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Rhodamine B degradation and reactive oxygen species generation by a ZnSe-graphene/TiO₂ sonocatalyst

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ABSTRACT

Nanostructured ZnSe-graphene/TiO₂ was synthesized by a hydrothermal-assisted approach. ZnSe-graphene/TiO₂ exhibited favorable adsorption of rhodamine B, a wide wavelength absorption range, and efficient charge separation. Reactive oxygen species were generated by the oxidation of 1,5-diphenyl carbazide to 1,5-diphenyl carbazone. The sonocatalytic reaction mechanism was proposed. These findings potentially broaden the applications of sonocatalytic technologies.

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1. Introduction

Industrial dyestuffs including textile dyes are a recognized environmental hazard. Physical, chemical, and biological methods have been used to treat such waste. Advanced oxidation processes include peroxone, non-thermal plasma, photo-Fenton, ultraviolet (UV)-O₃, UV/H₂O₂, and semiconductor treatments. These organic degradation processes can achieve the complete elimination and mineralization of various pollutants.

TiO₂ is an attractive material for photoelectric conversion and photocatalysis because of its low cost, ease of production, high photochemical and biological stability, and low toxicity [1,2]. Much effort has focused on extending the absorption of TiO₂ into the visible region, and thus increasing its photocatalytic activity. Semiconductor quantum dots have attracted enormous interest because of their potential in single electron transistors [3], lasers [4], light emitting diodes [5], and infrared photodetectors [6] operated at low current and high tempera-

ture. CdS [7], Ag₂S [8], ZnSe [9], Bi₂S₃ [10], and CdSe [11,12] all have been used to sensitize TiO₂.

Graphene-based composites have attracted much attention for their potential in electronics, photocatalysis, and photovoltaic devices [13–15]. Graphene can enhance charge transport in devices. This is because its delocalized electrons within its conjugated *sp*²-hybridised framework impart high conductivity. Graphene-based nanocomposites containing Pd, Ag, Au, TiO₂, and metal selenides have all been reported [16–20]. Metal selenides can impart interesting electronic and optical properties in potential applications. ZnSe has a direct band gap of ~2.7 eV, making it well suited for solar absorption. Chen et al. [21] synthesized a N-doped graphene/ZnSe nanocomposite (GN-ZnSe) by a one-pot hydrothermal process at low temperature. GN-ZnSe exhibited favorable electrochemical performance in the oxygen reduction reaction, and favorable photocatalytic activity for bleaching methyl orange under visible-light irradiation.

Sonocatalytic technologies have been proposed in recent

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years. Their high efficiency without additional oxidants can lower the cost of treatment [22]. The sonocatalytic decomposition of organic pollutants can be enhanced in the presence of a photocatalyst. Combining ultrasound with solid photocatalyst particles can provide additional nuclei for cavitation bubble formation. Ultrasound can also enhance the mass transfer of organic pollutants between the liquid phase and catalyst surface and increase the active surface area by ultrasonic de-aggregating. Photocatalysts can be excited by ultrasound-induced luminescence. Such luminescence has a wide wavelength range and increases the production of hydroxyl radicals ($\cdot\text{OH}$) in the reaction mixture [23]. Reactive oxygen species (ROS) such as superoxide radical anions ($\cdot\text{O}_2^-$), $\cdot\text{OH}$, hydrogen peroxide (H_2O_2), and singlet oxygen ($^1\text{O}_2$) are also generated [24].

Understanding the sonocatalytic degradation and ROS formed during ultrasonic irradiation may enhance the degradation efficiency and yield new sonocatalysts. Herein, we hydrothermally prepared a ZnSe-graphene/ TiO_2 sonocatalyst [8,19,20]. The composite was used to ultrasonically degrade aqueous rhodamine B (RhB). The generated ROS were estimated by oxidation-extraction photometry. The reasons for the high sonodegradation activity of ZnSe-graphene/ TiO_2 are discussed.

