

NANO EXPRESS

Open Access



Fabrication of Z-scheme $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ Heterostructures for Enhancing Visible Photocatalytic Activity

Wenhui Liu, Dengdeng Liu, Kun Wang, Xiaodan Yang, Shuangqi Hu* and Lishuang Hu*

Abstract

In this paper, a synthetical study of the composite $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ photocatalyst, synthesized by simple two-step method, is carried out. Supplementary characterization tools such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and UV-vis diffuse reflectance spectroscopy were adopted in this research. The outcomes showed that highly crystalline and good morphology can be observed. In the experiment of photocatalytic performance, $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ shows the best photocatalytic activity, and the photocatalytic degradation rate reached almost 100% after illuminating for 25 min. The reaction rate constant of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ is the largest, which is 0.02286 min^{-1} , twice that of Ag_3PO_4 and 6.6 times that of the minimum value of $\text{TiO}_2/400$. The degradation effect of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ shows good stability after recycling the photocatalyst four times. Trapping experiments for the active catalytic species reveals that the main factors are holes (h^+) and superoxide anions ($\text{O}_2^{\cdot -}$), while hydroxyl radical ($\cdot\text{OH}$) plays partially degradation. On this basis, a Z-scheme reaction mechanism of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ heterogeneous structure is put forward, and its degradation mechanism is expounded.

Keywords: Composite, Heterostructures, Superoxide anion, Photocatalytic degradation

Background

Semiconductor photocatalysts have attracted increasing interest due to extensive use in organic pollutant degradation and solar cells [1–6]. As the representative of semiconductor-based photocatalysts, TiO_2 has been extensively investigated because of its excellent physical-chemical properties [7, 8]. However, the pure TiO_2 photocatalyst has certain disadvantages in practical applications such as its wide band gap (3.2 eV for anatase and 3.0 eV for rutile), which leads to poor visible response.

A silver-based compound such as Ag_2O , AgX ($X = \text{Cl}, \text{Br}, \text{I}$), Ag_3PO_4 , Ag_2CrO_4 , have been recently used for photocatalytic applications [9–12]. Among others, silver orthophosphate (Ag_3PO_4) has already attracted attention from many researchers because Ag_3PO_4 has a band gap of 2.45 eV and strong absorption at less than 520 nm. The quantum yield of Ag_3PO_4 is over 90%. It is a good visible-light photocatalyst. However, due to the formation

of Ag^0 on the surface of the catalyst ($4\text{Ag}_3\text{PO}_4 + 6\text{H}_2\text{O} + 12\text{h}^+ + 12\text{e}^- \rightarrow 12\text{Ag}^0 + 4\text{H}_3\text{PO}_4 + 3\text{O}_2$) during the photocatalytic reaction, the reuse of Ag_3PO_4 is a major problem. Therefore, it is a common practice to reduce photocatalytic corrosion of Ag_3PO_4 and ensure good catalytic activity of Ag_3PO_4 . Based on literature precedence, it is known that compounding can effectively improve the photocatalytic performance of both semiconductor materials. After compounding, the separation effect of photogenerated electrons and holes is strengthened, contributing to enhance the photocatalytic activity of composite materials. Numerous researchers have investigated heterojunctions such as $\text{Bi}_2\text{O}_3\text{-Bi}_2\text{WO}_6$, $\text{TiO}_2/\text{Bi}_2\text{WO}_6$, ZnO/CdSe , and $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ [2, 13–15]. Compared with single-phase photocatalysts, heterojunction photocatalysts can expand the light response range by coupling matched electronic structure materials. And because of the synergistic effect between components, charge can be transferred through many ways to further improve heterojunction photocatalytic activity.

* Correspondence: shuangqihuzb@163.com; hlsly1314@163.com
Environmental and Safety Engineering Institute, North University of China,
Taiyuan 030051, Shanxi, People's Republic of China

Based on the above analysis, Ag_3PO_4 -based semiconductor composites with synergistic enhancement effect were designed to improve carrier recombination defects and Ag_3PO_4 -based semiconductor composites catalytic performance. In this paper, nano-sized TiO_2 was prepared by solvothermal method, and then the nanoparticles of $\text{TiO}_2/400$ were deposited on the surface of Ag_3PO_4 at room temperature to obtain $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ composites. The photocatalytic activity of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ composite was tested using RhB dye (rhodamine B).

Methods

Hydrothermal Preparation of Nano-sized TiO_2

0.4 g P123 was added to a mixed solution containing 7.6 mL absolute ethanol and 0.5 mL deionized water and stirred until P123 was completely dissolved. The clarified solution was labeled as A solution. Then a mixed solution containing 2.5 mL butyl titanate (TBOT) and 1.4 mL concentrated hydrochloric acid (12 mol/L) was prepared and labeled as B solution. The solution B was added to solution A by drop. After stirring for 30 min, 32 mL ethylene glycol (EG) was added to the solution and stirred for 30 min. Then, the solution was placed in oven, at 140 °C, high temperature, and high pressure for 24 h. Natural cooling, centrifugal washing, separation, collection of sediments, and drying at 80 °C oven for 8 h. The white precipitation was calcined in muffle furnace at different temperatures (300 °C, 400 °C, 500 °C) and marked as standby of $\text{TiO}_2/300$, $\text{TiO}_2/400$, and $\text{TiO}_2/500$, respectively.

