Ag@AgBr/Ag₃PO₄ Nanocomposites as Photocatalyst for Degradation of Rhodamine B

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Ternary nano-Ag@AgBr/Ag₃PO₄ was synthesized via an approach involving ion interchange– precipitation and in situ photo-assisted reduction. It was then characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDX), selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), and UV-Vis diffuse reflectance spectroscopy (DRS). Under visible light irradiation, Ag@AgBr/Ag₃PO₄ had high photocatalytic activity and stability with respect to the decomposition of rhodamine B (RhB). $0.1Ag@AgBr/Ag_3PO_4$ showed the best photocatalytic performance and degraded 96% of RhB after 30 min of irradiation. It is known from the effects that different capture factors have on the photocatalytic reaction of RhB by $0.1Ag@AgBr/Ag_3PO_4$, holes (h⁺) and superoxide anions (O₂⁻⁻) are primarily responsible for the degradation of RhB. To explain the photocatalytic degradation process of RhB, a Ztype photocatalytic degradation mechanism was proposed.

Keywords: Nanocomposites; Photocatalytic degradation; RhB; Z-type

1. INTRODUCTION

As China's economy has rapidly developed, environmental problems with the air, water, and solid waste pollution have become increasingly prominent. Among of them, environmental issues that are caused by wastewater from printing and dyeing have high concentrations of organic matter and are increasingly serious problems. Particularly, as a common pollutant released in textile wastewater with

stable chemical properties, RhB has been degraded with traditional processing methods such as biological methods, membrane separation, and chemical precipitation[1, 2]. However, the above approaches have the disadvantages of high operating costs and secondary pollution.

In the last few decades, photocatalysts have received widespread attention because of their environmental friendliness and cost-effectiveness[3]. TiO₂ is one of the most common and promising photocatalysts and has high photocatalytic activity, low cost, and high chemical stability; however, because of its large band gap, it can only absorb sunlight in the ultraviolet region (only 5% of solar energy)[4]. Therefore, to more efficiently harness sunlight, visible-light-driven photocatalysts must be designed.

Ag₃PO₄ is a narrow band gap photocatalyst with the forbidden bandwidth of 2.45 eV and has been used to degrade organic pollutants using visible light[5, 6]. It strongly absorbs wavelengths shorter than 520 nm with a maximum quantum efficiency of 90%, which is much higher than other metal oxides. However, during photocatalytic reactions, Ag₃PO₄ easily decomposes into Ag⁰ and PO₄³⁻ because of photocorrosion. Also, Ag⁰ precipitates on the catalyst surface and inhibits its photocatalytic activity, which decreases the catalyst's reusability[7, 8]. Recently, Ag₃PO₄ composite photocatalysts have been prepared to obtain materials that have improved photocatalytic activity and reusability[9, 10], including Ag/Ag₃PO₄[11], TiO₂/Ag₃PO₄[12], ZnO/Ag₃PO₄[13], and Ag₃PO₄/CeO₂[14].

Ag@AgX (X = Cl, Br, and I) visible-light-driven photocatalysts have been widely studied because of their photocatalytic performance[15-17]. The presence of metallic Ag enhances the visible light absorption efficiency of Ag@AgX, while it also prevents the decomposition of AgX. Ag is in close contact with AgX, and the photogenerated electrons generated after excitation of AgX are transferred to Ag nanoparticles, which can reduce the recombination of AgX photogenerated electron-hole pairs. The photogenerated holes in Ag@AgBr can combine with Br⁻ to form strongly oxidative bromine radicals (Br·); these can degrade organic pollutants and sterilize and reduce heavy metal ions[10, 18]. According to literature reports, coupling Ag@AgBr with other semiconductors can increase the quantum yield and catalytic activity of materials[19, 20]. For example, Zhang et al. prepared an Ag/AgBr/TiO₂ composite that had excellent photocatalytic activity for the decomposition of gaseous benzene and acetone[21]. Jin et al. synthesized the Ag-AgBr/Bi₂O₂CO₃ photocatalyst that had visible-light-driven photocatalytic properties for rhodamine B (RhB) degradation[22].