2. Experimental

2.1. Materials

Ethylene glycol and anhydrous ethanol were purchased from Daejung Chemical Co. (Korea). ZnCl_2 , selenium metal powder, and NH_4OH (28%) were purchased from Daejung Chemicals & Metal Co., Ltd. (Korea). Anhydrous Na_2SO_3 (95%) was purchased from Duksan Pharmaceutical Co., Ltd. (Korea). Titanium(IV) *n*-butoxide (TNB, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, Kanto Chemical Company, Tokyo, Japan) was used as the Ti source in the preparation of TiO_2 and graphene/ TiO_2 composites. Anatase TiO_2 (99.7%, Sigma-Aldrich, USA) with a particle size of <25 nm was used as a comparative sample. RhB (99.99+%, Samchun Pure Chemical Co., Ltd., Korea) was used as a model pollutant. All chemicals were used without further purification, and distilled water was used throughout experiments.

2.2. Synthesis of ZnSe-graphene/ TiO_2

Graphite oxide (GO) was prepared from graphite according to the Hummers-Offeman method [19]. In brief, graphite powder (10 g) was dispersed in cold concentrated sulfuric acid (230 mL, 98 wt%, dry ice bath). KMnO_4 (30 g) was gradually added under cooling and vigorous stirring to prevent the temperature from exceeding 293 K. The dry ice bath was replaced with a water bath, and the mixture was heated to 308 K for 30 min under continuous stirring, with gas allowed to release. Deionized water (460 mL) was slowly added, which rapidly increased the solution temperature up to 371 K. The reaction was allowed to proceed for 40 min to increase the degree of GO oxidation. Reaction of the resulting bright-yellow suspension was terminated by adding distilled water (230 mL) followed by

hydrogen peroxide (30%, 250 mL). The solid product was collected by centrifugation (3000 rpm), washed with 5% HCl until SO_4^{2-} was no longer detectable with BaCl_2 , washed three times with acetone, and air dried overnight in a vacuum oven. GO was transformed into graphene oxide sheets by sonication for 30 min at 308 K.

In a typical procedure, about 300 mg of GO and 22 mg of ZnCl_2 were ultrasonically dispersed in 100 mL of ethylene glycol for 1 h using a digital sonifer. This yielded a graphene oxide nanosheet (GONS)/ Zn^{2+} solution (denoted solution A) [25]. Na_2SO_3 (5 g) and Se powder in 30 mL of water were refluxed for 1 h to form a Na_2SeSO_3 solution (denoted solution B). Solution B and 6 mL of NH_4OH (28 wt%) were added to solution A, which was heated to 333 K for several minutes. A colloidal TiO_2 solution in 35:15:4 ethanol: H_2O :TNB (denoted solution C) was added to the above mixture. The resulting solution was transferred to a polytetrafluoroethylene-lined stainless steel autoclave, which was then sealed. The contents were heated to 433 K for 6 h. The reaction was allowed to cool to room temperature. The precipitate was collected by filtration, washed thoroughly with water, dried in a vacuum oven at 353 K for 12 h, and then heated to 773 K for 1 h. ZnSe/ TiO_2 [26] and GR- TiO_2 [19] were similarly prepared with a little modification.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra (FTS 3000MX, Biorad Co., Korea) were recorded on a Perkin-Elmer spectrometer from KBr pellets. Spectra were recorded over the range 4000–400 cm^{-1} at 4 cm^{-1} resolution, with forward and reverse mirror speeds of 10 and 6.2 kHz, respectively. Crystal structures were observed by X-ray diffraction (XRD, Shimadzu XD-D1, Japan) at room temperature with $\text{Cu K}\alpha$ radiation. Diffuse reflectance ultraviolet-visible (DRS UV-vis) spectra were recorded using a spectrophotometer (Neosys-2000) equipped with an integrating sphere assembly. Morphologies were analyzed by scanning electron microscopy (SEM, JOEL JSM-5200, Japan) at an operating voltage of 3.0 keV. The SEM microscope was equipped with an energy dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM, JEOL JEM-2010, Japan) images were collected at an accelerating voltage of 200 kV and were used to examine particle sizes and distributions. Specific surface areas were determined using the BET method from N_2 adsorption isotherms at 77 K using a BET analyzer (Monosorb, USA).

