GQD/Bi_2O_3 Composite for high-efficient photocatalysts

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Abstract: Bismuth oxide (Bi_2O_3) is one of the potential visible-light photocatalytic materials, however, due to low electron mobility and short minority carrier diffusion length, the photocatalytic activity of Bi_2O_3 is restricted. The GQD/Bi_2O_3 composites were synthesized stably depositing single-crystalline graphene quantum dots (GQDs) with absorption edge at ~10nm, prepared by using a top-down method. The GQD-Bi_2O_3 heterojunctions were successfully established, the photo-generated electrons transfer from the Bi_2O_3 to the GQDs at the interface of the GQD-Bi_2O_3 heterojunctions, result in efficient electron-hole pairs separation and higher photocatalytic efficiency. The optimum visible performance is achieved at GQD content of 1.0 wt %, the RhB dye was nearly completely decoloured after 90 min of visible-light irradiation, and then decrease at higher doping levels due to the thicker GQD layer will cover the active sites of Bi_2O_3, thus leading to the greatly reduced catalytic activity.

1 Introduction

The degradation of organic pollutants by using semiconductor photocatalysts has been extensively studied during the past years because of its advantages of high efficiency, energy conservation and no secondary pollution[1-3]. Bismuth oxide (Bi2O3), a semiconductor that has a narrow bandgap of 2.8 eV, has recently received considerable attentions as potential visible-light photocatalytic materials [4-5]. However, Bi2O3 alone exhibits a poor photocatalytic activity primarily because its conduction band is too low for the oxidation of the surface O2 to O^{-}, leading to a high recombination rate of the electron hole pairs [6-7]. To improve the photocatalytic activity of Bi2O3, several strategies have been attempted in the literatures, e.g. element doping, surface modification with noble metal , coupling with other semiconductors or quantum dots (QDs) like CdS, GaAs, CdTe, ZnS, etc. [8-10]. In this paper, GQDs/Bi2O3 nanocomposite was successfully synthesized by a facile and green method, and its photocatalytic performance for degrading Rhodamine B (RhB) with different GQD contents was evaluated under visible-light irradiation.

2 Materials and Methods

2.1.Reagents and chemicals

All the reagents were of analytical grade and used without further purification. Water-soluble graphene oxide (GO) sheets were prepared from natural graphite powders by using a hydrothermal method. Graphene sheets (GSs) were obtained by the thermal deoxidization of GO sheets in a tube furnace at 200-300℃ for 2 h with a heating rate of 5 °C·min-1 in a nitrogen atmosphere.

2.2.Preparation of Bi_2O_3 nanoparticles

Bi2O3 nano-particles were prepared by using a facile solvothermal method. 0.364 g of Bi(NO3)3.5H2O and 0.6 g of Polyvinylpyrrolidone (PVP) were dissolved into a 55 mL ethylene glycol solution of nitric acid (1 M). The mixture was continuously stirred for 0.5 h, and then transferred to a Teflon-lined stainless-steel autoclave (100 mL). The solvothermal treatment was conducted at 433 K for 12 h. Afterwards, the mixture was cooled to room temperature and then separated by centrifugation, the resulted solid was washed three times by using deionized (DI) water and absolute ethanol, dried at 333 K for 12 h and calcined at 543 K for 3 h in air to obtain the final product.

2.3.Preparation of GQDs

In a typical procedure to prepare GQDS, 0.1 g of GSs were oxidized in a mixture of concentrated H2SO4 (10 ml) and HNO3 (30 ml) for 24 h under ultrasonication. The mixture was then diluted with DI water (250 ml) and filtered through a 0.22 μm microporous membrane to remove the acids. Then the pH value of the mixture was adjusted to 8 by using NaOH and transferred to a Teflon-lined autoclave (50ml) and heated at 200 °C for 10 h. After being cooled to room temperature, the resulting black suspension was filtered through a 0.22 μm microporous membrane. The obtained colloidal solution was further dialyzed in a dialysis bag (molecular weight cut off = 3500 Da) overnight to give the strongly fluorescent GQDs.

2.4.Synthesis of GQDs/Bi_2O_3Composites

The composites were prepared by using a hydrothermal deposition method. Typically, Bi2O3 (0.1g) was added to 10 mL of GQD solution under stirring for 1h at room temperature to obtain a homogeneous suspension. Afterwards, the suspension was transferred into a Teflon-lined autoclave (20 ml), heated at 150 °C for 4 h and dried in a vacuum oven at 80 °C overnight to obtain the GQDs/Bi2O3 composites containing 1.0 wt% of GQDs.

