Enhanced visible light photocatalytic activity of AgI/TiO_2 composite fabricated by a grinding method

Jin Xu, Dasheng Gao, Shuang Cui, Xiaohua Wang and Ningning Liu

ABSTRACT

Through a simple grinding method, AgI/TiO_2 composites were successfully synthesized. The as-prepared AgI/TiO_2 composites were used as photocatalysts for Rhodamine B (RhB) degradation under visible light irradiation and exhibited excellent photocatalytic performance. In the presence of composites, almost 100% RhB was decomposed after 60 min. The photocatalytic activity of AgI/TiO_2-0.5 composite was optimal, which was 9.5 times higher than that of pristine TiO_2, and 15.6 times higher than that of AgI. Moreover, experimental results revealed that the improved photocatalytic activity was not only ascribed to the loading AgI but also resulted from the method that enabled the exposure of more active sites in the composites. In addition, the intimate interfacial contact obtained by this method could also promote the efficient separation of photogenerated electron-hole pairs. Moreover, the possible photocatalytic active species and the stability of the photocatalyst were investigated in detail.

Key words | AgI, photocatalysis, rhodamine B, TiO_2, visible light

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INTRODUCTION

Semiconductor photocatalysts with high photocatalytic performance are considered to be one of the most promising materials for solving environmental issues and the energy crisis (Han *et al.* 2018a, 2018b, 2018c). Recently, TiO_2 as a traditional photocatalyst has attracted considerable attention owing to its high efficiency, low cost, non-toxicity and high stability (Fujishima 1972; Chen *et al.* 2012; Dahl *et al.* 2014; Zhang *et al.* 2018). Unfortunately, TiO_2 can only adsorb UV light which accounts for about 4% of the total solar energy, limiting its wide application. To sufficiently utilize solar energy, various strategies including noble metal deposition, doping process, surface sensitization and composite systems have been developed to fabricate efficient TiO_2-based composite photocatalysts (Kumar & Devi 2011; Wang *et al.* 2014; Chen *et al.* 2017; Gao *et al.* 2018). However, developing the desirable visible light responsive TiO_2-based composite is still a challenge.

Silver halides are well-known photosensitive materials and are widely employed as source materials in photographic films. As a member of the silver halides, AgI has a smaller band gap than AgCl and AgBr, and it could be considered a promising photocatalyst (Cheng *et al.* 2010). Under ambient condition, there are two main phases of AgI, β and γ phases (Jiang *et al.* 2014). β-AgI as a visible light photocatalyst has become a research hotspot due to its photocatalytic performance for dye degradation. However, AgI could be subject to labile photodecomposition when it is exposed to illumination. It has been reported that the presence of a support (e.g. TiO_2, Al_2O_3, SiO_2, carbon nanotube (CNT) and g-C_3N_4) could stabilize AgI by inhibiting the photographic process (Li *et al.* 2008; Hu *et al.* 2010; Guo *et al.* 2011; An *et al.* 2013; Shi *et al.* 2013; Xu *et al.* 2013; Yi *et al.* 2015; Xia *et al.* 2016; Yang *et al.* 2017). Among these supports, coupling TiO_2 with AgI has

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been a subject of intense investigation because of its remarkably high photocatalytic activity in removal of organic dyes under visible light irradiation (Hu *et al.* 2007; Song *et al.* 2012; Wang *et al.* 2015, 2016; Xue *et al.* 2015; Yang *et al.* 2016; Yu *et al.* 2016; Shao *et al.* 2017). To date, the synthetic methods of fabrication of the AgI/TiO_2 composite are still complicated, high cost and environmentally unfriendly. Thus, it is necessary to develop a simple approach to fabricate the AgI/TiO_2 photocatalyst.

