensity visible lamp of 40W instead of 90W lamp used in prior experiment. It was found that the degradation rate of MO was not majorly affected by varying the power of source, which elucidate that the degradation of MO is not solely depend on the power of light source (Figure S4). For

comparison, the photodegradation of MO was assessed under illumination to UV radiations also and it was observed that MO was entirely degraded in 60 min of exposure. Interestingly, photodegradation of MO was absolutely high in NIR radiations compared to both UV and visible radiations. The excellence of GR-ZnO nanocatalyst under exposure to NIR laser could be narrated to PTE that could generate during the process of photocatalysis. It is known that NIR radiations are mainly responsible for PTE.³⁷ Therefore, to explore the influence of PTE which could play a decisive role in enhanced degradation of MO, this study has been further extended to emphasis over PTE. The GR-ZnO nanocatalyst is composed of GR nanosheets and it is identified that GR is a promising candidate of PTE in presence of NIR radiations.¹⁸ Under this influence, we measured the PTE or rise in the temperature of catalytic mixture comprised of GR-ZnO nanocatalyst and MO solution identical to prior photocatalysis experiments without external circulation of water employed to prevent from heating-up of catalytic suspension (Figure S5). To elucidate PTE in detail, rise in temperature of pure water, MO solution alone and a suspension containing the mixture of GR and MO solution were measured under illumination to NIR laser for 40 min. Overall, a raise of 4.6 °C was perceived for the suspension containing mixture of GR-ZnO nanocatalyst and MO solution. It was higher than the value measured for pure water, MO solution and the suspension containing the mixture of GR and MO solution (Figure S5). Moreover to reveal any possibility of PTE under exposure to either UV or visible radiations, we measured the change in temperature of the samples by exposing to UV and visible lights distinctly, and found a minute elevation in both cases (Figure S6).

Fascinatingly, degradation of MO under exposure to NIR radiations in darkness was significantly lower than the rate measured in NIR radiations in addition to lamps present in laboratory (Figure 9). So, it is obvious that NIR radiations play a decisive role in enhanced photocatalytic activity of GR-ZnO nanocatalyst. It seems the degradation of MO could not occur with NIR radiations alone in darkness, instead it need supplement of both UV and visible radiations. In general, NIR radiations necessitate the support of both UV and visible radiations to enhance the activity of a photocatalyst. Based on this important evidence, it could be assessed that, excitation of electrons could not ensue with NIR radiations alone without coupling of UV and visible radiations.²

Since NIR radiations are unable to accelerate either ZnO or MO, almost no electrons could be generated, and MO could not degrade under dark. However, in combination with UV and visible radiations, heat generated by NIR light could remarkably speed up the process of degradation. So that, NIR radiations play an important auxiliary role in enhancing the photocatalytic activity of GR-ZnO nanocatalyst, since the NIR light alone cannot produce the photodegradation of MO. The key role played by PTE in enhanced photodegradation of MO could be explained as the cause for photocatalysis is separation and transfer of photo-generated charge carriers. Herein PTE lead to rise in temperature and facilitates the mobility of charge carriers in GR-ZnO nanocatalyst, which results to rapid photodegradation of MO. In detail, illumination of the suspension containing GR-ZnO nanocatalyst with NIR laser heat-up GR sheets by PTE and accelerate the photo-generated electrons. It brings rapid degradation of MO molecules over the surface of GR-ZnO nanocatalyst.

The degradation of MO was performed with constant circulation of water, even under this condition PTE could influence over photodegradation, so we attempted to quantify the effect of PTE. The hot carrier relaxation transpire in GR nanosheets could be the reason for rise in temperature found in presence of NIR laser.³⁸ The relaxation of photo-generated carriers usually consists of several processes, *viz.*, carrier-carrier interaction, carrier-phonon scattering (mainly optical phonon emission), Auger recombination, and carrier trapping.^{38,39} It is reported by Ruzicka et al. that the relaxation of a hot carrier in GR nanosheets is independent of temperature³⁸ and the carriers have a hot distribution immediately after photo-excitation. Subsequently the energy relaxation is dominated by carrier-phonon scattering and a large number of optical phonons are emitted and give rise to significant deviation of the phonon distribution in excitation spot away from the equilibrium distribution dictated by temperature of the sample. As photothermal process is the collective electronic effect, so the lattice temperature rapidly reaches equilibrium. Therefore, the hot carriers experiences, a much higher lattice temperature than the temperature of other parts of the sample, and the finite temperature variation has no influence on the carrier dynamics.² It might lead to PTE and raise the local temperature of the photocatalytic mixture through illumination to NIR laser even under the condition of constant circulation of water. Hence the PTE caused significant degradation of MO in presence of NIR laser compared to degradation rate in UV and visible light.