Preparation of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ Photocatalyst

The 0.1 g TiO_2 powder was added to the 30-mL silver nitrate solution containing 0.612 g AgNO_3 and then treated by ultrasound for 30 min to make TiO_2 dispersed uniformly. We added 30-mL solution containing 0.43 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and stirred for 120 min at ambient temperature. By centrifugation, cleaning with deionized water and anhydrous ethanol, the precipitates were separated, collected, and dried at 60 °C. The products were named as $\text{TiO}_2/300/\text{Ag}_3\text{PO}_4$, $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, and $\text{TiO}_2/500/\text{Ag}_3\text{PO}_4$, respectively. Ag_3PO_4 was prepared without adding TiO_2 under the same conditions as the above process.

Characterization

The X-ray diffraction (XRD) patterns of the resulted samples were performed on a D/MaxRB X-ray diffractometer (Japan), which has a 35 kV Cu-K α with a scanning rate of 0.02° s⁻¹, ranging from 10 to 80°. Scanning electron microscopy (SEM), JEOL, JSM-6510, and JSM-2100 transmission electron microscopy (TEM) assembly with energy dispersive X-ray spectroscopy (EDX) were used to study its morphology at 10-kV acceleration

voltage. X-ray photoelectron spectroscopy (XPS) information were collected by using an ESCALAB 250 electron spectrometer under 300-W Cu K α radiation. The basic pressure was about 3×10^{-9} mbar, Combine to refer to the C1s line at amorphous carbon 284.6 eV.

Photocatalytic Activity Measure

The photocatalytic performance of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ catalysts was tested by using the photodegradation of RhB in aqueous solution as the research object. Fifty milligrams of the photocatalyst was mixed with 50 mL of RhB aqueous solution (10 mg L⁻¹) and stirred in darkness for a certain time before illumination to ensure adsorption balance. In the reaction process, cooling water is used to keep the system temperature constant at room temperature. A 1000-W Xenon lamp provides illumination to simulate visible light. LAMBDA35 UV/Vis spectrophotometer was used to characterize the concentration (C) change of RhB solution at $\lambda = 553$ nm. The decolorization rate is indicated as a function of time vs C_t/C_0 . Where C_0 is the concentration before illumination, and C_t is the concentration after illumination. Used catalysts were recollected to detect the cycle stability of the catalysts. The experiment was repeated four times.

Results and Discussion

XRD analysis is used to determine the phase structure and crystalline type of catalyst. The XRD spectra of the prepared catalysts were shown in Fig. 1, including $\text{TiO}_2/400$, Ag_3PO_4 , $\text{TiO}_2/\text{Ag}_3\text{PO}_4$, $\text{TiO}_2/300/\text{Ag}_3\text{PO}_4$, $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, and $\text{TiO}_2/500/\text{Ag}_3\text{PO}_4$. It can be obtained from the figure that the crystal structure of $\text{TiO}_2/400$ is anatase (JCPDS No. 71-1166). In the XRD spectra of Ag_3PO_4 , the diffraction peaks located at 20.9°,

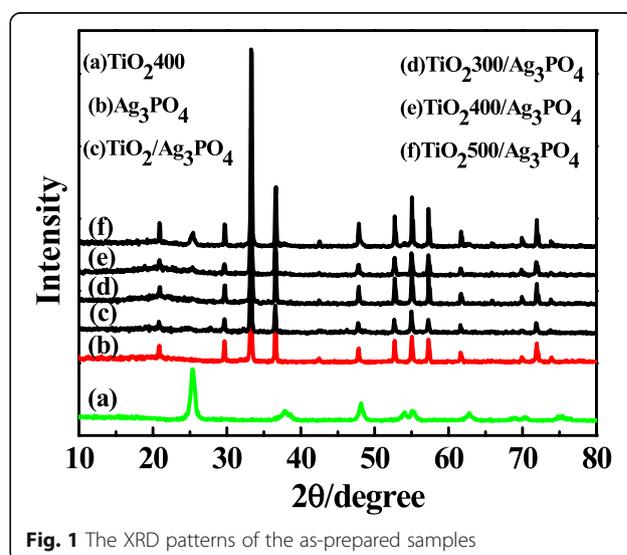


Fig. 1 The XRD patterns of the as-prepared samples

29.7°, 33.3°, 36.6°, 47.9°, 52.7°, 55.1°, 57.4°, 61.7°, and 72.0° belong to the characteristic peaks of (110), (200), (210), (211), (310), (222), (320), (321), (400), and (421) planes of Ag_3PO_4 (JCPDS No. 70-0702), respectively. The synthesized composite photocatalysts showed characteristic peaks consistent with TiO_2 and Ag_3PO_4 , and the characteristic peaks of TiO_2 were 25.3° at the composite TiO_2 , $\text{TiO}_2/300/\text{Ag}_3\text{PO}_4$, $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, $\text{TiO}_2/500/\text{Ag}_3\text{PO}_4$, which was consistent with the calcination temperature of TiO_2 rise, the crystallinity of TiO_2 becomes higher.

