Degradation of Acid Orange 7 using magnetic AgBr under visible light: The roles of oxidizing species

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ABSTRACT

AgBr was creatively immobilized on a magnetic substrate (SiO₂-coated Fe₃O₄ nanoparticle, SFN) to achieve magnetic separation after visible light-driven photocatalytic oxidation (PCO). The resulted Ag/AgBr/SFN was characterized by TEM, vibrating sample magnetometer and other techniques. It is found that the average diameter of the Ag/AgBr/SFN particle is less than 20 nm. The typical superparamagnetic behavior of Ag/AgBr/SFN implies that the catalyst can be magnetically separated. The physicochemical features of the used Ag/AgBr/SFN after visible light irradiation were not dramatically changed by X-ray diffraction, UV–Vis diffuse reflectance spectra and Fourier transform-infrared analysis. SiO₂ interlayer was proven to slightly increase the degradation efficiency for an azo dye Acid Orange 7. UV–Vis spectra and HPLC analysis indicated that the dye was oxidized and decomposed. The photoactivity of Ag/AgBr/SFN was partly maintained after successive PCO under visible light. In order to evaluate the roles of e[−]–h⁺ pairs and reactive oxygen species, the quenching effect was examined by employing Ag/AgBr/SFN and commercial TiO₂ (P-25) under visible light ($\lambda > 400$ nm) and UV-A irradiation, respectively. Active h⁺ and the resulting ·OH played the major roles for degradation. The effect of active h⁺ and ·OH were proven to be highly dependent on the concentration of photocatalysts. The effect of ·OH was more obvious for P-25, while that of active h⁺ was more predominant for Ag/AgBr/SFN.

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1. Introduction

Sustainable and ever-increasing interests have been focused on photocatalytic degradation of toxic substances for the purification of water and air using titania. Being one of the key AOPs (advanced oxidation processes), photocatalytic process is subjected to extensive studies and considered to be potentially applied for decontamination. Nevertheless, there are still two fundamental drawbacks hindering its development. One is the recovery of photocatalyst. It is difficult to recover and reuse these catalysts due to their small size especially in slurry system, which needs the further filtration step of high cost. The other is the inefficient utilization of visible light. TiO₂ only absorbs wavelengths at the near-UV region ($\lambda < 400$ nm), which consists of only 5% of solar spectrum. However, visible light covers as much as 45% of the total solar energy.

Photocatalysts are preferably used in slurry system due to its high surface area and decontamination efficiency (Chung et al., 2004). In order to solve the problem of recovery and reuse of used photocatalysts, these photocatalysts were usually immobilized on inert substrates such as sand, zeolite, resins and even metal substrates by coating, soaking, precipitating or spinning methods (Matthews, 1987; Anpo et al., 1997; Kominami et al., 2001). Though the immobilized photocatalysts were easy to be recovered, the remarkable reduction on their photocatalytic activities was observed to a considerable extent due to the lack of effective surface area and low mass transfer rate (Chung et al., 2004). Recently, magnetically separable photocatalysts were suggested and proven to be a good solution for the catalyst separation (Chen et al., 2001; Gao et al., 2003; Xu et al., 2007). The size of the photocatalyst could be intentionally manipulated by controlling the size of the magnetic core materials. Thus, magnetic nano-sized photocatalysts can be synthesized to increase their effective working area and improve their photoactivities.

The magnetic photocatalysts always refer to those with a ternary structure including a magnetic core, a silica membrane

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mid-layer and photocatalysts outer-layer. The SiO_2 mid-layer was also proven to be a great need. The bandgap of SiO_2 is as much as 9.0 eV. Consequently, the passive SiO_2 layer can not only inhibit the oxidation of the Fe_3O_4 core by the holes photogenerated by the out-layer, but also can weaken the adverse effect of $\gamma\text{-Fe}_2\text{O}_3$ such as conglomeration (Gao et al., 2003). It was proven that the SiO_2 mid-layer helped to improve the photoactivity by inhibiting the charges injection from the out-layer photocatalyst (Xu et al., 2007). As a result, the nano-sized ternary structure of magnetic photocatalyst was preferably selected for practical use.

Titania has been frequently employed as the out-layer photocatalyst in literature (Chen et al., 2001; Beydou and Amal, 2002; Chung et al., 2004), which renders the difficulty of lack of photoactivity when utilizing visible light. Others (Zou et al., 2001; Kim et al., 2004; Fu et al., 2005) have reported interesting work on efficient utilizing of visible light by employing non-titania photocatalyst. Moreover, the use of silver halides such as AgBr, a series of photosensitive materials for photography, emerges to be capable of inactivating pathogenic material and destruction of azo dye under visible light (Rodrigues et al., 2005; Hu et al., 2006; Elahifard et al., 2007; Lan et al., 2007; Zang and Farnood, 2008). However, there are few studies on the immobilization of these typical non-titania photocatalyst on magnetic support for decontamination under visible light so far. In this study, magnetic AgBr was prepared by immobilizing AgBr on SiO_2 -coated Fe_3O_4 nanoparticles (SFN) in order to achieve both photocatalyst recovery and visible light utilization.

