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Photocatalytic activity of attapulgite–TiO₂–Ag₃PO₄ ternary nanocomposite for degradation of Rhodamine B under simulated solar irradiation

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Abstract

An excellent ternary composite photocatalyst consisting of silver orthophosphate (Ag₃PO₄), attapulgite (ATP), and TiO₂ was synthesized, in which heterojunction was formed between dissimilar semiconductors to promote the separation of photo-generated charges. The ATP/TiO₂/Ag₃PO₄ composite was characterized by SEM, XRD, and UV-vis diffuse reflectance spectroscopy. The co-deposition of Ag₃PO₄ and TiO₂ nanoparticles onto the surface of ATP forms a lath-particle structure. Compared with composite photocatalysts consisting of two phases, ATP/TiO₂/Ag₃PO₄ ternary composite exhibits greatly improved photocatalytic activity for degradation of rhodamine B under simulated solar irradiation. Such ternary composite not only improves the stability of Ag₃PO₄, but also lowers the cost by reducing application amount of Ag₃PO₄, which provides guidance for the design of Ag₃PO₄- and Ag-based composites for photocatalytic applications.

Keywords: Photocatalyst, Attapulgite, TiO₂, Ag₃PO₄, Composite

Background

Organic pollutant degradation has been a critical process towards resolving environmental pollution. Fujishima et al. reported in 1972 that TiO₂ has the capability of utilizing solar energy for water splitting and hydrogen production [1]. Since then, semiconductor-based photocatalytic technology has become a promising, and yet effective approach to resolve environment pollution. Over the past decades, a number of semiconductors, such as TiO₂, Ag₃PO₄, BiVO₄, WO₃, and g-C₃N₄, have been extensively investigated for photocatalytic application [2]. Among them, TiO₂ has received extensive attention due to its good chemical stability, non-photocorrosion, low cost, and nontoxicity. Because of its wide band gap (3.2 eV) and lacking visible light absorption, however, TiO₂ exhibits low photocatalytic efficiency.

The application of TiO₂-based photocatalysts was thus hampered severely.

The photocatalysts, such as Ag₃PO₄ [3], Bi₂MoO₆ [4], WO₃ [5], and g-C₃N₄ [6], can exhibit high-efficiency under visible light irradiation, and thus have drawn extensive research efforts. For example, Ye et al. reported that silver orthophosphate (Ag₃PO₄) exhibited much stronger photooxidative capabilities and higher efficiency for photocatalytic degradation [3] than most other known photocatalysts such as WO₃ [5] and BiVO₄ [7]. However, the photocatalytic stability of Ag₃PO₄ could be deteriorated by the photoreduction of Ag⁺ into metallic Ag. The low photostability and high cost of Ag₃PO₄ are concerning issues that will limit its photocatalytic applications. In this context, Ag₃PO₄-based composite photocatalysts have been investigated with the goal of improving its photostability and photocatalysis, such as TiO₂/Ag₃PO₄ [8], Ag₃PO₄/graphene [9], and Ag₃PO₄/Ag/WO_{3-x} [10].

Attapulgite (ATP) is a kind of rod-shaped fiber hydrated magnesium aluminum silicate non-metallic mineral, which has remarkable physical and chemical

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properties, such as exchangeable cations, water absorption, adsorption discoloration, and large specific surface area [11]. ATP is thus considered to be an ideal catalyst carrier with rod morphology, and its high surface area is benefit for absorbing catalyst and pollutant. Although Ag_3PO_4 - and TiO_2 -based and attapulgite/ Ag_3PO_4 binary composite photocatalysts have been reported, attapulgite-based ternary composite materials have rarely been investigated.

In this work, the ATP/ TiO_2 / Ag_3PO_4 ternary composites were synthesized by a facile two-step method for improving the photostability and photocatalysis of Ag_3PO_4 and suppressing the consumption of noble metal Ag. The crystalline structure and microstructure of novel ternary composites were characterized by XRD and SEM, respectively, while their photocatalytic activities and stability were measured by degradation of organic dye rhodamine B (RhB) under simulated solar irradiation. This ternary composite exhibits higher photocatalytic efficiency than pure silver phosphate and excellent photocatalytic stability.