Figure 2 shows the SEM, TEM, and EDX diagrams of the catalysts of $\text{TiO}_2/400$, Ag_3PO_4 , and $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$. Figure 2a is the spherical nanostructure $\text{TiO}_2/400$ prepared by solvothermal method with a diameter ranging from 100 to 300 nm. Figure 2b is the Ag_3PO_4 crystal with a regular hexahedral structure. Its particle size

ranges from 0.1 to 1.5 μm and has a fairly smooth surface. Figure 2c is the SEM image of the composite $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$. It can be seen that the nanoparticles of $\text{TiO}_2/400$ are deposited on the surface of Ag_3PO_4 . The morphology of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ was further explored with TEM and the TEM diagram of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ is displayed in Fig. 2d. It can be observed that 200-nm nano-sized TiO_2 particles adhere to the surface of Ag_3PO_4 . Figure 2e is the HRTEM of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$. It can be founded that TiO_2 particles are closely bound to Ag_3PO_4 , and the lattice spacing of $\text{TiO}_2/400$ and Ag_3PO_4 are 0.3516 and 0.245 nm, respectively, corresponding to (101) and (211) surfaces of TiO_2 and Ag_3PO_4 . Figure 2f is the EDX diagram of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$. It can be seen that the sample consists of four elements: Ti, O, Ag, and P. The obvious diffraction peak of copper element is

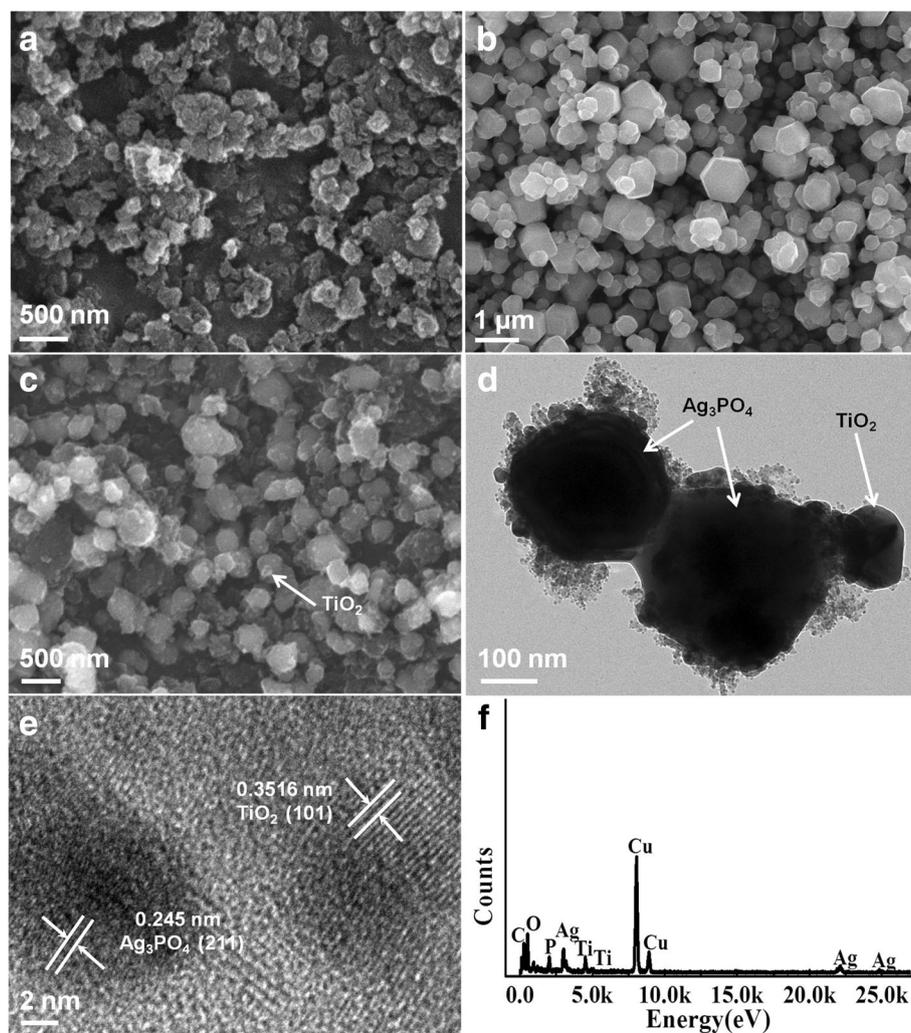


Fig. 2 SEM images of prepared photocatalysts: **a** $\text{TiO}_2/400$, **b** Ag_3PO_4 , **c** $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, **d** TEM image of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, **e** HRTEM image of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$, and **f** corresponding EDX pattern of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$

produced by the EDX excitation source, Cu K α . EDX confirmed the corresponding chemical elements of TiO₂400/Ag₃PO₄. In conclusion, it can be clearly judged that TiO₂ is loaded on the surface of Ag₃PO₄ crystals in granular form and has a good hexahedron morphology.

The product X-ray photoelectron spectroscopy (XPS) is investigated in Fig. 3. Figure 3a is the survey XPS spectrum of the product. Ti, O, Ag, P, and C five elements can be observed in the graph, of which C is the base, implying that composite coexisted with TiO₂ and Ag₃PO₄. Figure 3b is the high-resolution spectrum of Ag 3d. The two main peaks centered at binding energy 366.26 eV and 372.29 eV, assigning to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. It shows that Ag is mainly Ag⁺ in

the photocatalyst of TiO₂400/Ag₃PO₄ [16]. Figure 3c shows the XPS peak of P 2p, which corresponds to P⁵⁺ in the PO₄³⁺ structure at 131.62 eV. Two peaks located at 457.43 eV and 464.58 eV can be attributed to Ti 2p_{3/2} and Ti 2p_{1/2} in the XPS spectrum of Ti 2p orbital (Fig. 3d). Figure 3e is the XPS of O 1s. The whole peak can be divided into three characteristic peaks, 528.9 eV, 530.2 eV, and 532.1 eV. The peaks at 528.9 eV and 530.2 eV are ascribed to oxygen in Ag₃PO₄ and TiO₂ lattices, respectively. The peaks at 532.1 eV indicate hydroxyls or the oxygen adsorbed on the surface of TiO₂/Ag₃PO₄. The results of XPS analysis further prove that Ag₃PO₄ and TiO₂ have been compounded.