In addition, a large number of oxidizing species are involved in photocatalytic oxidation (PCO) and they are expected to play the key roles in decontamination. These reactive oxygen species (ROSs) such as $\cdot\text{OH}$ and H_2O_2 are basically transformed from the initial generation of charge carriers, active holes and electrons. Generation of $\cdot\text{OH}$ is widely accepted as a characteristic of AOPs (Andreozzi et al., 1999). However, to date, it is still unclear in which roles these oxidizing species play in aqueous PCO reaction under different reaction conditions. The visible light-induced and ultraviolet-induced PCO reaction may differ for the generation of oxidizing species. Photocatalyst concentration is another influencing factor for PCO. In this research, the roles of active holes and ROSs was comparatively investigated using magnetic AgBr and P-25 (TiO_2) under visible light ($\lambda > 400\text{ nm}$) and UV-A irradiation, respectively. Most of the oxidizing species have a short lifetime and their instantaneous measurement becomes difficult. As a result, a series of scavengers were employed and the quenching effect was investigated as a diagnostic tool to evaluate their roles by decolorizing an azo dye, Acid Orange 7 (AO7). AO7 is commonly selected as an organic contaminant for evaluating a degradation process and AO7 degradation has been studied in detail (Styliadi et al., 2004; Velegraki et al., 2006). As a result, it is convenient to study AO7 degradation to investigate the roles of these oxidizing species involved.

2. Experimental

2.1. Preparation of Fe_3O_4 nanoparticles and silica-coated Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 nanoparticles were synthesized by method of chemical co-precipitation. First, 100 mL distilled water was heated up to about 70°C . $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a molar ratio of 2:1.6 were added to the solution with vigorous stirring (Meng et al., 2005). Then, 2 M NaOH was added drop-wise into the above solution until the pH reached approximately 11. The resulting solution became black and was constantly stirred at 70°C for 1 h to ensure complete growth of the nanoparticle crys-

tals. Before the precipitate was magnetically separated, the solution was cooled in air to room temperature ($\sim 25^\circ\text{C}$). The precipitate was then rinsed with distilled water in order to obtain a product with a neutral pH. Finally, the black Fe_3O_4 particles were rinsed with absolute ethanol three times, and the particles were allowed to dry at $\sim 25^\circ\text{C}$.

The SFN were prepared by the following procedure. First, approximately 1 g of Fe_3O_4 nanoparticles was dispersed in 20 mL of 0.1 M sodium dodecyl sulfate (98.5%, Sigma). The slurry was sonicated for 10 min, followed by 30 min of vigorous stirring. Subsequently, 20 mL of absolute ethanol, 6 mL of concentrated ammonia and 5 mL of tetraethyl orthosilicate were added successively to the solution. The reaction was allowed to proceed for 3 h at 50°C before the nanoparticles were magnetically separated and rinsed with distilled water. Finally, the resulting particles were rinsed with absolute ethanol three times and dried at room temperature, yielding grey silica-coated Fe_3O_4 nanoparticles.

2.2. Preparation of magnetically separable Ag/AgBr/SFN

The magnetic Ag/AgBr/SFN was prepared by a deposition-precipitation method similar to procedures found in literature (Hu et al., 2006). First, 0.5 g of SFN was added to 100 mL of deionized water, and the suspension was dispersed with the aid of ultrasonication for 30 min. Then 0.6 g of cetyltrimethylammonium bromide was added to the solution and was stirred magnetically for over 30 min. Subsequently, 0.105 g of AgNO_3 in 2.3 mL of NH_4OH (25 wt.% NH_3) was quickly added, and the magnetic stirring was maintained at room temperature for over 12 h. The suspension was centrifuged, washed and dried at 110°C for 1 h. Finally, the product was calcined at 500°C in air for 3 h.

2.3. Characterization

TEM images were recorded on a Tecnai F20 (FEI, 200 kV) microscope coupled with an energy dispersive X-ray (EDX) (Oxford Instruments) spectrometer. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-diffractometer ($\text{Cu K}\alpha$, $\lambda = 0.15406\text{ nm}$). The UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained by employing a UV-Visible spectrophotometer (Perkin-Elmer). Magnetization with the applied magnetic field was measured by vibrating sample magnetometer (VSM-7300, Lakeshore, USA). Fourier transform-infrared spectroscopy (FT-IR) investigations were made on a FT-IR spectrometer (Nicolet Impact 420).

2.4. Degradation of Acid Orange 7 under visible light irradiation

AO7 was obtained from Sigma (purity $>80\%$) and used without any purification. Commercial TiO_2 P-25 was kindly provided by Degussa Co. (Germany). Catalase for quenching was a fluorescent catalase detection kit (Cell Technology, Mountain View, USA). Isopropanol (R.D.H., Germany) used was of GC assay grade. Ultrapure azide was purchased from United States Biochemical Co. (USA).

The PCO of AO7 (20 mg L^{-1}) was carried out in a flask under visible light irradiation produced by a 300 W Xenon lamp (Beijing Changtuo Scientific and Technological Corporation, Ltd., Beijing, China). A UV cut-off filter was employed to remove the light with wavelength shorter than 400 nm. The visible light (369.5 mW cm^{-2}) was focused on a 50 mL beaker from one side and passed through the Pyrex glass to induce the PCO reaction. Vigorous stirring was maintained to prevent settling of the magnetic photocatalyst. P-25 and UV lamps (15 W, maximum emission at 365 nm) were used for UV-induced PCO reaction. The light intensity for UV-A irradiation was fixed at 0.39 mW cm^{-2} . All the

reaction mixture was stirred at dark for over 60 min to reach adsorption/desorption equilibrium and continued stirring was maintained during the whole PCO process. The pH of reaction solution was adjusted with HCl or NaOH as required, and determined with a pH meter (Thermo Orion 420A Benchtop meter, USA). The reaction temperature was increased from room temperature to about 40 °C when the reaction was ceased at 60 min. All the reactions were conducted at least in duplicate.