In this paper, a series ternary $Ag@AgBr/Ag_3PO_4$ nanocomposite was prepared via a two-step *in situ* photoreduction method. The photocatalytic activity and stability of $Ag@AgBr/Ag_3PO_4$ were evaluated by decomposing RhB under the irradiation of visible light.

2. EXPERIMENTAL PART

2.1. Reagents

Sodium bromide (NaBr), polyvinylpyrrolidone (PVP), silver nitrate (AgNO₃), disodium hydrogen phosphate (Na₂HPO₄·12H₂O), p-benzoquinone (C₆H₄O₂), triethanolamine (N(CH₂CH₂OH)₃), isopropanol ((CH₃)₂CHOH), absolute ethanol (C₂H₅OH), and RhB were all analytically pure.

2.2. Preparation of catalyst

2.2.1. Preparation of Ag₃PO₄

AgNO₃ (0.612 g) was added to a beaker that contained 30 mL of ultrapure water, and the mixture was stirred to dissolve AgNO₃. Then, 30mL of a solution that contained 0.43g of Na₂HPO₄·12H₂O was added, and the mixture was stirred for 120min. The precipitate was centrifuged, and the product was washed with ultrapure water and absolute ethanol. Then, the precipitate was collected and dried for 10 h. The obtained product was Ag₃PO₄.

2.2.2. Preparation of Ag@AgBr/Ag₃PO₄ Composite

AgNO₃ (0.17g) was dissolved in 80mL of a solution of alcohol water (V water: V ethanol = 3: 5). Ag₃PO₄ (0.05g, 0.1g, 0.15g) and 0.111g of polyvinylpyrrolidone (PVP) surfactant were added under stirring, placed in a reaction kettle, and kept in an oven for 3h. After it was left to cool, 20 mL of an aqueous solution that contained 0.0515 g of NaBr was added; then hydrochloric acid (30%) was used to adjust the pH to 2.5. The solution was stirred overnight and then reduced under a 1000W xenon light for 30 min. The product was washed with ultrapure water and absolute ethanol, and then Ag@AgBr/Ag₃PO₄ with different content of Ag₃PO₄ was obtained after precipitation was collected and dried for 10 h. The samples were named as 0.05Ag@AgBr/Ag₃PO₄, 0.1Ag@AgBr/Ag₃PO₄, and 0.15Ag@AgBr/Ag₃PO₄. Ag@AgBr was prepared under the same conditions as above except without the addition of Ag₃PO₄.

2.3. Characterization

The X-ray diffraction (XRD) patterns were collected by an X-ray diffractometer (Rigaku D/max-2500) using Cu-K α radiation source at 35 kV, ranging from 10 to 80°. The JSM-6510 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectra (EDX) and the JSM-2100 highresolution transmission electron microscope (HRTEM) were used to study the samples morphologies. X-ray photoelectron spectroscopy (XPS) data were collected with an ESCALAB 250 X-ray photoelectron spectrometer. The UV-Vis diffuse reflectance spectra (DRS) was collected using a UV-2550 with wavelength between 200 and 850nm.

2.4. Photocatalytic degradation experiment

Photocatalytic degradation experiments were performed in a JOYN-GHX-DC photochemical reactor. A 1000W xenon lamp was used as the visible light source. The prepared photocatalyst (50mg) was weighed and dispersed in a test tube that contained 50mL of 10mg/L RhB. The test tube was put in the photochemical reactor, and the door was closed to avoid the stray light. The mixture was stirred for 20min to ensure that the catalyst was evenly dispersed. Then, the light source was turned on, and a 4mL sample was taken every 6 min. The sample was centrifuged, and the supernatant is sampled. Before and after reaction, the absorbance of a solution of RhB was measured using a UV-visible spectrophotometer.

During the reaction, the temperature of the reaction solution was controlled to be about 10 $^{\circ}$ C using cooling water. The degradation rate of RhB via photocatalytic degradation was calculated using Beer Lambert's law (1). The photocatalytic degradation of RhB was characterized using kinetics, according to equation (2). These were used to judge the photocatalytic degradation performance of the photocatalyst.

$$C_t/C_0 = A_t/A_0$$
(1)

$$A_t + Kt = -\ln(C_t/C_0)$$
(2)

where A_0 and A_t represent the initial absorbance and the absorbance at time t after illumination, respectively, and C_0 and C_t represent the corresponding initial concentration of the solution and the concentration of the solution at t time, respectively.