Here, we report that AgI/TiO_2 composites were successfully fabricated through a simple grinding method. The as-prepared AgI/TiO_2 composites were characterized by X-ray diffraction, scanning electron microscopy and UV-Vis spectroscopy. The photocatalytic performance was evaluated by RhB degradation under visible light irradiation. The as-prepared AgI/TiO_2 composites exhibited good visible light absorption and enhanced photocatalytic activities under visible light irradiation. In order to further explain this phenomenon, the photocurrent response properties of photocatalysts were also analyzed. Importantly, possible photocatalytic active species and the stability of the photocatalyst were investigated in detail.

METHODS

Chemicals and materials

All chemicals throughout the experiments were analytical grade and used as received from commercial suppliers without further purification. Ethanol (99%) and isopropyl alcohol (99.7%) (IPA) were obtained from Tian Jin Yong Da Chemical Reagent Co., Ltd. Titanium (IV) butoxide and silver nitrate (99.8%) were supplied by Sinopharm Chemical Reagent Co., Ltd. Disodium ethylene diamine tetraacetic acid (EDTA), benzoquinone (BQ) and KI were obtained from Tian Jin Bo Di Chemical Reagent Co., Ltd.

Preparation of photocatalysts

Preparation of TiO_2

Firstly, 200 mL distilled water was added to a 250 mL beaker, and the pH solution was adjusted to 3 using HNO_3 solution (1 mol L^{-1}). A mixture of 20 mL ethanol and 20 mL titanium (IV) butoxide was added to the above solution. Then, a white suspension was obtained and aged at 70 °C for 48 h. Subsequently, the product was collected by centrifugation and washed thoroughly with water. Finally, the white TiO_2 nanoparticles were collected and dried at 60 °C for 24 h.

Preparation of AgI

Under dark conditions, AgI nanoparticles were fabricated using a simple precipitation method. Briefly, 0.2 mol L^{-1} $AgNO_3$ aqueous solution (10 mL) was added dropwise into 0.2 mol L^{-1} KI (10 mL) aqueous solution under stirring, and then the mixed solution was stirred for 3 h. Afterward, the yellow product was washed with water three times and dried for 24 h.

Preparation of AgI/TiO_2 composites via a simple grinding method

To obtain the AgI/TiO_2-0.1 composite, 0.05 g of AgI sample and 0.5 g of TiO_2 were added to a mortar, and the mixture was ground for 15 min. AgI/TiO_2 composites with mass ratio of 0.5:1 (denoted as AgI/TiO_2-0.5), 1:1 (denoted as AgI/TiO_2-1) and 2:1 (denoted as AgI/TiO_2-2) were also fabricated following a similar process. The mass ratio of AgI/TiO_2 composites is listed in Table 1.

Characterization

The powder X-ray diffractometer (XRD) patterns were carried out on a Rigaku XRD D/max-2500PC instrument with Ni-filtered Cu Kα irradiation. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained by a PerkinElmer UV WinLab spectrophotometer with $BaSO_4$ as a reflectance standard. The product morphologies were analyzed using a SSX-50 scanning electron microscope (SEM; Shimadzu, Japan). Fourier transform infrared (FT-IR) spectra of the samples were

Table 1 | Mass ratio of AgI/TiO_2 composites

Name	AgI/ (g)	TiO_2/(g)
AgI/TiO_2-0.1	0.05	0.5
AgI/TiO_2-0.5	0.25	0.5
AgI/TiO_2-1	0.5	0.5
AgI/TiO_2-2	1.0	0.5

monitored by FT-IR spectrophotometer (VERTEX 70, Bruker, Germany) in the range of 4,000–500 cm^{-1} with KBr as reference sample. X-ray photoelectron spectroscopy (XPS, Kratos, ULTRA AXIS DLD) was recorded by a Kratos AXIS $Ultra^{DLD}$ system with monochrome Al Kα (hν = 1,486.6 eV) radiation. Photocurrent measurements were evaluated at a CHI electrochemical workstation (Shanghai). The working electrode was prepared on an ITO glass. Furthermore, 0.2 mol L^{-1} of Na_2SO_4 solution was used as electrolyte.