Experimental section

Materials

ATP nanofibers with an average diameter less than 100 nm and an average length less than 1 μm (Fig. 1) was pursued from Jiangsu Qingtao Energy Science and Technology Co., Ltd. RhB (A.R.), EDTA disodium salt dehydrate (GR, 99%), tert-Butanol (GR, $\geq 99.5\%$), stearyl trimethyl ammonium chloride (STAC, 98%), silver nitrate (AR), and disodium dihydrogen phosphate

hydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, AR, 99%) were purchased from Macklin. Titanium oxide, anatase (nanopowders, 5–10 nm particle size, 99.8% metals basis, hydrophilic/lipophilic) was purchased from Aladdin.

Synthesis of samples

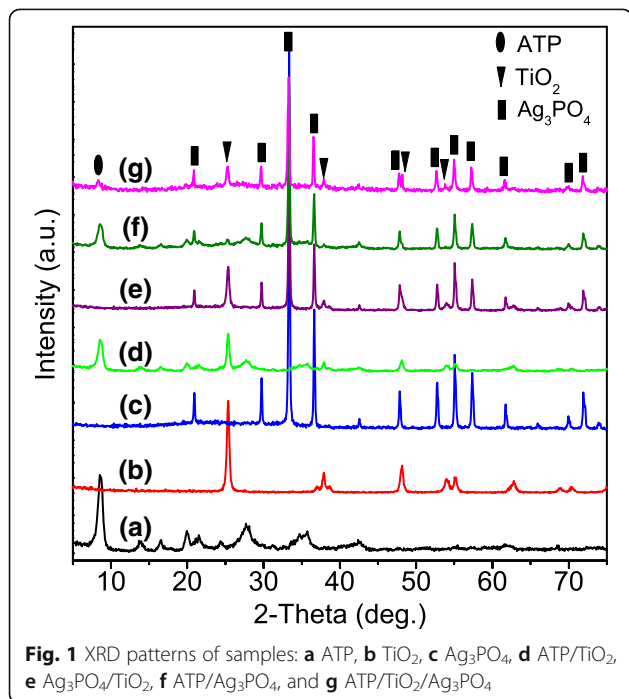
The ATP/ TiO_2 / Ag_3PO_4 ternary composite was synthesized by a facile two-step method. Well-dispersed ATP nanorods and TiO_2 nanoparticles with mass ratio of 5:2 were first added into deionized water and stirred for 4 h. Through physical and surface electronic absorption, the TiO_2 nanoparticles were attached to the surface of ATP nanorods. After centrifugal separation, the precipitate was washed with deionized water and then dried at 60 $^\circ\text{C}$ for 6 h to obtain ATP/ TiO_2 composites. By a simple precipitation method, Ag_3PO_4 nanoparticles were deposited on the surface of ATP/ TiO_2 and ATP/ TiO_2 / Ag_3PO_4 ternary composites were then prepared. [12] In a typical preparation process, 20 ml silver nitrate solution (0.1 mol/L) was dissolved in ATP/ TiO_2 aqueous suspension with 0.7 g ATP/ TiO_2 composites and 50 ml deionized water by ultrasonic stirring for 30 min. 20 ml Na_2HPO_4 aqueous solution (0.1 mol/L) was then added slowly into the above solution with ultrasonic stirring in dark condition for another 40 min. Then, the light yellowish-brown precipitate was centrifuged, washed several times with ethanol absolute, and dried at 60 $^\circ\text{C}$ for 12 h, to obtain ATP/ TiO_2 / Ag_3PO_4 ternary composites. The powder samples of Ag_3PO_4 , Ag_3PO_4 /ATP, Ag_3PO_4 / TiO_2 , and ATP/ TiO_2 were also synthesized using the similar method.

Characterization

X-ray diffraction was collected using XRD Rigaku D/max-RB) for phase analysis of the powders under 40 kV and 30 mA. The microstructures were evaluated by scanning electron microscopy (SEM, INSPECTF FEL, Netherlands). Ultraviolet-visible (UV-vis) diffuse reflection spectroscopy of the photocatalyst was investigated using U-3010 Hitach UV-vis spectrophotometer using BaSO_4 as reference.

Photocatalytic experiment

Photocatalytic degradation of RhB was tested under simulated solar irradiation. 50 mg ATP/ TiO_2 / Ag_3PO_4 was added to 100 ml RhB solution with a concentration of 5 mg/L and stirred in dark for 40 min to ensure adsorption-desorption equilibrium. The light source was a 300 W Xe lamp (Microsolar300, PerfectLight, Beijing, China) at about 150 mW/cm^2 (as tested by a radiometer FZ-A, Photoelectric Instrument Factory of Beijing Normal University, China). After opening the lamp, 4 ml solution was taken out at known time intervals and separated through centrifugation (10,000 rpm, 10 min). The supernatants were analyzed by recording variations of absorption



peak (554 nm) in the UV-vis spectra using UV-vis spectrophotometer (T6, PERSEE, Beijing, China).

