Highly efficient solar photocatalytic degradation of a textile dye by TiO₂/graphene quantum dots nanocomposite

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Abstract

Herein, two sunlight responsive photocatalysts including TiO₂ nanoparticles (NPs) and TiO₂/graphene quantum dots (GQDs) nanocomposite for degrading a textile dye, Reactive Black 5 (RB5), were prepared. The results showed that 100% of 50 ppm RB5 could be degraded by TiO₂ NPs and TiO₂/GQDs within 60 and 30 min sunlight irradiation, respectively. Hence, much better photocatalytic activity in degradation of RB5 was achieved by TiO₂/GQDs under sunlight irradiation compared with pure TiO₂ NPs due to its lower band gap (2.13 eV) and electron/hole recombination rate. The photocatalytic degradation mechanism of RB5 by TiO₂ NPs was elucidated by adding some scavengers to the solution. The main reactive species contributing to RB5 degradation were surface hydroxyl radicals. The first-order solar degradation rate constant of RB5 for TiO₂/GQDs is greater than that of TiO₂ NPs under sunlight illumination.

Keywords Azo dye · Kinetic · Photocatalysis · Mechanism · TiO₂/graphene quantum dots nanocomposite

1 Introduction

Visible-light photocatalysis is an advanced, green, and most efficient technique for environmental pollutants elimination in water and air [1]. Metal oxides such as TiO₂ and ZnO have been used as photocatalysts because of their high photosensitivity, stability, and great potential in water and air remediation [2]. Among metal oxides, TiO₂ is one of the extensively studied photocatalysts due to its low toxicity, low cost, high physicochemical stability, strongly oxidizable, and biocompatibility [3–5]. However, because of two major drawbacks, its practical application is hampered. These drawbacks are: (1) poor visible light absorption capacity due to its wide band gap (2) rapid recombination of photogenerated

electron/hole (e⁻/h⁺) pairs leading to reduce the quantum efficiency significantly [6, 7]. To solve these problems, effective strategies such as structural modification and band gap manipulation were devised [8–15]. The photocatalyst modification techniques include coupling with a narrow band gap semiconductor [16, 17], dye sensitization [18], noble metal deposition [19, 20], hydrogenation [21], and doping with metal and non-metal ions [22, 23]. Jia et al. [24] synthesized N-doped TiO₂/C nanocomposite to decompose Rhodamine B (RhB) under visible light. The dye photodegradation rate was greater for N-doped TiO₂/C nanocomposite with respect to pure TiO₂ and N-doped TiO₂. Wei et al. [25] prepared mesoporous TiO₂/graphitic carbon nitride (g-C₃N₄) hollow microspheres for degradation of phenol under visible light irradiation. The photocatalytic activity of TiO₂/g-C₃N₄ in degrading phenol under visible light irradiation was fivefold better than that of g-C₃N₄ alone.

Ton et al. [26] showed the photocatalytic efficiency of TiO₂/reduced graphene oxide (rGO) nanocomposites for degradation of methylene blue (MB) under visible light is 15 and 5 times greater than that of TiO₂-P25 and TiO₂/rGO nanocomposite, respectively. Hunge et al. [27] prepared WO₃/TiO₂ nanocomposite to decompose oxalic acid under sunlight irradiation. It was found that the 42 and 83% photodegradation of oxalic acid occur for WO₃ and WO₃/TiO₂ after 320 and 180 min sunlight irradiation,