Evaluation of photocatalytic activity

The activity of photocatalysts was evaluated by RhB degradation, and the concentration of RhB was determined by the peak at 554 nm with a spectrometer (PerkinElmer UV WinLab spectrophotometer). Typically, 30 mg of photocatalyst powder was mixed with 100 mL of RhB aqueous solution (1×10^{-5} mol L^{-1}) in a quartz reactor (Beijing PerfectLight Technology Co., Ltd, China, http://www.perfectlight.cn/) with a water cooling jacket. The cooling jacket was maintained at 5 °C throughout the photocatalysis. Then, the suspension was magnetically stirred in the dark for 60 min to reach adsorption-desorption equilibrium. The suspension was irradiated by a 300 W Xe lamp (Perfect Light PLS-SEX300) with a UV cut filter. The distance between the reactor and light source was 10 cm. At certain time intervals, 3 mL of the specified dispersions was sampled and centrifuged at 8,000 rpm for 5 min. The concentration of the solution was determined by a UV spectrometer. After each cycle of photocatalytic test, the catalysts were recovered. The suspension was centrifuged at 8,000 rpm for 10 min, the obtained catalysts were soaked in ethanol overnight, and then the catalysts were washed with acetone and distilled water three times and dried under vacuum at 60 °C for 24 h.

RESULTS AND DISCUSSION

Characterization

AgI/TiO_2 composites with different mass ratio were fabricated via a simple grinding method for 15 min (Figure 1). Figure 2 shows the characteristic morphology of AgI/TiO_2-0.5 composite. It can be seen from Figure 2 that AgI/TiO_2-0.5 composite displays nonuniform particles, and the size of these particles ranges from several hundred nanometers to several micrometers. The result might be attributed to the grinding method and the introduction of AgI nanoparticles.

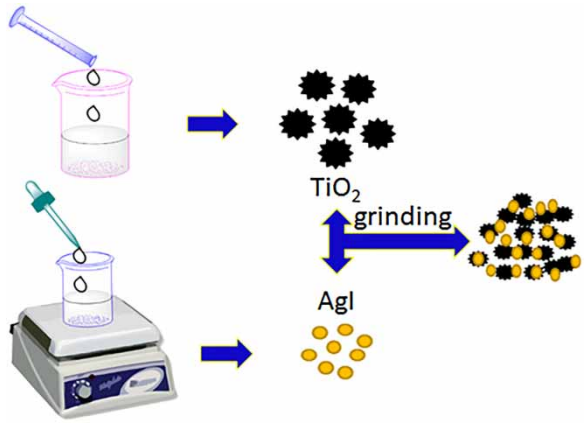

Figure 1 | Illustration of the synthetic route to AgI/TiO_2 composites.

Figure 3 shows powder XRD patterns of pristine TiO_2 and AgI/TiO_2 composites. For pristine TiO_2, the peaks at 25.6°, 38.4°, 48.4°, 54.6° and 62.7° indexed as (101), (004), (200), (211) and (204) reflections associated with anatase TiO_2 (JCPDS no. 21-1272) can be clearly observed. For the sample of AgI/TiO_2 composites, apart from the characteristic peaks of anatase TiO_2, several new peaks associated with AgI (JCPDS no. 09-0374) can also be observed, indicating the existence of AgI nanoparticles in the samples. Additionally, the peak intensity of TiO_2 decreased, meaning that the AgI content increased gradually in the system.