The concentration of AO7 was determined by measuring the absorbance at a fixed wavelength of 484 nm, which corresponds to the maximum absorption wavelength of AO7 in visible region. The UV–Vis spectra of the samples were recorded from 200 to 700 nm using a UV–Vis spectrophotometer (Cary 100 Scan, Varian). Analyses of AO7 and its degradation products were carried out on a HPLC (Waters 996 photodiode array detector and 2695 separations module) analysis. The other experimental parameters can be referred to our previous study (Li et al., 2006).

3. Results and discussion

3.1. Characterization

3.1.1. TEM of SFN and Ag/AgBr/SFN

Fig. 1a and b shows the typical bright-field TEM images of the SFN and Ag/AgBr/SFN powder. It is clearly seen that the average diameters of the Ag/AgBr/SFN particles are less than 20 nm from the light patches. Compared with SFN in Fig. 1a, the morphologies of Ag/AgBr/SFN were almost not changed after Ag/AgBr immobilization on it. In addition, the dark core structure is obvious, as observed from Fig. 1b, and the other can be assigned to the other parts of core-shell structure such as the outer-layer coating of Ag/AgBr and the mid-layer SiO₂ and γ -Fe₂O₃. This suggests a good combination between Ag/AgBr and SFN particles. The selected-area electron diffraction pattern (inset of Fig. 1b) demonstrates the distinct diffraction rings of the crystalline structure, which is the typical spinel structure of the inner Fe₃O₄ nanoparticles (Matthews, 1987; Kominami et al., 2001). By EDX analysis, the atomic ratios of Si and Fe on SFN are 24.1% and 7.5%, respectively. In accordance, the Si and Fe contents were found to be 30.0 and 19.1 wt.%, respectively. Other research indicated that the silica content in TiO₂/SiO₂/ γ -Fe₂O₃ was only 1.9 wt.% (the mass ratio between TiO₂ and silica-coated SiO₂/ γ -Fe₂O₃ was 1:1) even though the incomplete SiO₂ membrane still improved the photocatalytic efficiency (Rodrigues et al., 2005). This indicates the existence of a SiO₂ mid-layer in Ag/AgBr/SFN will help to restrain the adverse effect of charge carrier recombination as well. For Ag/AgBr/SFN, the atomic ratios of Si,

Fe, Ag and Br are 54.7%, 40.7%, 2.9% and 1.7%, respectively, as measured by EDX analysis. This reveals that Ag⁰ was generated in the Ag/AgBr/SFN during the preparation of the visible light active catalyst.

3.1.2. Magnetic properties of Ag/AgBr/SFN

The magnetic properties of the Ag/AgBr/SFN and SFN powders were investigated with a VSM. The representative magnetic hysteresis loops of Ag/AgBr/SFN and SFN measured at room temperature and illustrated in Fig. 2, which suggests a typical superparamagnetic behavior with zero coercivity and remanence. This superparamagnetism is very useful in technical applications, and these photocatalysts can be separated from water when an external magnetic field is applied. A comparatively lower magnetic property of the Ag/AgBr/SFN particle is observed in comparison with that of the SFN powder. This indicates the existence of Ag/AgBr coating on SFN to some extent.

3.1.3. XRD, UV–Vis DRS and FT-IR measurement

Both Ag/AgBr/SFN and SFN totally became orange in color after being calcined at 500 °C for 3 h, indicating that a large amount of Fe₂O₃ was generated due to calcination. Only two wide, weak peaks are clearly observed for XRD patterns of SFN, revealing the nanocrystalline nature of SFN. Typical peaks occurring at 63.1° and 35.7° (Joint Committee on Powder Diffraction Standards (JCPDS), No. 25-1402) also show that the SFN surface was oxidized by calcinations and γ -Fe₂O₃ phase was formed. The main phases are pure maghemite (Lan et al., 2007). The characteristic diffraction peaks of amorphous SiO₂ between 20° and 30° are not so obvious as demonstrated in literature (Xu et al., 2007). The diffraction peaks attributed to AgBr are obviously detected (JCPDS No. 79-0149), while the characteristic diffraction peak of Ag⁰ at 64.4° is also clearly observed in the fresh Ag/AgBr/SFN sample, indicating the existence of an Ag/AgBr structure. The existence of Ag/AgBr structure has been documented by other studies using the similar preparation procedures (Hu et al., 2006; Zang and Farnood, 2008). After visible light irradiation, the intensities of AgBr peaks were not dramatically reduced. No relevant peaks of SiO₂ were observed for both used SFN and Ag/AgBr/SFN, which implies the amorphous SiO₂ interlayer and AgBr outlayer were well dispersed and stable enough, but not fragmented due to vigorous stirring and PCO reaction.