The UV-Vis diffuse reflectance absorption spectra of the catalysts of TiO₂400, Ag₃PO₄, and TiO₂400/Ag₃PO₄ are

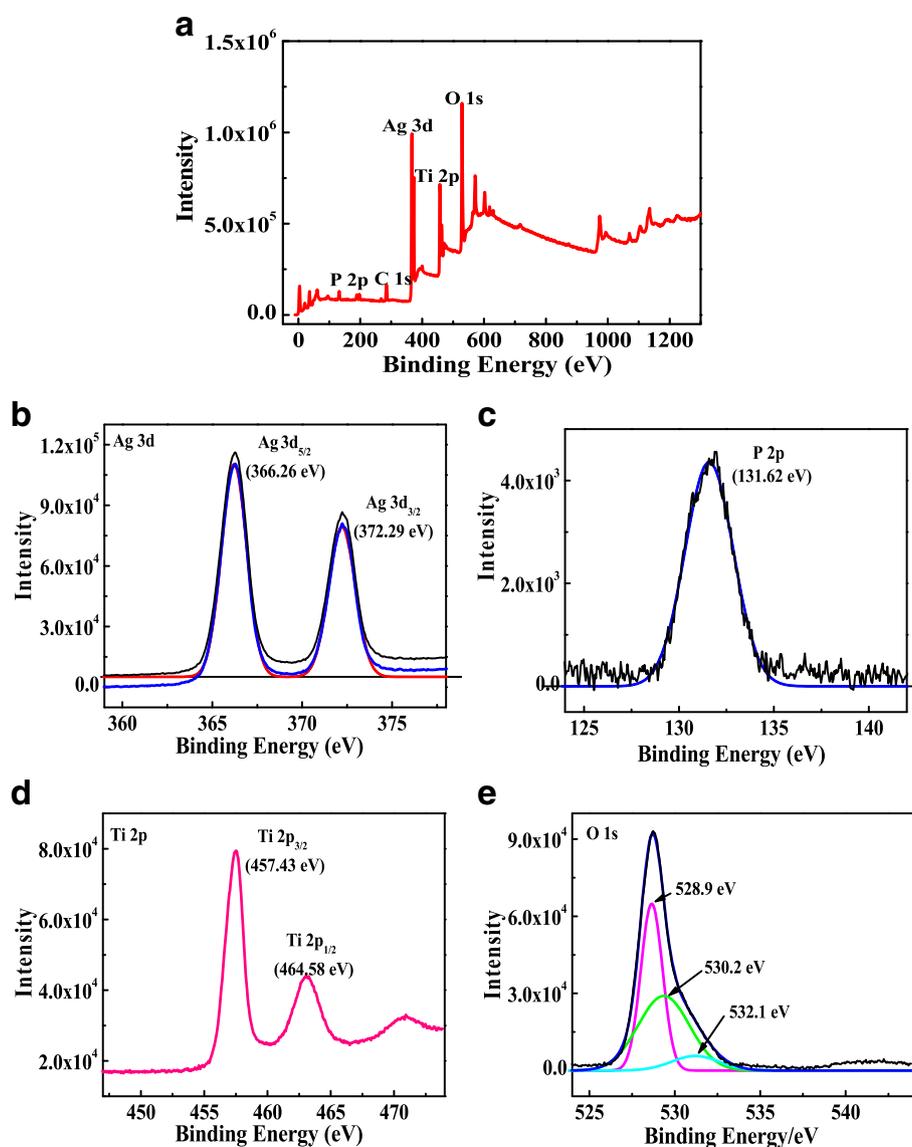


Fig. 3 XPS spectrum of TiO₂400/Ag₃PO₄: **a** survey scan, **b** Ag 3d, **c** P 2p, **d** Ti 2p, and **e** O1s

exhibited in Fig. 4a. It can be seen from the figure that the optical absorption cutoff wavelengths of TiO₂400 and Ag₃PO₄ are 400 and 500 nm, respectively. When Ag₃PO₄ is loaded on TiO₂400, the light absorption range of the composite obviously broadens to 500–700 nm, indicating that there is interaction between Ag₃PO₄ and TiO₂400 in the composite system of TiO₂400/Ag₃PO₄, and the mechanism needs further study. Bandwidth of Ag₃PO₄, TiO₂400, and TiO₂400/Ag₃PO₄ catalysts is computed with the Kubelka-Munk formula [17]:

$$A_{hv} = c(h\nu - E_g)^n$$

where A , $h\nu$, c , and E_g are the absorption coefficient, incident photon energy, absorption constant, and band gap energy, respectively. The value of n for direct semiconductor is 1/2, and that for indirect semiconductor is 2. Anatase TiO₂ and Ag₃PO₄ are indirect semiconductors, so n takes 2.

