Research Article

Photodegradation of Methyl Orange Using Magnetically Recoverable AgBr@Ag$_3$PO$_4$/Fe$_3$O$_4$ Photocatalyst under Visible Light

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A novel magnetically recoverable AgBr@Ag$_3$PO$_4$/Fe$_3$O$_4$ hybrid was prepared by a simple deposition-precipitation approach and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV-Vis diffuse reflectance spectroscopy (DRS). The results revealed that the photocatalytic activity and stability of AgBr@Ag$_3$PO$_4$/Fe$_3$O$_4$ composite toward decomposition of methyl orange (MO) dye were superior to those of pure Ag$_3$PO$_4$ under visible light irradiation. The photocatalytic activity enhancement of AgBr@Ag$_3$PO$_4$/Fe$_3$O$_4$ is closely related to the efficient separation of electron-hole pairs derived from the matching band potentials between Ag$_3$PO$_4$ and AgBr, as well as the good conductivity of Fe$_3$O$_4$. Moreover, the photocatalyst could be easily separated by applying an external magnetic field due to its magnetic property. The quenching effects of different scavengers proved that active h$^+$ and $\cdot$O$_2^-$ played the major role for the MO degradation. This work would provide new insight for the construction of visible light responsible photocatalysts with high performance, good stability, and recoverability.

1. Introduction

As a promising way to meet the challenges of environmental pollution, photocatalysis has attracted considerable interest over the past few decades [1–4]. With the shortage of energy sources becoming severe, significant efforts have now been directed toward the exploitation of highly efficient visible light responsible photocatalysts which can potentially utilize solar energy [5–8]. Very recently, Ag$_3$PO$_4$ has been put forward as a novel photocatalyst with excellent oxidative capability for the purification of water under visible light irradiation, which thus inspired great enthusiasm [9–13]. It seems to be a promising material for efficient photodecomposition of organic contaminants. Nevertheless, it should be noted that, in the present Ag$_3$PO$_4$ photocatalytic system, Ag$_3$PO$_4$ is prone to be photochemically decomposed to Ag if no sacrificial reagent is involved [14], which inevitably becomes a main obstacle for Ag$_3$PO$_4$ in practical application.

Recent reports indicated that epitaxial growth of an AgX (X = Br, I) nanoshell on the surface of Ag$_3$PO$_4$ could greatly enhance the chemical stability and activity of Ag$_3$PO$_4$ [15–17]. For instance, Bi et al. introduced AgX (X = Cl, Br, I) for the modification of Ag$_3$PO$_4$ by a simple in situ ion-exchange method and revealed the enhanced photocatalytic properties and stability [16]. Cao et al. successfully synthesized AgBr/Ag$_3$PO$_4$ as highly efficient and stable photocatalyst [17]. This is mainly because AgX and Ag$_3$PO$_4$ have matching band potentials, which could promote the transfer and separation of photoexcited carriers through their heterojunctions. Other researchers also confirmed the enhancement in AgBr-based composites [16]. Thus, combining Ag$_3$PO$_4$ with AgX is a more promising and fascinating visible light response photocatalyst than pure Ag$_3$PO$_4$.

For nano- or microsized photocatalysts, another problem that restrains their application is how to effectively separate the used photocatalysts from the mixed system in a simple way [18, 19]. Immobilizing catalysts on magnetic substrates by feasible methods is proven to be an effective approach for removing and recycling particles [20–23]. Moreover, Fe$_3$O$_4$ has excellent conductivity. Thus, Fe$_3$O$_4$ could act as an
electron-transfer channel and acceptor, which would suppress the photogenerated carrier recombination [24]. Therefore, given the magnetic separation ability and conducting properties of Fe₃O₄, it can be foreseen that fabrication of AgBr@Ag₃PO₄/Fe₃O₄ heterostructures could combine the advantages of activity of AgBr@Ag₃PO₄ with the merit of easy separation due to the incorporation of Fe₃O₄.