The UV–Vis DRS of fresh Ag/AgBr/SFN, used Ag/AgBr/SFN and SFN were measured for comparison in Fig. 3. It is obvious that they all appear to show a good absorbance of visible light even with the magnetic support SFN. For fresh Ag/AgBr/SFN and SFN, their absorbance

Fig. 1. Representative TEM images of (a) SFN and (b) Ag/AgBr/SFN.

Fig. 2. Magnetic hysteresis loop of the Ag/AgBr/SFN and SFN.

Fig. 3. UV-Vis diffuse reflectance spectra of (a) fresh Ag/AgBr/SFN, (b) used Ag/AgBr/SFN and (c) SFN.

in the visible region is similar due to the strong absorbance of SFN support. As proven by XRD patterns, there is evident γ -Fe₂O₃ phase that exists on the photocatalyst surface. SFN appears to be orange color and the strong absorption can be attributed to that of γ -Fe₂O₃. This indicates that both Ag/AgBr/SFN and SFN are potentially photoactive in the visible region. AgBr is a pale yellow solid, and its color is not as dark as that of the orange γ -Fe₂O₃. However, the absorption of fresh Ag/AgBr/SFN is a little higher than that of SFN, especially from 600 to 800 nm. It can be deduced that it is the existence of Ag⁰ that made its absorbance stronger, which is consistent with the EDX analysis. In addition, the used Ag/AgBr/SFN exhibits an especially stronger absorbance from 600 to 800 nm than both fresh Ag/AgBr/SFN and SFN, which suggests the increased content of Ag⁰ after photocatalytic reaction. The increased metallic silver content on AgBr/TiO₂ was also observed after cyclic run irradiation by other study (Zang and Farnood, 2008), which caused a decrease of photoactivity but a considerable photoactivity was still maintained.

The FT-IR spectra of Ag/AgBr/SFN and used Ag/AgBr/SFN were detected in the range from 400 to 2500 cm⁻¹. The used Ag/AgBr/SFN was not subjected to any post-treatment. It is observed that there was not obvious FT-IR difference for Ag/AgBr/SFN before and after photocatalytic reaction, which indicates that the magnetic photocatalyst was stable enough to some extent. The characteristic absorption bands at around 800 and 1100 cm⁻¹ are attributed to the symmetric vibration and asymmetric stretching vibration of Si–O–Si, respectively (Dutoit et al., 1995). On the one hand, it reveals the existence of SiO₂ on the catalyst surface, though SiO₂ is generally regarded as an interlayer between Ag/AgBr and magnetic core. On the other hand, it also suggests the coexistence of SiO₂ with Ag/AgBr and Fe₂O₃ on the photocatalyst

surface. The orange color of Fe₂O₃ has suggested the existence of surface Fe₂O₃ besides the XRD indication. In addition, the bending vibration of adsorbed water was observed at 1613–1645 cm⁻¹, but the typical absorption bands of aromatic groups were not evidently demonstrated.

3.2. Degradation of AO7

3.2.1. Effect of SiO₂ mid-layer

In order to investigate the effect of SiO₂ interlayer, Ag/AgBr/FN (without SiO₂ interlayer) was prepared and its degradation efficiency was compared with that of Ag/AgBr/SFN. The apparent rate constant (pseudo-first-order) for AO7 degradation was enhanced from $2.6 \times 10^{-2} \text{ min}^{-1}$ in the absence of SiO₂ interlayer to $3.3 \times 10^{-2} \text{ min}^{-1}$ with the interlayer. It reveals that the SiO₂ interlayer is capable of improving the photoactivity of the magnetic photocatalyst, which is consistent with other studies (Chen et al., 2001; Xu et al., 2007). However, the apparent rate constant using SFN ($1.4 \times 10^{-3} \text{ min}^{-1}$) achieved $1.4 \times 10^{-3} \text{ min}^{-1}$, which was especially lower compared with those of Ag/AgBr/FN and Ag/AgBr/SFN. This suggested that though Fe₂O₃ was expected to be photoactive under visible light, the contribution of Fe₂O₃ to the total photoactivity of Ag/AgBr/SFN was not dominant. Meanwhile, it can be deduced that AgBr is mainly responsible for the photoactivity of Ag/AgBr/SFN.

3.2.2. Effect of initial solution pH

For metal oxide such as TiO₂, the solution initial pH could influence adsorption and degradation efficiency through affecting the surface complexation and the electrostatic interactions between the adsorbate and the oxide surface. As a photocatalyst, Ag/AgBr/SFN is different from metal oxide because AgBr is mainly responsible for the degradation. The degradation efficiencies of Ag/AgBr/SFN were investigated under pH 5.0, 7.0 and 9.0. It is observed that the color removal at 60 min decreased gradually from pH 5.0 (93%) to pH 9.0 (82%). Apparently, solution pH did not significantly influence the degradation using Ag/AgBr/SFN at around neutral pH, which is similar to the performance of P-25 under UV irradiation (So et al., 2002). On the other hand, it indicates that Ag/AgBr/SFN is comparatively stable for PCO.

3.2.3. Destruction of AO7

The UV/Vis spectral changes of AO7 degradation at pH 7 was recorded within 120 min, as illustrated in Fig. 4a. AO7 has four absorbance bands in which two in visible region and the other two in ultraviolet region. In visible region, a major band locates at 484 nm and a shoulder band at 430 nm due to the hydrazone form and azo form of AO7, respectively. The other two bands at 230 and 310 nm in ultraviolet region are ascribed to the benzene and naphthalene rings of the dye, respectively (Stylidi et al., 2004).