The degradation degree of RhB dye was determined according to the following equation: $D\% = (c_0 - c)/c_0 \times 100\% = (A_0 - A)/A_0 \times 100\%$, where c_0 and c are the initial concentration and concentration after photocatalysis of the solution, respectively; and A_0 and A are the absorbance values of the solution before and after photocatalytic reaction, respectively.

Results and discussion

Characterization of the ATP-Ag₃PO₄-TiO₂ composites

The XRD patterns of ATP, TiO₂, Ag₃PO₄, and nanocomposites are shown in Fig. 1. The diffraction peaks in Fig. 1a can be indexed as ATP phase with monoclinic structure (JCPDS # 21-0958), which implies that the ATP had been specially purified and no impurity phases exist. Figure 1b displays typical diffraction peaks of anatase TiO₂ without any impurities, while Fig. 1c shows the diffraction peaks corresponding to pure Ag₃PO₄ phase, in good agreement with JCPDS # 06-0505. There are not any impurity phases or structure destabilization for all the nanocomposite samples of ATP/TiO₂ (Fig. 1d), Ag₃PO₄/TiO₂ (Fig. 1e), ATP/Ag₃PO₄ (Fig. 1f), and ATP/TiO₂/Ag₃PO₄ (Fig. 1g). In XRD patterns of ATP/TiO₂/Ag₃PO₄ (Fig. 1g), main characteristic peaks associated with both Ag₃PO₄ and TiO₂ can be detected, while the diffraction peaks from ATP phase are much weaker. The phenomenon implies that the ATP nanorods are cladded by TiO₂ and Ag₃PO₄ nanoparticles.

The morphological and microstructure of the composite photocatalysts are shown in Fig. 2. ATP nanorods exhibited an average length less than 1 μm and a diameter less than 100 nm (Fig. 2a). Due to surface physical and chemical adsorption, TiO₂ nanoparticles with diameter of about 40 nm attached to the surface of ATP nanorods and formed ATP/TiO₂ composites, as shown in Fig. 2b. In Fig. 2c, the ATP nanorods were fully covered by Ag₃PO₄ and TiO₂ particles in ATP/TiO₂/Ag₃PO₄ ternary composite, while Ag₃PO₄ appeared on the surface of ATP/TiO₂ composites in the form of uniform spheroidal particles with diameter of about 50 nm.

Absorption spectra

The UV-vis absorption spectra of Ag₃PO₄, ATP, TiO₂, and ATP/TiO₂/Ag₃PO₄ are shown in Fig. 3a. Similar with the reported results, [3] Ag₃PO₄ exhibits good absorption from the UV to the visible light region with a wavelength up to about 500 nm. On the other hand, TiO₂ exhibits an excellent UV absorption without obvious absorption in visible light region. ATP shows a lower UV absorption and little absorption in visible light region. As expected, ATP/TiO₂/Ag₃PO₄ ternary nanocomposite exhibits a strong UV absorption benefiting from TiO₂ and ATP and the enhanced visible-light absorption imposed by Ag₃PO₄. The optical band gap (E_g) can be estimated from the optical absorption edge according to the Eq. (1). [13, 14]

$$\alpha hv = A(hv - E_g)^m, \quad (1)$$

where α is the spectral absorption coefficient, " hv " is the photon energy, A is a constant, and m is equal to 0.5 or 2 for direct and indirect transitions, respectively. TiO₂ [15] is generally regarded as an indirect bandgap semiconductor, and its indirect E_g is determined by the interception of a straight line fitted through the low-energy side of the curve $(\alpha hv)^{1/2}$ versus hv as shown in Fig. 3b, with an estimated value of about 3.20 eV. Ag₃PO₄ was reported as an indirect bandgap semiconductor, and its direct gap at the Gamma point and the indirect gap are very close in terms of the calculated results. [16] Its direct gap of about 2.45 eV was regarded as the bandgap of Ag₃PO₄ in most reports. Here, the indirect E_g and direct E_g are determined by the interception of the straight line fitted through the low-energy side of the curve $(\alpha hv)^{1/m}$ ($m = 2$ and 0.5) versus hv , respectively. The results of Ag₃PO₄ reveal an indirect bandgap of 2.33 eV (Fig. 3b) and a direct bandgap of 2.49 eV (Fig. 3c). The direct E_g of 2.49 eV is more matched with its absorption band edge than the indirect bandgap of 2.33 eV. Thus, the E_g of Ag₃PO₄ is determined as 2.49 eV. Similarly, ATP shows an indirect bandgap of 3.37 eV (Fig. 3b) and a direct bandgap of 3.75 eV (Fig. 3c), and the E_g of ATP is determined as 3.75 eV. The above bandgap values of TiO₂, Ag₃PO₄ and ATP are quite close to the reported results. [17] In the ATP/TiO₂/Ag₃PO₄ ternary