The recycling used ability: The photocatalyst was cycled 3 times to examine the cycling stability.

Free radical capture experiments: The experiments can be used to analyze the active substances in degrading pollutants. Isopropanol (IPA) was used as a hydroxyl radical (OH \cdot) capture agent; triethanolamine (TEOA) was used as a hole (h⁺) capture agent; p-benzoquinone (BQ) was used as a superoxide anion (O₂⁻) capture agent.

3. RESULTS AND DISCUSSION



Figure 1. XRD patterns of the as-prepared samples

The phase and crystal structure of the catalyst were examined using XRD. The XRD spectra of the prepared Ag₃PO₄, Ag@AgBr, 0.05Ag@AgBr/Ag₃PO₄, 0.1Ag@AgBr/Ag₃PO₄, and 0.15Ag@AgBr/Ag₃PO₄ catalysts are shown in Fig. 1. It is known that in the XRD spectrum of Ag₃PO₄, the main diffraction peaks are observed at 20.9°, 29.7°, 33.3°, 36.6°, 47.9°, 52.8°, 55.1°, 57.4°, 61.7°, and 72.0° and belong to the Ag₃PO₄ (JCPDS No 70-0702) characteristic peaks of the (110), (200), (210),

(211), (310), (222), (320), (321), (400), and (421) crystal planes, respectively. For the card of AgBr (JCPDS No. 79-0148), the characteristic diffraction peaks of the Ag@AgBr/Ag₃PO₄ and Ag@AgBr catalysts at 26.9°, 31.1°, and 44.6°, and these correspond to the (111), (200), and (220) crystal planes of the cubic crystal of AgBr. Also, the characteristic diffraction peaks that belong to Ag₃PO₄ in the XRD pattern of Ag@AgBr/Ag₃PO₄ became increasingly obvious as the amount of Ag₃PO₄ increased. In addition, no independent diffraction peaks of metallic Ag are observed in the spectra. This may be because the Ag content is too low, the dispersion of the Ag is high, or the diffraction peaks of Ag are masked by the diffraction peaks of AgBr[23].



Figure 2. SEM images of prepared photocatalysts: (a) Ag@AgBr microspheres, (b) Ag₃PO₄ nanoparticles, (c) Ag@AgBr/Ag₃PO₄microspheres, (d) TEM image of Ag@AgBr/Ag₃PO₄, (e,f) HRTEM image of Ag@AgBr/Ag₃PO₄, (g) SAED pattern of Ag@AgBr/Ag₃PO₄, and (h) corresponding EDX pattern of Ag@AgBr/Ag₃PO₄

Fig. 2 shows the SEM, TEM, SAED, and EDX images of the Ag₃PO₄, Ag@AgBr, and Ag@AgBr/Ag₃PO₄ catalysts. Fig. 2a shows the Ag@AgBr nanoparticles with a particle size range of

100-600nm. The regular hexahedral structure of the Ag₃PO₄ crystal has a particle size ranging from 0.5 to 1 μ m, as observed in Fig. 2b. An SEM image of 0.1Ag@AgBr/Ag₃PO₄ after the composite formed is displayed in Fig. 2c, and the nanoparticles Ag@AgBr and Ag₃PO₄ are tightly bound together. Fig. 2d is a TEM image of 0.1Ag@AgBr/Ag₃PO₄; it can be seen in the figure that 10-50 nm of nano-Ag and AgBr particles are attached to the Ag₃PO₄ surface. Fig. 2e and 2f are HRTEM images of 0.1Ag@AgBr/Ag₃PO₄.



