Application of silver phosphate-based photocatalysts: Barriers and solutions

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**HIGHLIGHTS**
- Fundamental mechanism for the excellent photocatalytic performance of Ag3PO4.
- Synthesis methods for Ag3PO4 with high photocatalytic performance.
- Barriers and solutions for the practical application of Ag3PO4.

**GRAPHICAL ABSTRACT**

**ABSTRACT**

Semiconductor photocatalysis is an extremely promising technology to deal with the far-reaching issues we need to face, such as the shortage of renewable-energy resources and the increasingly serious worldwide environmental problems. Ag3PO4 is an excellent visible-light-driven photocatalyst, showing an extraordinary photoactivity for oxygen evolution in water splitting and degradation of pollutant in aqueous solution. However, due to the uncontrollable photocorrosion phenomenon, the Ag3PO4-based photocatalysis is still at laboratory scale. To remove the obstacles for practical application and to further improve its photocatalytic performance, this review summarized the achievements that have been made in this field. We began with an effort to introduce the reasons for Ag3PO4 exhibiting excellent photocatalytic performance. Subsequently, the different synthesis methods of Ag3PO4 were discussed. Finally, we outlined the barriers that hindered the practical application of Ag3PO4 and proposed the ways to remove these barriers. This review also underlined the crucial problems that should be addressed prior to practical applications.

1. Introduction

Facing the increasingly serious environmental issues, many methods have been developed to solve these problems, such as adsorption, bioremediation, and advanced oxidation processes [1–17]. Among them, photocatalysis is a promising method that has attracted more and more attention, because it represents an easy way to take advantage of solar energy and it could be abundantly available everywhere in the world [18–24]. It is undoubted that the semiconductor photocatalysis is an extremely promising technology to handle the far-reaching issues faced by us, e.g., the growing renewable-energy shortage crisis and environmental problems [23]. The photocatalytic industry has ushered
in an era of flourishing ever since Fujishima and Honda \[25\] reported that TiO₂ could be used as an electrode under ultra-violet radiation for photoelectrochemical water splitting back in 1970s.

Give the credit to the properties of TiO₂ (e.g., electronic structure, chemical stability, and low cost), it is unquestionable that TiO₂ is an extremely promising photocatalyst. However, restrained by its wide band gap energy (E₀ = 3.23 eV), TiO₂ is mainly excited under ultra violet irradiation, suggesting that it could only utilize 4% of solar energy at most \[26\]. To promote the efficiency of solar energy utilization, extending the corresponding region to visible-light is a practicable solution. To achieve this goal, there are generally two ways: One is the combination of TiO₂ with other materials such as non-metal ions (e.g., N, C, and S) \[27–29\], halogen \[30,31\], transition metal ions (e.g., Fe, Cr, Mn, and V) \[32,33\], noble metal ions \[34\], graphene \[35–37\], and semiconductor (e.g., CdS-TiO₂ \[38\], CdSe-TiO₂ \[39\], Bi₂O₃-TiO₂ \[40\], WO₃-TiO₂ \[41\], Cu₂O-TiO₂ \[42\], and SnO₂-TiO₂ \[43\]) or doping other elements into the crystal of TiO₂ \[44–47\]; another is the development of some novel semiconductor photocatalysts such as tungsten-containing photocatalyst \[48\], bismuth-based photocatalyst \[49,50\], g-C₃N₄ \[51\], and Ag₃PO₄ \[52\]. Among them, Ag₃PO₄ was demonstrated to have a superior performance in the field of oxygen rate and dye degradation. Thus, Ag₃PO₄ has attracted great attention ever since Ye and coworkers \[52\] discovered its photocatalytic application in 2010.

Ag₃PO₄ is a photocatalyst which can be excited by visible light. Its band gap energy is approximately 2.43 eV \[52\]. Generally, pure Ag₃PO₄ photocatalyst could absorb solar energy with a wavelength shorter than 530 nm. The valence band of Ag₃PO₄ is approximately +2.9 V vs. normal hydrogen electrode (NHE, pH = 0), suggesting that it possesses strong oxidizing property. Moreover, quantum efficiency of Ag₃PO₄ could reach approximately 90% in water oxidation (while using AgNO₃ as scavenger). This is greater than the widely known photocatalysts such as N-doped TiO₂ and BiVO₄ \[53\]. Ag₃PO₄ could serve as an efficient photocatalyst for the treatment of environmental contaminants, such as phenol and phenol derivatives \[53–56\], humic acid \[57\], Cr(VI) \[58\], dyes \[15,59,60\], endocrine disrupting compounds \[61\], pharmaceuticals and personal care products \[21,62–64\]. Despite these benefits, practical application of Ag₃PO₄-based photocatalysis has not been achieved to date, due to several key barriers such as the high cost of raw materials, the slightly soluble in water, and the self-photocorrosion phenomenon \[65,66\]. Herein, in this review, we aim to offer a systematically summarization and reasonable suggestions about how to remove the obstacles that impede the practical application of Ag₃PO₄ in a full-scale situation.

2. Why does Ag₃PO₄ show excellent photocatalytic performances?

The crystal structure of Ag₃PO₄ is a body-centered cubic (BBC) which is composed of several isolated, regular PO₄ tetrahedral unit cells, with its P-O bonds distance being about 1.539 Å. The space group of Ag₃PO₄ is P4-3n with a lattice parameter of approximately 6.004 Å. The large electron clouds overlapping of PO₄ makes the CBM mainly be correlated to the oxygen atoms of PO₄. By comparing to the semiconductors with anisotropic distribution, first, the crystal structure of Ag₃PO₄ makes it more likely to draw holes and reject electrons, which reduced the transportation of photogenerated charge carriers, and enhanced the photocatalytic activity. Second, native defects such as Ag vacancies are favorable for the photocatalytic activity \[74\]. Ag vacancies may increase the chance of meeting photoinduced holes decreases compare to the semiconductors with anisotropic distribution. Second, the inductive effect of PO₄− ions makes it more likely to draw holes and reject electrons, which reduced the recombination of photogenerated charge carriers, and enhanced the photocatalytic activity.

![Fig. 1. Schematic diagram of photocatalytic redox process of Ag₃PO₄. Inset: ball and stick configuration of Ag₃PO₄ (the inset is cited from Ref. \[71\].)](image-url)
3. How to synthesize Ag₃PO₄-based photocatalysts?

There are four fundamental steps for a photocatalysis process: the generation of electron-hole pairs, the separation of photoinduced electron-hole pairs, the migration of electron-hole pairs to the surface, and the redox reactions. The migration of electron-hole pairs to the surface process normally would be affected by the particle size, surface state, crystallinity, crystal texture, and so on. For instance, a short transfer distance of charge carriers is undoubtedly beneficial to the decrease of the recombination. On the other hand, the surface of photocatalysts is the place where the photocatalysis process occurs. The synthesis process of photocatalyst is closely related to those influence factors. In recent years, lots of synthesis methods have been proposed to fabricate Ag₃PO₄-based photocatalyst [57,74–81], and we summarized the most commonly used approaches in the following texts (Table 1).

3.1. Ion-exchange method

Ion-exchange method is the mostly used method for the fabrication of Ag₃PO₄. It takes advantage of the different solubility of raw materials such as AgM and NPO₄ (M and N are the ions or ionic group except for Ag⁺ and PO₄³⁻, respectively), to replace M⁻ or N³⁺ by PO₄³⁻ or Ag⁺, thereby forming Ag₃PO₄ particles. The operation condition is simple, and the cost is low. It synthesizes Ag₃PO₄ samples at room temperature without special equipment. The choice of raw material is the key technology in this method. Yu et al. [74] recently synthesized a one-dimensional Ag₃PO₄ hollow microrods with extremely high photocatalytic performance and self-stability through anion exchange method. Ag₂WO₄ was utilized as Ag⁺ ion sources instead of AgNO₃ or CH₃COOAg. Ag₃PO₄ has lower solubility compared to Ag₂WO₄, and thus Ag₂WO₄ could react with HPO₄²⁻ ions to form Ag₃PO₄ in a thermodynamically favored direction. In this reaction procedure, the released Ag⁺ ions are really close to the Ag₂WO₄. The inward HPO₄²⁻ is slower compared to the outward Ag⁺, which favors the formation of a hollow interior (Fig. 3). The as-obtained Ag₃PO₄ has perfect and regular 1D structure with 2 μm in diameter and 2 μm in length, which is similar to the Ag₂WO₄ microrods precursor. The Ag₃PO₄ samples as synthesized could thoroughly photodegrade Rh B within 60 s and MO in 60 s, whilst spherical particles needed 14 min and 28 min, respectively. In addition, the 5-cycle run test demonstrated that this structure could serve as a viable way to enhance the stability of Ag₃PO₄.