2.4. Ultrasonic degradation of organic dye solutions

A controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea) was used to irradiate the RhB solution. The apparatus was operated at an ultrasonic frequency of 20 kHz and output power of 750 W through manual adjusting (3.04×10^6 J). In a typical experiment, 0.2 g of control sample and nanocomposite were added to 100 mL of RhB solution (2×10^{-5} mol/L). The suspension was magnetically stirred for 120 min in the dark to establish adsorption equilibrium. The concentration of adsorbed RhB (C_{ads}) was then measured, and the

suspension was subjected to ultrasonic irradiation to commence degradation. The temperature was controlled at about 298 K by a water bath. A glass reactor vessel of 5 cm in diameter and 7 cm in height was used and was placed on the magnetic churn dasher. The diameter of the ultrasound tip was 1.90 cm, and the ultrasound irradiation area was 26.86 cm². Ultrasonic irradiation of the reactor vessel was carried out for 30, 60, 90, 120, and 150 min. Samples (3 mL) were withdrawn regularly from the reactor, and the dispersed material was collected by centrifugation and analyzed by UV-vis spectrophotometry (Optizen Pop Mecasys Co., Ltd., Korea).

2.5. Evaluation of ROS

Six 10-mL 1,5-diphenyl carbazide (DPCI) stock solutions (0.01 mol/L) were added into three 100-mL volumetric flasks. ZnSe-GR/TiO₂ and TiO₂ (50 mg) were added to the above DPCI solutions. All three solutions were diluted to 50 mL with water. The DPCI and ZnSe-GR/TiO₂ concentrations of the three solutions were 2×10^{-3} mol/L and 1.00 g/L, respectively. After 180 min of ultrasonic irradiation, 10 mL of each solution was extracted with benzene and diluted to 10 mL with benzene for analysis by UV-vis spectrophotometry.

3. Results and discussion

3.1. Growth and characterization of ZnSe-GR/TiO₂

ZnSe-GR/TiO₂ was synthesized by the ethylene glycol-assisted hydrothermal dissociation of Na₂SeSO₃ in the presence of GO and ZnCl₂. TiO₂ nanoparticles adhered to GO functional groups on graphene oxide. Epoxy (C–O–C), hydroxyl (–OH), carbonyl (C=O), and carboxylic acid (–COOH) groups existed on the GO surface, so Zn²⁺ was strongly electrostatically adsorbed. Generated selenium ions caused nucleation and promoted the formation of ZnSe-GR. TiO₂ was deposited on GO sheets or ZnSe-GR surfaces and then crystallized into anatase nanocrystals during heat-treatment. Figure 1 shows the deposition of ZnSe and TiO₂ on graphene.

Figure 2(a) shows XRD patterns of TiO₂, GR-TiO₂, ZnSe-TiO₂, and ZnSe-GR/TiO₂. The pattern of TiO₂ contained diffractions at 37.9°, 47.8°, 54.3°, 55.0°, and 62.7°, which were indexed to the characteristic (004), (200), (105), (101), (211), and (204)

Fig. 2. (a) XRD patterns of TiO₂, GR-TiO₂, ZnSe-TiO₂, and ZnSe-GR/TiO₂; (b) FT-IR spectra of GO and ZnSe-GR/TiO₂.

peaks of anatase TiO₂ [JCPDS 21-1272] [27]. The (111), (220), and (311) diffraction peaks originated from the zinc blende structure [JCPDS 21-1272], in agreement with previous reports [28]. Weak new peaks appeared at 30° and 34° after reaction at 433 K for 6 h. These may have been indicated the presence of ZnO in the composite at shorter reaction times, in agreement with Gharibe et al. [29]. No diffractions of GO(001) or graphene(002) phase were detected in the GR-TiO₂ and ZnSe-GR/TiO₂. GO can be reduced to graphene during solvothermal reaction, and graphene sheets can then restack to form poorly ordered graphite. If the regular stacking of GO or graphite is broken, for example by exfoliation, their diffraction

Fig. 1. Schematic illustration of the deposition of ZnSe and TiO₂ nanoparticles on a GONS.

peaks can reportedly weaken or disappear [19].