Figure 3. XPS spectra of Ag@AgBr/Ag₃PO₄: (a) survey scan and (b) Ag 3d, (c) O 1s, (d) Br 3d, and (e) P 2p spectra



Figure 4. (a) Ag_3PO_4 , Ag@AgBr, $0.05Ag@AgBr/Ag_3PO_4$, $0.1Ag@AgBr/Ag_3PO_4$, $0.15Ag@AgBr/Ag_3PO_4$ UV-Vis DRS results. (b) Plots of $(\alpha hv)^2$ versus energy (hv) for the band gap energy of Ag_3PO_4 . (c) Plots of $(\alpha hv)^{1/2}$ versus energy (hv) for the band gap energy of Ag@AgBr

The spacings of the lattice fringe are 0.235, 0.2029, and 0.3002 nm and correspond respectively to the (111), (220), and (200) crystal planes of Ag, AgBr, and Ag₃PO₄. SAED results of 0.1Ag@AgBr/Ag₃PO₄ are shown in Fig. 2g, and the bright diffraction rings of 0.1Ag@AgBr/Ag₃PO₄ indicate that it is polycrystalline. In addition, in Fig. 2g, it can be seen that the lattice spacings of the three crystal planes are 0.235, 0.2029, and 0.3002 nm, respectively. Also, the results are consistent with HRTEM results. The EDX diagram of 0.1Ag@AgBr/Ag₃PO₄ is shown in Fig. 2h, and four elements are seen: Br, O, Ag, and P. The apparent Cu element diffraction peak was generated by the Cu mesh that was used to prepare the test sample for the TEM test. We can know from the above analysis that Ag@AgBr is dispersed and supported on the Ag₃PO₄ crystal surface in a granular form and that is has a good hexahedral morphology.

To study the surface chemical state of 0.1Ag@AgBr/Ag₃PO₄, we used XPS to analyze the surface chemical state (Fig. 3). The full-spectrum of the 0.1Ag@AgBr/Ag₃PO₄ composite is shown in Fig. 3a.

There are five elements Br, O, Ag, P and C, where C is the substrate, and this indicates that Ag₃PO₄ and Ag@AgBr are in the composite. From Fig. 3b, the XPS peaks of Ag 3d are composed of Ag $3d_{5/2}$ peaks at 367.75 eV (divided into two peaks at 367.7 eV and 368.1 eV) and Ag $3d_{3/2}$ at 373.8 eV (divided into two peaks at 373.6 eV and 374.2 eV), respectively[24]. The peaks at 367.7 eV and 373.6 eV can be attributed to Ag⁰, whereas the peaks at 368.1 and 374.2 eV can be attributed to the Ag⁺ of Ag@AgBr/Ag₃PO₄. The presence of Ag 3d in this way indicates the formation of AgBr and Ag in the catalyst[24]. Fig. 3c shows the XPS peaks of O 1s; the O 1s XPS spectrum of Ag@AgBr/Ag₃PO₄ is composed of two multi-state peaks that correspond to 531.95 eV and 533.3 eV, respectively. The 531.95 eV peak corresponds to oxygen in the lattice of Ag₃PO₄, and the peak at 533.3 eV indicates the adsorption of H₂O or OH⁻ on the surface. Fig. 3d is the XPS analysis of Br 3d. Br 3d was fitted with two main peaks at 68.45 eV and 69.35 eV, and these represent Br $3d_{5/2}$ and Br $3d_{3/2}$, respectively. This distribution explains that Br is present as Br⁻[25]. The XPS analysis of P 2p is shown in Fig. 3e, and it represents P⁵⁺ in the PO₄³⁺ structure at 133.8eV. From the above analysis, it is further proved that Ag₃PO₄ was combined with Ag@AgBr.

Fig. 4a shows the DRS of the Ag_3PO_4 , Ag@AgBr, $0.05Ag@AgBr/Ag_3PO_4$, $0.1Ag@AgBr/Ag_3PO_4$, and $0.15Ag@AgBr/Ag_3PO_4$ catalysts. The cut-off wavelength of Ag_3PO_4 light absorption is about 500 nm, whereas Ag@AgBr shows strong absorption at wavelengths of 200 to 800 nm. When Ag_3PO_4 was supported on Ag@AgBr, the optical absorption range was broader, and the optical absorption intensity over the whole range of wavelengths increased. Among them, the optical absorption effect of $0.1Ag@AgBr/Ag_3PO_4$ is the best, and this indicates that Ag_3PO_4 and Ag@AgBr have a synergistic effect.