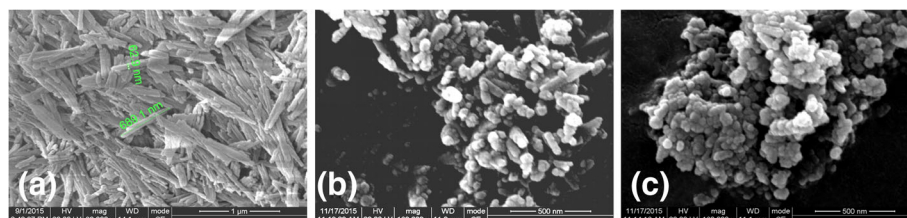


Fig. 2 SEM images of **a** ATP, **b** ATP/TiO₂, and **c** ATP/TiO₂/Ag₃PO₄ powders

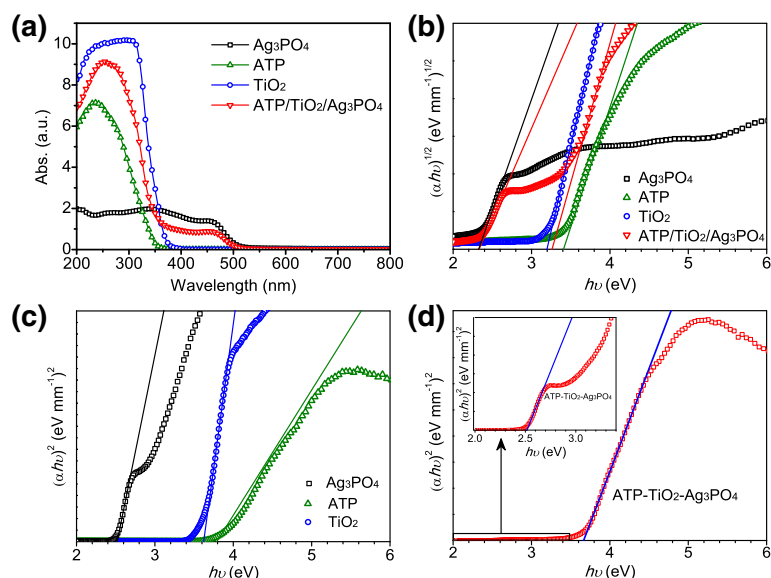


Fig. 3 **a** UV-vis absorption spectra and **b** plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ of Ag₃PO₄, ATP, TiO₂ and ATP/TiO₂/Ag₃PO₄ ternary nanocomposite; **c** plots of $(\alpha h\nu)^2$ versus $(h\nu)$ of Ag₃PO₄, ATP and TiO₂; **d** plots of $(\alpha h\nu)^2$ versus $(h\nu)$ of ATP/TiO₂/Ag₃PO₄ ternary nanocomposite, and the inset in **d** is the partial enlarged detail of the plots in **d**

nanocomposite, there are two different optical absorption band edges of about 385 and 510 nm in the UV-vis absorption spectra, from which two different E_g values can be estimated. From the absorption band edge of 385 nm, a direct E_g of about 3.64 eV is obtained, which is in between those of TiO₂ and ATP as a result of composite effect. Corresponding to the absorption edge of 510 nm, a direct E_g of about 2.49 eV is obtained, in according with the direct E_g of Ag₃PO₄. As a result, the ternary composite retained the similar outstanding absorption in visible light as Ag₃PO₄, as well as good UV absorption derived from TiO₂ and ATP. This result implies the ATP/TiO₂/Ag₃PO₄ ternary composite has the potential to be an excellent photocatalyst in the wavelength range from UV light to visible light.