Owing to importance of PTE in photocatalysis, PTE of GR-ZnO nanocatalyst was quantified under exposure to 980 nm laser and compared with its individual components *viz.*, GR and ZnO. Figure 10 illustrate the profile of time dependent temperature rise of samples in response to illumination of 980 nm laser at their concentration level of 2 mg/mL. After 7 mins of irradiation, an elevation of 47.3 °C was found for aqueous dispersion of GR-ZnO nanocatalyst. Under identical conditions, temperature of GR was raised by 43.7 °C and it was 39.2 °C for ZnO. While, rise in temperature found for water was 8.3 °C. Since the ability of water to absorb NIR radiations is very low, that caused its minute PTE. Hence, contribution of water in the enhanced PTE of GR-ZnO nanocatalyst is extremely low. Comparatively it can be perceptible that PTE of GR-ZnO nanocatalyst is higher than GR and ZnO, it demonstrates the unique structure generated by coupling of GR with ZnO NTs has radically improved the absorption ability to NIR radiations and made GR-ZnO nanocomposite as a robust photocatalyst. In addition, PTE of GR-ZnO nanocatalyst measured in five consecutive cycles was virtually constant, so, no photo bleaching found in GR-ZnO nanocatalyst (Figure 11). It was also observed that PTE of GR-ZnO nanocatalyst was linearly depends on its concentration level (Figure S7).

Subsequently, the photothermal conversion efficiency of GR-ZnO nanocatalyst was evaluated using the equation proposed by Roper with some modifications.¹ For this purpose, variation in temperature of the aqueous dispersion of GR-ZnO nanocatalyst (2 mg/mL) was measured as a function of time under exposure to laser for 7 min, at this juncture, rise in temperature was reached to a steady condition. Then shut off of laser leads to drop in temperature and it was monitored to find the rate of heat transfer from aqueous dispersion of GR-ZnO nanocatalyst to surrounding environment using the following equation (1).

$$\eta = \frac{hS(T_{max} - T_{amb}) - Q_{dis}}{I(1 - 10^{-A_{980}})} \quad (1)$$

where η is the photothermal efficiency, h is heat transfer coefficient and S is the surface area of the sample container. T_{max} is the maximum temperature attained by system of aqueous dispersions and T_{amb} is the ambient surrounding temperature in °C. While, I is the power of laser source, A_{980} is the absorbance of aqueous dispersions of GR-ZnO nanocatalyst measured at 980 nm and Q_{dis} is the rate of heat dissipated due to absorption of light by solvent and container. The value for all these parameters is provided in Table 1.

To find the value of hS , a dimensionless driving force of temperature, θ is introduced and scaled using the maximum system temperature, T_{max} and the ambient surrounding temperature, T_{amb} .

$$\theta = \frac{T - T_{amb}}{T_{max} - T_{amb}} \quad (2)$$

and the sample system time constant, τ_s was evaluated using the following equation (3)

$$t = -\tau_s \ln(\theta) \quad (3)$$

Then the value of τ_s was calculated by Figures S8 and S9, and using its value the unknown parameter, hS was evaluated with the help of equation (4).

$$hS = \frac{m_D C_D}{\tau_s} \quad (4)$$

where m_D and C_D are mass and heat capacity of water, respectively. The value of Q_{dis} was measured separately using quartz cuvette containing only DI water without any sample. Hence the photothermal conversion efficiency (η) estimated for GR-ZnO nanocatalyst was found to be 48.6%.