The band gaps of Ag₃PO₄ and Ag@AgBr can be calculated according to the Kubelka-Munk formula[26], which is as follows:

 $\alpha hv = A(hv - Eg)^{n/2}$ (3)

 α is the absorption coefficient, h is Planck's constant, v is the frequency of light, Eg represents the band gap energy, and A is a constant. The value of n is determined by the type of semiconductor material. When the material has an indirect band gap, n is 4, and when the semiconductor has a direct band gap, n is 1. The values of n for Ag₃PO₄ and Ag@AgBr are 1[27] and 4[28], respectively. Fig. 4b shows (α hv)² versus energy (hv) diagrams of the band gap energy of Ag₃PO₄ (band gap width of 2.45 eV), and Fig. 4c shows the (α hv)^{1/2} versus energy (hv) diagrams of the band gap energy of Ag@AgBr (band gap width of 2.6 eV).

To reveal the photogenerated electron transfer of $Ag@AgBr/Ag_3PO_4$ in the photocatalytic reaction, the VB (valence band) and CB (conduction band) of AgBr and Ag_3PO_4 were predicted using the following formulas[29]:

$$\begin{split} E_{CB} &= X - Ee - 0.5Eg \qquad (4) \\ E_{VB} &= E_{CB} + Eg \qquad (5) \end{split}$$

The absolute electronegativity is represented by X; Ee is the free electron energy at the hydrogen electrodes (approximately 4.5 eV); Eg is the band gap energy; E_{CB} and E_{VB} are the CB and VB potentials, respectively. The X value of AgBr is 5.81 eV, and the E_{VB} value of AgBr is calculated to be 2.61 eV. The E_{CB} value of AgBr is estimated to be 0.01 eV. Similarly, when the X value of Ag₃PO₄ is 6.17 eV, the E_{VB} value is 2.9 eV, and the E_{CB} value is about 0.45 eV.



Figure 5. (a) Visible light scanning pattern of Ag@AgBr/Ag₃PO₄ degradation of RhB. (b) Effects of different catalysts on photocatalytic degradation of RhB under visible light. (c) First-order kinetic fitting plots for degradation of RhB using different catalysts. (d) Cycling runs of Ag₃PO₄ and Ag@AgBr/Ag₃PO₄ for degradation of RhB

Table 1. Photo degradation rate constants and linear regression coefficients of different catalysts using the equation $-\ln(C/C_0) = kt$

	k(min ⁻¹)	Regression equation	\mathbb{R}^2
0.1Ag@AgBr/Ag ₃ PO ₄	0.06545	$-\ln(C/C_0) = 0.06545x + 0.43992$	R ² =0.74063
Ag@AgBr	0.04492	$-\ln(C/C_0)=0.04492x+0.40574$	R ² =0.83218
0.05Ag@AgBr/Ag ₃ PO ₄	0.03395	$-\ln(C/C_0) = 0.03395x + 0.3063$	R ² =0.82514
0.15Ag@AgBr/Ag ₃ PO ₄	0.02726	$-\ln(C/C_0)=0.02726x+0.23241$	R ² =0.81706
Ag ₃ PO ₄	0.01797	-ln(C/C ₀)=0.01797x+0.16992	R ² =0.84582

Table 2. Comparision of the Ag@AgBr/Ag₃PO₄ with similar photocatalyst for degradation of rhodamine B.

