Magnetically Separable Fe$_3$O$_4$/AgBr Hybrid Materials: Highly Efficient Photocatalytic Activity and Good Stability

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Abstract
Magnetically separable Fe$_3$O$_4$/AgBr hybrid materials with highly efficient photocatalytic activity were prepared by the precipitation method. All of them exhibited much higher photocatalytic activity than the pure AgBr in photodegradation of methyl orange (MO) under visible light irradiation. When the loading amount of Fe$_3$O$_4$ was 0.5 %, the hybrid materials displayed the highest photocatalytic activity, and the degradation yield of MO reached 85 % within 12 min. Silver halide often suffers serious photo-corrosion, while the stability of the Fe$_3$O$_4$/AgBr hybrid materials improved apparently than the pure AgBr. Furthermore, depositing Fe$_3$O$_4$ onto the surface of AgBr could facilitate the electron transfer and thereby leading to the elevated photocatalytic activity. The morphology, phase structure, and optical properties of the composites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–visible diffuse reflectance spectra (UV–vis DRS), and photoluminescence (PL) techniques.

Keywords: AgBr; Fe$_3$O$_4$; Magnetic separation; Visible light; Photocatalysis

Background
Up to now, most of the silver oxide and silver halide have attracted much attention because of their strong visible light absorption performance [1–7]. Particularly, AgBr, which has a band gap of 2.6 eV, is well known as a photosensitive material and has been extensively applied to photographic films, which demonstrated excellent performance in degradation of dye pollutants and decomposition of water [8–10]. For example, Ag/AgBr/TiO$_2$ [11], Ag–AgBr/TiO$_2$/RGO [12], AgBr(I)/Ag [13], Fe(III)/AgBr [14], and Ag/AgBr/ZnO [15] have been successfully fabricated by diverse techniques, and their novel and unique photocatalytic properties have been extensively explored.

For the nanosized or microsized photocatalysts, effective separation from the mixed system and recycle using are important problems to restrain their real applications [16, 17]. Immobilizing catalysts on magnetic substrates by feasible methods is proven to be an effective approach for removing and recycling particles [18–21]. Moreover, Fe$_3$O$_4$ has excellent conductivity, so it could act as an electron transfer channel and acceptor, which could suppress the photo-generated carrier recombination. For instance, Ye et al. reported that the hierarchical core–shell-structured Fe$_3$O$_4$/WO$_3$ has a more effective photoconversion capability than pure WO$_3$ or Fe$_3$O$_4$ [22]. The Ag halides such as AgBr and AgI are photactive to visible light. When they were immobilized on SiO$_2$@Fe$_3$O$_4$ magnetic supports, they exhibited faster degradation rates for 4-chlorophenol than N-TiO$_2$ [23]. However, the Ag halides were easily photoreduced and lost their stability quickly.

The motivation of the present research originated from the idea that Fe$_3$O$_4$ has high conductivity and its CB level (1 V vs. NHE) makes it become a good candidate for coupling with AgBr. Based on the above reason, we prospect their combination could improve the photocatalytic performance by enhancing charge transport. Herein, conductive Fe$_3$O$_4$ particles and visible light active AgBr were coupled together to prepare the magnetically recyclable Fe$_3$O$_4$/AgBr composites with visible light activity. Studies of their photocatalytic performance in the decomposition of methyl orange (MO) indicated that Fe$_3$O$_4$/AgBr photocatalysts exhibited excellent catalytic activity under visible...
light illumination. Meanwhile, the stability of AgBr was improved when it was coupled with Fe₂O₄.

**Methods**

**Preparation of the Photocatalyst**

**Synthesis of Fe₂O₄ Nanospheres**

The Fe₂O₄ nanospheres were prepared according to the literature reported previously [24]. In a typical synthesis, 0.5 g of 1 g FeCl₃·3H₂O, 3.0 g NaAc, and 10 mL oleic acid were added to 30 mL ethylene glycol into a three-necked flask, and then a red solution was formed. The mixture was stirred vigorously at 50 °C for 20 min until all reagents were dissolved completely. Then, the mixture was transferred into a Teflon-lined autoclave and heated at 200 °C for 20 h. The products were cooled down to room temperature, washed with ethanol for several times, and dried under vacuum to give a black solid.