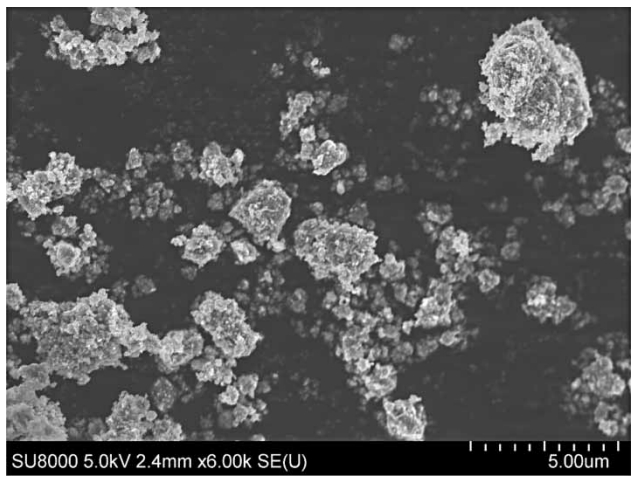

Figure 2 | SEM image of AgI/TiO_2-0.5 composite.

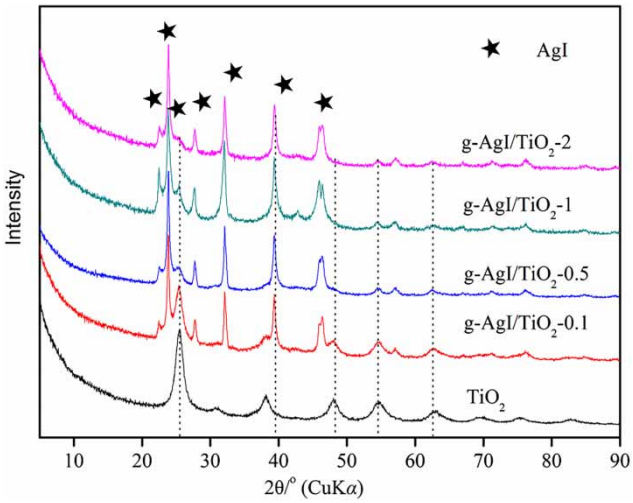

Figure 3 | XRD patterns of TiO_2 and AgI/TiO_2 composites.

The nature of species and the chemical states of elements on the surface of AgI/TiO_2-0.5 composite were obtained by XPS analysis. As shown in Figure 4(a), the composite is mainly composed of Ti, Ag, I and O elements. Figure 4(b) shows the XPS of Ti 2p region with peaks appearing at 458.5 eV and 464.1 eV. These two peaks are attributed to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ of Ti^{4+} in TiO_2. Two main peaks are observed at the binding energies of around 367.7 eV and 373.7 eV, corresponding to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ (Figure 4(c)), respectively. As for I 3d of AgI/TiO_2-0.5 composite (Figure 4(d)), two peaks appear at 618.9 eV ($3d_{5/2}$) and 630.4 eV (I $3d_{3/2}$) and are ascribed to I^- of AgI. Besides, no peaks corresponding to I_2 and Ag^0 are observed. Thus, it can be confirmed that the AgI/TiO_2 composites were fabricated through the simple grinding method.

The optical absorption property is a significant parameter for a photocatalyst to determine its photocatalytic activity. Figure 5(a) displays the UV-Vis diffuse reflectance spectra of the pristine TiO_2, AgI and AgI/TiO_2 composites. It can be clearly seen that the pristine TiO_2 shows a broad