The FT-IR spectrum of graphene was rather simple, which suggested extensive oxidation. The spectra of the crystalline material contained well-distinguished sharp bands, whereas the spectra of the amorphous material were less resolved. The hydration results established the importance of defined conditions for FT-IR (Fig. 2(b)). The strong band at about 3400 cm^{-1} in the GO was assigned to the -OH stretching vibration, and that at 1619 cm^{-1} to the vibration of adsorbed water. The C=O , C-OH , and C-O stretching bands were observed at 1728 , 1226 , and 1050 cm^{-1} , respectively. In the spectrum of ZnSe-GR/TiO_2 , weak peaks at 1224 and 1367 cm^{-1} were assigned to the C-OH and C-H bands, respectively. The C=O stretching vibration was observed at 1739 cm^{-1} . Compared to the spectrum curves the intensities of peaks attributed to functional groups of oxidized graphene were weak and decreased. This was because some of functional groups had combined with ZnSe and TiO_2 particles, resulting in a reduction of these groups content. This was in agreement with the XRD results.

The composite was characterized by SEM, as shown in Fig. 3. GO had a flaky morphology, which reflected its layered microstructure, as shown in Fig. 3(a,b). ZnSe/TiO_2 and ZnSe-GR/TiO_2 were also hydrothermally synthesized for comparison. The morphology of ZnSe/TiO_2 is shown in Fig. 3(c,d). A homogeneous distribution with some agglomeration was observed. The SEM images of ZnSe-GR/TiO_2 are shown in Fig. 3(e,f), and they exhibited the well-known properties of surface nanostructures. This suggested that ZnSe and TiO_2 particles were well-dispersed on the layered graphene nanosheet. Elemental compositions were analyzed by EDX, and the results are shown in Fig. 3(g). The main elements present were Ti and O , as evidenced by the strong peaks at 4.51 , 4.92 , and 0.52 keV . The Zn and Se contents of the composite were much lower. According to a former study [30], a small concentration of dopant in the TiO_2 matrix can prevent the formation of electron-hole recombination centers and increase negative charge capability.

TEM images of ZnSe/TiO_2 and ZnSe-GR/TiO_2 are shown in Fig. 4. The composite exhibited uniform particle sizes. The TiO_2 particles were cubic with an average size of $15\text{--}20\text{ nm}$. The average size of the well-dispersed ZnSe nanoparticles was $10\text{--}15\text{ nm}$. The lattice spacing of 0.35 nm was assigned to the (101) plane of anatase [31]. The interplanar spacings of (110) lattice plane families of ZnSe , with a lattice parameter of $a =$

Fig. 3. SEM micrographs of as-prepared samples. (a,b) Graphene; (c,d) ZnSe/TiO_2 ; (e,f) ZnSe-GR/TiO_2 ; (g) EDX elemental microanalysis and (h) element weight of ZnSe-GR/TiO_2 .

0.567 nm [32]. The presence of the GR template resulted in a lower aggregation of the TiO_2 and ZnSe nanoparticles. The TiO_2 and ZnSe nanoparticles also prevented the agglomeration of GR sheets after reduction.

UV-vis absorption spectra of the different samples were measured to investigate their visible light response and are shown in Fig. 5. TiO_2 , ZnSe/TiO_2 , and ZnSe-GR/TiO_2 strongly absorbed in the UV region. The spectrum of TiO_2 exhibited the characteristic sharp absorption edge at 400 nm (3.2 eV). The absorption bands of ZnSe-GR/TiO_2 differed from those of nanoscale TiO_2 and ZnSe/TiO_2 . TiO_2 had a white appearance, whereas ZnSe/TiO_2 was pale yellow and ZnSe-GR/TiO_2 was

Fig. 4. TEM images of ZnSe/TiO_2 (a) and ZnSe-GR/TiO_2 (b,c).

Fig. 5. (a) UV-vis absorption spectra of TiO_2 , ZnSe/TiO_2 , and $\text{ZnSe-GR}/\text{TiO}_2$; (b) Variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) of TiO_2 and ZnSe/TiO_2 .

gray-black. Therefore, the quantitative consideration is void between TiO_2 , ZnSe/TiO_2 , and $\text{ZnSe-GR}/\text{TiO}_2$. The enhanced light-harvesting efficiency of GR-TiO_2 could have arisen from chemical bonding between TiO_2 and GR. Ti–O–C bonding could have facilitated charge transfer upon excitation of ZnSe and TiO_2 [33,34].