3.2. Precipitation method

The precipitation method is also frequently used for Ag₃PO₄ fabrication. Keisuke et al. [57] demonstrated that the samples fabricated by precipitation methods possessed higher photooxidation ability in the degradation of humic acid than those prepared by ion-exchange method. Although the bulk properties (e.g., light absorbance and crystalline size) are almost the same, it was calculated that the specific surface area of the synthesized Ag₃PO₄ fabricated through precipitation method is nearly 7 times larger than that through the ion-exchange method (8.7 m²/g and 1.2 m²/g for precipitation method prepared and ion-exchange method prepared, respectively). In addition, the particle size of the former one is mainly centered on 0.3–0.4 μm, while the latter one is predominantly ranging from 6 to 10 μm. It was reported that the Ag₃PO₄ samples prepared by precipitation method showed 95% DOC removal rate for humic acid degradation after 2 h visible light (λ = 451 nm) irradiation.

3.3. Hydrothermal method

Using hydrothermal method to prepare Ag₃PO₄ photocatalyst is also a noteworthy approach. Hydrothermal method is utilizing the chemical reaction between the reagents at a particular temperature and pressure [82–84]. Owing to the specific condition of this method, it could
<table>
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<tr>
<th>Method</th>
<th>Morphology</th>
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<th>Experimental conditions</th>
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<tr>
<td>Ion-exchange method</td>
<td>1D hollow porous microrod</td>
<td>Under vigorous magnetic stirring, 0.01 M Na2WO4 aqueous solution was added into 0.05 g AgNO3 aqueous solution, then 0.05 M Na2HPO4 aqueous solution was added by drop into the above solution.</td>
<td>0.2 g photocatalysts were added into 100 mL 8 mg/L Rh B and MO solution, respectively. Light source: 300 W Xe arc lamp.</td>
<td>Rh B was completely degrade within 60 s; MO was completely degrade in 60 s.</td>
<td>[74]</td>
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<td>porous nanotube</td>
<td>40 mL 0.05 M NaHCO3 was added slowly into 1 mmol AgNO3 and 2.0 g PVP mixture solution, and stirring for 1 h at room temperature. Then, collected the precipitates and transferred into 30 mL distilled water. Added 20 mL 0.03 mmol Na2HPO4 solution drop by drop (5/s/d) into the above solution under vigorous stirring for 3 h, collect the precipitates and dried at 60°C.</td>
<td>30 mg photocatalysts were added into 50 mL Rh B (10 mg/L) and phenol (20 mg/L) solution, respectively.</td>
<td>Rh B was completely degrade in 8 min; 87% phenol was degrade in 80 min.</td>
<td>[80]</td>
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<td>Precipitation method</td>
<td>particle</td>
<td>Under magnetic stirring at room temperature, an appropriate amount of Ca10(PO4)6(OH)2 were added into AgNO3 solution (the Ag/P atomic ratio was 3.0).</td>
<td>0.02 g photocatalysts were added into 10 mg/L HA solution. Light source: 300 W Xe lamp.</td>
<td>93% DOC was removed after 2 h.</td>
<td>[57]</td>
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<td>cubic enclosed completely</td>
<td>0.1 M ammonia aqueous solution was added drop by drop into 0.2 g AgNO3 aqueous solution to form a transparent solution, then added 0.15 M Na2HPO4 aqueous solution into the above solution.</td>
<td>0.2 g photocatalysts were added into 100 mL 8 mg/L MB solution. Light source: 300 W Xe lamp.</td>
<td>MB was completely degrade in 3 min.</td>
<td>[78]</td>
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<td>by six perfect (1 0 0) facets</td>
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<td>Hydrothermal method</td>
<td>rhombic dodecahedral</td>
<td>0.15 M Na2HPO4 aqueous solution was added drop by drop into 0.2 g CH3COOAg aqueous solution.</td>
<td>0.2 g photocatalysts were added into 100 mL 8 mg/L MB solution. Light source: 300 W Xe lamp.</td>
<td>MO was completely degrade in 4 min; Rh B was completely degrade in 4 min.</td>
<td>[79]</td>
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<td>tetrapod</td>
<td>2.5 mmol AgNO3 were added in 3 mmol 85% H3PO4 aqueous solution, then added 37.5 mmol area into the above solution. Transferred the resulting precursors into a Teflon-lined stainless steel autoclave and maintained at 80°C for 24 h.</td>
<td>0.1 g photocatalysts were added into 100 mL 8 mg/L Rh B solution. Light source: 300 W Xe lamp.</td>
<td>98% Rh B was degrade after 18 min.</td>
<td>[75]</td>
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<td></td>
<td>irregularly spherical</td>
<td>0.25 M Na2PO4 solution was added into 0.75 M AgNO3 solution with vigorous stirring for 10 min, and adjust the pH value by 1 M H2PO4 and 1 M NaOH solution. Transferred the above solution into Teflon-lined stainless steel autoclave and maintained at certain temperature for certain time. Variate: temperature (100°C, 150°C, 200°C, 250°C), pH (3, 5, 7, 9), feedstock concentration (0.75 M, 0.375 M, 0.075 M, 0.0075 M for AgNO3), and reaction time (2 h, 6 h, 12 h, 24 h).</td>
<td>0.15 g photocatalysts were added into 180 mL 0.02 M AgNO3 solution, and purged with helium gas to eliminate air before light irradiation. Kept the temperature of the system around 30°C by the mostatic circulating water. Light source: 300 W Xe arc lamp.</td>
<td>The initial rate of O2 evolution determined to be 1156 μmol g−1 h−1 and apparent quantum yield at 420 nm amounted to 3.69%.</td>
<td>[81]</td>
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<td>Colloidal method</td>
<td>colloidal</td>
<td>0.02 M AgNO3 were added into 0.02 M Na2HPO4 aqueous solution, then collect the catalyst and dried at 70°C for 12 h.</td>
<td>0.125 g photocatalysts were added into 125 mL EY (0.042 mM) and MB (0.05 mM) solution, respectively. Light source: 500 W halogen linear lamp.</td>
<td>EY was completely degrade after 10 min; 90% MB was degrade after 15 min.</td>
<td>[76]</td>
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<td>Heteroepitaxial</td>
<td>concave trisoctahedral</td>
<td>Ammonia solution was added into 0.2 g AgNO3 aqueous solution, then, the Au@Ag nanorods with high aspect ratio and 0.15 M Na2HPO4 aqueous solution was added in order.</td>
<td>0.2 g photocatalysts were added in 100 mL 8 mg/L Rh B solution. Light source: 300 W Xe arc lamp.</td>
<td>Rh B was completely degrade within 3 min.</td>
<td>[77]</td>
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Note: Rh B (rhodamine B); MO (methyl orange); PVP (poly vinyl pyrrolidone); HA (humic acid); dissolved organic carbon (DOC); EY (Eosin Y); MB (methylene blue).
The basic synthesis parameter such as hydrothermal temperature and intensity of pressure, Ag$_3$PO$_4$ products with few defects, good direction, regular morphology, and high purity could be obtained. The products have superior crystalline and the size is easy to control. Meanwhile, this method is beneficial to the generation of intermediate and special valence state compounds, and could equally realize the doping process, because the atmosphere of surrounding under hydrothermal condition is liable to control. Wang et al. [75] first used this method with the assistance of urea to prepare a highly uniformed Ag$_3$PO$_4$ with tetrapod morphology at 2012. Production of tetrapod Ag$_3$PO$_4$ undergoes three steps. (i) precipitation process: the addition of urea could neutralize the phosphoric acid to form H$_3$PO$_4$~ to react with Ag$^+$ produce Ag$_3$PO$_4$ microrod; (ii) the dissolution process: with the reaction time increase, microrod Ag$_3$PO$_4$ would dissolve by the ammonia released from urea hydrolysis; (iii) recrystallization process: through the reaction between dissolved Ag(NH$_3$)$_2$$^{+}$ and PO$_4^{3–}$, the tetrapod Ag$_3$PO$_4$ was shaped up. The uniform tetrapod Ag$_3$PO$_4$ possess four cylindrical microrods arms grow along the [110] direction with an average diameter of 5 μm and a length of 15–30 μm, and its specific surface areas is 38.0 m$^2$/g. The degradation rate of RhB by as-obtained Ag$_3$PO$_4$ particles was more than 2 times higher than the Ag$_3$PO$_4$ samples prepared by ion-exchange method. Reaction conditions have been of great influence on the morphology and facets of as-prepared samples. For instance, Cui et al. [87] have discussed the effect of temperature in hydrothermal synthesis procedure of Ag$_3$PO$_4$. The authors found out that with the temperature increased from 20°C to 120°C, the intensity of (1 1 0) peaks becomes sharper and stronger, which means an increased ratio of exposed (1 1 0) facets. Generally, more exposed (1 1 0) facets means higher photocatalytic activity of Ag$_3$PO$_4$, which is conducive to the photocatalytic performance.