Photocatalytic activities

The photocatalytic activity of the resulting samples was evaluated by the degradation of RhB under Xe light irradiation, Fig. 4. After immersing photocatalysts, RhB solutions were stirred for 40 min in dark condition to establish adsorption-desorption equilibrium with the goal of eliminating the interference of adsorption. Figure 4a shows the evolution of absorption spectra during the photodegradation of RhB solutions by ATP/TiO₂/Ag₃PO₄ ternary nanocomposite under Xe light illumination as a function of time. The absorption peaks centered at 554 nm correspond to the characteristic absorption peak of RhB. Due to the photodegradation of RhB, the peak strength decreased as the concentration of RhB decreased. After stirring the solution for 40 min in dark condition,

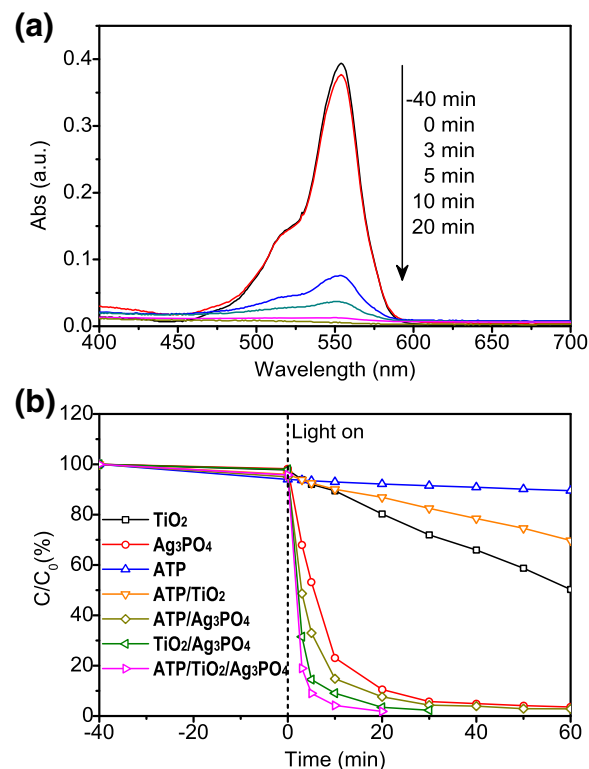


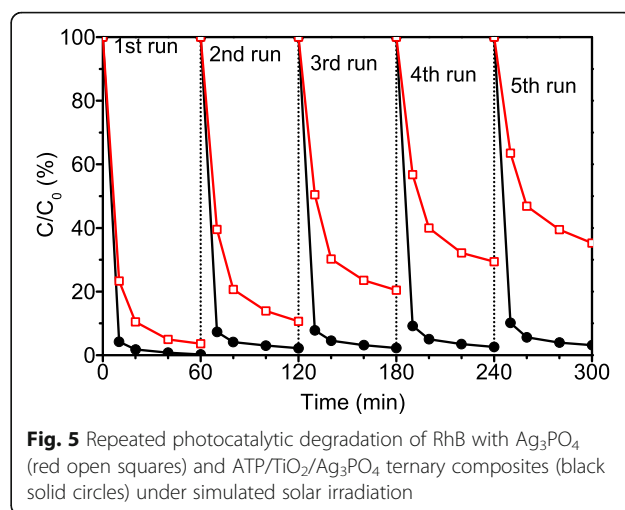
Fig. 4 **a** UV-vis absorption spectra of the photocatalytic degraded RhB solutions by the ATP/TiO₂/Ag₃PO₄ ternary nanocomposite at different times. **b** Photocatalytic degradation of RhB with different photocatalysts under simulated solar irradiation