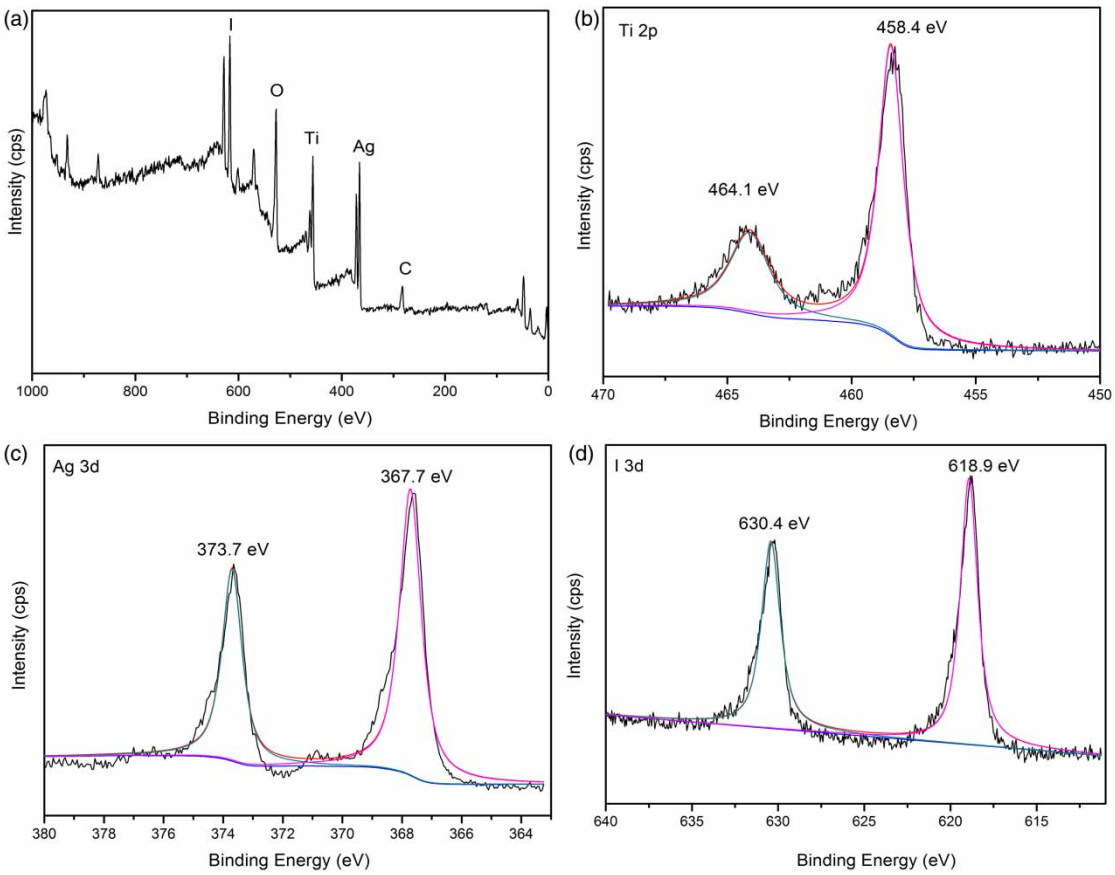

Figure 4 | XPS patterns of AgI/TiO_2-0.5 composite.

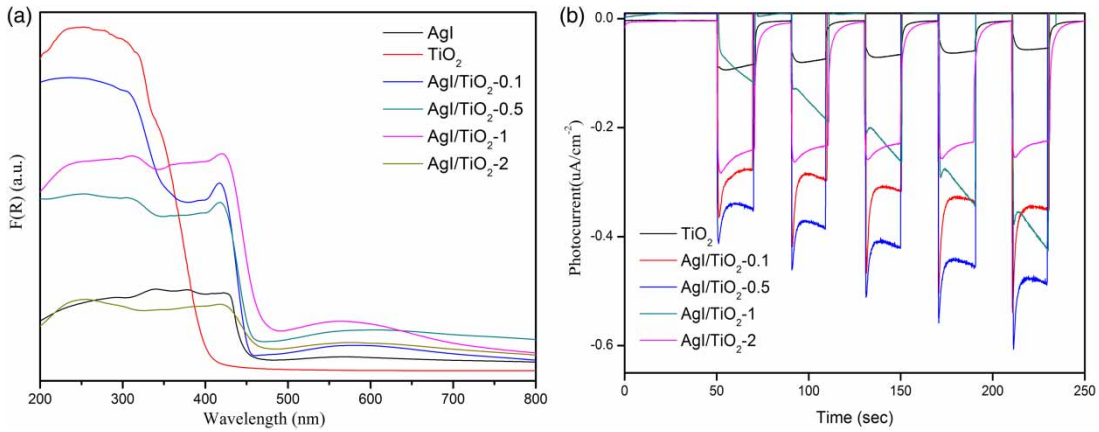

Figure 5 | (a) UV-Vis spectra of AgI, TiO_2 and AgI/TiO_2 composites; (b) photocurrent response of TiO_2 and AgI/TiO_2 composites.