The four bands were weakened simultaneously by PCO using magnetic Ag/AgBr/SFN, which indicates that the structure units corresponding with the four bands were destructed rather than accumulated. However, there was a new absorbance band at 254 nm generated in the ultraviolet region at the very beginning, though the decay in visible region occurred concurrently. The strongest absorbance intensity at 254 nm was achieved at about 20 min and then shrank step by step. Quinonic compounds were speculated to contribute to the peak, which have a characteristic UV-Vis absorption at around 255 nm (Huang and Yu, 1988).

The degradation intermediates of AO7 were monitored by HPLC and their variations are presented in Fig. 4b. For AO7, it has a typical chromatogram peak with a retention time t_R at 7.0 min, as can be seen from the chromatograms of the AO7 solution before reaction. When photocatalytic reaction occurred, it is obvious that the intensity of AO7 dramatically declined and intermediates with t_R at

Fig. 4. (a) UV/Vis spectral changes of AO7 as a function of irradiation time and (b) HPLC chromatograms of AO7 as a function of irradiation time. Experimental conditions: [AO7] = 20 mg L⁻¹, [Ag/AgBr/SFN] = 500 mg L⁻¹, visible light >400 nm, pH 7.

2.0 and 3.0 min were generated concurrently. At 45 min, the chromatogram peak of AO7 almost disappeared and those of the intermediates began to shrink gradually with the prolonged reaction time. The above suggests that AO7 was completely decomposed by PCO using Ag/AgBr/SFN.

3.2.4. Recovery and reuse of Ag/AgBr/SFN

By means of magnetic separation, the used Ag/AgBr/SFN can be recovered immediately by a magnet for successive use. The recovered catalyst was not subjected to any further treatment and used for PCO reaction by addition of AO7 solution. The degradation efficiency declined continually from 94% to 39% in the six runs of recovery and reuse. The recovered Ag/AgBr/SFN became a little darker than the newly-prepared Ag/AgBr/SFN, which revealed the increased content of Ag⁰ on the used Ag/AgBr/SFN due to PCO. This is consistent with the results of UV–Vis DRS. The similar experimental results were demonstrated using AgBr/TiO₂ and a decline of photoactivity was observed as well (Zang and Farnood, 2008). The above indicated that AgBr was not stable enough during PCO. Even this, a limited photoactivity of Ag/AgBr/SFN was still maintained after six runs of PCO reaction.

3.3. Roles of oxidizing species

3.3.1. Predominant roles of active holes and the resulting hydroxyl radicals

During PCO reaction, the generation of e⁻–h⁺ pairs is the beginning of all the oxidation processes. Active h⁺ is the primary oxidizing species directly produced by photocatalyst under illumination. A series of ROSs are subsequently generated on the basis of active holes and electrons. These ROSs including ·OH, H₂O₂, ¹O₂, ·HO₂ and ·O₂⁻ are capable of oxidizing organic and biological pollutants to achieve water and air purification. They are indispensable for PCO reactions because these reactions will come to a stop without

active h⁺ and ROSs. As a result, the generation of ROSs will directly determine the performance of PCO.

In order to evaluate the effect of these primary oxidizing species, a series of quencher were employed to scavenge the counterpart active holes and ROSs, as presented in Table 1. Their quenching effect has been a diagnostic tool for evaluating the roles of these oxidizing species, and their dosages were referred to the previous studies (Martin et al., 1995; Sun and Pignatello, 1995; Rabani et al., 1998; Ilisz and Dombi, 1999; Wu et al., 1999; Ishibashi et al., 2000; Chen et al., 2005; Zhang et al., 2008). As a consequence of quenching, PCO reaction will be partly suppressed and *k*_{app} (apparent rate constant) is lowered. The more the *k*_{app} is reduced, the more important the role the oxidizing species play is in the reaction. Though the roles of ROS are only quantitatively determined by indirect method, it has been employed by many researchers due to lack of direct determination.

Table 2 shows the *k*_{app} (pseudo-first-order) when the reaction was quenched by KI, isopropanol, catalase, azide. The roles of the counterpart species quenched can be calculated and indicated by *k*_{app}/*k*_{app} (no quenching) (Zhang et al., 2006). Obviously, the *k*_{app} of KI quenching decreased to only 12% of no quenching, indicating the overwhelming role of h⁺/adsorbed ·OH for AO7 degradation. The weak quenching effect of isopropanol, catalase and azide implies that other ROSs such as ·OH, H₂O₂ and ¹O₂ played comparatively insignificant roles for AO7 degradation. ·OH (*E*⁰ (·OH, H⁺/H₂O) = 2.72 V/NHE) is more reactive than other oxidizing species. However, it is worthwhile pointing out that ·OH was not the prevailing oxidizing species generated by Ag/AgBr/SFN under visible light. Active h⁺ was confirmed to be the dominating oxidant, which is consistent with other studies (Mao et al., 1991; Ishibashi et al., 2000; Chen et al., 2005). Therefore, though ·OH was largely produced in this PCO reaction, the degradation of AO7 by active h⁺ process was more dominant.