### 3.5. Facet control

There are generally three low-index facets of Ag$_3$PO$_4$ (i.e., (1 0 0), (1 1 0), and (1 1 1)), which show comparable photocatalytic performance but exhibit better stability compared to high-index facets. The main difference between these three low-index facets of Ag$_3$PO$_4$ is the surface states such as the concentration of Ag$^+$ cations, the concentration of oxygen vacancies, and the concentration of dangling phosphorus-oxygen bonds. For (1 0 0) facets, the proportion of P atoms and Ag$^+$ cations is 1:2, without any O$^{2–}$ anions in the planes. The enriched Ag$^+$ cations could be converted to Ag by the photoexcited electrons, which could enhance the segregation of photogenerated carriers, thereby improving their photocatalytic performance [78]. Additionally, the (1 1 0) facets of Ag$_3$PO$_4$ possess a metal-like electronic property, which might be conducive to the promoted harvesting efficiency of photons. Compare to (1 1 0) facets, regular rhombic dodecahedral shaped (1 1 0) facets Ag$_3$PO$_4$ had more oxygen vacancies created, more active sites generated, and larger adsorption amounts on these sites on the surface [79]. Wang et al. [75] found that the Ag atoms on the (1 1 0) planes contained threefold-coordinated with one dangling bond and two-coordinated with two dangling bonds, whilst in the (1 0 0) planes, all the Ag atoms were coordinative saturated, which explained the reason for (1 1 0) facets exhibiting the higher reactivity than the (1 1 0) facets. As for tetrahedron Ag$_3$PO$_4$ with (1 1 1) facets, the planes consisted of over-abundance of dangling phosphorus-oxygen bonds, which could act as oxidation sites for a better reactivity. Besides, the hole mass along (1 1 1) is smaller than other directions in Ag$_3$PO$_4$ crystals [89]. That would improve the hole mobility of the tetrahedrons samples, and enhance the separation efficiency, thus improving the photocatalytic activity. It is generally recognized that Ag$_3$PO$_4$ exposed with one more of these three facets have great photocatalytic activity, and tetrahedral Ag$_3$PO$_4$ with exposed (1 1 1) facets are more photocatalytically active than rhombic dodecahedrals with (1 1 0) facets and cubes with (1 0 0) facets. However, Hsieh et al. [90] demonstrate that there might be controversies about this recognition. The authors tested the photodecomposition capability of MO solution of Ag$_3$PO$_4$ with different morphology (cubes, rhombic dodecaheda and tetrahedrons). Interestingly, the results show that the Ag$_3$PO$_4$ cubes show the best photodecomposition capability of MO, Ag$_3$PO$_4$ rhombic dodecahedra shows a little over half of that, and Ag$_3$PO$_4$ tetrahedrons are completely inactive after 90 min of reaction. The authors conclude that this is because (1 1 1) surface have the highest barrier for electron transport to the surface (the most steep upward band bending among these three facets), hence there may no photogenerated electrons and holes arrived in the (1 1 1) faces of Ag$_3$PO$_4$ to participate in the photocatalysis. On the contrary, (1 0 0) facet have the least degree of upward band bending, which indicate its have the best electron transmission capacity among these three facets, and the upward band bending degree of (1 1 0) facet is between (1 1 1) and (1 0 0) facet, signify less efficiency of photogenerated electron transfer than that of (1 0 0) facet. In addition, Kim et al. [91] exhibit that tetrahedron Ag$_3$PO$_4$ have the fastest oxidation capability of amplex red compare to Ag$_3$PO$_4$ with mixed facet and cube. The authors state that this is owing to the (1 0 0) faces have coordinatively saturated Ag atoms, whereas the Ag atoms on (1 1 1)
facets are located at three-coordinated sites with one dangling bond. Once the \([\text{Ag}_2 = \text{O} \rightarrow \text{Ag}_\text{surface}]\) combined with \(h^+\), the \((1 1 1)\) surface would be less stable than that of \((1 0 0)\) surface, leading to higher recombination rate of photoexcited electrons and holes. To date, there was no consistent recognition of which the crystal structure of \(\text{Ag}_3\text{PO}_4\) is better for the photocatalytic degradation of pollutants or water splitting, which need researchers put more strength in this aspect in the future study.

4. Summary

The synthesis method plays a significant role in determining the morphology of photocatalysts and its photocatalytic performance. The growth procedure of \(\text{Ag}_3\text{PO}_4\) was largely rest with the \(\text{Ag}^{+}\) source in morphology of photocatalysts and its photocatalytic performance. The once the \([\text{Ag}_2=\text{O} \rightarrow \text{Ag}]\) surface combined with \(h^+\), the \((111)\) surface facets are located at three-coordinated sites with one dangling bond. X. Li, et al. [92] also taken into considering. For instance, Sulaeman et al. [92] proved introduced some specific features of these methods. In the synthesis process, other influential factors such as the additives and \(pH\) should be also taken into consideration. For instance, Sulaeman et al. [92] proved that the content of ethanol as the solvent could influence the \(\text{Ag}/\text{P}\) atomic ratio of \(\text{Ag}_3\text{PO}_4\), thus influence the formation of \(\text{Ag}\) vacancies on the surface of \(\text{Ag}_3\text{PO}_4\). Hsieh et al. [90] confirmed that the formation of \([\text{Ag}(\text{NH}_3)_2]^+\) complex has great influence for the morphology control of precipitation method. The molar ratio of \(\text{NH}_4\text{NO}_3/\text{NaOH}/\text{AgNO}_3/\text{K}_2\text{HPO}_4\) was controlled at 2:1:8:1:2 in a sequence adding order to synthesis \(\text{Ag}_3\text{PO}_4\) cubes. By adjusting the molar ratio of \(\text{NH}_4\text{NO}_3\) and \(\text{AgNO}_3\), the authors successfully fabricate \(\text{Ag}_3\text{PO}_4\) particles with different morphology (e.g., rhombic dodecahedra, \((100)\)-truncated rhombic dodecahedra, tetrahedra, and tetrapods). Forming \([\text{Ag}(\text{NH}_3)_2]^+\) complexes before adding phosphate could distinctly reduce the driving force toward \(\text{Ag}_3\text{PO}_4\) production, thus efficiently controlled the shape of products. Besides, different morphology of \(\text{Ag}_3\text{PO}_4\) also was a significant parameter for the photocatalytic activity needs to carefully considered. The porous and hollow structure is conducive to the enhancement of light harvesting, the photogenerated electron-hole separation efficiency, and immersing of reactants to the photocatalysts. In the design stage, researchers should carefully take all these influence parameters into consideration, choose a specific method for a specific purpose. In addition, researchers also should make unremitting efforts to develop simple and green synthesis methods for the full-scale fabrication of \(\text{Ag}_3\text{PO}_4\) photocatalyst with high photocatalytic performance in the future.

5. What hinder the practical application of \(\text{Ag}_3\text{PO}_4\)?

\(\text{Ag}_3\text{PO}_4\) is an excellent photocatalyst because it can be excited by visible light and possess strong photooxidation capability. However, to date, application of \(\text{Ag}_3\text{PO}_4\) in treating organic pollutants in real-world scenarios has not yet been achieved. Thus, one might want to know what hinders the practical application of \(\text{Ag}_3\text{PO}_4\). There are indeed several barriers that need to be removed. One big challenge is the severe self-photocorrosion, which strongly limits its cyclic utilization. The photocorrosion phenomenon gives rise to a series of severe issues. Firstly, in large-scale applications, consumption of bare \(\text{Ag}_3\text{PO}_4\) photocatalyst is high because silver is a noble metal. Price of \(\text{TiO}_2\) is ¥30.72 per gram (without considering the cost of \(\text{PO}_4^{3-}\) source and other additives), which is 8 times more expensive than \(\text{TiO}_2\) (CODE # 51026962. Sinopharm Chemical Reagent Co., Ltd.). That makes using bare \(\text{Ag}_3\text{PO}_4\) as photocatalyst for water purification impracticable. Secondly, \(\text{Ag}_3\text{PO}_4\) is slowly soluble in water (\(K_{sp} = 1.6 \times 10^{-16}\)), and dissolved in nitric acid or ammonia solution, thus its reclamation in real-world situation is difficult. Lastly, the photogenerated electrons under light irradiation could be absorbed by the \(\text{Ag}^+\) released from \(\text{Ag}_3\text{PO}_4\), and consequently reduced to metallic silver, which would deposit on the surface of \(\text{Ag}_3\text{PO}_4\) (\(4\text{Ag}_3\text{PO}_4 + 6\text{H}_2\text{O} + 12h^+ + 12e^- \rightarrow 12\text{Ag} + 4\text{H}_3\text{PO}_4 + 3\text{O}_2\)). This is owing to the position of conduction band of \(\text{Ag}_3\text{PO}_4\) is +0.45 V, which is much more positive than the potential of \(\text{H}_2\text{O}/\text{H}_2\) and more negative than that of \(\text{Ag}/\text{Ag}^+\), thus the photoinduced electrons would be adopted by \(\text{Ag}^+\) released from the lattice of \(\text{Ag}_3\text{PO}_4\) instead of \(\text{H}_2\text{O}\) if there were no scavengers exist. As a result, the structure of \(\text{Ag}_3\text{PO}_4\) could be destroyed, and thus the photocatalytic activity would decrease after several photocatalysis reactions, which greatly hindered its practical application. According to the high-resolution 3d XPS spectra of pure \(\text{Ag}_3\text{PO}_4\) after one run of degradation of \(\text{Rh B}\) (Fig. 4), Chang et al. [66] calculated that more than 27% of metallic Ag would be formed on the surface of \(\text{Ag}_3\text{PO}_4\). Teng et al. [65] reported that \(\text{Rh B}\) was completely degraded by \(\text{Ag}_3\text{PO}_4\) within 4 min under Xe lamp irradiation. After three cyclic experiments, however, only 34% of \(\text{Rh B}\) was degraded under the same situation.