The plots depicting $(\alpha h\nu)^{1/2}$ versus incident photon energy ($h\nu$) from Fig. 4b indicates the band gap energy diagrams (E_g) of Ag₃PO₄, TiO₂400, and TiO₂400/Ag₃PO₄ catalysts are 2.45 eV, 3.1 eV, and 2.75 eV, respectively. This further proves that TiO₂400/Ag₃PO₄ is a good visible-light photocatalyst with suitable band gap width and visible light capture ability.

Photocatalytic degradation of RhB by TiO₂400, Ag₃PO₄, TiO₂300/Ag₃PO₄, TiO₂400/Ag₃PO₄, and TiO₂500/Ag₃PO₄ was investigated in Fig. 5a. The results showed that pure TiO₂400 had the worst photocatalytic effect, and the photocatalytic degradation rate was only 30% within 25 min. The photocatalytic degradation efficiency of pure Ag₃PO₄ was 69% after 25 min of irradiation. The photocatalytic degradation rate of TiO₂300/Ag₃PO₄ reached 40% after 25 min. The photocatalytic degradation rate of TiO₂500/Ag₃PO₄ was 80% after 25 min

of irradiation. The best photocatalytic activity was TiO₂400/Ag₃PO₄, and 100% of RhB was decomposed after 25 min of illumination.

Figure 5b studied the kinetics model of photocatalytic degradation of RhB. From the figure, the photodegradation of RhB was followed pseudo-first-order kinetics and the reaction rate constant (k) was calculated with the slope of fitting curves. The reaction rate constant (k) values of each sample were shown in Table 1. The reaction rate constants of TiO₂400, Ag₃PO₄, TiO₂300/Ag₃PO₄, TiO₂400/Ag₃PO₄, and TiO₂500/Ag₃PO₄ were 0.00345 min⁻¹, 0.01148 min⁻¹, 0.00525 min⁻¹, 0.02286 min⁻¹, and 0.01513 min⁻¹, respectively. The sample TiO₂400/Ag₃PO₄ has the largest reaction rate constant, which is 0.02286 min⁻¹, twice that of Ag₃PO₄ and 6.6 times that of the minimum value of TiO₂400. This indicates that the combination of Ag₃PO₄ and TiO₂ can greatly contribute to the improvement of Ag₃PO₄ photocatalytic activity.

Figure 5c is the stability test result of four times of degradation of RhB solution by recycling of TiO₂400/Ag₃PO₄. The degradation effect of TiO₂400/Ag₃PO₄ shows good stability in four times of recycling, and in the fourth cycle experiment, the degradation effect of TiO₂400/Ag₃PO₄ was slightly higher than that of the third cycle. This may be due to the formation of composite material between Ag₃PO₄ and TiO₂ to accelerate photogenerated electron-hole pair transfer and in situ formation of a small amount of Ag in Ag₃PO₄ during photocatalysis to inhibit further photo-corrosion.

The results of TiO₂/Ag₃PO₄ capture factors are shown in Fig. 5d. After the addition of trapping agent IPA, the degradation activity decreased partially. When BQ and TEOA were added, the degradation degree of RhB decreased significantly, even close to 0. Therefore, we can infer that the main factors are holes (h^+) and superoxide anions ($O_2^{\cdot -}$), while hydroxyl radical ($\cdot OH$) plays partially degradation.