Material	t(min)	Degradation efficiency	Ref
0.1Ag@AgBr/Ag ₃ PO ₄	30	96%	This work
Ag ₃ PO ₄ (3.0 wt.%)/ZnO	40	95%	[30]
0.2Ag@AgCl/ZnCo ₂ O ₄	120	99.4%	[31]
Ag/AgBr/ZnO-2	180	100%	[32]
Ag/AgBr/NiFe ₂ O ₄	60	100%	[33]

Figure 5a uses UV-visible full-wavelength scanning to analyze the changes of RhB molecule during the photocatalytic degradation of 0.1Ag@AgBr/Ag₃PO₄. With prolonged reaction time, the characteristic peak intensity of RhB, which is at 553nm, became gradually weaker. After 30min of light irradiation, the peak intensity at 553nm gradually decreased, and this indicates that the chromophore group of RhB was destroyed.

shows effects different Fig. 5b the that the catalysts $(Ag_3PO_4,$ Ag@AgBr, $0.1 Ag@AgBr/Ag_3PO_4$, and $0.05 Ag@AgBr/Ag_3PO_4$, $0.15 Ag@AgBr/Ag_3PO_4$) have on the photocatalytic degradation of RhB. The results show that the degradation rates of Ag₃PO₄, Ag@AgBr, 0.05Ag@AgBr/Ag3PO4, and 0.15Ag@AgBr/Ag3PO4 at 30 min were 57%, 88%, 81%, and 72% respectively; of these, the worst effect was that of pure Ag₃PO₄. The photocatalytic degradation rate of 0.1Ag@AgBr/Ag₃PO₄ reached 96% within 30 min, and RhB almost completely degraded. The results illustrate that Ag₃PO₄ obviously improved the photocatalytic performance of the Ag@AgBr photocatalyst. To illustrate the excellent photocatalytic performance of the 0.1Ag@AgBr/Ag₃PO₄, a detailed comparison on the 0.1Ag@AgBr/Ag₃PO₄ with previous reported various similar photocatalysts for degradation of rhodamine B was summarized in Table 2. Obviously, the 0.1Ag@AgBr/Ag₃PO₄ shows highly efficient photocatalytic performance.

The decomposition of RhB by $Ag@AgBr/Ag_3PO_4$ follows the pseudo-first-order kinetic model (Fig. 5c), and the Table 1 shows the k values that were calculated from linear fitting. The reaction rate constants of Ag_3PO_4 , Ag@AgBr, $0.05Ag@AgBr/Ag_3PO_4$, $0.1Ag@AgBr/Ag_3PO_4$, and $0.15Ag@AgBr/Ag_3PO_4$ are $0.01797min^{-1}$, $0.04492min^{-1}$, $0.03395min^{-1}$, $0.06545min^{-1}$, and $0.02726min^{-1}$, respectively. The largest reaction rate constant is that of $0.1Ag@AgBr/Ag_3PO_4$ ($0.06545min^{-1}$), which shows that the combination of Ag_3PO_4 and Ag@AgBr enhance their photocatalytic performance.



Figure 6. SEM image of 0.1Ag@AgBr/Ag₃PO₄ after 4 cycles of use

The stability test results for Ag₃PO₄ and 0.1Ag@AgBr/Ag₃PO₄ are shown in Fig. 5d. After 4 cycles the degradation rate of RhB by Ag₃PO₄ is only 25%, while the degradation rate of RhB by 0.1Ag@AgBr/Ag₃PO₄ can stabilize at 71% since the second cycle. This result indicates that the composite of Ag₃PO₄ and Ag@AgBr improves the stability performance. Fig. 6 shows an SEM image of 0.1Ag@AgBr/Ag₃PO₄ after 4 cycles of use. As seen from the figure, the product is basically stable,

and this indicates that the microstructure of the product is basically stable, which is consistent with the stability of the light catalytic degradation performance after 4 cycles[34].

Fig. 7 shows the effects of different capture factors on the photocatalytic reaction. Adding IPA has only a small impact on the degradation of RhB. However, when BQ and TEOA were added to the reaction system, the photocatalytic process was evidently inhibited. Thus, it can be speculated that the oxidation process of a hole (h^+) and superoxide anion (O_2^-) are the main active species in the 0.1Ag@AgBr/Ag_3PO_4 photocatalytic degradation process on RhB.