6. How to remove these barriers?

6.1. Surface modification

6.1.1. Plasmonic effect

Metal deposition is a commonly used method for the enhancement of photocatalytic performance. There are mainly two mechanisms for the metal/semiconductor composites, namely, Schottky junction and plasmonic effect. Generally, Schottky junction was formed when there is a direct contact between the metal and semiconductor, while the plasmonic effect could influence the charge transfer of semiconductor even there was an insulating interlayer in the middle of metal and semiconductor. While the metal and the semiconductor have matched work functions and were stuck together intimately, a metal-semiconductor Schottky junction was formed, which can facilitate the separation of electron-hole pairs for charge transfer between these components [93,94]. However, improved separation efficiency was cost of the redox ability of carriers. Owing to the difference of Fermi levels of...
metal and the conduction band of n-type semiconductor or valence band of p-type semiconductor, the energy of carriers was inevitably lost during the transfer process from semiconductor to metal [95]. Normally, the plasmonic metals were defined as Au, Ag and Cu, and the others were generally considered as non-plasmonic metals in the photocatalytic research field [95]. The localized surface plasmon resonance (LSPR) effects could result in collective oscillation of the free electrons, which can induce strong absorption of the electromagnetic energy, hence enhancing the absorption and photocatalytic performances of the semiconductor [96]. For metal/Ag3PO4 composites, generally, the electrons would flow into metal from Ag3PO4 crystal until it came to the equilibrium of the two systems and formed a new Fermi level as long as the heterostructures were formed. Meanwhile, bands of Ag3PO4 bend upward to the surface and an internal electric field directed from Ag3PO4 to metal were established. The electrons would accumulate on the metal instead of the surface of Ag3PO4, thereby mitigating its photocorrosion. These electrons could merge with the trapped surface oxygen molecules to generate O2− reactive species for photooxidation reaction. Moreover, insoluble metal deposited on Ag3PO4 could guard the Ag3PO4 from dissolution in aqueous solution.

Ag nanoparticles could be generated in both production and photocatalysis processes. In Ag/Ag3PO4 composites system, the photogenerated electrons would be transferred to Ag, and the holes remain on the Ag3PO4 lattice surface during the irradiation, owing to the existence of PO43− ions, thereby boosting the separation efficiency of photexcited electron/hole pairs and achieving high stability [97]. The main function of Ag in this system is to accelerate the transfer of photogenerated electrons from Ag3PO4 conduction band to the Ag nanoparticles and forming O2− or O22− reactive species by trapping O2 and H2O for degradation of organic contaminants [98]. Ag/Ag3PO4 showed a more efficient and stable photocatalytic performance compared to pure Ag3PO4 even after five cycles [99]. The XRD patterns of Ag/Ag3PO4 after cycling photodegradation experiments (Fig. 5) showed that the change of the phase structure was inappreciable (the content of Ag nanoparticles were 5.73% and 5.84% before and after cycling experiments), and no more Ag nanoparticles were generated. The reduction ability of Ag3PO4 could also be promoted by Ag deposition. Patil et al. [100] reported that Ag/Ag3PO4 glass nanocomposites could be used for H2 production from H2S, with maximum H2 output being 3920.4 μmol·h−1·g−1. The overvoltage of hydrogen of Ag metal is −0.22 V vs. NHE, which is more negative compared to pristine Ag3PO4 (+0.285 V vs. NHE), which makes the H2 yield over Ag seems profitable and reasonable. However, in such a composite system, the stability issue was still not fully solved, because some photogenerated electrons inevitably stayed in the conduction band of Ag3PO4, which could reduce Ag+ of Ag3PO4 to form metallic Ag.

Apart from Ag, the deposition of other noble metals on Ag3PO4 has also been studied by researchers [101–103]. Similar to Ag/Ag3PO4, the photoinduced electrons could be accumulated in noble metal through the established electric field between Ag3PO4 and noble metal, inhibition of the recombination of photogenerated carriers. The photocatalytic activity of the M/Ag3PO4 (M = Pt, Pd, Au) is followed by the order: Pt/Ag3PO4 > Pd/Ag3PO4 > Au/Ag3PO4, which is owing to their different work functions [101]. The larger difference between noble metal and Ag3PO4, the faster transformation of electrons from Ag3PO4 to noble metal. For Au/Ag3PO4, the introduce of Au particles could not only facilitate the electron transfer from Ag3PO4 to Au (owing to the higher electrical conductivity) and acting as electron reservoirs to separate the photexcited charge carriers, but also could extend the light absorption range up to 800 nm. Liu et al. [103] demonstrated that Au nanorod coupled Ag3PO4 could completely decompose Rh B dye after 50 min under solar light irradiation, while 78% for the pure Ag3PO4 under the same condition. In this composite, the electrons in the 6sp band of Au could transfer to a higher-energy state owing to the surface plasmon resonance (SPR) effect, and react with O2 to generate ‘O2−’ radical. Besides, photexcited electrons in the conduction band of Ag3PO4 could transfer into the Au nanorod, consumed by the vacancies of the Au nanorod, thus facilitate the space separation of the photoexcited electrons and holes. Rh B could be efficiently decomposed by the generated ‘O2−’ and h+ radicals. In addition, under a 300 W Xe lamp with a cutoff light filter of 645 nm, the as-prepared Au/Ag3PO4 samples still show efficient degradation rate of Rh B, which further verified the light absorption range is amplified to 800 nm.

6.1.2. Constructing multiple semiconductor composites heterojunction

Coupling semiconductor with other is a valid way for the enhancement of photocatalytic performance. The hybrid photocatalysts may have complementary features and have optimal performances than single component. The separation and transportation of photogenerated charges could be improved, and semiconductors with larger band gaps could be sensitized through introducing semiconductors with smaller band gaps. Moreover, the stability of semiconductors could be increased by coupling with some semiconductors with superb electrochemical/photochemical stability. During the past decades, numerous studies of semiconductor coupled with Ag3PO4 were reported, showing improved separation efficiency of photoinduced charge carriers, strengthened photostability of Ag3PO4, enhanced photoreduction ability, and simultaneously increased photocatalytic performance. We simplified present the two types of connection mechanism between semiconductors and Ag3PO4 (type II and Z-scheme-like), carbon materials or polymers coupled Ag3PO4, and some novel ternary or multi-component Ag3PO4 hybrid composites in this section.

There are generally three types heterostructure based on the bandgaps and electronic affinity of semiconductors, namely, type I (straddling), type II (staggered), and type III (broken) (Fig. 6). The former two types are more commonly used in practical heterostructure devices. For type I, photocatalyst I (PC I) has narrower band gap compare to photocatalyst II (PC II), and both the location of conduction band and valence band of PC I was within PC II (Fig. 6A). This type of heterostructures is conducive to the accumulation of electrons and holes in PC I, and were mostly utilized in optical devices such as light emitting diodes and lasers [104,105]. As for Type II heterojunction, photogenerated electrons in the conduction band of PC I could transfer to the conduction band of PC II, accompanied by the transformation of the photogenerated holes from the valence band of PC II to the valence band of PC I (Fig. 6B). Similar to the Schottky junction of metal/semiconductor composites, in the interface of two semiconductors, a built-in field would be generated, which is conducive to the separation of photoexcited electron-hole pairs in this region, leading to the

Fig. 5. XRD patterns of (a) Ag/Ag3PO4 composite, (b) Ag/Ag3PO4 after the 5th cycling photodegradation of Rh B (cited from Ref. [99]).
enhancement of photocatalytic performance. The elevated photocatalytic capability could also be attributed to the augmented surface area and enhanced absorption of reactants. Charge transfer directions were depending on the position of the conduction band and valence band of the two semiconductors. In this heterojunction system, we preferred that Ag₃PO₄ to act as PC II to transfer the photoinduced electrons to other semiconductor, which may show a better inhibition capability for the photocorrosion than the type II heterojunction where Ag₃PO₄ act as the PC I. It should be noted that metallic Ag could be still generated in the photocatalysis process, reducing the cyclic utilization capability of Ag₃PO₄. Yao et al. [106] reported that the type II heterojunction Ag₃PO₄/TiO₂ composites showed 90% degradation rate of the methylene blue (MB) after 6 min under irradiation, which was higher than that of Ag₃PO₄ samples. This composite system reduced the loading of metallic Ag from 77 wt% to 47 wt%, which could be regarded as significant progress for reducing photocorrosion phenomenon.