In addition, double-quenching using both KI and isopropanol was conducted so as to judge the total effect of both active h⁺ and ·OH. ·OH involved in double-quenching consists of those adsorbed on the photocatalyst and those generated in bulk solution. Compared with KI quenching alone, the *k*_{app} by double-quenching was only reduced slightly <1%. This suggests that the effect of ·OH, generated in bulk solution, was almost negligible. Due to the

Table 1
Scavengers used and oxidizing species quenched.

	ROSs quenched	Scavenger dosage
KI	h ⁺ /adsorbed ·OH	0.01 M
Isopropanol	·OH	0.01 M
Catalase	H ₂ O ₂	935 000 units L ⁻¹
Azide	¹ O ₂	0.025 M
Double-quenching (KI + isopropanol)	h ⁺ /·OH	0.01 M KI and 0.01 M isopropanol

Table 2
*k*_{app} after quenched by a series of scavengers. Experimental conditions are same as those in Fig. 4.

	<i>k</i> _{app} (×10 ⁻² min ⁻¹)	<i>R</i>	<i>k</i> _{app} / <i>k</i> _{app} (no quenching) (%)
No quenching	3.3	0.93	100
KI	0.4	0.98	11.8
Isopropanol	2.8	0.99	86.9
Catalase	2.5	0.93	75.8
Azide	2.8	0.99	87.0
Double-quenching (KI + isopropanol)	0.4	0.99	11.2

longer lifetime of active e^- compared to that of active h^+ (Hoffman et al., 1995), $\cdot OH$ generated in bulk solution is accepted to be produced by the following equations:

As a result, $\cdot O_2^-$ and H_2O_2 come from conduction band electrons and they constitute the main products of active e^- . However, as seen from the quenching results, the effect of these products of active e^- in bulk solution was very limited as well. Besides, heterogeneous photocatalysis consists of three steps: adsorption of organics, surface reaction and desorption of final products. PCO reaction is accepted to mainly occur on the catalyst surface (Ishibashi et al., 2000; Hu et al., 2003). Due to the short lifetime of active h^+ and the resulting $\cdot OH$ on the photocatalyst, the contribution of oxidizing species in the bulk solution could be especially insignificant, which is consistent with the analysis made above. Totally, the effect of active h^+ and the adsorbed $\cdot OH$ was dominant for PCO and it mainly occurred on the catalyst surface.

3.3.2. Effect of photocatalyst concentration on the roles of oxidizing species

AgBr is well accepted as a high-quality photosensitive and imaging material, and it is widely applied as source materials in photographic films (Belloni et al., 1999). In Ag/AgBr/SFN, silver bromide is mainly responsible for its photoactivity. Different from the traditional titania-based photocatalyst, Ag/AgBr/SFN may demonstrate a special performance in PCO reaction under visible light. For comparison, the quenching test was conducted under UV-A irradiation using TiO_2 (P-25) with a concentration of 100 and 500 $mg\ L^{-1}$. Both P-25 and Ag/AgBr/SFN achieved similar degradation efficiencies in the same concentration. KI and isopropanol quenching were conducted due to their leading roles of active h^+ and $\cdot OH$ in PCO reaction.

For isopropanol quenching, as illustrated in Fig. 5a and b, the k_{app} of P-25 and Ag/AgBr/SFN (100 $mg\ L^{-1}$) decreased to 51% and 60% of no quenching, respectively. The contribution percentage of $\cdot OH$ on P-25 was about 1.2 times that on Ag/AgBr/SFN. Nevertheless, the k_{app} of P-25 and Ag/AgBr/SFN at 500 $mg\ L^{-1}$ increased to 69% and 87% of no quenching, respectively. Therefore, the contribution percentage of $\cdot OH$ on P-25 and Ag/AgBr/SFN both declined with an increase of catalyst concentration from 100 to 500 $mg\ L^{-1}$. Accordingly, the contribution percentage of $\cdot OH$ on P-25 was about 2.4 times that on Ag/AgBr/SFN at 500 $mg\ L^{-1}$. It implies that the effect of $\cdot OH$ was more obvious on P-25 compared with Ag/AgBr/SFN, despite the fact that the effect of active holes was still dominant for P-25 at 500 $mg\ L^{-1}$.

For KI quenching, the k_{app} of P-25 and Ag/AgBr/SFN (100 $mg\ L^{-1}$) decreased to 62% and 18% of no quenching, respectively. The contribution percentage of h^+ /adsorbed $\cdot OH$ generated on Ag/AgBr/SFN was about 2.2 times that on P-25. On P-25 and Ag/AgBr/SFN, the contribution percentage of h^+ /adsorbed $\cdot OH$ both increased with an increase of catalyst concentration from 100 to 500 $mg\ L^{-1}$. The contribution percentage of h^+ /adsorbed $\cdot OH$ generated on Ag/AgBr/SFN still achieved about 1.2 times that on P-25 at 500 $mg\ L^{-1}$. Due to the weak effect of $\cdot OH$ in most cases, the total effect of h^+ /adsorbed $\cdot OH$ is mainly attributed to active h^+ . These suggest that the effect of active h^+ is more predominant for Ag/AgBr/SFN than for P-25 especially at high catalyst concentration.