absorption in the UV region, which is in agreement with a previous report (Yi *et al.* 2015). Compared with the spectra of pristine TiO_2, the spectra of AgI/TiO_2 composites show a strong broad absorption band in the range of 400 nm to 800 nm. That is, the absorption band of AgI/TiO_2 composites expands to the visible light region (around 425 nm), which is caused by the loading of AgI nanoparticles.

To evaluate the efficient separation of photogenerated electron-hole pairs, photocurrent experiments were carried out under visible light irradiation. As illustrated in Figure 5(b), the photocurrent density on AgI/TiO_2 composites is higher than that on the pristine TiO_2, indicating that the loading of AgI leads to the enhancement of visible light response. It is clear from Figure 5(b) that the highest photocurrent density is observed on the AgI/TiO_2-0.5 composite, indicating its highest photocatalytic activity among these catalysts. Therefore, the result suggests that these photogenerated electron-hole pairs could be efficiently separated in this system under visible light irradiation.

Photocatalytic degradation of RhB

In order to evaluate the photocatalytic activities of different catalysts, RhB degradation experiments were carried out under visible light irradiation. Before irradiation, all photocatalysts in the RhB solution were stirred in the dark for 60 min to reach adsorption-desorption equilibrium. As shown in Figure 6(a), about 6.8% and 7.6% of RhB molecules were adsorbed onto the pristine TiO_2 and AgI, respectively. However, the adsorption capacities of AgI/TiO_2 composites are higher than those of pristine TiO_2 and AgI. About 11.4%, 31.3%, 19.2% and 19.7% of RhB molecules were adsorbed on the surface of AgI/TiO_2-x (0.1, 0.5, 1, 2) composites, respectively. The discrepancy in the adsorption could be

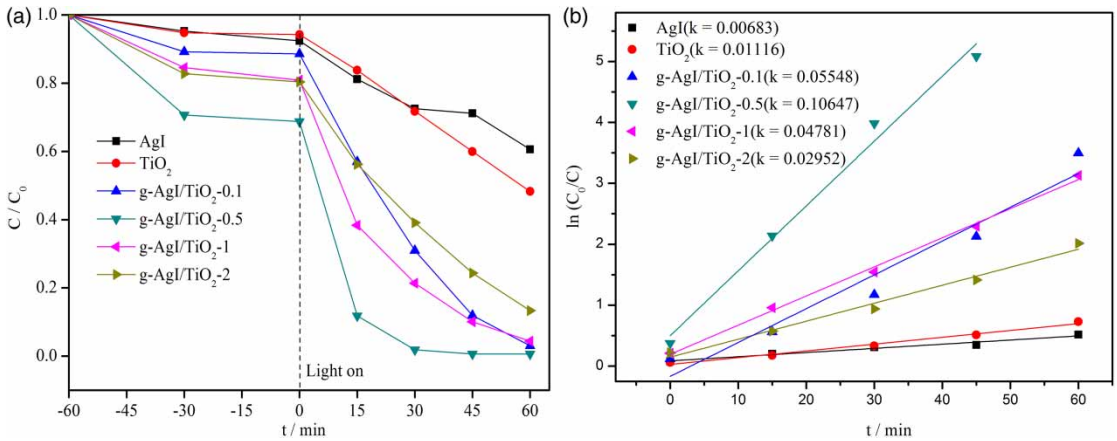

Figure 6 | (a) Photocatalytic performance for RhB degradation over AgI, TiO_2 and AgI/TiO_2 composites under visible light irradiation; and (b) their reaction rate constants (k).