Although the recombination of photoinduced electron-hole pairs is restrained by the type II heterojunctions, the redox ability of the charges in this system is weakened. The Z-scheme-like photocatalytic system may be an ideal candidate to solve this problem [107]. Similar to type II heterojunction photocatalytic systems, the separation of photoexcited electron/hole pairs could be also enhanced in the Z-scheme-like photocatalytic system. Photogenerated electrons in the conduction band of PC I could encounter with the photogenerated holes in the valence band of PC II through either a conductor or a direct contact (Fig. 7 A and B). The photoinduced electrons still remain in the more negative conduction band of PC II for photoreduction process, while the photogenerated holes remain in the more positive valence band of PC I for photooxidation reaction. The driving force energy needed for this system is reduced which could make the hybrid photocatalyst utilize visible-light more efficiently.

Transition metal sulfides (e.g. MoS₂ and WS₂) recently attracted more and more attention from researchers. Considering the band gap energy of transition metal sulfides and Ag₃PO₄, it is reasonable to believe that the composition of these semiconductors could constructing a Z-scheme-like heterojunction, which could effectively restrain the oxidation of transition metal sulfides and the reduction of Ag₃PO₄, hence improve both the photocatalytic activity and stability. The two dimensional graphene-like materials MoS₂ have a suitable band edges (E_{CB} = −0.12 V, E_{VB} = 1.78 V), which is well matched with Ag₃PO₄ to form Z-scheme-like photocatalytic system [108,109]. Zhu et al. [110] reported that Ag₃PO₄/MoS₂ composite photocatalyst exhibited excellent photocatalytic degradation rate of organic contaminants and ascendant stability according to the recycling experiments. MoS₂ could effectively accept electrons and form strong interaction with Ag₃PO₄. Photogenerated electrons of Ag₃PO₄ could recombine with the photoexcited hole of MoS₂ in Ag particles which were formed by the photocorrosion of Ag₃PO₄. The Ag particles serve as charge recombination center and are favorable to the development of the Z-scheme-like system. The holes remaining in Ag₃PO₄ and electrons in MoS₂ could...
simultaneously be utilized for the redox reactions. The separation efficiency was improved and the photocatalytic performance was also enhanced.

Metal-free graphitic carbon nitride (g-C3N4) is a material with stable, abundant, responsive to visible-light, and exhibits splendid electronic properties. The band gap width of g-C3N4 is about 2.7 eV (the conduction band position of g-C3N4 is ~1.12 V and the valence band position of it is 1.57 V) [18, 111–114]. He et al. [115] reported that the Z-scheme-like Ag3PO4@g-C3N4 composite could transfer CO2 to fuel. Photoinduced holes in g-C3N4 and the photoexcited electrons in Ag3PO4 would combine in Ag nanoparticles. The photogenerated electrons in g-C3N4 could reduce H2 or CO2 while the photogenerated holes in Ag3PO4 could be used to oxidize H2O to O2 or degrade pollutants. The biggest CO2 conversion rate of Ag3PO4@g-C3N4 photocatalyst 57.5 μmol·h−1·gcat−1, which was almost 6.1 and 10.4 times higher than that of g-C3N4 and P25 under the same conditions, respectively.

Besides the two kinds of hybrid mechanisms introduced above, other materials such as carbon materials (e.g., fullerenes and graphene) [116, 117], polymers [118–121], and metal-organic frameworks [122–124] could be used as the conductor for the improvement of photocatalytic performance. Given credit to the good electron transport of carbon compounds, it may be a kind of the most appropriate material to combine with Ag3PO4 [125–127]. In the carbon-based materials, graphdiyne with π-conjugated structure of sp- and sp2-hybridized carbon atoms have attracted tremendous attention. Its electron and hole mobility is about 2 * 10^5 cm^2 V−1 s−1 [128] and 10^3 cm^2 V−1 s−1 [129] order of magnitude, respectively, and the conductivity of graphdiyne is measured as 2.516 * 10−4 S/m [130]. The graphdiyne has uniformly distributed pores and a tunable band gap in the range of 0.46–1.22 eV [131]. Guo et al. [132] studied the promoted photocatalytic activity of graphdiyne/Ag3PO4 pickering emulsion. The abundant butadiyne bonds (–C≡C–C≡C–) makes graphdiyne works as an excellent acceptor (formed a large π-conjugated system) for the photoexcited electrons of Ag3PO4, and an appropriate amount of the precursor Ag+ could be reduced to Ag0 by the introduction of graphdiyne due to the low work function of it. According to the authors, MB solution could be completely photodegraded within 10 min by this graphdiyne/Ag3PO4 emulsion system under visible light irradiation, while only 75% MB were photodegraded by carbon nanotube/Ag3PO4 or graphene/Ag3PO4 photocatalyst under the same condition.

Coupling Ag3PO4 with polymers may be an efficient way to restrain the photocorrosion of Ag3PO4, because it could function as a passivation layer to cut down the number of surface recombination sites and prevents the photocorrosion of semiconductor [133]. For instance, Yuse et al. [121] synthesized a core-shell structure Ag3PO4@benzoxazine soft gel nanocomposite for the improvement of interface properties and stability of Ag3PO4. The silver amine complex ion formed through the amino group of benzoxazine and Ag+ ions on the surface of Ag3PO4 could consuming the photogenerated electrons of Ag3PO4 with the O2 evolution. The graphdiyne could boost the oxygen generation by acting as conductive electron mediator bridge as well as to stabilize Ag3PO4 as a promising substrate. The O2 evolution of this composite could reach 753.1 μmol·h−1·gcat−1, which is 12.2 times higher than that of pure Ag3PO4 photocatalyst.

Shao et al. [143] improved the photocatalytic performance of Ag3PO4@benzoxazine by synthesizing Ag3PO4 tetrapods with more exposure of (1 1 0) facet and decorated of carbon quantum dots (CQDs) on the surface of Ag3PO4. The CQDs could act as an “exciter” by expanding light absorption and strengthening energy conversion via up-converted photoluminescence effect, thus activate more photogenerated charge carriers from the (1 1 0) facet of Ag3PO4 tetrapod. Simultaneously, it could facilitate the electron transfer from the conduction band of Ag3PO4 to the conduction band of itself. The silver amine complex formed between Ag3PO4 and benzoxazine is beneficial for the free radical chain reaction. This 3D core-shell structure decreased the solubility of Ag3PO4. The photocatalytic activity of this composite still remains 95% removal rates of sulfamethoxazole with 10 min even after 9 cycles.

Except the abovementioned ternary Ag3PO4 hybrid composites system, other multi-component Ag3PO4 hybrid composites were also been studied by researchers. For example, Pan et al. [147] introduced TiO2 into the laminar Ag3PO4/Ag/MoS2 Z-scheme-like heterojunction photocatalyst to prevent the aggregation. Comparing with traditional heterojunctions, the part of Ag3PO4/Ag/MoS2 in this composite still forms a Z-scheme-like structure. Additionally, credit to the lamellar structure, the conduction band of MoS2 may be higher than that of TiO2, which could lead the photogenerated electrons from MoS2 transferred into the conduction band of TiO2, further promote the separation efficiency of photoinduced charge carriers. The photoluminescence of Ag3PO4/Ag/MoS2/TiO2 is obvious weaker than others (Fig. 8), which proved this conjecture. Direct Z-scheme-like photocatalysts for water splitting suffer from charge separation and photocatalytic backward reaction issues [148, 149]. Li et al. [150] announced that the synergetic effect of a type II heterostructure could efficiently suppress the backward reaction. The authors deposit Ag3PO4 nanoparticles on CeO2/TiO2 hierarchical branched nanowires, and speculated that the cascade energy level alignment in CeO2/TiO2 hierarchical branched nanowires facilitates the spatial charge separation, thus inhibit the backward reaction, and further improved the photocatalytic activity. Other novel multi-component photocatalytic system such as quasi-type II p-n/n-n dual heterojunction Ag@Ag3PO4@g-C3N4/NiFe layered double hydroxide (LDH) nanocomposites [151] and dual Z-scheme-like g-C3N4/Ag3PO4/Ag/MoS2 [152] composites were also been investigated by researchers, and their proposed mechanism for charge transfer pathways (including the abovementioned Ag3PO4/Ag/MoS2/TiO2 and Ag3PO4/CeO2/TiO2) were show in Fig. 9.