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respectively. Rajender et al. [28] prepared TiO_2 /graphene quantum dots (GQDs) to decompose MB under visible light. They showed TiO_2 /GQDs has much better photocatalytic efficiency against MB than that of TiO_2 . The photocatalytic efficiency of TiO_2 /GQDs composite in destroying methyl orange (MO) under UV–vis light irradiation was investigated. The photocatalytic activity of TiO_2 /GQDs composite was significantly improved compared with that of pure TiO_2 [29]. Sun et al. [30] synthesized N-doped GQDs/ TiO_2 composites (g-NGQDs (green solids)/ TiO_2 and y-NGQDs (yellow solution)/ TiO_2) for degrading RhB solutions under visible light irradiation. The degradation performance of g-NGQDs/ TiO_2 composite was 9.4 times better than that of P25 TiO_2 . Monga et al. [31] prepared mono/bimetallic loaded TiO_2 nanocomposites of copper and gold to reduce 3-nitroacetophenone and 1-chloro-3-nitrobenzene and oxidation of salicylic acid under illuminating by visible light. They claimed the bimetallic/ TiO_2 nanocomposites exhibit higher photocatalytic activity compared with monometallic counterparts. Hao et al. [32] fabricated TiO_2 /g- C_3N_4 heterojunction composites which exhibited greater photocatalytic activity against RhB than that of pure g- C_3N_4 or TiO_2 under Xenon arc lamp with UV-cutoff filter. Shafaei et al. [33] prepared TiO_2 nanoparticles (NPs) and TiO_2 /GQDs nanocomposites for degradation of RhB under visible/solar light. They showed that the photocatalytic performance of TiO_2 /GQDs nanocomposites is much better than that of TiO_2 NPs. Chandra et al. [34] reported the synthesis of CuS/TiO_2 nanocomposites for hydrogen production by photocatalytic water splitting under UV–vis light irradiation. The H_2 production rate for CuS/TiO_2 nanocomposites was higher than those of pure TiO_2 nanospindles and CuS nanoflakes, respectively.

Herein, we designed two solar light active photocatalysts including TiO_2 NPs and TiO_2 /GQDs nanocomposite via a facile hydrothermal process to decompose an anionic azo dye, Reactive Black 5 (RB5), under sunlight irradiation. GQDs was synthesized by pyrolysis of citric acid (CA), similar to our previous work [35]. GQDs are two-dimensional sheets of graphene with a size smaller than 100 nm. They are non-toxic, free of heavy metals, having high thermal and electrical conductivity, good dispersibility in different solvents, and photoinduced-electron transfer properties [35].

1.1 Materials and methods

1.1.1 Materials

Titanium tetraisopropoxide (TTIP, 97.0%) from Sigma Aldrich, hydrochloric acid (37.0%), potassium iodide (99.0%), methanol (99.0%) and ethylene glycol (EG, 99.0%) from Merck, cetyl trimethylammonium bromide (CTAB, 99.0%) from BDH, ethanol (99.9%) from Bidestan, isopropanol (99.0%) from Mojallali Company, sodium fluoride

(99.0%) from Riedal, citric acid (99.5%) and sodium hydroxide ($\geq 97.0\%$) from Fluka, terephthalic acid (TPA, $\geq 98.0\%$) and p-benzoquinone (99.0%) from Riedel Company, and RB5 dye from Germany (Dystar Company) were used without further purification. For preparation of solutions deionized (DI) water was used.

1.2 Equipments

The Electrothermal MY6404 Heating Mantle (200 W) was used for the pyrolysis of CA. The Sigma 3–30 K centrifuge instrument was used to separate the photocatalysts from the solutions and in the photodegradation measurements. To determine the phase purity, the X-ray powder diffraction (XRD) pattern of the samples was provided by means of a Bruker/D8 Advanced diffractometer in the 2θ range from 5° to 80° , by 0.04° steps, with monochromatic CuK_α ($\lambda = 0.15406$ nm) radiation. The Fourier transform infrared (FTIR) spectra of the prepared nanomaterials were obtained with a KBr pellet on a Thermo Nicolet-Avatar 370 Spectrometer. The Unico UV-2100 spectrophotometer was used to record the UV–vis absorption spectra of the samples at room temperature. The TEM images of the samples were taken by an LEO 912 AB instrument. The acceleration voltage was 120 kV. Hitachi S4160 (Cold Field Emission) instrument was used to provide the field emission scanning electron microscopy (FE-SEM) images of the samples. The freeze-dryer (ALPHA 1–2 LD PLUS) was used for the preparation of GQDs. Temperature and pressure of freeze-dryer were set at -50°C and 0.05 mbar for 72 h. The nitrogen adsorption/desorption isotherms for prepared photocatalysts were obtained using the BELSORP-mini instrument at liquid nitrogen temperature (77.36 K) after being degassed at 300°C for 5 h. The zeta potential of the photocatalysts as a function of pH was measured by the Zeta sizer (Nano-ZS) from the Malvern instrument. The photoluminescence (PL) spectra of the photocatalysts were recorded by photoluminescence spectrometer RF-1501, Shimadzu. The total organic carbon (TOC) was measured by TOC-V_{CPH} Shimadzu analyzer.