Generally speaking, the contribution percentage of $\cdot OH$ was observed to be especially lower than that of active h^+ under the reaction conditions examined for both photocatalysts. However, the contribution percentage of $\cdot OH$ and h^+ /adsorbed $\cdot OH$ on degrada-

Fig. 5. Effects of KI and isopropanol on k_{app} for AO7 degradation using P-25 (TiO_2) and Ag/AgBr/SFN at 100 and 500 $mg\ L^{-1}$. Experimental conditions: [AO7] = 20 $mg\ L^{-1}$, visible light >400 nm, pH 7.

tion using 100 $mg\ L^{-1}$ P-25 amounted to 49% and 38%, respectively, which demonstrates that $\cdot OH$ is more dominant than active h^+ at low concentration of P-25. Meanwhile, for Ag/AgBr/SFN, the contribution percentage of active h^+ was evidently enhanced from 82% to 88% when its concentration increased from 100 to 500 $mg\ L^{-1}$. Other study (Chen et al., 2005) reported that the active h^+ play a major role in AO7 degradation using P-25 (1000 $mg\ L^{-1}$) under UV-A irradiation, which indicates that the effect of active h^+ is more dominant for high catalyst concentration as well. These point out that the effect of $\cdot OH$ is more obvious at low concentration of P-25, while that of active h^+ /adsorbed $\cdot OH$ becomes more dominant with the increasing photocatalyst concentration for both catalysts.

4. Conclusions

Magnetic Ag/AgBr/SFN was prepared and used for degradation of AO7 under visible light irradiation. It is found that the PCO reaction did not dramatically changed the physicochemical features Ag/AgBr/SFN. SiO_2 interlayer is capable of improving the photoactivity of Ag/AgBr/SFN and SFN substrate demonstrated a very weak photoactivity. A limited photoactivity of Ag/AgBr/SFN was still maintained after successive runs of PCO reaction under visible light. The roles of active $\cdot OH$ and h^+ /adsorbed $\cdot OH$ were highly dependent on the concentration of photocatalysts. The effect of active h^+ was more predominant for Ag/AgBr/SFN especially at high catalyst concentration, while that of $\cdot OH$ was observed to be more obvious for TiO_2 (P-25) at low catalyst concentration.