6.2. Doping

Introducing heteroatoms into the lattice of host material is considered as an excellent way to adjust the photocatalytic performance of semiconductors. Unlike surface modification such as metal deposition, doping is a physical or chemical method, which introduces ions into the internal of host material lattice. It could efficiently modify the surface structure of host material, form some defects (acting as capture centers to inhibit the recombinaction of photoinduced electron/hole pairs), increase some spectral response, cause significant changes in the band gap (introducing levels), influence the kinetic state of photoinduced charge carriers (causing linear expansion of the transition of charge carriers, and prolong the life time of photoinduced charges), hence is conducted to the improvement of photocatalytic performance [153–156]. However, doping does not always play a positive role in
energy band engineering. Dopants could act as carrier recombination centers when the concentration of dopants exceeds the optimum value, and thus decrease the photocatalytic properties. Doping could also destroy the local symmetry, and the chemical mismatch between the dopant and host may result in the formation of deep defect levels [157]. Therefore, choosing proper dopants for precise engineering the energy band configuration is at a camera position.

Generally, doping could introduce an impurity level or replace some elements in the original crystal. For instance, an impurity energy band would be formed in the doping process of Ni$^{2+}$-doped Ag$_3$PO$_4$ [158]. The additional Ni$^{2+}$ could facilitate the utilization of photons as well as the separation efficiency of photoinduced charge carriers. The

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**Fig. 8.** The photoluminescence of the samples with different excitation wavelength, (A) 325 nm, (B) 450 nm (cited from Ref. [147]).

**Fig. 9.** The proposed mechanism for charge transfer pathways (A) Ag$_3$PO$_4$/Ag/MoS$_2$/TiO$_2$ (adapted from Ref. [147]), (B) Ag$_3$PO$_4$/CeO$_2$/TiO$_2$ (adapted from Ref. [150]), (C) Ag@Ag$_3$PO$_4$/$\gamma$-C$_3$N$_4$/NiFe LDH (adapted from Ref. [151]), (D) $\gamma$-C$_3$N$_4$/Ag$_3$PO$_4$/Ag$_2$MoO$_4$ (adapted from Ref. [152]).
photodegradation rate of methyl orange (MO 40 mg/L) could be reached at 89% by Ni$^{2+}$-doped Ag$_3$PO$_4$ after 4 min under visible light irradiation, whereas 12% of MO (40 mg/L) was only degraded by pure Ag$_3$PO$_4$ photocatalyst under the same situation. Five cycling experiments showed that the photodegradation rate of MO (20 mg/L) was still up to 92%. The introduction of copper atoms could substitute silver atoms in the crystalline lattice of Ag$_3$PO$_4$, thus create defects that influence the structural ordering, stabilize the cubic structure, and prevent the reduction of Ag$^+$ by acting as recombination centers to trap photogenerated electrons [159]. Introducing Bi$^{3+}$ ions could replace the P$^{5+}$ ions of Ag$_3$PO$_4$ [160]. The valance band level of Ag$_3$PO$_4$ could be decreased by bismuth doping, and the band gap energy of Bi$^{3+}$-Ag$_3$PO$_4$ could be reduced to 1.954 eV. Doping Bi$^{3+}$ ions in Ag$_3$PO$_4$ suppressed the formation of excess OH defects. High-concentration OH defect is not good for the electronic transitions, and could destroy Ag-O bonds in Ag$_3$PO$_4$ to accelerate electronic recombination. Notably, in an aqueous solution, MO molecules carry a negative charge while the Bi$^{3+}$ ions carry a positive charge in doped Ag$_3$PO$_4$. Hence, adsorption capability could be accelerated because of the internal attraction between these two groups, which facilitated the photocatalytic reaction. P (V) of Ag$_3$PO$_4$ could be substituted by Mo (VI) cations, and new intermediate levels in the forbidden band would be formed after doping procedure of molybdenum [161]. Electronic repulsion capability of Ag$_3$PO$_4$ could be improved by Mo doping due to the Mo (VI) cations are more positive than the P (V) cations. Mo doping could break in degeneracy in the Ag 4d orbitals, and Mo 4d orbitals in the conduction band provokes the decrease of the band gap value. Appropriate amount of Mo doping could create an appropriate amount of defects, which could serve as traps to delay the recombination of charge carriers, and forming intermediate states in the forbidden band to lower the $E_c$. The $E_c$ could be reduced to 2.07 eV for 0.5% Mo doped Ag$_3$PO$_4$, and shows two time faster degradation rates than pure Ag$_3$PO$_4$ microcrystals toward RH B solution.

Lanthanides doped semiconductors could form crystalline defects, which could enhance visible wavelengths emission and inhibit the recombination of photogenerated electron-hole pairs [156]. The surface structure of Ag$_3$PO$_4$ could be affected by La doping [162]. As the concentration of La dopant increased, more surface defects and pores would be generated. Enhanced photocatalytic capability of La-doped Ag$_3$PO$_4$ was aided by the increased porosity, surface defects, and surface area. Other lanthanides like Dy or Er doped Ag$_3$PO$_4$ were also been reported [163,164]. Gadolinium cations could replace Ag$^{3+}$ ions for the Gd-doped Ag$_3$PO$_4$ photocatalysts [164]. The M$^{3+}$ (M = Gd, Dy, and Er) ions in this system combined with an electron to form M$^{2+}$, which would further react with O$_2$ to increase the formation of O$_2^{-}$.

Ba-doped Ag$_3$PO$_4$ hollow nanosheets with high photocatalytic activity and photoconversion efficiency were synthesized by Yu et al. [165] via a one-step cation exchange method. This synthesis method was conducive to the dispersion of Ba$^{2+}$ ions. Ba-doped Ag$_3$PO$_4$ could completely degrade Rh B solution within 5 min and MO solution in 2.5 min, which was more active than that of cubic or spherical Ag$_3$PO$_4$ particles. After five cycling runs, the time for complete degradation was in the range of 5–7 min for Rh B, and 2.5–4 min for MO. Ba doping might greatly increase the amount of oxygen defects, which could inhibit the recombination of the photoinduced charge carriers. An alternative explanation was that doping Ba in the Ag$_3$PO$_4$ created a charge imbalance, which caused more OH$^{-}$ to trap more holes, thereby restraining the recombination of charge pairs and generating more OH$^{-}$.

To date, some cationic metal (e.g. Ni, Bi, Ba, Cu, Mo, La) has been successfully doped into Ag$_3$PO$_4$ lattice, and effectively enhanced the photocatalytic performance. However, the metal doping generally introduce localized energy levels in the band gap to modification host material, which may also bring the risk of impairing charge separation and transport by acting as a recombination center. In this regard, one might want to know the anionic nonmetal doping behavior in Ag$_3$PO$_4$ since there are plenty of convincing research paper proved the anionic nonmetal doping in TiO$_2$ and other photocatalytic could obtain a better photocatalytic performance [166–168]. Recently, a fluorine-doped Ag$_3$PO$_4$ photocatalyst with boosting activity and stability by a facile in-situ fluorination was reported by Li et al. [169]. Doping F elements with moderate amount have no effect on the basic crystal structure of cubic Ag$_3$PO$_4$ and did not introduce impurity phases. Besides, the average crystallite size and crystallinity was improved when the fluoride ions was introduced into Ag$_3$PO$_4$, which is benefit for the dissolution and recrystallization processes. Higher crystallinity degree in conducive to the suppressing of bulk charge recombination, and promoting charge separation and transportation. Most of F$^{-}$ ions would substitute O$^{2-}$ ions in Ag$_3$PO$_4$ lattice, and forming a stronger F-P-F bond compare to the P-O bond. The Fermi level of F-doped Ag$_3$PO$_4$ would move toward the conduction band, which is in favor of the charge separation. Small amount of fluorine would adsorbed on the surface of Ag$_3$PO$_4$, and absorb more H$_2$O owing to the fluorine induced $\cdot$F...(H–OH), group involving hydrogen-bonding interactions. F doping would induce more surface defects such as oxygen vacancies, which enhance the capture of surface O$_2$ as well as the activation of O$_2$ by photoinduced electrons. In addition, the band gap of F-doped Ag$_3$PO$_4$ was raised. Accordingly, the band gap of Ag$_3$PO$_4$ and F-doped Ag$_3$PO$_4$ is about 2.41 eV and 2.44 eV, respectively. The reduction potential of photogenerated electrons was enhanced and oxidation potential of photogenerated holes was reduced in the F-doped Ag$_3$PO$_4$.