only a little decrease in the absorption peak intensity is observed for RhB, which indicates a weak dye adsorption of the nanocomposite. After irradiation for 20 min, the characteristic absorption peak of RhB nearly disappeared, implying almost complete degradation of the dye in the solution. Under similar Xe light irradiation condition, the photocatalytic degradation of RhB with different photocatalysts is compared in Fig. 4b. The photocatalysts of single-phase TiO_2 and ATP showed lower degradation rate than 50% under 60 min irradiation, while Ag_3PO_4 displayed much stronger and faster photocatalytic degradation, in good agreement with previous reports on photocatalysis of TiO_2 and Ag_3PO_4 [18]. Ag_3PO_4 was reported as a strong photocatalyst, but its stability of photocatalytic activity is low and its cost is high. The ternary nanocomposites revealed a fast degradation rate of around 81.1% only after 3 min irradiation and almost complete degradation after 20 min irradiation, which are obviously higher than that of single-phase Ag_3PO_4 and other binary composite photocatalysts including ATP/ Ag_3PO_4 and $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ as seen in Fig. 4b. ATP has little photocatalytic activity, but it has been reported with good ability of adsorption, [19] which facilitates dye molecules adhering to its surface, and results in a higher degradation rate of RhB by the ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ ternary nanocomposite photocatalysts. Interestingly, the ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ photocatalysts showed stronger photocatalytic degradation efficiency than $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ or Ag_3PO_4 with the same weight. As a result, the application amount of high-cost Ag_3PO_4 is reduced.

The stability of the photocatalysts for photodegradation of RhB under Xe light irradiation was evaluated by repeated photocatalytic experiments. Similar test was also performed on Ag_3PO_4 for comparison. After each run of photocatalytic degradation, the photocatalysts were separated, washed, dried, and then recycled for the next run. The initial concentration of RhB and the dosage of photocatalyst were kept consistent during each run of photocatalytic degradation. The results are shown in Fig. 5. After every run, the activity of Ag_3PO_4 significantly decreased as expected [20]. In the photocatalytic process, the active sites were covered by Ag appearing on the surface of Ag_3PO_4 particles. The photocatalytic activity of the ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ ternary nanocomposite remained unchanged even after five cycling runs of photodegradation of RhB. This result indicates that the photocatalysis is very stable in ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ ternary nanocomposites.

Possible mechanism in photocatalytic process

In photocatalytic degradation processes, the common reactive oxygen species include $\cdot\text{OH}$ radicals, $\text{O}_2^{\cdot-}$ radicals and holes (h^+). [2] The trapping experiments were carried out to monitor the reactive oxygen species involved in



photocatalytic process of ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ composites over RhB. Three chemicals of tert-butanol (TBA), benzoquinone (BQ), and disodium ethylenediaminetetraacetate ($\text{Na}_2\text{-EDTA}$) were used as scavengers of $\cdot\text{OH}$ radicals, $\text{O}_2^{\cdot-}$ radicals and holes, respectively. [9] The experimental results under Xe light irradiation are shown in Fig. 6. The introduction of 1 mM TBA ($\cdot\text{OH}$ radical scavenger) has no obvious influence on the photocatalytic activity of the composite photocatalyst (Fig. 6b). This result indicated that $\text{OH}\cdot$ radicals are not the main active oxygen species in the photocatalytic process. The addition of 1 mM BQ ($\text{O}_2^{\cdot-}$ radical scavenger) reduces the photocatalytic degradation degree of RhB to 42% in 60 min (Fig. 6c), which indicates that $\text{O}_2^{\cdot-}$ radicals make an important but only segmental contribution to photocatalytic performance. After adding the hole scavenger $\text{Na}_2\text{-EDTA}$ (1 mM) into the photocatalytic system, the photocatalytic degradation activity of ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ nanocomposites is almost completely suppressed (Fig. 6d), and the degradation degree of RhB decreases to less than 5% after 60 min. This result implies that holes play a key role in photocatalytic

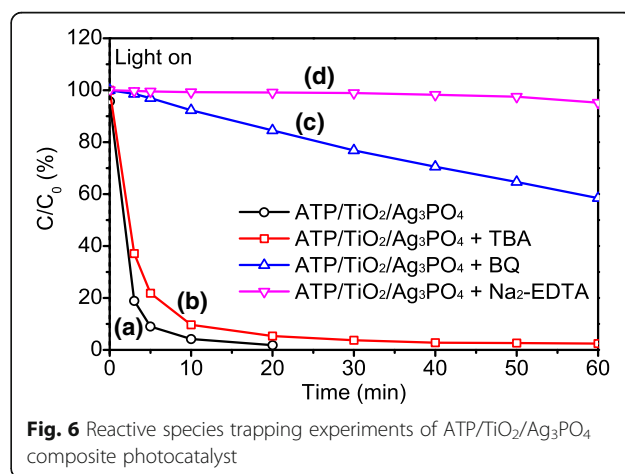
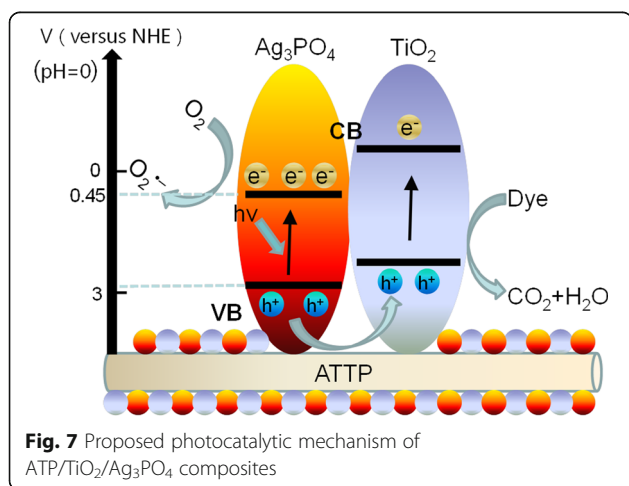