1.3 Preparation of photocatalysts

1.3.1 TiO_2 NPs

TiO_2 NPs were prepared by one-pot hydrothermal method similar to our previous work [33]. Briefly, 0.004 mol TTIP as titanium source was added into HCl solution under stirring (bottle 1) and then 50 mL of EG was added into bottle 1. Then, 0.003 mol CTAB was added in 5 mL deionized water (bottle 2). After stirring for 30 min, the bottle 2 was added to bottle 1, stirred for 60 min, transferred into an autoclave, and was heated at 150°C for 20 h. The autoclave was cooled to

room temperature. The obtained white powder was washed with DI water and ethanol several times and dried at vacuum oven at 80 °C for 20 h.

1.3.2 GQDs

GQDs were prepared by the pyrolysis of CA using a heating mantle device [36–38]. In a typical process, 0.01 mol CA was put into a beaker and heated for about 5 min. Subsequently, the CA was liquated. The obtained liquid was cooled to room temperature. Then, 100 mL NaOH (0.25 M) solution was added dropwise to neutralize the solution to pH 7 under vigorous stirring. Finally, the solution was dialyzed in a dialysis bag of 3500 Da for 4 days. Then, the solvent was removed by freeze-drying.

1.3.3 TiO₂/GQDs nanocomposite

0.2437 g of TiO₂ NPs and 0.0062 g of GQDs were sonicated in 20 mL of deionized water and 10 mL of anhydrous ethanol for 30 min. The colloid was transferred into a 100 mL Teflon autoclave and heated to 160 °C for 4 h. Then, the autoclave was cooled to room temperature. The white powder was washed with deionized water and ethanol several times and dried in a vacuum oven at 60 °C for 20 h.

1.4 Photodegradation measurement

The photocatalytic activity of four photocatalysts (TiO₂ NPs, P25, GQDs, and TiO₂/GQDs) was investigated by the degradation of the aqueous solution of RB5 under sunlight irradiation. For this purpose, 60 mL aqueous solution of RB5 with a specified concentration was placed in a pyrex glass vessel. Then, a desired amount of the photocatalyst was added to the solution. The photocatalytic reaction was performed in the dark for 30 min to establish adsorption/desorption equilibrium between the photocatalyst and RB5. The results showed that 22.53% of RB5 was adsorbed within 30 min in dark. Then, the reaction vessel was exposed to sunlight. The experiments were performed on sunny days. The experiments were carried out by different initial dye concentrations (50–100 ppm), pHs (1–10), and a dose of catalyst (0.2–1.0 g/L). The temperature of the solution was in the range of 35–39 °C. During each experiment, roughly 5 mL solution was extracted into a centrifugal tube at certain time intervals and centrifuged to separate the photocatalyst. Then, the absorbance of the filtered supernatant was measured with a UV–vis spectrophotometer at maximum wavelength, $\lambda_{\max}$, of RB5 (598 nm). The degradation efficiency, DE%, of RB5 is calculated using the following equation:

$$DE\% = \frac{C_0 - C}{C_0} \times 100, \quad (1)$$

where C_0 and C are the dye concentration at the initial and time t , respectively.

In this study, the amount of hydroxyl radicals ($\cdot\text{OH}$) formed on the surface of TiO₂ was analyzed by using TPA as a chemical prob [39]. It has been well known that TPA reacts with $\cdot\text{OH}$ radicals quickly produce 2-hydroxyterephthalic acid (2-HTPA) which is a highly fluorescent adduct. In a typical procedure, 0.8 g/L of TiO₂ NPs was added into 100 mL of 5×10^{-4} M TPA solution in 2×10^{-3} M NaOH. After exposing to sunlight, the suspension was stirred. After each 15 min, 5 mL solution was extracted into a centrifugal tube and centrifuged to separate the photocatalyst. The solution was analyzed using a photoluminescence spectrometer. The PL emission intensity of the 2-HTPA was recorded at 430 nm after excitation at 315 nm. The PL intensity of the peak at 430 nm is directly proportional to the amount of $\cdot\text{OH}$, which is formed on the surface of TiO₂.