caused by different surface area and different 'chemical affinity' for the pristine TiO_2, AgI and AgI/TiO_2 composites. As the reaction proceeded, all catalysts showed non-negligible photocatalytic performance for RhB degradation. However, the photocatalytic activities of AgI/TiO_2 composites showed high activity, and RhB was almost completely decomposed in 60 min. It is found that AgI/TiO_2-0.5 composite displayed the highest photocatalytic activity and its degradation efficiency reached almost 100% within 45 min. To further confirm the above results, the degradation kinetics equation was used to describe the process of photocatalytic reaction. The function of ln (C/C_0) versus time (t) is a linear relationship, indicating that the process of RhB degradation follows the pseudo-first-order reaction kinetics model:

$$\frac{-\mathrm{d}(C/C_0)}{\mathrm{d}t} = \mathrm{k}t$$

where C_0 is the initial concentration of RhB before irradiation, C is the concentration of RhB at t time, and k is a rate constant. As demonstrated in Figure 6(b), comparison of the rate constants for RhB degradation over the catalysts reveals a similar trend as discussed previously. The photocatalytic activity of AgI/TiO_2 composite rose with the increasing mass ratio of AgI and TiO_2 from 0.1:1 to 0.5:1, which might be attributed to the increased number of active sites in the AgI/TiO_2 composite. However, when the AgI loading mass is greater than or equal to 1:1, the photocatalytic activity decreased. A possible reason might be that excessive AgI could not sufficiently contact with TiO_2, so that the formation of intimate interfacial contact is difficult. In addition, the excessive AgI might aggregate on the catalyst surface to reduce the available active sites, resulting in the decrease in photocatalytic activity. Therefore, the optimum AgI content in the composite is 0.5:1. The rate constants of AgI/TiO_2-0.5 composite for RhB degradation are 9.5 and 15.6 times higher than those of pristine TiO_2 and AgI, respectively.

Possible photocatalytic mechanism

To give further evidence to the role of active species under visible light, the main reactive species including •OH, $\bullet O_2^-$, and h^+ were investigated during the photocatalysis process. Isopropanol (IPA), disodium ethylene diamine tetraacetic acid (EDTA) and benzoquinone (BQ) were applied as scavengers of •OH, h^+ and $\bullet O_2^-$, respectively. As shown in Figure 7(a), the degradation efficiency of RhB significantly decreased in the presence of BQ. Since BQ is a $\bullet O_2^-$ quencher, $\bullet O_2^-$ could be one of the main active species during the photocatalysis process. However, the presence of IPA and EDTA did not cause obvious changes in the RhB degradation efficiency, suggesting that •OH and h^+ do not play an important role in the photocatalytic process. Thus, $\bullet O_2^-$ is the main active species during the RhB degradation process.

Stability and reusability of AgI/TiO_2-0.5 composite

Figure 7(b) shows the stability of AgI/TiO_2-0.5 composite for RhB degradation under visible light irradiation. AgI/TiO_2-0.5 composite was easily recycled by simple centrifugation and ethanol treatment in these recycling experiments. After five cycles, the photocatalytic activity did not decrease significantly in the RhB degradation under visible light irradiation. The results demonstrate that AgI/TiO_2-0.5 composite is an effective and stable photocatalyst during the degradation process. However, we find that the color of spent AgI/TiO_2-0.5 composite changes from yellow to grey, indicating the occurrence of AgI decomposition. To further confirm the result, the spent AgI/TiO_2-0.5 composite collected after five cycles was analyzed by XRD. XRD patterns in Figure 7(c) show that several new peaks are observed in the spent samples. These new peaks are consistent with Ag^0 species (JCPDS no. 04-0783). Therefore, it is confirmed that the AgI content in the composite might slightly decrease after five cycles.