Fig. 6 Reactive species trapping experiments of ATP/ $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ composite photocatalyst

degradation. In consequence, holes and $O_2^{\cdot-}$ radicals are the main reactive radicals in the ATP/TiO₂/Ag₃PO₄ photocatalytic process degrading RhB under Xe light irradiation.

Based on the discussion mentioned above, a possible photocatalytic mechanism was proposed to explain the photocatalytic degradation of RhB by ATP/TiO₂/Ag₃PO₄ ternary composite photocatalysts, as shown in Fig. 7. The potentials for conduction band (CB) and valence band (VB) of TiO₂ are -0.5 eV vs. NHE, and $+2.70$ eV vs. NHE, respectively [21, 22]. These values are more negative than that of both Ag₃PO₄ (CB $+0.45$ eV vs. NHE, VB $+2.97$ eV vs. NHE) [3, 16] and ATP (CB -0.25 eV vs. NHE, VB $+3.50$ eV vs. NHE). Therefore, the photo-generated electrons in the CB of TiO₂ can easily transfer to that of Ag₃PO₄, while the photo-induced holes in the VB of Ag₃PO₄ will migrate to that of TiO₂, which promotes the effective separation of photo-generated electron-hole pairs and decreases the recombination probability of electrons and holes. As a result, the ATP/TiO₂/Ag₃PO₄ composite photocatalyst can exhibit higher photocatalytic activities than single phase Ag₃PO₄. Meanwhile, the holes in VB of TiO₂, which has strong oxidation characteristics, not only could significantly accelerate the photocatalytic reaction rates of RhB degradation, but also could oxidize H₂O to generate O₂. The reduction potential of $O_2^{\cdot-}$ is -0.28 eV, while the potentials of CB for TiO₂ and Ag₃PO₄ are -0.3 and $+0.45$ eV, respectively. Therefore, the resulting O₂ at the surface of photocatalysts then could capture photogenerated electrons to produce $O_2^{\cdot-}$ radicals, and the Ag⁺ ions in Ag₃PO₄ could be protected from photoreduction into metallic Ag ($Ag^+ + e^- \rightarrow Ag$) since the electrons were consumed in the reaction with O₂. In consequence, the composite photocatalyst with TiO₂ and Ag₃PO₄ shows much higher stability than single-phase Ag₃PO₄ photocatalyst.



Conclusions

In conclusion, we synthesized ATP/TiO₂/Ag₃PO₄ ternary composite through a simple method: TiO₂ nanoparticles were absorbed on the surface of ATP to form a binary structure, and then Ag₃PO₄ nanoparticles were deposited on ATP/TiO₂ composite through electrostatic interaction. The heterogeneous junction formed in the ternary composite improves the photocatalytic efficiency and stability. In comparison with pure Ag₃PO₄ phase, this kind of composite photocatalyst not only reduces the consumption of the precious metal silver to a larger extent, but also improves the efficiency of photocatalysts. Our results will provide guidance to design Ag-based composites for photocatalytic application.

Abbreviations

ATP: Attapulgite; BQ: Benzoquinone; CB: Conduction band; Na₂-EDTA: Disodium ethylenediaminetetraacetate; RhB: Rhodamine B; TBA: Tert-butanol; VB: Valence band

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Availability of data and materials

All data are fully available without restriction.

Authors' contributions

HH designed the experiment and drafted the manuscript. HH, ZJ, and ZH carried out the sample preparation and the photocatalytic measurements. EL and BWL participated in the discussion and the characterization of SEM, XRD, and UV-vis diffuse reflectance spectroscopy. All the authors have read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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