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References

- Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999. Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today* 53, 51–59.
- Anpo, M., Zhang, S.G., Mishima, H., Matsuoka, M., Yamashita, H., 1997. Design of photocatalysts encapsulated within the zeolite framework and cavities for the decomposition of NO into N₂ and O₂ at normal temperature. *Catal. Today* 39, 159–168.
- Belloni, J., Treguer, M., Remita, H., Keyzer, R.D., 1999. Enhanced yield of photoinduced electrons in doped silver halide crystals. *Nature* 402, 865–867.
- Beydoun, D., Amal, R., 2002. Implications of heat treatment on the properties of a magnetic iron oxide–titanium dioxide photocatalyst. *Mater. Sci. Eng. B – Solid* 94, 71–81.
- Chen, F., Xie, Y.D., Zhao, J.C., Lu, G.X., 2001. Photocatalytic degradation of dyes on a magnetically separated photocatalyst under visible and UV irradiation. *Chemosphere* 44, 1159–1168.
- Chen, Y.X., Yang, S.Y., Wang, K., Lou, L.P., 2005. Role of primary active species and TiO₂ surface characteristic in UV-illuminated photodegradation of Acid Orange 7. *J. Photochem. Photobiol. A* 172, 47–54.
- Chung, Y.S., Park, S.B., Kang, D., 2004. Magnetically separable titania-coated nickel ferrite photocatalyst. *Mater. Chem. Phys.* 86, 375–381.
- Dutoit, D.C.M., Schneider, M., Baiker, A., 1995. Titania–silica mixed oxides. 1. Influence of sol–gel and drying conditions on structural properties. *J. Catal.* 153, 165–176.
- Elahifard, M.R., Rahimnejad, S., Haghghi, S., Gholami, M.R., 2007. Apatite-coated Ag/AgBr/TiO₂ visible-light photocatalyst for destruction of bacteria. *J. Am. Chem. Soc.* 129, 9552–9553.
- Fu, H.B., Pan, C.S., Yao, W.Q., Zhu, Y.F., 2005. Visible-light-induced degradation of Rhodamine B by nanosized Bi₂WO₆. *J. Phys. Chem. B* 109, 22432–22439.
- Gao, Y., Chen, B.H., Li, H.L., Ma, Y.X., 2003. Preparation and characterization of a magnetically separated photocatalyst and its catalytic properties. *Mater. Chem. Phys.* 80, 348–355.
- Hoffman, M.R., Martin, S.T., Choi, W.Y., Bahnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 95, 69–96.
- Hu, C., Tang, Y.C., Yu, J.C., Wong, P.K., 2003. Photocatalytic degradation of cationic blue X-GRL adsorbed on TiO₂/SiO₂ photocatalyst. *Appl. Catal. B – Environ.* 40, 131–140.
- Hu, C., Lan, Y.Q., Qu, J.H., Hu, X.X., Wang, A.M., 2006. Ag/AgBr/TiO₂ visible light photocatalyst for destruction of Azodyes and bacteria. *J. Phys. Chem. B* 110, 4066–4072.
- Huang, L., Yu, D.Q., 1988. *Application of UV–Vis Spectra in Organic Chemistry*. Science Press, Beijing, pp. 339–354.
- Ilisz, I., Dombi, A., 1999. Investigation of the photodecomposition of phenol in near-UV-irradiated aqueous TiO₂ suspensions. II. Effect of charge-trapping species on product distribution. *Appl. Catal. A – Gen.* 180, 35–45.
- Ishibashi, K., Fujishima, A., Watanabe, T., Hashimoto, K., 2000. Quantum yields of active oxidative species formed on TiO₂ photocatalyst. *J. Photochem. Photobiol. A* 134, 139–142.
- Kim, H.G., Hwang, D.W., Lee, J.S., 2004. An undoped, single-phase oxide photocatalyst working under visible light. *J. Am. Chem. Soc.* 126, 8912–8913.
- Kominami, H., Kumamoto, H., Kera, Y., Ohtani, B., 2001. Immobilization of highly active titanium(IV) oxide particles: a novel strategy of preparation of transparent photocatalytic coatings. *Appl. Catal. B – Environ.* 30, 329–335.
- Lan, Y.Q., Hu, C., Hu, X.X., Qu, J.H., 2007. Efficient destruction of pathogenic bacteria with AgBr/TiO₂ under visible light irradiation. *Appl. Catal. B – Environ.* 73, 354.
- Li, G.T., Qu, J.H., Zhang, X.W., Liu, H.J., Liu, H.N., 2006. Electrochemically assisted photocatalytic degradation of Orange II: influence of initial pH values. *J. Mole. Catal. A – Chem.* 259, 238–244.
- Mao, Y., Schoneich, C., Asmus, K.D., 1991. Identification of organic acids and other intermediates in oxidative degradation of chlorinated ethanes on titania surfaces en route to mineralization: a combined photocatalytic and radiation chemical study. *J. Phys. Chem.* 95, 10080–10089.
- Martin, S.T., Lee, A.T., Hoffmann, M.R., 1995. Chemical mechanism of inorganic oxidants in the TiO₂/UV process: increased rates of degradation of chlorinated hydrocarbons. *Environ. Sci. Technol.* 29, 2567–2573.
- Matthews, R.W., 1987. Solar-electric water purification using photocatalytic oxidation with TiO₂ as a stationary phase. *Sol. Energy* 38, 405–413.
- Meng, J.H., Yang, G.Q., Yan, L.M., Wang, X.Y., 2005. Synthesis and characterization of magnetic nanometer pigment Fe₃O₄. *Dyes Pigments* 66, 109–113.
- Rabani, J., Yamashita, K., Ushida, K., Stark, J., Kira, A., 1998. Fundamental reactions in illuminated titanium dioxide nanocrystallite layers studied by pulsed laser. *J. Phys. Chem. B* 102, 1689–1695.
- Rodrigues, S., Uma, S., Martyanov, I.N., Klabunde, K.J., 2005. AgBr/Al-MCM-41 visible-light photocatalyst for gas-phase decomposition of CH₃CHO. *J. Catal.* 233, 405–410.
- So, C.M., Cheng, M.Y., Yu, J.C., Wong, P.K., 2002. Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation. *Chemosphere* 46, 905–912.
- Stylidi, M., Kondarides, D.I., Verykios, X.E., 2004. Visible light-induced photocatalytic degradation of acid orange 7 in aqueous TiO₂ suspensions. *Appl. Catal. B – Environ.* 47, 189–201.
- Sun, Y., Pignatello, J.J., 1995. Evidence for a surface dual hole-radical mechanism in the titanium dioxide photocatalytic oxidation of 2,4-D. *Environ. Sci. Technol.* 29, 2065–2072.
- Velegraki, T., Poullos, I., Charalabaki, M., Kalogerakis, N., Samaras, P., Mantzavinos, D., 2006. Photocatalytic and sonolytic oxidation of acid orange 7 in aqueous solution. *Appl. Catal. B – Environ.* 62, 159–168.
- Wu, T.X., Liu, G.M., Zhao, J.C., Hidaka, H., Serpone, N., 1999. Evidence for H₂O₂ generation during the TiO₂-assisted photodegradation of dyes in aqueous dispersions under visible light illumination. *J. Phys. Chem. B* 103, 4862–4867.
- Xu, S.H., Shangguan, W.F., Yuan, J., Chen, M.X., Shi, J.W., 2007. Preparations and photocatalytic properties of magnetically separable nitrogen-doped TiO₂ supported on nickel ferrite. *Appl. Catal. B – Environ.* 71, 177–184.
- Zang, Y.J., Farnood, R., 2008. Photocatalytic activity of AgBr/TiO₂ in water under simulated sunlight irradiation. *Appl. Catal. B – Environ.* 79, 334–340.
- Zhang, X.W., Li, G.T., Wang, Y.Z., Qu, J.H., 2006. Microwave electrodeless lamp photolytic degradation of acid orange 7. *J. Photochem. Photobiol. A* 184, 26–33.
- Zhang, X.W., Sun, D.D., Li, G.T., Wang, Y.Z., 2008. Investigation of the roles of active oxygen species in photodegradation of azo dye AO7 in TiO₂ photocatalysis illuminated by microwave electrodeless lamp. *J. Photochem. Photobiol. A* 199, 311–315.
- Zou, Z.G., Ye, J.H., Sayama, K., Arakawa, H., 2001. Direct splitting of water under visible light irradiation with an oxide semiconductor photocatalyst. *Nature* 414, 625–627.