The overall degradation of MO employing GR-ZnO nanocatalyst under exposure to UV, visible light and NIR laser could be ascribed to its high surface area, which enhances the adsorption of MO molecules due to π - π interaction between the aromatic ring of the MO molecules and GR nanosheets, that leads to noncovalent adsorption of dye molecules.⁴⁰ Additional crucial factor that could contributed in significant photocatalytic activity of GR-ZnO nanocatalyst was narrowing in its band gap, which extends the optical or light absorption of GR-ZnO nanocatalyst and results in efficient transfer of photo-generated electrons from ZnO to GR nanosheets.⁴¹ Therefore, the bandgap measured for ZnO and GR-ZnO nanocatalyst was found to be 3.37 and 3.35 eV, respectively. The band gap in ZnO is

reduced by its conjugation with GR nanosheets. Moreover, the GR in GR-ZnO nanocatalyst behaves as a source for trapping and shuttling of photo-generated electrons. The mechanism underlying photocatalytic activity of GR-ZnO nanocatalyst in the degradation of MO under exposure to NIR laser is schematically demonstrated in Figure 12 and also narrated with possible mechanism in UV and visible radiations (Figure S10). The valence band (VB) and conduction band (CB) in ZnO are located at -7.39 and -4.19 eV (vs. vacuum), respectively⁴² and the work function of GR is -4.42 eV (vs. vacuum).⁴³ The exposure of aqueous solution of GR-ZnO nanocatalyst and MO to light produces pairs of electrons (e^-) and holes (h^+) and the ZnO promotes the electrons from VB to CB by leaving the holes in VB. It follows efficient interfacial transfer of electrons from CB of ZnO to GR nanosheets as the Fermi level of GR is lower than CB minimum of ZnO. This process remarkably reduces recombination probability of photo-excited electrons and holes in ZnO. Therefore, number of photo-excited holes retained to a large extent, which participate in oxidation of MO and enhances the photocatalytic activity. Simultaneously, more photo-generated holes can react with adsorbed water to form a hydroxyl radical ($OH^\bullet$), which can promote the decomposition of MO. In addition, the oxygen adsorbed on the surface of ZnO can accept the electrons and form superoxide radical anions ($O_2^{\bullet -}$), which also causes the formation of $OH^\bullet$ upon protonation. These hydroxyl radicals and superoxide radical anions are responsible for decomposition of MO into non-toxic products under simulated light irradiation.⁴⁴ From these predictions, possible degradation reactions can be summarized as follows:

For better quantification of photocatalytic activity of GR-ZnO nanocatalyst, the kinetic analysis was used. It is assumed that the photocatalytic degradation of MO in presence of catalysts follows pseudo-first order kinetics and which can be described in terms of Langmuir–Hinshelwood (L-H) model:^{1,45,46}

$$-\frac{dC}{dt} = kr \frac{K_a C}{1 + K_a C} \quad (5)$$

where $(-dC/dt)$ and C are degradation rate and concentration of MO, respectively, t is the reaction or exposure time, k_r is rate constant of the reaction, and K_a is the adsorption coefficient of the reactant. The initial concentration of MO used in the photocatalytic experiments was very low ($C_0 = 10$ mg/L), so that the $K_a C$ term becomes negligible and

equation (5) can be described with the first-order kinetics. Then modifying the equation (5) at the initial conditions of the photocatalytic procedure, *viz.*, $t = 0$, $C = C_0$ as:

$$\ln[C_0/C] = k_{app} \cdot t \quad (6)$$

where C_0 is initial concentration of MO, k_{app} is apparent rate constant of the reaction and t is the time of exposure to light.

The L-H plots obtained on the basis of equation 6 for photodegradation of MO under exposure to NIR laser have provided a linear relationship with concentration and exposure time (Figure S11). The linearity of L-H plots reveals photodegradation of MO follow the pseudo-first-order reaction kinetics. Further, the apparent rate constants (k_{app}) calculated for GO, ZnO and GR-ZnO nanocatalyst using L-H plots are summarized in Table 2. It was found that the value of k_{app} for GR-ZnO nanocatalyst (0.1128 min^{-1}) was about twelve times higher than GR (0.0092 min^{-1}) and six times greater than ZnO (0.0188 min^{-1}). Hence the perfect blending of GR with ZnO has brought the tremendous improvement in the activity of GR-ZnO nanocatalyst. Moreover, the L-H plots acquired for UV, visible, NIR and NIR in darkness were also found linear (Figure S12). The value of k_{app} calculated for UV light was 0.0693 min^{-1} (Table 3), which was higher than the value of visible light (0.0446 min^{-1}). Whereas the value of k_{app} assessed for NIR laser in presence of laboratory lights was significantly higher (0.1128 min^{-1}) than the value obtained under exposing to NIR laser in darkness (0.0038 min^{-1}).