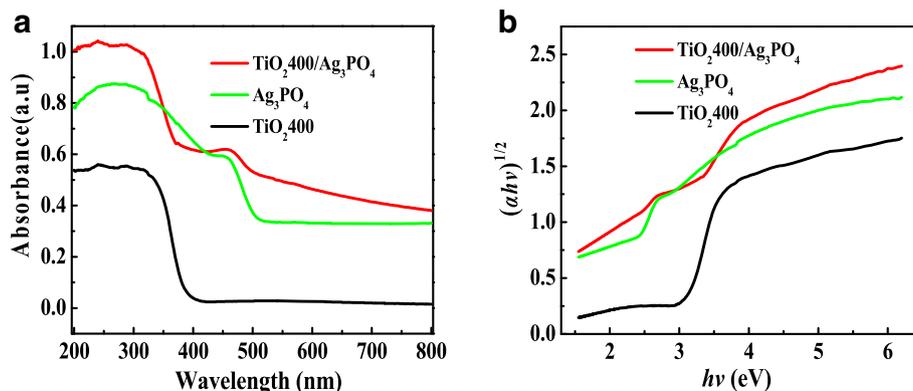
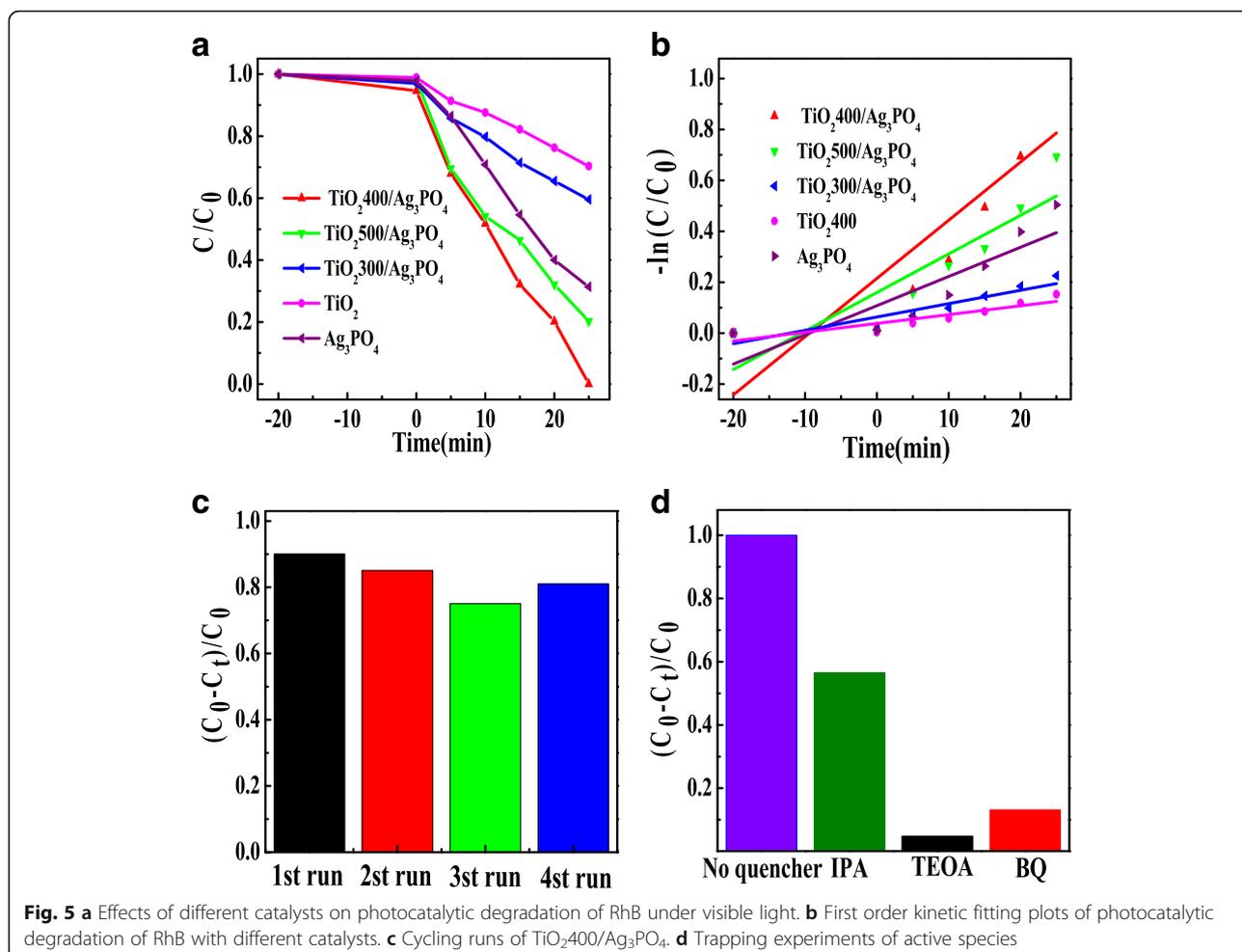


Fig. 4 TiO₂400, Ag₃PO₄, and TiO₂400/Ag₃PO₄ catalysts: **a** UV-Vis DRS, **b** plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$)

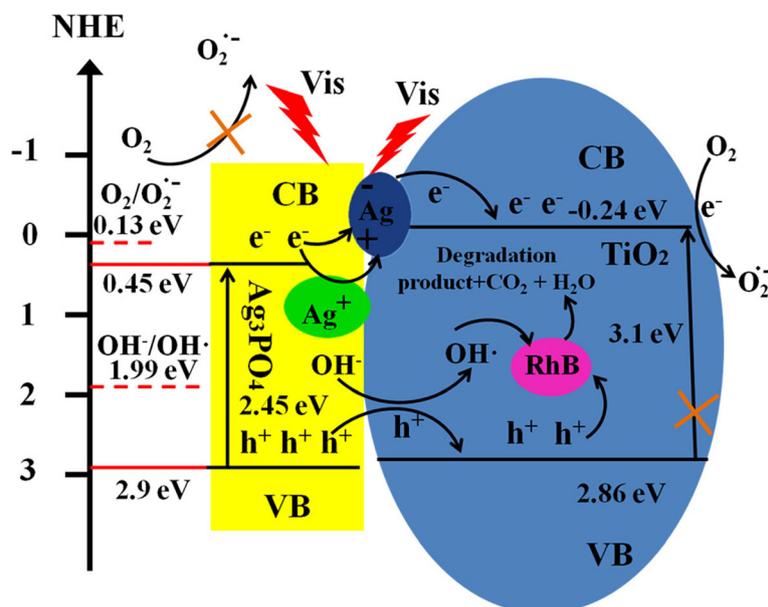


A possible Z-scheme photocatalytic degradation mechanism was proposed in Scheme 1 to expatiate the photocatalytic degradation of RhB by TiO₂/Ag₃PO₄ based on free radical capture and photodegradation experiments. The band gap of Ag₃PO₄ is 2.45 eV, and its E_{CB} and E_{VB} potential are ca.0.45 eV and 2.9 eV (vs. NHE) [18], respectively. As shown in Scheme 1, under visible light irradiation, Ag₃PO₄ is stimulated by photons with energy greater than its band gap to produce photogenerated electron-hole pairs. The holes left in the valence band of Ag₃PO₄ migrated to the