**Synthesis of Fe₂O₄/AgBr Hybrid Materials**

Fe₂O₄ nanospheres (0.01 g) were dispersed in 20 mL deionized water and then ultrasonically dispersed evenly. AgNO₃ (1.18 g) was added into the solution, and then NaBr (0.1 mol/L) was added dropwise slowly. The resulting suspensions were filtered, washed several times with distilled water, and finally dried in vacuum. Different Fe₂O₄/AgBr samples were obtained by adjusting the mass ratio of Fe₂O₄ and AgBr, and the sample was denoted as Fe₂O₄/AgBr-x (x means the percentage of Fe₂O₄).

**Characterization**

X-ray diffraction (XRD) patterns were measured on an X’Pert Philips diffractometer (Cu Kα radiation, 2θ range 10°–90°, step size 0.08°, accelerating voltage 40 kV, applied current 40 mA). The morphology of the samples was taken on a Hitachi S-4800 scanning electron microscope (SEM). UV–visible diffuse reflectance spectra (UV–vis DRS) were obtained on a Shimadzu U-3010 spectrometer, using BaSO₄ as a reference. The photoluminescence (PL) spectra were recorded on a F-7000 FL spectrophotometer.

**Evaluation of the Photocatalytic Activity**

MO was selected as the model pollutant to evaluate the photocatalytic activity of the Fe₂O₄/AgBr hybrid materials. In a typical experiment, 0.1 g of the photocatalyst was put into a 120 mL quartz reactor containing 100 mL MO aqueous suspension (20 mg/L, pH = 7). Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption–desorption equilibrium. A 300-W Xe arc lamp with a 420 cutoff filter was used as the light source (λ ≥ 420 nm, I₄20 = 8.0 mW/cm²). At 2-min intervals, 5 mL of the suspension was collected and centrifuged for 3 min to remove the catalyst particles for analysis. The residual MO concentration was detected at 464 nm using a UV–vis spectrophotometer (722, Shanghai Jingke Instrument Plant, China).

**Results and Discussion**

**Phase Structure and Morphology of the Samples**

Figure 1a shows that the size of Fe₂O₄ nanospheres was about 100 ~ 200 nm. The surface of Fe₂O₄ particles was rough, and each magnetic microsphere was constructed with many small magnetic grains. From Fig. 1b, we can clearly see that the obtained AgBr particles by the precipitation method easily agglomerate to large particles and their size was more than 300 nm. Figure 1c displays that when Fe₂O₄ was coupled with AgBr, the particle size of the composite increased apparently than the pure AgBr particles. The magnetic property of the surface Fe₂O₄ would result in the agglomeration of the particles. The EDS spectrum of Fe₂O₄/AgBr-0.5 hybrid materials indicates that the atomic ratio of Fe and Ag is approximately 1:134, which is a little larger than the designed value.

**Optical Properties of the Photocatalysts**

The UV–vis spectra of Fe₂O₄/AgBr hybrid materials are illustrated in Fig. 3. The pure Fe₂O₄ particles show strong absorption both in ultraviolet and visible light regions, which may be attributed to its small band gap. The absorption band edge of AgBr at 26.8°, 30.9°, 44.3°, 55.0°, and 64.5° were assigned to the (111), (200), (220), and (400) crystal planes of AgBr (JCPDS 06-4308) [14]. With increasing Fe₂O₄ content, no characteristic peaks were ascribed to Fe₂O₄ emerging with AgBr phase, which should be due to the lower content of Fe₂O₄.