The DRS spectra of TiO_2 and ZnSe/TiO_2 were transformed using the Kubelka-Munk function of the measured reflectance:

$$K = (1 - R)^2 / 2R = F(R)$$

where K is the transformed reflectance, R is the reflectance (%), and $F(R)$ is the remission or Kubelka-Munk function. The band gap (E_g) and absorption coefficient (α) were related by:

$$\alpha h\nu = A (h\nu - E_g)^{1/2}$$

where ν and A are the frequency and a constant, respectively. If the compound scattered in a perfectly diffuse manner, then $K = 2\alpha$. The following expression then applies:

$$[F(R)h\nu]^2 = A(h\nu - E_g)$$

The E_g of ZnSe/TiO_2 was estimated to be 2.5 eV, which was red-shifted from the typical E_g of TiO_2 (3.25 eV) in Fig. 5(b).

3.2. Degradation of RhB

3.2.1. Adsorption ability

To evaluate the adsorption ability of the composite, the reactor was placed on a magnetic churn dasher and stirred for 30 min in the dark to establish sorption equilibrium, as shown in Fig. 6. The amount of RhB adsorbed by $\text{ZnSe-GR}/\text{TiO}_2$ was higher than that adsorbed by TiO_2 . This was attributed to the larger surface area of $\text{ZnSe-GR}/\text{TiO}_2$, as shown in Table 1. The

Fig. 6. UV-vis absorption spectra of samples at sorption equilibrium, showing RhB absorption features.

surface area of ZnSe-TiO_2 was 25.34 m^2/g , which was higher than that of TiO_2 . GR/TiO_2 had the largest surface area and therefore adsorbed the most RhB. After establishing adsorption equilibrium, GR-TiO_2 and $\text{ZnSe-GR}/\text{TiO}_2$ removed 68% and 55% of the RhB from solution, respectively. TiO_2 removed only 11% of RhB.

3.2.2. Sonocatalytic activity

Sonocatalysis is an alternative to photocatalysis for degrading pollutants in waste water [32]. The effects of ultrasonic irradiation on RhB degradation in the presence of TiO_2 , GR-TiO_2 , ZnSe/TiO_2 , and $\text{ZnSe-GR}/\text{TiO}_2$ were investigated. After ultrasonic irradiation 150 min, $\text{ZnSe-GR}/\text{TiO}_2$ exhibited the highest degradation of RhB (82.9%), as shown in Fig. 7(a). GR-TiO_2 and ZnSe/TiO_2 degraded 47.3% and 34.1% of RhB, respectively. Calculated $-\ln(C_t/C_{\text{ads}})$ values were approximately linear with increasing irradiation time, as shown in Fig. 7(b) and Table 1. The RhB degradation rate constant for $\text{ZnSe-GR}/\text{TiO}_2$ was $10.32 \times 10^{-3} \text{ min}^{-1}$ under ultrasonic irradiation, which was much higher than those for TiO_2 , GR-TiO_2 , and ZnSe/TiO_2 .

Cycling experiments of the sonocatalytic degradation of RhB in the presence of $\text{ZnSe-GR}/\text{TiO}_2$ were conducted to investigate the stability of the sonocatalytic activity. Figure 8 shows that $\text{ZnSe-GR}/\text{TiO}_2$ exhibited no significant loss in photocatalytic activity after four successive RhB degradations. This indicates that $\text{ZnSe-GR}/\text{TiO}_2$ was stable and could not be photocorroded during the photocatalytic oxidation of RhB. Thus, $\text{ZnSe-GR}/\text{TiO}_2$ is a promising sonocatalyst for environmental purification. The modification of graphene improved the photocatalytic performance and increased the stability of ZnSe and TiO_2 nanocrystals.

Table 1

Sonodegradation rate (k_{app}) constants and BET surface areas of TiO_2 , GR-TiO_2 , ZnSe/TiO_2 , and $\text{ZnSe-GR}/\text{TiO}_2$.