2.5.Photocatalytic Test

The degradation of Rhodamine B (RhB) was evaluated by adding 0.01 g of the prepared GQDs/Bi2O3 photocatalysts in 100 ml of RhB solution (10 mg·L-1) at room temperature. The visible light was obtained from a 350W xenon lamp equipped with a 420 nm ultraviolet cutoff filter.

2.6.Characterization.

TEM observations were performed on a JEOL JEM-2010F electron microscope operating at 200 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were performed on Thermo Nicolet Avatar 370 FT-IR.

3 Results and Discussion

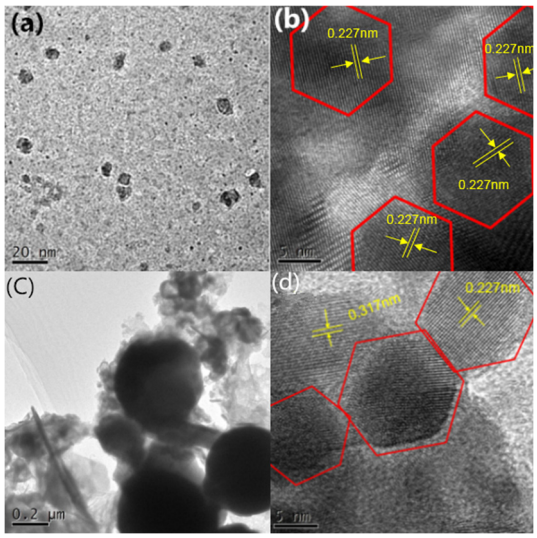


Fig. 1. TEM and HRTEM images of GQDs (a, b) and1.0 wt % doping GQDs/ Bi_2O_3 composites (c, d)

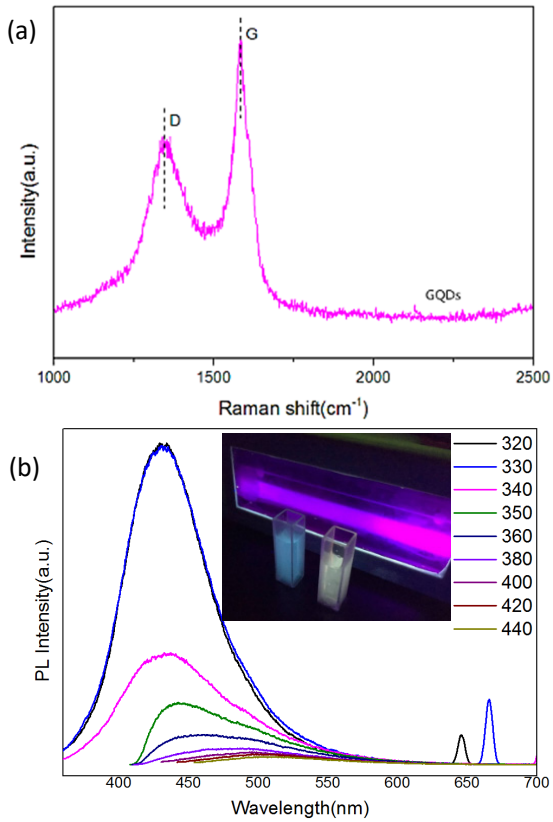
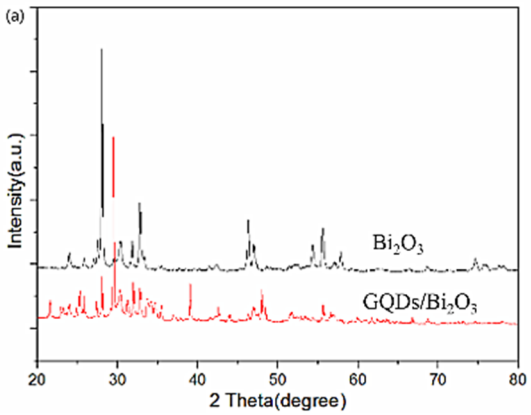


Fig. 2. Raman (a) and PL (b) spectrum of GQDs

TEM images in Fig.1a shows that the prepared GQDs have a relatively uniform particle distribution with an average lateral size of 10nm. As displayed in the HRTEM images (Fig.1b), an obvious single-crystal structure is observed for the GQDs, with an interplanar spacing of 0.227 nm. Moreover, the successful synthesis of GQDs was also verified by the Raman and PL analysis. The two characteristic D and G bands at 1355 cm-1 and 1580 cm-1, which are attributed, respectively, to disordered carbon and ordered sp^2 carbon, can be clearly observed in the Raman spectrum (Fig. 2a). The PL spectra for the aqueous suspension of GQDs (Fig. 2b) shows the typical excitation-dependent PL behaviors, exhibiting blue color (inset in Fig. 2b) when being excited at 325 nm.