2 Results and discussion

2.1 Characterization of photocatalysts

The XRD technique was performed to evaluate the phase purity and crystallinity of the prepared nanomaterials. The XRD patterns of TiO₂ NPs, GQDs, and TiO₂/GQDs are shown in Fig. 1a. TiO₂ NPs and TiO₂/GQDs have the same diffraction peaks centered about 2θ values of 25.1°, 37.9°, 48°, 62°, 62.8°, 70.1°, and 75° indexed to (101), (004), (200), (105), (204), (220) and (215) crystal planes with a tetragonal crystal structure of the anatase phase, respectively. The XRD pattern of GQDs represents a broad peak centered at $2\theta = 32^\circ$ assigned to the graphite (002) plane. The peak is broad due to the small size and low crystallinity of GQDs. The average crystallite size, D_{hkl} , of the samples was calculated using the Debye–Scherrer formula [40]:

$$D_{hkl} = \frac{k \times \lambda}{B_{hkl} \cos \theta_{hkl}}, \quad (2)$$

where λ is the X-ray wavelength, β is the full width at half maximum, θ is the Bragg angle, and k is the so-called shape factor which is equal to 0.9. The calculated average crystallite size of TiO₂ NPs and TiO₂/GQDs was calculated as 7.81 and 9.96 nm, respectively. As Fig. 1a shows no extra peak is observed for TiO₂/GQDs compared with pure that of TiO₂. Also, the position and intensity of the diffraction peaks were not changed indicating the GQDs did not change the crystal

Fig. 1 **a** The XRD patterns, **b** FTIR spectra, **c** UV–vis spectra, **d** Tauc plots of the GQDs, TiO₂ NPs, and TiO₂/GQDs, **e** the N₂ adsorption/desorption isotherms of TiO₂ NPs, **f** the N₂ adsorption/desorption isotherms of TiO₂/GQDs

structure of TiO₂. The peak of GQDs was not observed in the TiO₂/GQDs which might be due to the small amount and low crystallinity of GQDs compared with TiO₂.

Figure 1b represents the FTIR spectra of TiO₂ NPs, GQDs, and TiO₂/GQDs. The FTIR spectrum of the TiO₂ NPs displays a broad band at the 3403.27 cm⁻¹ corresponding to the hydrogen-bonded O–H stretching vibrational from the surface hydroxyl group. The characteristic absorption peak at ~2958.75 cm⁻¹ is assigned to the C–H stretching vibration. The peak at the 1630.94 cm⁻¹ is attributed to the hydroxyl groups of water. A weak band at about 751.06 cm⁻¹ originates from the Ti–O–Ti stretching and

bending vibrational modes. As Fig. 1b shows the FTIR spectrum of GQDs reveals the presence of some functional groups at the surfaces and edges of GQDs. A broad band around 3443.37 cm⁻¹ is attributed to the stretching vibration of O–H. The band at 2950.00 cm⁻¹ is assigned to the stretching vibration of C–H bond. The peak at the 1729.80 cm⁻¹ reveals the existence of a C=O functional group in the GQDs. The peaks at 1389.45 cm⁻¹ and 1582.49 cm⁻¹ originate from C=C bonds of the aromatic and COO⁻ bonds proving the existence of the COOH group. The peak band at 1079.70 cm⁻¹ is associated with the C–OH bond. The FTIR spectrum of the TiO₂/GQDs represents the broad absorption

band at $\sim 3403.41\text{ cm}^{-1}$ which is corresponding to O–H stretching vibration. The band at 1634.05 cm^{-1} is related to bending vibration of –OH. The bands at $\sim 1089.90\text{ cm}^{-1}$ and $\sim 992.04\text{ cm}^{-1}$ are related to the C–O–C bonds and epoxy groups, respectively. A weak band at 735.44 cm^{-1} is attributed to the stretching vibration of Ti–O–Ti. The FTIR results indicating that GQDs were successfully attached to the TiO₂ NPs.

Figure 1c presents the UV–vis spectra of the TiO₂ NPs, GQDs, and TiO₂/GQDs nanocomposite. As Fig. 1c shows TiO₂ NPs have a band edge at 507.89 nm while for those of GQDs and TiO₂/GQDs are at 275.92 and 568.63 nm, respectively. The peak around 228 nm for GQDs could be assigned to the $\pi \rightarrow \pi^*$ transition of aromatic C=C bonds.