Owing to the strong P-O bond, incorporating S into Ag$_3$PO$_4$ lattice is difficult, which need much energy input to inset those dopants into PO$_4$ matrix. Therefore, some researchers proposed using oxoanion groups to modulate semiconductor to get an enhanced photocatalytic activity as an alternative way [170,171]. Cao et al. [172] successfully doped SO$_4^{2-}$ ions into Ag$_3$PO$_4$ lattice by a precipitation method. It was feasible to replace PO$_4^{3-}$ by SO$_4^{2-}$ experimentally because the ionic radius of SO$_4^{2-}$ and PO$_4^{3-}$ are similar (0.218 nm of SO$_4^{2-}$ and 0.230 nm for PO$_4^{3-}$). The S element in SO$_4^{2-}$ had strong electronic interactions with Ag, P and O elements. Give credit to the higher electronegative of S compared to the P atom, the additional SO$_4^{2-}$ would decrease the electron densities around Ag and P elements. Doped SO$_4^{2-}$ created impurity states were mainly distributed in the valence band region, and no impurity state appeared in the forbidden band gap. The Fermi level of SO$_4^{2-}$-doped Ag$_3$PO$_4$ was significantly shifted towards the conduction band. As the concentration of dopant increased, both the VBM and the CBM gradually shifted towards lower energy regions, which were conducted to the enhancement of oxidative capability of photoexcited holes and suppressed the reduction capability of photoexcited electrons. The photodegradation rate of Rh B solution of SO$_4^{2-}$-doped Ag$_3$PO$_4$ was 4.5 times higher compared to Bi$^{3+}$-doped Ag$_3$PO$_4$. Although the photodegradation rate slightly decreased after two cycling runs, the degradation of Rh B solution is still up to 98% after six cyclic runs. Luo et al. [173] proposed a doughnut-like carbonate-doped Ag$_3$PO$_4$ with high photocatalytic activity through an ion-exchange method. Similar to the Ba-doped Ag$_3$PO$_4$ aforementioned, the authors took advantage of the lower solubility of Ag$_3$PO$_4$ ($K_{sp}=8.45 \times 10^{-12}$) compared to Ag$_2$CO$_3$ ($K_{sp}=8.45 \times 10^{-12}$) to get a hollow hexagon doughnut-like structure. The CO$_3^{2-}$-doping introduced impurity levels which could narrow the energy gap of Ag$_3$PO$_4$ and enhanced its photocatalytic activity. Photoexcited electrons and holes can be efficiently separated and migrated through CO$_3^{2-}$-doped doughnut-like Ag$_3$PO$_4$. The photodegradation rate of Rh B solution still maintained 85% of its original activity after five cyclic running.

7. Summary

In this section, we systematically discussed various strategies to enhance photocatalytic performance of Ag$_3$PO$_4$, including the deposition of metals, combination with other semiconductors, and doping specific amount of elements into the lattice of Ag$_3$PO$_4$. The main purpose of these methods was to boost the separation/transition efficiency.
of photoexcited electron-hole pairs, and inhibit its recombination. These methods provide efficient ways to overcome the photo instability and improve the photocatalytic performance of Ag$_3$PO$_4$, as well as prevents the dissolution of Ag$_3$PO$_4$. Metal/Ag$_3$PO$_4$ hybrid photocatalyst provide a solid way to enhance the photoactivity of Ag$_3$PO$_4$. To date, however, most of the researches published only focused on the plasmonic effect of Ag/Ag$_3$PO$_4$ composite, other nonplasmonic metals were barely studied. We hope that researchers would put more strength in that aspect, and put forward some other metal/Ag$_3$PO$_4$ hybrid photocatalyst with high photoactivity and photoactivity for practical application. Besides, for the metal/semiconductor system, the particle size, shape, and surrounding environment has a large influence of the plasmonic bands of metal nanoparticles, which also need researchers spend time on the study of the aspect in the future.

Constructing enhanced photocatalytic performance of Ag$_3$PO$_4$ based hybrid photocatalyst usually relies on the matched band structures which improve the separation efficiency of photogenerated charge carriers, and the synergistic effects on the aspect of improved visible light absorption and reactants adsorption. Given the high cost of raw material of Ag$_3$PO$_4$, decorated small number of Ag$_3$PO$_4$ with other inexpensive materials could efficiently cut down the cost, which seems to be a promising way for the industrial application of Ag$_3$PO$_4$. However, studies of semiconductor/Ag$_3$PO$_4$ were still in its primary stage, only a few researchers have put attention on the combination of metal or semiconductor with a specific facet of Ag$_3$PO$_4$ as well as the homo-junction of Ag$_3$PO$_4$. For instance, researchers demonstrated that TiO$_2$ with well-defined $\{10\overline{1}1\}/\{00\overline{1}\}$ facet junction (p-n junction) of epitaxial interface is conducive to the separation, transfer and surface reaction of charge carriers for more efficient photocatalysis reaction [86]. This also could be an efficient way for the enhancement of photoactivity and stability of Ag$_3$PO$_4$. Recently, Xie et al. [174] constructed an Ag$_3$PO$_4$ morphological homojunction with enhanced photocatalytic activity. The Ag$_3$PO$_4$ homojunction consist of submicron spherical and rhombic dodecahedron particles, introduce an internal field between them, which facilitates the transfer of charge carriers and separation of photoinduced electron-hole pairs. However, the authors were using a simple physical combination process to synthesize the Ag$_3$PO$_4$ homojunction, a more sophisticated method and explanation for the homojunction of Ag$_3$PO$_4$ should be further studied. In addition, the structures of metal or semiconductor modified Ag$_3$PO$_4$ also is a vital parameter for the photocatalytic performance. Numerous structures were proposed to further enhance the photocatalytic activity. For instance, one-dimensional necklace-like Ag nanowires/Ag$_3$PO$_4$ cubes were fabricated by Bi et al. [175] in 2012. The authors compared the photocatalytic activity of this composite with core-shell coaxial hetero-nanowires Ag/Ag$_3$PO$_4$ and pure Ag$_3$PO$_4$ by the degradation of Rh B. The degradation results shows that the necklace-like Ag nanowires/Ag$_3$PO$_4$ cubes only need 2 min for the complete degradation of Rh B, while the core-shell coaxial hetero-nanowires Ag/Ag$_3$PO$_4$ and pure Ag$_3$PO$_4$ need 6 and 8 min, respectively. Improved photocatalytic activity could attribute to the effectively export of enriched electrons on the Ag nanowires and the remained high concentration of holes on Ag$_3$PO$_4$ cubes. The position and number of Ag$_3$PO$_4$ cubes could be easily controlled in this composite. Novel collective photocatalytic properties could be achieved by the necklace-like structure. Research on novel structure such as isolated structure, multi-segmented heterojunction structure, porous core-shell structure half core-shell stack structure of Ag$_3$PO$_4$ should not be ignored in the future studies. In addition, discussion of multiple hybrid composites should also take into consideration. For instance, Zhu et al. [176] successfully synthesized P/Ag/Ag$_2$O/Ag$_3$PO$_4$/TiO$_2$ composites. The authors declared that the photogenerated electrons of Ag$_3$PO$_4$ and Ag$_2$O in this composite could flow to the Fermi level of Ag, while the photoexcited holes of TiO$_2$ and Ag$_3$PO$_4$ could transfer to the valence band of Ag$_2$O under sunlight irradiation. In addition, the SPR effect of Ag could lead to generation of energetic electrons, and injected to the TiO$_2$ to produce superoxide anion radicals and holes for the improved photocatalytic activity of this composite. Thus, the recombination rate of electron-hole pairs was largely decreased, and the photocatalytic activity and stability were largely enhanced.

There is no doubt that doping is an efficient way for the modification of Ag$_3$PO$_4$. Doping appropriate amount of dopants into Ag$_3$PO$_4$ could efficiently affect the light absorption as well as the charge dynamics. However, there are still some shortcomings in this method. For example, it is hardly to obtain a high doping level owing to the difference of ionic radii of doped and host ions. Dopants could serve as recombination centers, and decrease the redox capability while the use of dopants is introducing electronic states under the CBM or above the VBM. It is worth mentioning that doping method like the aforementioned Ba-doped Ag$_3$PO$_4$ and CO$_2^{2−}$-doped Ag$_3$PO$_4$ represents a simple and effective way for the full-scale fabrication of photocatalysts with morphology control and elements doping. In addition, the selectivity of modified Ag$_3$PO$_4$ also needs to be taken into consideration. For instance, the CO$_2^{2−}$-doped Ag$_3$PO$_4$ could completely degrade Rh B solution within 8 min and MO within 14 min [173]. This is also important for the practical application of Ag$_3$PO$_4$. Moreover, to date, researches about element doped Ag$_3$PO$_4$ are really lacking, especially for the nonmetal doped Ag$_3$PO$_4$ and co-doping effect, which needs researchers investigated more at this side, and hopefully researchers could summarize general rules for the doping effect of Ag$_3$PO$_4$. Furthermore, combined Ag$_3$PO$_4$ with other doped materials were abundant studied in the past decade. However, combined doped Ag$_3$PO$_4$ with other materials were barely reported, which seems to be a notable aspect for the modification of Ag$_3$PO$_4$ photocatalyst.