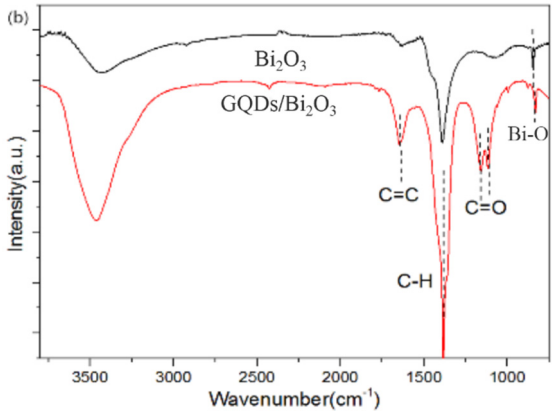
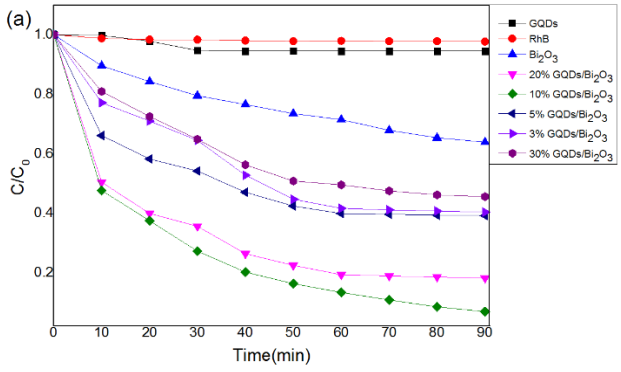


Fig. 3. XRD (a) and FT-IR (b) spectrum of Bi_2O_3 alone and 1.0 wt % $GQDs/Bi_2O_3$ composite.

Under the hydrothermal "sintering" conditions, GQDs were stably deposited on the surface of Bi2O3 nanoparticles. TEM and HRTEM images (Fig.1c and 1d) of the GQDs/Bi2O3 composites with 1.0 wt% GQD loading demonstrate that GQDs are well dispersed on Bi2O3 nanoparticles. The structure of the $GQDs/Bi_2O_3$ composites is further characterized by using the XRD, FT-IR. As shown in Fig.3a, the XRD patterns of both Bi_2O_3 and $GQDs/Bi_2O_3$ exhibit the typical diffraction of anatase Bi_2O_3 [JCPDS: 41-1449]; while the interaction between GQDs and Bi_2O_3 during the hydrothermal process leads to the shift of the diffraction peaks to the higher angles in the XRD pattern of the $GQDs/Bi_2O_3$ composites. Compared with that of Bi_2O_3, the characteristic peaks attributed to C=C vibration at 1647 cm-1, C-H vibration at 1384 cm-1, C=O vibration at 1160 cm-1, and C-O vibration at 1116 cm-1 are observed in the IR spectrum of the $GQDs/Bi_2O_3$ composites (Fig.3b), confirming the existence of GQDs in the composites.



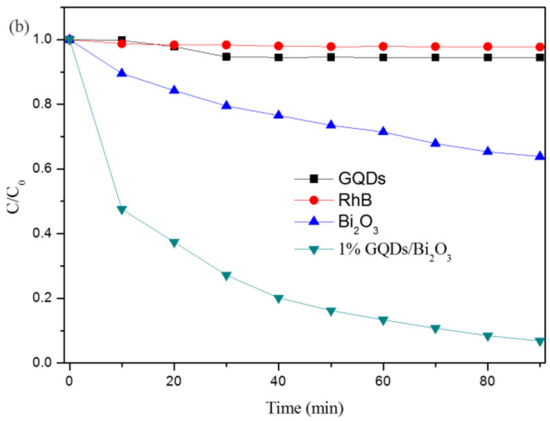


Fig.4.(a) Photocatalystic degradation rate curves of RhB using $GQDs/Bi_2O_3$ composites with different contents of GQDs as catalysts under the visible light . (b)Phtocatalystic degradation rate curves of RhB using GQD, Bi_2O_3, and $GQDs/Bi_2O_3$ as photocatalysts under the visible light.