The band gap of the samples is determined by fitting the optical transition at the absorption edges using the Tauc/David–Mott model described by the equation [41]:

$$(ah\nu)^n = B(h\nu - E_g), \quad (3)$$

where h is the Planck's constant, ν is the frequency of vibration, α is the absorption coefficient, E_g is the band gap, B is a proportionality constant and n is equal to 2 or 1/2 for an allowed indirect and direct transitions, respectively. By plotting $(ah\nu)^n$ vs. the photon energy and extrapolating the linear part of the plot to the x-axis, the band gap can be calculated. The Tauc plots of the photocatalysts are shown in Fig. 1d. The band gaps of GQDs, TiO₂ NPs, and TiO₂/GQDs were calculated as 4.40, 2.23, and 2.13 eV, respectively. The band gap of TiO₂ NPs is less than that of the TiO₂ (P25) bulk (3.2 eV). Doping of TiO₂ with metal or nonmetal elements and manipulating its structure and size are two main methods used for narrowing its band gap. Wang et al. [42] prepared TiO₂ NPs with the band gap of 2.75 eV by engineering its structure and morphology. Our preparation procedure for TiO₂ NPs used in this work is very similar to that of Wang et al. [42].

The surface area of the photocatalyst is a key factor in a photocatalytic degradation reaction. The specific surface area for the TiO₂ NPs and TiO₂/GQDs was estimated from their nitrogen adsorption/desorption isotherms by Brunauer–Emmett–Teller (BET) method (Fig. 1e, f). The specific surface area of TiO₂ NPs and TiO₂/GQDs was 235.87 and 133.32 m²g^{−1}, respectively. The nitrogen adsorption/desorption isotherms of TiO₂ NPs and TiO₂/GQDs are the characteristics of mesoporous materials. The specific surface area, average pore size, and total pore volume of TiO₂ NPs and TiO₂/GQDs are listed in Table 1.

Figure 2a–c illustrates the TEM images of the TiO₂ NPs, GQDs, and TiO₂/GQDs. The insets of Fig. 2a–c are the particle size distribution (PSD) histogram for TiO₂ NPs, GQDs, and TiO₂/GQDs nanocomposite calculated by Digimizer software [43]. TiO₂ NPs (Fig. 2a) are nearly spherical with

Table 1 The surface properties of TiO₂ NPs and TiO₂/GQDs

Sample	Specific surface area (m ² g ^{−1})	Average pore size (nm)	Total pore volume cm ³ g ^{−1}
TiO ₂ NPs	235.87	7.4286	0.4381
TiO ₂ /GQDs	133.32	9.2996	0.3100

an average particle size of about 4.04 nm. As Fig. 2b shows, the homogeneous GQDs are well dispersed. The PSD histogram in the inset of Fig. 2b shows the GQDs have an average particle size of 18.17 nm with a narrow size distribution. As shown in Fig. 2c the TiO₂ NPs retain the morphology after incorporating with GQDs. The average particle size of TiO₂/GQDs was calculated as about 12 nm.

The morphology of the TiO₂ NPs, GQDs and TiO₂/GQDs was investigated by FE-SEM and shown Fig. 3a–j. As this figure shows, the TiO₂ NPs possess a near-spherical shape with diameters in the range of 4.9–7.7 nm (Fig. 3a). The elemental mapping confirms the presence of Ti and O elements in TiO₂ NPs as shown in Fig. 3b–d.

Figure 3e shows the FE-SEM image of the GQDs. The particles have sheet-like shapes. The elemental mapping of GQDs (Fig. 3f) clearly shows the elements of C and O distributed in the GQDs.

The morphology of the TiO₂/GQDs is given in Fig. 3g–j. Figure 3g shows that TiO₂/GQDs has spherical morphology. To further confirm the formation of the nanocomposite, the elemental mapping of TiO₂/GQDs nanocomposite was shown in Fig. 3h–j and confirm the existence of C, O, and Ti elements.

2.2 Degradation of RB5 by TiO₂ NPs under sunlight irradiation

The most important parameters for the degradation process of RB5 including catalyst loading, pH, and dye concentration were investigated.