Nowadays, toxic organic dyes and their effluents are among the largest groups of water pollutants. The removal of these nonbiodegradable dye molecules from the environment is a crucial ecological problem, for their toxicity and potential carcinogenicity. To solve such pollution, the methyl orange (MO), which is a typical azo dye for textile industry, is chosen as the targeted pollutant in this paper. Herein, we prepared a novel magnetically separable AgBr@Ag₃PO₄/Fe₃O₄ composite via a simple deposition-precipitation approach. The catalysts can be easily recovered by applying an external magnetic field. Furthermore, we demonstrate that this composite favors the separation of electron-hole pairs and exhibits the enhancement of stability and activity in the photocatalytic decomposition of MO under visible light.

2. Experimental

2.1. Materials. All chemicals were of analytical grade and used as received without purification. Nano Fe₃O₄ (particle size <50 nm) was purchased from Sigma-Aldrich.

2.2. Sample Preparation. Firstly, the Fe₃O₄ nanoparticles were dispersed in distilled water (20 mL, 7.5 mM) and then added to the AgNO₃ solution (10 mL, 0.1 M). The solution was sonicated for 10 min. Subsequently, Na₂HPO₄ aqueous solution (5 mL, 0.5 mM) was added dropwise to the above suspension. After sonicated for 10 min, a definite concentration of NaBr solution was added slowly into the above mixture. The theoretical molar percentage of added Br/original P was controlled to be 80%. The reaction was allowed to proceed for 10 min under sonication. Finally, the obtained precipitate was separated by an external magnetic field, washed thoroughly with deionized water, and then dried at 60°C for 12 h. The final sample was labeled as AgBr@Ag₃PO₄/Fe₃O₄.

For comparison, pure Ag₃PO₄ particles were prepared by a simple precipitation method according to the previous study [14]. Ag₃PO₄/Fe₃O₄ and AgBr@Ag₃PO₄ were also prepared by the same conditions by replacing the NaBr or Fe₃O₄ solution with water.

2.3. Characterization. For XRD studies, the samples were recorded on X’Pert Pro PANalytical automatic diffractometer, using Cu-Kα radiation (λ = 0.154 nm) in the 2θ range of 10°–80°. TEM images were taken on a JEM-1200 (JEOL) microscope with an acceleration voltage of 80 kV. The UV-Vis diffuse reflectance spectra in the range of 230–700 nm were recorded on a Geneseral TU-1901 PC spectrometer, using BaSO₄ as a standard.

2.4. Photocatalytic Tests. The photocatalytic activity of the sample was evaluated by photodegradation of MO at room temperature. Briefly, 60 mg of photocatalyst was added to an aqueous solution of MO (100 mL, 20 mg/L). The suspension was mechanically stirred for 45 min in dark conditions to reach complete adsorption–desorption equilibrium. Then, it was irradiated with a 150 w Xe lamp with a 400 nm light filter. During the illumination, at given time intervals, about 3 mL aliquots were sampled, magnetically separated, and centrifuged at 10,000 rpm for 5 min to remove the remaining particles. The concentrations of MO were analyzed on a UV-Vis spectrophotometer at 461 nm.

Additionally, the recycling experiments were performed for three consecutive cycles to test the stability and reusability of the as-prepared AgBr@Ag₃PO₄/Fe₃O₄ composite. After each cycle, the photocatalyst was separated by an external magnetic field, washed thoroughly with deionized water, and then dried at 60°C for the next test.

3. Results and Discussion

3.1. Structural Characterization. XRD was used to investigate the different crystalline structures of the as-prepared photocatalysts. As shown in Figure 1(a), all the characteristic diffraction peaks can be readily indexed as the different crystalline planes of Ag₃PO₄ (JCPDS, card number 06-0505). From Figure 1(b), the diffraction peaks can be well indexed to magnetite Fe₃O₄ (JCPDS, card number 19-0629). For the pattern of AgBr@Ag₃PO₄/Fe₃O₄ (Figure 1(c)), besides the peaks of Ag₃PO₄ and Fe₃O₄, the diffraction peaks of AgBr at 26.6°, 30.9°, 44.3°, and 64.4° corresponding to the (111), (200), (220), and (400) have also been detected, confirming that AgBr have been formed on the Ag₃PO₄ surface after reaction with NaBr. The diffraction peaks of Fe₃O₄ at 35.5°, 43.2°, and 62.8° correspond to the (311), (400), and (440). However, as shown in Figures 1(b) and 1(c), the diffraction peaks from Fe₃O₄ turn weaker in the as-prepared AgBr@Ag₃PO₄/Fe₃O₄ composite due to the low content of Fe₃O₄. These observations indicate the successful synthesis of AgBr@Ag₃PO₄/Fe₃O₄ heterostructure.