CONCLUSIONS

In summary, AgI/TiO_2 composite photocatalysts were synthesized by a simple grinding process. The as-prepared AgI/TiO_2 composites were used as photocatalysts for RhB degradation under visible light irradiation and exhibited excellent photocatalytic performance. The enhanced photocatalytic activity was not only attributed to the loading AgI but also resulted from the method that enabled the exposure

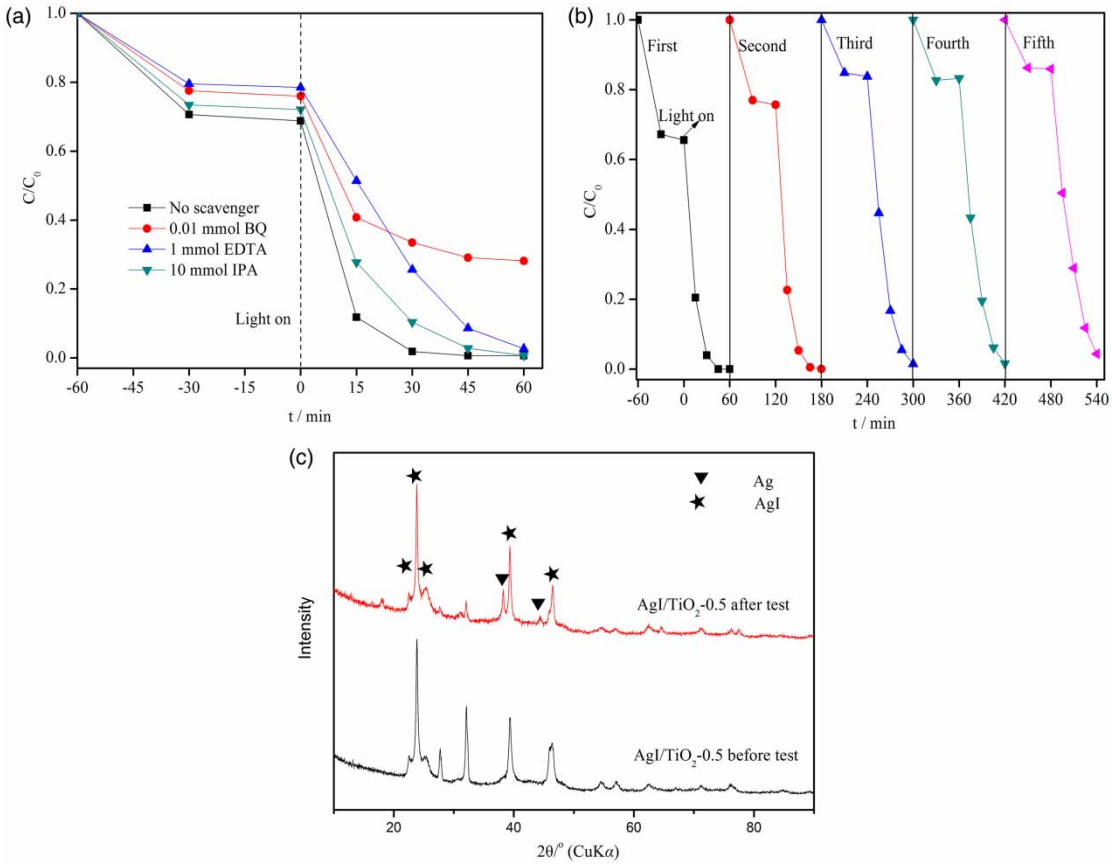

Figure 7 | (a) Effects of different scavengers over AgI/TiO_2-0.5 composite for RhB degradation; (b) reusability of AgI/TiO_2-0.5 composite for RhB degradation; (c) comparison of XRD patterns of AgI/TiO_2-0.5 composite before and after photocatalytic test.

of more active sites in the composites. In addition, the intimate interfacial contact obtained by this method could also promote the efficient separation of photogenerated electron-hole pairs. The photocatalytic mechanism demonstrated that the $\cdot O_2^-$ was the dominant active species during the photocatalytic process. Moreover, the photocatalytic activity of AgI/TiO_2 composite could still remain after four cycles, indicating the potential application in wastewater treatment. This work may offer an efficient way for large-scale synthesis of high-efficiency, visible light photocatalysts.

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