2.2.1 Catalyst loading

In this work, the concentration of TiO₂ NPs was changed from 0.2 to 1.0 g/L. The concentration of RB5 (50 ppm) was kept constant during all experiments. As shown in Fig. 4a, the RB5 dye was photodegraded with 60 min irradiation with sunlight with different amounts from 63.00 to 100.00% when the photocatalyst concentration was increased from 0.2 to 0.8 g/L. This means the number of active sites increases which in turn enhances the degradation of dye. By increasing the concentration from 0.8 to 1.0 g/L, the degradation of RB5 dye decreased due to the agglomeration of NPs, resulting in a reduction in the

Fig. 2 TEM images of **a** TiO₂ NPs, **b** GQDs, **c** TiO₂/GQDs. The insets are the corresponding PSD

photocatalyst surface area. Hence, we chose 0.8 g/L for the photocatalyst concentration for the next experiments.

2.2.2 Initial dye concentration

The RB5 concentration was varied in the range of 50–100 ppm. The results illustrated that the complete photocatalytic degradation of RB5 dye was achieved for 50 ppm of the dye. By further increase of RB5 dye concentration from 50 to 100 ppm, the percentage of degradation of RB5 decreased to 48.80% (Fig. 4b). At high dye concentrations, more active sites of TiO₂ are covered by dye molecules leading to the reduction in photon absorption. Hence, the degradation rate decreases.

2.2.3 Initial solution pH

The zero-point charge, pH_{zpc} , of TiO₂ NPs was determined by plotting the zeta potential vs. solution's pH as shown in Fig. 4c. The pH_{zpc} of TiO₂ is about 3.3. At the $pH < pH_{zpc}$ and $pH > pH_{zpc}$, the surface of the TiO₂ NPs was positively and negatively charged, respectively. RB5 is an anionic dye. Hence, it is expected it is more degraded at $pH < 3.3$. In this work, the initial solution pH was changed from 1 to 10 by adding HCl (0.1 M) or NaOH (0.1 M) into the solution (Fig. 4d). The natural pH of the RB5 dye aqueous solution was 4.9. When the pH of the solution decreased from 10.0 to 4.9, the percentage of RB5 degradation dye increased from 8.92 to 17.32%. When the pH of the solution was reduced from 4.9 to 2.0, the percentage

Fig. 3 FE-SEM images and the elemental mapping of **a–d** TiO₂ NPs, **e, f** GQDs, **g–j** TiO₂/GQDs

of RB5 dye degradation increased from 17.32 to 100.00%. When pH of the solution was decreased from 2.0 to 1.0, the percentage of degradation of RB5 dye was decreased to 96.00%. At $\text{pH} < \text{pH}_{\text{zpc}}$, RB5 anions were easily adsorbed to TiO₂ with a positive surface charge. At $\text{pH} > \text{pH}_{\text{zpc}}$, RB5 anions were excluded from the surface of the photocatalyst because of the presence of more negatively charged sites and electrostatic repulsion. Hence, pH 2 was chosen as the optimum value.

2.3 Photocatalytic degradation kinetics

The experimental data were fitted well with the first-order kinetics model. The first-order rate constant can be calculated from the equation as follow:

$$\ln \frac{C_t}{C_o} = -kt, \quad (4)$$

Fig. 4 Effect of **a** catalyst loading, **b** initial dye concentration (dose of catalyst = 0.8 g/L, pH 2) on the degradation efficiency of RB5 dye, **c** zeta potential versus pH for TiO₂ NPs, **d** degradation of RB5 at vari-

ous initial pH (C_0 = 50 ppm, dose of catalyst = 0.8 g/L). The sunlight irradiation time = 60 min and temperature 35–39 °C is the same in **a**, **b**, **d**

where k is rate constant. C_0 and C_t are the concentration of dye at initial and time, t . Table 2 gives the degradation rate constants of RB5 with different initial concentrations by TiO₂ NPs and TiO₂/GQDs under sunlight irradiation. As Table 2 shows the rate constant of photocatalytic degradation of RB5 by TiO₂/GQDs is larger than that of pure TiO₂ NPs. Also, a complete RB5 degradation was approximately reached in a shorter time when TiO₂/GQDs was utilized.

2.4 Mechanism

Some experiments were designed to determine the mechanism of degradation of RB5 dye such as the effect of

Table 2 The first-order rate constants of photocatalytic degradation of RB5 by TiO₂ NPs and TiO₂/GQDs with different concentrations of RB5 (C_0 = 50–100 mg/l, dose of catalyst = 0.8 g/L, pH 2, sunlight irradiation time = 60 min for TiO₂ NPs and 30 min for TiO₂/GQDs, 35–39 °C)

Initial dye concentration (ppm)	k (min ⁻¹)	R^2
TiO ₂		
60	0.026	0.91
70	0.021	0.88
100	0.009	0.89
TiO ₂ /GQDs		
50	0.160	0.93

different radical scavengers, UV–vis spectra of RB5 during the photodegradation process, and desorption.