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

	K (min ⁻¹)	Regression equation	R^2
TiO ₂ /400/Ag ₃ PO ₄	0.02286	$-\ln(C/C_0) = 0.02286x + 0.21496$	$R^2 = 0.68755$
TiO ₂ /500/Ag ₃ PO ₄	0.01513	$-\ln(C/C_0) = 0.01513x + 0.15984$	$R^2 = 0.753$
Ag ₃ PO ₄	0.01148	$-\ln(C/C_0) = 0.01148x + 0.1079$	$R^2 = 0.71128$
TiO ₂ /300/Ag ₃ PO ₄	0.00525	$-\ln(C/C_0) = 0.00525x + 0.06354$	$R^2 = 0.82635$
TiO ₂ /400	0.00345	$-\ln(C/C_0) = 0.00345x + 0.0383$	$R^2 = 0.78461$

valence band of TiO₂ and then directly participated in the RhB oxidation and decomposition process, which adsorbed on the surface of TiO₂. At the same time, during the migration of photogenerated holes, the H₂O and OH⁻ adsorbed on the composite surface can also be oxidized to form ·OH, and the highly oxidizing ·OH can further oxidize and degrade pollutants. This is mainly due to the energy of holes in the valence band of Ag₃PO₄ which is 2.9 eV, higher than the reaction potential energy of OH⁻/OH (E(OH⁻/OH) = 1.99 eV (vs. NHE)). However, the conduction potential of Ag₃PO₄ is 0.45 eV, the energy of photogenerated electrons is 0.45 eV, and the activation energy of single electron oxygen is E(O₂/O⁻·) = 0.13 eV (vs. NHE). The photogenerated electrons on Ag₃PO₄ conduction band cannot be captured by dissolved oxygen. With the accumulation of photogenerated electrons on Ag₃PO₄ conductive band, a small amount of Ag nanoparticles has been formed due to the photocatalytic corrosion of Ag₃PO₄ photocatalyst. The formed Ag nanoparticles can also be stimulated by light energy to form photogenerated electron-hole pairs.

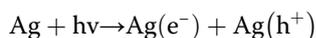
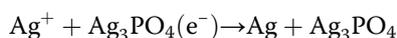


Scheme 1 Schematic illustration of the photocatalytic mechanism of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$

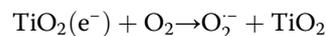
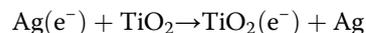
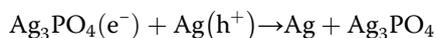
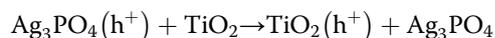
Then the electrons migrated to the conduction band of TiO_2 , while the holes left on the Ag nanoparticles can be compounded with the photogenerated electrons generated on the conduction band of Ag_3PO_4 , thus preventing the further corrosion of Ag_3PO_4 photocatalyst. Due to the forbidden band of TiO_2 is 3.1 eV, it cannot be excited under visible light and the E_{CB} and E_{VB} are ca. -0.24 eV and 2.86 eV (vs. NHE), respectively. Electrons injected into TiO_2 conduction band can degrade pollutants through trapping the oxygen adsorbed onto the TiO_2 surface. This is mainly due to the $E_{\text{CB}} = -0.24$ eV (vs. NHE) which is more negative than $E(\text{O}_2/\text{O}_2^{\cdot-}) = 0.13$ eV (vs. NHE). The results are in accordance with the trapping experiments. The main factors are holes (h^+) and superoxide anions ($\text{O}_2^{\cdot-}$), while hydroxyl radical ($\cdot\text{OH}$) plays partially degradation.

Basing on the above discussion, the degradation reaction of $\text{TiO}_2/\text{Ag}_3\text{PO}_4$ is expressed by the chemical equation as follows:

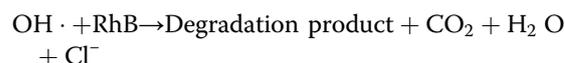
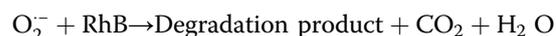
Generation of photoelectron hole pairs:



Migration and transformation of photogenerated hole electron pairs:



Degradation of pollutants:



Conclusions

In summary, a comprehensive investigation of the composite $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ photocatalyst, prepared by a simple two-step method is presented. Complementary characterization tools such as 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), X-ray photoelectron spectroscopy (XPS), and UV-vis diffuse reflectance spectroscopy (DRS) were utilized in this study. The results showed that the composite $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ photocatalyst is highly crystalline and has good morphology. For $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ degradation of RhB, $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ shows the highest photocatalytic activity. After 25 min of reaction, the photocatalytic degradation rate reached

almost 100%. The reaction rate constant of $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ is 0.02286 min^{-1} , which is twice that of Ag_3PO_4 and 6.6 times that of the minimum value of $\text{TiO}_2/400$. The $\text{TiO}_2/400/\text{Ag}_3\text{PO}_4$ also exhibits good stability after recycling four times. The main active catalytic species are holes (h^+) and superoxide anions ($\text{O}_2^{\cdot-}$), while hydroxyl radical ($\cdot\text{OH}$) plays partially degradation from trapping experiments. In addition, a Z-scheme reaction mechanism of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ heterogeneous structure is proposed to explain the RhB degradation mechanism. The accumulation of photogenerated electrons on Ag_3PO_4 conductive band causes photoetching of Ag_3PO_4 photocatalyst to form a small amount of Ag nanoparticles, consequently, accelerating photogenerated electron transfer in the Ag_3PO_4 conduction band, thus preventing further Ag_3PO_4 photocatalyst corrosion.