Fig.4 shows that the photocatalytic activity of the composites to degrade RhB are significantly enhanced by coupling GQDs with Bi2O3. By using the GQDs/Bi2O3 composites with the optimum GQD loading of 1 wt%, 91% RhB can be decoloured after 90 min of visible-light irradiation. For comparison, by using the same amount of pure Bi2O3 or GQDs as the photocatalysts, only 28% or 6% RhB can be degraded within the same irradiation time (Fig. 4b). As expected, the visible-light response of pure Bi2O3 is limited by its nature of wide-band gap and high recombination rate of the electron hole pairs. The poor catalytic performance of pure GQDs can be ascribed to the large exciton binding energy (~0.8 eV estimated for 2 nm GQDs) that greatly increases the recombination rate of photoexcited electrons and holes. It also can be observed from Fig.4a that the optimum GQD loading for the composites as the photocatalysts is 1 wt%, a further increase in the GQD loading beyond the optimum value will cause a significant decrease of the photocatalytic activity of the composites.

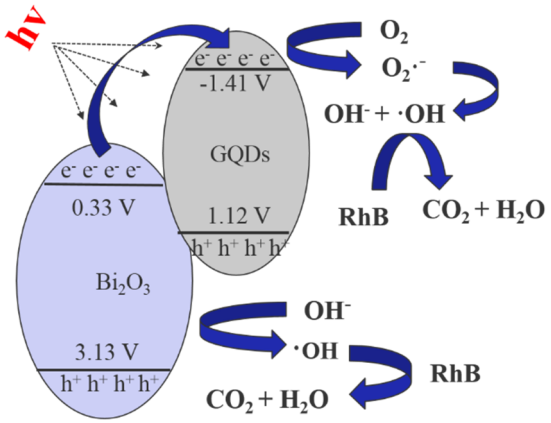


Fig. 5. Schematic of $GQDs/Bi_2O_3$nanocomposites combined with the possible reaction mechanism of photocatalytic procedure under Visible-Light Irradiation.

The photocatalytic mechanism of the GQDs/Bi2O3 composites can be lustrated in Fig.5. Under the irradiation of visible light, electrons can be excited from the VB to the CB in both GQDs and Bi2O3. Electrons in the CB of GQDs and holes in the VB of Bi2O3 could combine with O2 and OH- in the solution, respectively, to form ·OH, which is the most important reactive specie to degrade RhB. The coupling of Bi2O3 and GQDs in the composites leads to the transfer of the photo-generated electrons from Bi2O3 to GQDs, which rest at the GQD-Bi2O3 interface, resulting in the efficient electron-hole pairs separation and higher photocatalytic efficiency. When the GQD loading in the composite is too high, a thicker GQD layer will cover the active sites of Bi2O3, thus leading to the greatly reduced catalytic activity. Therefore, for the design of GQD-based hybrid photocatalysts with superior visible-light catalytic performance, it is crucial importance to construct monodispersed nanoparticle heterojunctions. We postulate that a monodispersion and thin monolayer of

soluble GQDs can be deposited on the surface of Bi2O3 nanoparticles by a hydrothermal process, and thus the optimum GQD-Bi2O3 heterojunctions at the nanoscale can be established at the low loading level.

Thus, the heterojunction material has alluring visible-light response, we can make a conclusion: on the one hand, the bandgap of GQDs is tuned as lowly as possible for harvesting more solar light, on the other hand, allow for construction of GQD-Bi2O3 heterojunctions at the interface of the two materials to drive the electron transfer between the GQDs and Bi2O3.

4 Conclusions

In summary, water-soluble GQDs are successfully loaded onto theBi2O3 in optimum density to form novel GQD sensitized Bi2O3 heterojunctions. The incorporation of GQDs can sensitize Bi2O3 and inhibit the fast recombination effectively, the photocatalytic activities under visible light irradiation obviously increased than pure Bi2O3. The optimum visible performance could be achieved when containing 1.0 wt % of GQD content, where the RhB dye was almost completely decolored after 90 min of visible-light irradiation. However, the catalytic activity of Bi2O3 would decrease when increasing the GQD content, since thicker GQD layer could cover the active sites of Bi2O3.

Acknowledgments

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