2.4.1 Radical scavengers

At first, all the experiments were performed in dark for 30 min to establish adsorption/desorption equilibrium. One experiment was performed for the aqueous RB5 solution in the absence of photocatalyst under sunlight irradiation. The results exhibited that the dye concentration did not change with increasing the irradiation time. This shows that the RB5 was stable versus light irradiation without photocatalyst. Different scavengers including methanol, isopropanol, p-benzoquinone, and fluoride were used as shown in Fig. 5a. Methanol as a hole scavenger could not inhibit the chromophore degradation implying that the hole did not play a role in the decolorization. By adding 60 mM isopropanol as OH_{bulk} scavenger, the degradation of RB5 did not change

significantly. This shows OH_{bulk} was not the main oxidant for dye photodegradation. By adding 60 mM NaF as $\cdot\text{OH}_{\text{ads}}$ scavenger, the degradation of RB5 was slowed down. When p-benzoquinone as a superoxide radical scavenger was added into the solution, the degradation rate of RB5 decreased. The results indicate that $\cdot\text{OH}_{\text{ads}}$ was the major species in the photocatalytic degradation process. We could prove these observations by theoretical calculations as follows. The relationship among the potentials of conduction and valence bands, band gap, and the energy of free electrons of a semiconductor can be calculated by the following equations:

$$E_{\text{CB}} = X - E_{\text{e}} - 0.5E_{\text{g}} \quad (5)$$

$$E_{\text{VB}} = E_{\text{CB}} + E_{\text{g}}, \quad (6)$$

where E_{CB} and E_{VB} are potential energy (eV) of the conduction and valence bands, respectively, X is the absolute

Fig. 5 **a** Effect of different scavengers on the degradation efficiency of RB5 by TiO_2 under different sunlight irradiation times, **b** UV–vis spectra of RB5, **c** the PL spectra of the TiO_2 in TPA solution at dif-

ferent times ($C_0 = 50$ ppm, pH 2, dose of catalyst = 0.8 g/L, sunlight irradiation time = 60 min, 35–39 °C)

electronegativity of a semiconductor, and E_e is the energy of free electrons in a standard hydrogen electrode (4.5 eV). For TiO_2 NPs, the absolute electronegativity and band gap energy are calculated 5.81 eV and 2.23 eV, respectively. E_{CB} and E_{VB} were calculated 0.195 eV and 2.425 eV, respectively. The results show that calculated E_{CB} is insufficient (0.195 eV) to reduce O_2 to $\cdot\text{O}_2^-$ at CB ($\text{O}_2/\cdot\text{O}_2^- = -0.33$ eV vs. NHE) and superoxide radicals are partially formed. On the other hand, the theoretical value of E_{VB} of TiO_2 is 2.425 eV. It is sufficiently higher than that required for the formation of $\cdot\text{OH}$ at VB ($\cdot\text{OH}/\text{OH}^-$ 1.99 eV vs NHE) which indicates the possibility of formation of $\cdot\text{OH}$. The theoretical and experimental data in Fig. 5a prove that $\cdot\text{OH}$ has a greater role than $\cdot\text{O}_2^-$ in photodegradation reaction. Hence, the $\cdot\text{OH}_{\text{ads}}$ is major species in the photocatalytic degradation process.

2.4.2 UV–vis spectroscopy

Figure 5b shows the UV–vis spectra of RB5 in an aqueous solution in the presence of TiO_2 NPs at different interval times. The UV–vis spectrum of RB5 generally exhibits three main peaks at wavelengths of 598, 312, and 254 nm attributed to chromophore containing along with conjugated π -system linked by two azo groups, naphthalene, and benzene components, respectively. As this figure shows the complete photodegradation of the three components of RB5 by TiO_2 NPs took place within 255 min. The rapid disappearance of the peak at 598 nm less than 45 min suggests that the chromophore component which is responsible for the characteristic color of RB5 has broken. After 255 min, the corresponding peaks of naphthalene and benzene groups have been disappeared. This peak is formed because of the reductive cleavage of azo bonds in RB5 [4, 44]. This could be related to the separation of sulfone, sulfonate, and amine groups from the dye molecule. With increasing irradiation time, the intensity of this peak decreased.