Abbreviations

BQ: *p*-benzoquinone; DRS: UV-vis diffuse reflectance spectroscopy; EDX: Energy dispersive X-ray spectrometer; HR-TEM: High-resolution transmission electron microscopy; IPA: Isopropanol; RhB: Rhodamine B; SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; TEOA: Triethanolamine; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

Acknowledgements

This work is greatly indebted to professors Shuangqi Hu for his meticulous instruction and Lishuang Hu who helped us with great encouragement.

Authors' Contributions

This work presented here was performed in collaboration of all the authors. All authors read and approved the final manuscript.

Funding

No funding support.

Availability of Data and Materials

The authors declare that materials and data are promptly available to readers without undue qualifications in material transfer agreements. All data generated in this study are included in this article.

Competing Interests

The authors declare that they have no competing interests.

Received: 17 April 2019 Accepted: 4 June 2019

Published online: 13 June 2019

References

- Li X, Fang S, Lei G, Han C, Ping Q, Liu W (2015) Synthesis of flower-like Ag/AgCl-Bi₂MoO₆ plasmonic photocatalysts with enhanced visible-light photocatalytic performance. *Appl Catal B Environ*:176, 62–177, 69
- Yao W, Bo Z, Huang C, Chao M, Song X, Xu Q (2012) Synthesis and characterization of high efficiency and stable Ag₃PO₄/TiO₂ visible light photocatalyst for the degradation of methylene blue and rhodamine B solutions. *J Mater Chem* 22:4050
- Fujishima A, Honda K (1972) Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* 238:37–38
- O'Regan B, Grätzel M, Fitzmaurice D (1991) Optical electrochemistry I: steady-state spectroscopy of conduction-band electrons in a metal oxide semiconductor electrode. *Chem Phys Lett* 183:89–93
- Li Z, Yu J, Fan J, Zhai P, Wang S (2009) Dye-sensitized solar cells based on ordered titanate nanotube films fabricated by electrophoretic deposition method. *Electrochem Commun* 11:2052–2055

- Shan Z, Wu J, Xu F, Huang FQ, Ding H (2008) Highly Effective Silver/Semiconductor Photocatalytic Composites Prepared by a Silver Mirror Reaction. *J Phys Chem. C* 112:15423–15428
- Xiaobo C, Lei L, Yu PY, Mao SS (2011) Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* 331:746–750
- Livraghi S, Votta A, Paganini MC, Giamello E (2005) The nature of paramagnetic species in nitrogen doped TiO₂ active in visible light photocatalysis. *Chem Commun* 4:498–500
- Yu L, Yu H, Mei C, Sun J (2012) Microwave hydrothermal synthesis of Ag₂CrO₄ photocatalyst for fast degradation of PCP-Na under visible light irradiation. *Catal Commun* 26:63–67
- Wang X, Li S, Yu H, Yu J, Liu S (2011) Ag₂O as a New Visible-Light Photocatalyst: Self-Stability and High Photocatalytic Activity. *Chemistry* 17: 7777–7780
- Lee S, Park Y, Pradhan D, Sohn Y (2016) AgX (X = Cl, Br, I)/BiOX nanoplates and microspheres for pure and mixed (methyl orange, rhodamine B and methylene blue) dyes. *J Ind Eng Chem* 35:231–252
- Zhiguo Y, Jinhua Y, Naoki K, Tetsuya K, Shuxin O, Hilary SW, Hui Y, Junyu C, Wenjun L, Zhaosheng L (2010) An orthophosphate semiconductor with photooxidation properties under visible-light irradiation. *Nat Mater* 9:559–564
- Yao W, Fang X, Guo D, Gao Z, Wu D, Kai J (2013) Synthesis of ZnO/CdSe hierarchical heterostructure with improved visible photocatalytic efficiency. *Appl Surf Sci* 274:39–44
- Peng Y, Yan M, Chen QG, Fan CM, Zhou HY, Xu AW (2014) Novel one-dimensional Bi₂O₃-Bi₂WO₆ p-n hierarchical heterojunction with enhanced photocatalytic activity. *J Mat Chem A* 2:8517–8524
- Li J, Guo Z, Yu W, Zhu Z (2014) Three-dimensional TiO₂/Bi₂WO₆ hierarchical heterostructure with enhanced visible photocatalytic activity. *Micro Nano Lett* 9:65–68
- Zheng C, Hua Y (2018) Assembly of Ag₃PO₄ nanoparticles on rose flower-like Bi₂WO₆ hierarchical architectures for achieving high photocatalytic performance. *J Mater Sci Mat Electron* 29:9291–9300
- Schuhl Y, Baussart H, Delobel R, Bras ML, Leroy JM, Gengembre L, Grimblot J (1983) Study of mixed-oxide catalysts containing bismuth, vanadium and antimony. Preparation, phase composition, spectroscopic characterization and catalytic oxidation of propene. *Chem Inf* 14:2055–2069
- An Y, Zheng P, Ma X (2019) Preparation and visible-light photocatalytic properties of the floating hollow glass microspheres – TiO₂/Ag₃PO₄ composites. *RSC Advances*

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► [springeropen.com](https://www.springeropen.com)