For practical implementation of a catalyst, its recycling and stability are crucial. So that after its application in degradation of MO, GR-ZnO nanocatalyst was recycled by centrifugation and employed in following four successive cycles. It was found that after its usage in five consecutive cycles, the efficiency of GR-ZnO nanocatalyst was not reduced significantly. In addition, XRD pattern of GR-ZnO nanocatalyst (Figure S13) acquired after its employment in five consecutive cycles couldn't show any prominent alteration. It elucidates the stability of GR-ZnO nanocatalyst, and no structural rupture and detachment between ZnO NTs and GR nanosheets occur.

CONCLUSIONS

In summary, a promising heterogeneous GR-ZnO nanocatalyst was prepared by in-situ reduction of GO to GR and successive nucleation of ZnO NTs through a facile hydrothermal process. In this approach, water has reduced GO to GR by promoting a favorable environment to the cleavage of heterolytic bonds of the functional groups such as -OH, C=O and C-O-C persists over the surface of GO. The GR-ZnO nanocatalyst has demonstrated that it is an excellent photocatalyst for complete degradation of hazardous MO. The enhanced photocatalytic activity of GR-ZnO nanocatalyst can be attributed to increase in the optical absorption, decrease in band gap, and effective separation of photo-generated charge carriers. The heterostructured GR-ZnO nanocatalyst could be easily recycled without any significant loss in its activity, hence GR-ZnO nanocatalyst is an excellent anti-photocorrosive catalyst. Overall, PTE has played an important crucial role in significantly

improved photocatalytic activity of GR-ZnO nanocatalyst under illumination to NIR laser. Further, the photo-excitation process of electrons could not occur alone under exposure to NIR radiations without the support of both UV and visible radiations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
ATR-IR spectra of (a) GO, (b) GR-ZnO nanocatalyst and (c) ZnO.

Figure 2. UV-vis-NIR absorption spectra of (a) GO, (b) ZnO and (c) GR-ZnO nanocatalyst.

Figure 3.
XRD patterns of (a) GO, (b) ZnO and (c) GR-ZnO nanocatalyst.

Figure 4. FESEM images of (a,b) graphene oxide (c-f) ZnO nanotrapezoids and (g-i) GR-ZnO nanocatalyst.

Figure5.
Raman spectra of (a) GO and (b) GR-ZnO nanocatalyst.

Figure6.
TGA profiles of (a) GO, (b) ZnO and (c) GR-ZnO nanocatalyst.

Figure7.
Absorption spectra of aqueous solution of methyl orange in presence of GR-ZnO nanocatalyst at different interval of illumination to NIR laser.

Figure8. Photocatalytic degradation profile of methyl orange over the surface of GR, ZnO and GR-ZnO nanocatalyst under exposure to NIR laser, and GR-ZnO nanocatalyst in darkness.

Figure9.
Photodegradation profile of methyl orange in presence of GR-ZnO nanocatalyst under exposure to UV light, visible light and NIR laser.

Figure 10.

Temperature rise of aqueous dispersion measured as a function of time under exposure to 980 nm laser.

Figure 11.
Temperature variation measured for aqueous dispersion of GR-ZnO nanocatalyst (2 mg/mL) for five cycles under illumination to NIR laser.

Figure 12.

The proposed mechanism for photocatalytic degradation of methyl orange in presence of GR-ZnO nanocatalyst under illumination NIR laser.

Table 1.

Values used in the calculation of photothermal efficiency (η) of GR-ZnO nanocatalyst.

$T_{max}(^{\circ}\text{C})$	$T_{amb}(^{\circ}\text{C})$	$I(\text{mW})$	A_{980}	$mD(\text{g})$	$CD(\text{J/g } ^{\circ}\text{C})$	$\tau S(\text{s})$	$hS(\text{mW}/^{\circ}\text{C})$	$Q_{Dis}(\text{mW})$	$\eta(\%)$
71.5	24.2	2000	1.195	1.01	4.179	219.5	19.8	25.9	48.6

Table 2.

Rate constants (k_{app}) calculated by Langmuir-Hinshelwood (L-H) plots for photodegradation of methyl orange under exposure to NIR laser.

	k_{app} (min ⁻¹)
GR	0.0092
ZnO	0.0188
GR-ZnO nanocomposite	0.1128

Table 3.

Rate constants calculated for photodegradation of methyl orange over the surface of GR-ZnO nanocatalyst under exposure to different light sources.

$k_{app} \text{ (min}^{-1}\text{)}$			
UV	Visible (90W)	NIR	NIR in dark
0.0693	0.0446	0.1128	0.0038