The PL spectra of the 2-HTPA were recorded at 430 nm after excitation at 315 nm at different sunlight irradiation times and shown in Fig. 5c. A broad peak was observed at around 430 nm of 2-HTPA for the TiO_2 photocatalyst. The increase in PL intensity with elapsing time reflects that as the degradation proceeds more $\cdot\text{OH}$ radicals are produced.

2.4.3 Mineralization

The TOC analysis was used to investigate the mineralization of the RB5. The % mineralization efficiency was calculated using the following formula:

$$\% \text{ Mineralization efficiency} = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100, \quad (7)$$

where TOC_0 and TOC_t are the values of TOC at $t=0$ and $t=t$, respectively. 92.39% of mineralization was achieved within 240 min under the experimental conditions.

2.5 Photocatalytic degradation of RB5 under sunlight irradiation by TiO_2/GQDs

The pH_{ZPC} of GQDs (Fig. 6a) and TiO_2/GQDs (Fig. 6b) was determined by plotting the zeta potential vs. pH. The pH_{ZPC} of GQDs and TiO_2/GQDs are 2.40 and 3.42, respectively. The photocatalytic activity of the TiO_2/GQDs nanocomposite against RB5 under sunlight irradiation was evaluated under the optimum conditions of TiO_2 ($C_0 = 50$ ppm, pH 2, dose of catalyst = 0.8 g/L, sunlight irradiation time = 60 min, 35–39 °C) and compared with the that of TiO_2 NPs, P25, and GQDs. Figure 6c shows 100.00% of RB5 was degraded by TiO_2/GQDs within 30 min whereas the complete degradation of dye occurred within 60 min for TiO_2 NPs. While, the percentage of dye degradation by P25 and GQDs within 60 min sunlight irradiation was 91.16% and 1.55%, respectively.

The PL spectra of TiO_2 NPs and TiO_2/GQDs were recorded and presented in Fig. 6d. The PL intensity is directly related to the recombination of e^-/h^+ pairs. TiO_2/GQDs has weaker PL intensity as compared to that of TiO_2 . It indicates the e^-/h^+ recombination rate for TiO_2/GQDs is less than that of TiO_2 .

The nanocomposite exhibited superior photocatalytic activity for RB5 degradation because of the following reasons:

1. TiO_2/GQDs has lower band gap ($E_g = 2.13$ eV) compared to that of TiO_2 ($E_g = 2.23$ eV). Here, it could harvest more sunlight.
2. During the photocatalytic process, GQDs serve as electron collectors in the nanocomposite which could reduce the e^-/h^+ recombination rate [45].
3. The π – π interactions between aromatic rings of RB5 and the conjugated structure of GQDs increase the adsorption of the dye on the surface of the TiO_2/GQDs [26].
4. The PL emission intensity of TiO_2/GQDs is less than that of TiO_2 . Hence, loading GQDs on TiO_2 could speed up the charge transfer and separation [46].

3 Conclusion

In this work, we successfully prepared sunlight-responsive photocatalysts for degrading RB5 including TiO_2 NPs and TiO_2/GQDs via a simple hydrothermal route. TiO_2/GQDs represented much better photocatalytic activity in degrading of RB5 under sunlight irradiation compared with pure TiO_2 NPs due to its lower bandgap (2.13 eV) and the e^-/h^+

Fig. 6 Zeta potential versus pH for **a** GQDs, **b** TiO₂/GQDs, **c** the comparative studies for P25, TiO₂, GQDs and TiO₂/GQDs (C_0 =50 ppm, pH 2, the dose of catalyst=0.8 g/L, sunlight irradiation

time=60 min, 35–39 °C), **d** PL spectra of TiO₂ and TiO₂/GQDs at 325 nm excitation wavelength

recombination rate. A series of radical-trapping experiments showed that the main reactive species contributing to RB5 degradation were $\cdot\text{OH}_{\text{ads}}$ radicals. The first-order solar degradation rate constant of RB5 for TiO₂/GQDs was greater than that of TiO₂ under sunlight illumination.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this article.

Availability of data and material All data generated or analyzed during this study are included in this published article.

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