Figure 7. Trapping experiments of active species during the photocatalytic reaction



Scheme 1. Schematic diagram of the photocatalytic mechanism of Ag@AgBr/Ag₃PO₄

On the basis of the aforesaid analysis, a Z-scheme reaction mechanism for the Ag@AgBr/Ag₃PO₄ photocatalytic degradation process was inferred. As shown in the Scheme 1, both AgBr and Ag₃PO₄ can absorb visible photons and form photoexcited electron-hole pairs. The valence and conduction band potential levels of Ag₃PO₄ are about 2.9 eV and 0.45 eV (vs. NHE), respectively, and the forbidden band width is 2.45 eV[35]. The photogenerated hole energy formed by Ag₃PO₄ is about 2.9 eV, which is higher than the reaction potential $E(OH^{-}/OH^{-})$. This indicates that the holes can be used directly in degrading pollutants. Because the photogenerated electron energy formed by Ag₃PO₄ is lower than $E(O_2/O_2^{-})$ for the activation energy of single electron oxygen, the photogenerated electrons cannot be trapped by dissolved oxygen. With a backlog of photogenerated electrons on the conduction band of Ag₃PO₄, the electrons can be transferred to the VB of AgBr by Ag nanoparticles. Then the electrons can be recombined with the photogenerated holes that accumulated in the VB of AgBr. The valence and conduction band levels of AgBr are about 2.61 eV and 0.01 eV (vs. NHE), respectively, and thus, the forbidden band width is 2.6 eV. The photogenerated electron energy generated by AgBr is higher than $E(O_2/O_2^-)$. Thus, the activity of electrons generated on the AgBr conduction band can be captured by dissolved oxygen to form the superoxide anion (O_2^{-}) , which further participates in the degradation reaction. Moreover, photogenic holes that are generated in the AgBr valence band can also combine with Br⁻ to form the Br· free radical, which has a strong oxidation property and can be more effectively involved in the RhB degradation. When a pollutant is mineralized into small inorganic molecules such as CO₂, Br · radicals are reduced to Br⁻, and then combine with Ag⁺ to form AgBr to ensure the self-stability of the system. This was consistent with the active factor capture results, showing the holes (h^+) and superoxide anions (O_2^-) as primary species responsible for the decomposition of RhB by 0.1Ag@AgBr/Ag₃PO₄.

During the photocatalytic reaction of Ag@AgBr/Ag₃PO₄, the decomposition pathway of RhB can be summarized as follows:

(1)Photogenerated electron-hole pairs

$$AgBr + hv \rightarrow AgBr (e^-) + AgBr (h^+)$$
$$Ag_3PO_4 + hv \rightarrow Ag_3PO_4 (e^-) + Ag_3PO_4 (h^+)$$

(2) Migration and conversion

$$\begin{array}{l} Ag + Ag_3PO_4(e^-) \rightarrow Ag_3PO_4 + Ag~(e^-) \\ AgBr(h^+) + Ag~(e^-) \rightarrow Ag + AgBr \\ AgBr(e^-) + O_2 \rightarrow AgBr + O_2^{--} \\ AgBr(h^+) + Br^- \rightarrow AgBr + Br^0 \end{array}$$

(3) Decomposition of RhB

 O_2^{-} + RhB → Degradation product + $CO_2 \pm H_2O$ AgBr(h⁺) + RhB → Degradation product + $CO_2 \pm H_2O$ Br⁰ + RhB → Degradation product + $CO_2 + H_2O + Br^-$

4. CONCLUSIONS

Nano-Ag₃PO₄ that was prepared via a precipitation method was chelated with AgBr, which was synthesized via ion interchange. Then, Ag^+ was reduced *in situ* to Ag via a photoreduction method to

form a ternary Ag@AgBr/Ag₃PO₄ heterocomplex. The photocatalytic activity and stability of Ag@AgBr/Ag₃PO₄ were analyzed by removal of RhB under visible light, and the results were used to propose a Z-type degradation mechanism for RhB. Under visible light, the Ag@AgBr surface plasmon has a synergistic effect with nano-Ag₃PO₄, which enhances the generation of electrons and holes. As photogenerated electrons accumulate in the CB of Ag₃PO₄, the electrons were transferred to Ag nanoparticles. They were then further transferred to the VB of AgBr before recombining with the holes in the VB of AgBr, and this enhanced the isolation efficiency of the Ag₃PO₄ electron-hole pairs. This study provides a facile and effective method for constructing and manufacturing composite photocatalysts.

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