**Photocatalytic Activity for MO Degradation on Fe₂O₄/AgBr Hybrid Materials**

The photocatalytic performances of the photocatalysts were evaluated by photoinduced decolorization of MO aqueous solution, as shown in Fig. 4. Prior to irradiation, the mixed solution of MO and photocatalyst was kept in the dark for 30 min to obtain an adsorption–desorption
equilibrium. For comparison, the photocatalytic activity of the pure AgBr was tested and the degradation yield reached approximately 55% in 12 min. When Fe₃O₄ nanospheres were loaded on AgBr particles, the photocatalytic activity increased apparently than the pure AgBr. The photocatalytic mechanism of Fe₃O₄/AgBr composites for MO degradation under visible light is illustrated in Fig. 5. The CB level of Fe₃O₄ (1 V vs. NHE) is much lower than that of AgBr (−1.1 V vs. NHE) [22–25], so the photo-excited electrons on the conduction band (CB) of AgBr can transfer to the CB of Fe₃O₄. And the conductivity of Fe₃O₄ is as high as 1.9 × 10⁶ S m⁻¹; the electrons on Fe₃O₄ particles would transfer out quickly and react with the surface pollutants. Meanwhile, Ag nanoparticles on the surface of AgBr can act as electron capture traps to improve the separation efficiency of the charge carriers and thereby improving the photocatalytic efficiency. These should be the main reason for the enhancement of the photocatalytic activity.
activity for Fe₃O₄/AgBr composites. In addition, the loading amount of Fe₃O₄ particles has an effect on the activity of the composites. The sample Fe₃O₄/AgBr-0.5 has the best photocatalytic activity; the degradation yield of MO reached nearly 85 % within 12 min. In order to clarify the reasons for this result, the active species in photodegradation process of MO were detected. Methanol, silver nitrate, and terephthalic acid solution were added into MO dye solution to capture electrons, holes, and ·OH, respectively. As can be seen from Fig. 6, when the active species of electrons, holes, and ·OH were captured, the degradation yield of MO decreased from 85 % to 68 %, 74 %, and 51 %, respectively. That indicated ·OH and electrons played more important roles comparing the holes in the photodegradation of MO.

As well known, AgBr is not stable, and it often suffers photo-corrosion. So, the stability of AgBr and Fe₃O₄/AgBr-0.5 was evaluated. As shown in Fig. 7, the photocatalytic activity on the pure AgBr decreased sharply in the consecutive three cycles. The degradation yield of MO on the pure AgBr particles in the three cycles was 0.52, 0.33, and 0.12, respectively. The photo-excited electrons on AgBr would reduce Ag⁺ to the metallic Ag, and the small Ag nanoparticles would cover on the surface of AgBr. And the surface Ag nanoparticles would prohibit the photo-absorption of the inner AgBr. When the amount of Ag was enough, the photo-excitation of the inner AgBr would be hold back, and as a result, the photocatalytic activity decreased remarkably as the reaction proceeding. However, for the Fe₃O₄/AgBr hybrid materials under visible light illumination

![Fig. 4](image1.png)

**Fig. 4** Visible light responded photodegradation of MO on the series of photocatalysts obtained. (a) Fe₃O₄. (b) AgBr. (c) Fe₃O₄/AgBr-0.1. (d) Fe₃O₄/AgBr-0.5. (e) Fe₃O₄/AgBr-1.

![Fig. 5](image2.png)

**Fig. 5** Photocatalytic mechanism of MO degradation on Fe₃O₄/AgBr hybrid materials under visible light illumination.

![Fig. 6](image3.png)

**Fig. 6** Detection of the active species of electrons, holes, and hydroxyl radicals.

![Fig. 7](image4.png)

**Fig. 7** The stability of the pure AgBr and Fe₃O₄/AgBr-0.5 hybrid materials on MO photodegradation in the consecutive three cycles. The inset shows that Fe₃O₄/AgBr-0.5 composites have a certain magnetic response to an applied magnetic field.
the highest. That was in accord with the photocatalytic activity result very well.

Conclusions

Fe$_3$O$_4$/AgBr hybrid materials with high photocatalytic efficiency under visible light were prepared through the precipitation method. The Fe$_3$O$_4$/AgBr samples showed much higher photocatalytic activity than the pure AgBr, which was due to the matched band structure of two components and the higher conductivity of Fe$_3$O$_4$. When the loading amount of Fe$_3$O$_4$ was 0.5%, the highest photocatalytic activity was obtained, and the degradation yield of MO reached 85% within 12 min. The PL spectra indicated that Fe$_3$O$_4$/AgBr hybrid materials had the higher separation efficiency of the photo-excited charge carriers, and that was in accordance with the photocatalytic activity very well. In addition, the stability of Fe$_3$O$_4$/AgBr composites was improved compared with the pure AgBr. The photo-excited electrons would transfer out quickly from the surface Fe$_3$O$_4$, so the self-reduction of AgBr to metallic Ag was prohibited, and as a result, the long-term stability of Fe$_3$O$_4$/AgBr was obtained.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
YC carried out the total experiment and wrote the manuscript. CL and JL participated in the data analysis. QL supervised the project. JY provided the facilities and discussions related to them. All authors read and approved the final manuscript.

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