Sample	BET surface area (m^2/g)	k_{app} (min^{-1})
TiO_2	11.59	6.95×10^{-4}
ZnSe/TiO_2	25.34	2.82×10^{-3}
GR-TiO_2	51.95	4.22×10^{-3}
$\text{ZnSe-GR}/\text{TiO}_2$	49.63	10.32×10^{-3}

Fig. 7. Removal of RhB (a) and $-\ln(C_t/C_{\text{ads}})$ plots (b) with increasing ultrasonic irradiation time in the presence of TiO_2 , ZnSe/TiO_2 , $\text{GR}-\text{TiO}_2$, and $\text{ZnSe-GR}/\text{TiO}_2$.

tals. This is beneficial for practical application, as the enhanced photocatalytic activity and suppressed catalyst deactivation will lead to more cost-effective operation.

3.2.3. Generation of ROS

Figure 9(a) shows the UV-vis absorption spectra of 1,5-di-phenyl carbazone (DPCO)-containing extracts from $\text{ZnSe-GR}/\text{TiO}_2$ sonocatalysis experiments. DPCI was oxidized to DPCO. Electrons were excited from the valence to conduction bands upon ultrasonic irradiation. Electron-hole pairs formed on the $\text{ZnSe-GR}/\text{TiO}_2$ surface. Electrons and holes reacted with dissolved O_2 and adsorbed H_2O to produce $\cdot\text{O}_2^-$ and $\cdot\text{OH}$, respectively. $\cdot\text{OH}$ then oxidized DPCI to DPCO. DPCO was extracted with benzene, and its absorbance at 560 nm was detected. The production of $\cdot\text{OH}$ was also detected. The DPCO absorbance increased with increasing time [35]. Figure 9(b) shows the UV-vis absorption spectra of DPCO-containing extracts in the presence of TiO_2 under ultrasonic irradiation. The results show that $\text{ZnSe-GR}/\text{TiO}_2$ was a more efficient sonocatalyst.

The sonocatalytic degradation of dyes in the presence of TiO_2 has been widely reported. Dye oxidation depends on $\cdot\text{OH}$ production [36] according to a mechanism involving hot spots and sonoluminescence. Cavitation first increases from the nucleation of bubbles, resulting in hot spots in solution. These hot

spots pyrolyze H_2O to form $\cdot\text{OH}$, as shown in Reaction (1) [37]. Sonoluminescence involves intense UV light. TiO_2 particles are excited and act as a photocatalyst during sonication. Usually sonochemical reaction pathways for the degradation of organic compounds by the sonolysis of water as the solvent inside the collapsing cavitation bubbles under extremely high temperature. In the presence of a sonocatalyst, ultrasound results in the sonolysis of water coupled with catalysts producing electron-hole pairs, as shown in Reaction (2). Electron-hole pairs produce $\cdot\text{OH}$ and $\cdot\text{O}_2^-$, which degrade the dyes to CO_2 , H_2O , and

Fig. 8. Successive sonocatalytic degradations of RhB by ultrasonic irradiation in the presence of $\text{ZnSe-GR}/\text{TiO}_2$.

Fig. 9. UV-vis absorption spectra of DPCO-containing extracts from ultrasonic irradiation in the presence of $\text{ZnSe-GR}/\text{TiO}_2$ (a) and TiO_2 (b) with increasing time.

Fig. 10. Proposed mechanism for the sonocatalytic degradation of RhB and generation of reactive oxygen species (ROS) by ZnSe-GR/TiO₂.

inorganic compounds, as shown in Reactions 3–5 [38].

A mechanism for the degradation of pollutants by ZnSe-GR/TiO₂ under ultrasonic irradiation is proposed in Fig. 10.

4. Conclusions

A ZnSe-graphene/TiO₂ composite was prepared by the ethylene glycol-assisted hydrothermal reaction of GONS/Zn²⁺, Na₂SeSO₃, and TiO₂. GONS acted as a precursor of graphene and as a dispersant and two-dimensional growth template for ZnSe and TiO₂ nanoparticles. ZnSe-graphene/TiO₂ exhibited intense red-shifted absorption compared with that of TiO₂ and ZnSe/TiO₂. The RhB degradation and ROS generation results suggested that ZnSe-graphene/TiO₂ was a more effective sonocatalyst than TiO₂. The high RhB degradation activity was attributed to a high charge mobility and red-shifted absorption edge of ZnSe-graphene/TiO₂.

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Graphical Abstract

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ZnSe-graphene/TiO₂ was hydrothermally prepared, and its degradation of rhodamine B and generation of reactive oxygen species (ROS) under ultrasonic irradiation were investigated.

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