![Figure 1: XRD patterns of (a) Ag₃PO₄, (b) Fe₃O₄, and (c) AgBr@Ag₃PO₄/Fe₃O₄.](image-url)
The morphological and microstructural details of the AgBr@Ag₃PO₄/Fe₃O₄ composite were then examined by TEM measurement. As shown in Figure 2(a), the Fe₃O₄ exhibits regular spherical shape with diameter of about 20–40 nm. Figure 2(b) reveals that the Ag₃PO₄ possess an irregularly spherical morphology with diameter of 100–500 nm. Some big particles can be attributed to the agglomeration of small particles. In the case of AgBr@Ag₃PO₄/Fe₃O₄ hybrid, as can be seen from Figures 2(c) and 2(d) in different magnification, it is evident that, alongside the Ag₃PO₄, the Fe₃O₄ nanoparticles are firmly anchored. This suggests a good combination between Ag₃PO₄ and Fe₃O₄ particles. Unfortunately, we failed to obtain TEM images of the AgBr@Ag₃PO₄/Fe₃O₄ samples, because AgBr nanoshells were easily destroyed by the high-energy electron beam during the measurements, as Wang et al. reported [25].

Figure 3 shows the UV-Vis diffuse reflectance spectra of Ag₃PO₄, Fe₃O₄, and the related complex photocatalysts. Pure Ag₃PO₄ shows a sharp fundamental absorption edge at about 520 nm, in accordance with the previous observation [26]. In contrast to pure Ag₃PO₄, the absorption of AgBr@Ag₃PO₄/Fe₃O₄ sample toward the visible light region is remarkably enhanced. It could be mainly attributed to the introduction of Fe₃O₄ nanoparticles, which is a well-performing light harvesting material as we can see in Figure 3.

3.2. Photocatalytic Performance. The photocatalytic activity of the as-prepared AgBr@Ag₃PO₄/Fe₃O₄ was evaluated by the degradation of MO under visible light irradiation. Figure 4 gives the absorption spectra of an aqueous solution of MO exposed to visible irradiation for various time periods. In the reaction process, the color of the MO solution gradually diminished (as the inset shows), and the typical absorption peak at 461 nm disappeared after 15 min, indicating that the chromophoric structure of the dye was completely destroyed assisted by AgBr@Ag₃PO₄/Fe₃O₄.
Figure 4: Absorption spectral changes of MO over AgBr@Ag₃PO₄/Fe₃O₄ composite as a function of irradiation time. The inset shows the color changes of the MO solutions corresponding to the degradation times.

Figure 5: Photocatalytic degradation curves of MO over different photocatalysts under visible light irradiation. For comparison, the photodegradation of MO was also performed with photolysis, pure Ag₃PO₄, Fe₃O₄, Ag₃PO₄/Fe₃O₄, and AgBr@Ag₃PO₄.

As can be seen from Figure 5, negligible degradation was detected under photolysis or using Fe₃O₄ as photocatalyst. Similar to the previous reports, the pure Ag₃PO₄ sample reveals a nice photodegradation performance under visible light (47.7% in 15 min). For comparison, after epitaxial growth of AgBr nanoshell on the surface of Ag₃PO₄, the AgBr@Ag₃PO₄ show much higher photocatalytic activity for the degradation of MO dye (94% in 15 min). This is mainly due to the effective coupling where the conduction band and valence band potentials of AgBr semiconductor are more negative than that of Ag₃PO₄, which could promote the transfer and separation of photoexcited electron-hole pairs [16]. In addition, the combination of Fe₃O₄ with Ag₃PO₄ also achieved good degradation efficiency (87.3% in 15 min). As Xi et al. explained, because of the excellent conductivity, the charge transport is improved after introduction of Fe₃O₄ into the composite, which would enhance the separation of electron-hole pairs [24]. Furthermore, just as the experimental results confirmed, once integrating the conductivity of Fe₃O₄ and the structural match of AgBr with Ag₃PO₄ particles, the AgBr@Ag₃PO₄/Fe₃O₄ exhibits the highest photocatalytic efficiency.

3.3. Stability and Recyclability of AgBr@Ag₃PO₄/Fe₃O₄. The stability of a photocatalyst is one of the most important parameters for its application. As our previous study demonstrated [27], Ag₃PO₄ is quite unstable at repeated use. However, as Figure 6(a) presents, the MO solution is quickly bleached after every MO decomposition experiment, and photocatalyst ternary AgBr@Ag₃PO₄/Fe₃O₄ is stable enough during the three repeated experiments without exhibiting any obvious loss of photocatalytic activity. Besides, the magnetic separation ability of the photocatalyst is impressive. As shown in Figure 6(b), the as-prepared AgBr@Ag₃PO₄/Fe₃O₄ can be...
conveniently collected from the solution by applying an external magnetic field within 3 min. This desirable property is what other conventional powder photocatalysts lack. Therefore, the as-prepared AgBr@Ag₃PO₄/Fe₃O₄ composite can work as an effective photocatalyst for pollutant degradation with good stability and recoverability.

3.4. Involved Active Species in the Photocatalysis. In order to investigate the photocatalytic degradation mechanism of AgBr@Ag₃PO₄/Fe₃O₄, it is necessary to verify the active species involved in the photocatalysis. Generally, photoinduced active species including h⁺, *OH radicals, and *O₂⁻ are expected to be involved in the photocatalytic process. Hence, i-PrOH was added to the reaction system as an *OH scavenger. EDTA-Na₂ was introduced as a scavenger of h⁺, and BQ was adopted to quench *O₂⁻ [28].

Figure 7 shows that, in the presence of EDTA, the photodegradation of MO was drastically inhibited with the degradation efficiency less than 5%. However, the employment of i-PrOH in the same photocatalytic system made a minor change caused in the photocatalytic degradation of MO. Furthermore, when the *O₂⁻ radical scavenger (BQ) was introduced, an evident decreasing photocatalytic activity of the AgBr@Ag₃PO₄/Fe₃O₄ composite was observed. These results indicate that active species h⁺ and *O₂⁻ contribute most to the photocatalytic system, and the presence of *OH radicals is considered to be of less importance to the reaction. Thus, we can anticipate the possible mechanism for the photocatalytic degradation of MO by AgBr@Ag₃PO₄/Fe₃O₄ composites. Under visible light irradiation, Ag₃PO₄ and AgBr can be simultaneously excited to form electron-hole (h⁺) pairs. As is known, AgBr and Ag₃PO₄ have matching band potentials; the photoinduced electrons can transfer from the CB bottom of AgBr to that of Ag₃PO₄, further migrate to Fe₃O₄ particles, and react with the adsorbed oxygen molecule to yield *O₂⁻. At the same time, the holes also move in the opposite direction from the VB top of Ag₃PO₄ to that of AgBr. The separated h⁺ then mainly participate in the degradation of MO by direct oxidation, which would be together with *O₂⁻. However, a small number of h⁺ can still react with water to produce *OH radicals to degrade MO.

4. Conclusions

In summary, we reported an investigation on the preparation and photocatalytic activity of a novel magnetically recoverable AgBr@Ag₃PO₄/Fe₃O₄ hybrid. Because of the magnetism of Fe₃O₄ and the matching band between AgBr and Ag₃PO₄, the as-synthesized AgBr@Ag₃PO₄/Fe₃O₄ nanoparticles exhibited efficient photocatalytic activity, good stability, and recyclability toward decomposition of MO under visible light irradiation. In addition, the quenching effects of different scavengers proved that reactive h⁺ and *O₂⁻ played the major role for the MO degradation. We expected that this kind of magnetically separable AgBr@Ag₃PO₄/Fe₃O₄ composite would provide new insight for the design and fabrication of high performance photocatalysts toward environmental protection.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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