8. Photoreactors

Another critical issue in the application of photocatalysis is the designing of photoreactors with satisfactory performances at full-scale. Undoubtedly, photocatalysis is a potential pollutant treatment technology. Subramanism et al. [177] calculated that up to 23,000 dollars could be saved by using a submerged membrane photoreactor with flux of 4000 L/m$^2$·h, and the demand for floor space of submerged membrane photoreactor is much smaller than the traditional aerobic/anaerobic ponding system. Up to now, several kinds of photoreactors have been developed, which all exhibit excellent photocatalysis performance. The first solar photoreactor designed for photocatalytic applications is parabolic trough reactor (PTR, Fig. 10A) which installed in Albuquerque (New Mexico, USA) back in 1989 which could concentrated the sunlight about 50 times on the photoreactor, and was used to treat polluted water containing chlorinated solvents and heavy metals [178,179]. Accordingly, chromium (IV) [180], dichloroacetic acid [181], phenol [182], 4-chlorophenol [183], dichlorophenol [184], pentachlorophenol [185], atrazine [183], and industrial wastewater [186] was successfully degraded by PTR. It favors mass transfer and could avoid possible photocatalyst sedimentation problems. Besides, PTR is a sealing system, and that means no evaporation of volatile compounds. However, there are certain disadvantages about this reactor. First, PTR can only make use of direct solar radiation, suggesting that it is practically useless on cloudy days. Second, the need of tracking system makes it usually expensive to install. Third, optical and quantum efficiency of PTR is low owing to the high recombination rate of electrons and holes. Last, concentrated solar radiation could make the reactor overheating, which can be problems for the efficiently photocatalytic decomposition of pollutants [187–189].

Non-concentrating reactors (NCRs, Fig. 10B) are static system without solar tracking system. The NCRs are able to capture diffuse light, which makes it more efficient compare to PTR. An experiment in Germany shows that for photosensitized cyclization of 1,1-dicarbonitrile under partly sunny or cloudy conditions confirmed this conclusion [190]. The NCRs are simpler systems, which mean that the manufacturing and maintenance cost is lower than that of PTR, makes it effective for small-scale operations [191]. However, the NCRs usually
work with laminar flow, which could cause mass transfer problems in photocatalysis and oversized floor space. In addition, the NCRs usually are open systems may lead to a highly volatile chemical and water loss by evaporation.

Compound parabolic collecting reactors (CPCRs, Fig. 10C) are stationary reactors with a parabolic reflective surface around a cylindrical reactor tube. It has both advantages of PTR and NCR. CPCR is a low concentrating system without solar tracking system, which significantly decreases the costs and complexity of this system. The reflective surface could reflect indirect light onto the reactor tubes, thus make it capture both direct and diffuse sunlight, as well as makes the reactor volumes smaller. The sanitary landfill leachate[192], olive mill waste[193], urban wastewater[194], toxic compounds such as pathogenic organisms[195], pesticides[196], chlorinated solvents[197], and biorecalcitrant compounds[198,199] could be removed from water by this photoreactor.

Except the abovementioned three photoreactors, several kinds of pilot photoreactors have been developed, which exhibit satisfactory photocatalysis performances at bench-scale. For instance, Abdel-Maksoud et al.[200] designed a tray photoreactor (Fig. 11A) based on using the sand supported TiO2 as photocatalysts for the degradation of phenol. The reactor is operated in a recirculating batch mode. The liquid could be recirculation pumped into the central vertical feeder which passes through the tray center. The inverted nozzle makes sure a radial flow of water along the tray. The tray side has 20 v-notch weirs which participate in the photocatalytic reaction. By subtly control the recirculation flow rate, formed polluted liquid film over the tray does not hinder the efficient light penetration. After the photocatalytic treatment, the liquid would fall down to the tank bottom ensuring water oxygenation, participate in the loop until it hit the water quality standards. This tray photoreactor is suitable for scale-up and commercialization owing to it modular design, integrated storage, and ease of continuous mode operation. Mosleh et al.[122] successfully applied Ag3PO4/AgBr/Ag-HKUST-1-MOF photocatalysts in a continuous flow photocatalytic rotating packed bed (Fig. 11B) for mixture dyes (methylene blue, auramine-O, and erythrosine) photodegradation under blue LED light irradiation. The degradation efficiency of these three dyes is 92.01%, 89.96%, and 89.57%, respectively. The optimum operating parameters are as follows: 75 min of irradiation time, 15 mg/L of each dye, 0.4 g/L of photocatalyst, 100 rpm of rotational speed, 0.3 L/min of solution flow rate and 25 L/min of aeration rate. The composite photocatalyst shows high stability under repeated photocatalytic reaction for 5 times. Besides, this photocatalytic reactor has less physical size and volume than conventional photocatalytic reactor because of the higher interfacial surface created by the device and highly efficient photocatalyst. The packed catalyst saves the cost of the filtration stage and avoids emission of Ag3PO4/AgBr/Ag-HKUST-1-MOF photocatalysts.
There are mainly two ways to use the photocatalysts in these reactors, i.e., using nanosized powder-like photocatalysts and using immobilized photocatalysts. The nanosized powder-like photocatalysts were often utilized in laboratory experiments, and was generally removed through precipitation or filtration methods. The reactors with dispersed photocatalysts have low pressure drop, large contact surface area for adsorption and reaction, and effective mass transfer of contaminants to nanosized powder-like photocatalysts [201]. However, the stirring of treated water and separation of nanosized powder-like catalysts from it after each run is difficult to be achieved, which greatly hinders its practical application in real-world wastewater situations. Lee et al. [202] successfully separated nanosized powder-like TiO2 photocatalysts dispersing in water by an optimal coagulant dose, proper flocculation, and sand filtration measurements. However, these methods are complicated, costly, and time consuming. For photocatalysis reaction, small particle sizes generally mean high photocatalytic activities, but smaller photocatalysts suspended in water are not easy to remove and recycle, and may permeate through filtration materials and block filter membranes. Combined Ag3PO4 with magnetic materials such as Fe3O4 [203,204], MnFe2O4 [205], and NiFe2O4 [206] appears to be an efficient way for the recycling of Ag3PO4 based composite photocatalysts. The magnetic composite could be totally separated from the solution by an extra magnetic field, which much simplified the recycle process.

For full-scale applications, immobilized photocatalysts seems to be a solution to avoid the recycle problem, but previous publications showed that the photocatalytic performance decreased significantly, as compared to the nanosized powder-like photocatalysts owing to the much smaller contact surface [207,208]. Therefore, it is vital to develop novel immobilized photocatalysts with enough photocatalytic activity for the pollutant treatment. Chen et al. [134] synthesized 3D graphene aerogels/Ag/Ag@Ag3PO4 heterstructure photocatalysts for the efficient adsorption-photocatalysis of different dyes in water. Graphene is an ideal supporting material for the construction of Ag3PO4 based composite photocatalysts. The macroscopic porous structure of 3D graphene aerogels makes it an easy and convenient recycling support for semiconductor photocatalysts. At the end of a photocatalytic cycle, workers could simply use tweezers to take out the photocatalyst, and could be employed into another photocatalytic cycle after rinsing. Zhu et al. [176] synthesized a novel P/Ag/Ag2O/Ag3PO4/TiO2 composite film on the inner-surface of glass tube for circulatory water purification and antibacterial application under solar light irradiation. The degradation rate of Rh B of this composite could reach 99.9% after 60 min, and showed no attenuation of degradation rate even after five running runs. Qu et al. [144] fabricated sandwich structural Ag3PO4 nanoparticle/polydopamine/Al2O3 porous small balls with excellent photocatalytic activity under natural irradiation. The role of polydopamine in this composite is to adhere between Al2O3 and Ag3PO4, and reduce a small part of Ag3PO4 to metallic Ag nanosphere for increased specific surface area and enhanced photocatalytic activity. The porous Al2O3 plays the role of the substrate for the Ag3PO4/Al2O3 heterojunction, and increase the specific surface area of this composite. The authors calculated the natural light intensity in an ordinary sunny day was 220 lx, which is 1/5 than that of 90 mW/cm2 Xe lamp and 1/9 than that of 180 mW/cm2 Xe lamp. In the natural irradiation, 5 ppm of MB, Rh B, and orange II could be completely degraded in 40, 60 and 30 min, respectively. Besides, the superhydrophilic surface of this composite provide an excellent antioil property, which greatly reduces secondary pollution, and a small ball structure photocatalyst is much more easy to use and recycle. In addition, membrane is a monolithic material, which is easy to recycle in aqueous solution. The photocatalytic performance of Ag3PO4 based composite photocatalyst membranes such as Ag3PO4/polyacrylonitrile composite electrospun fiber membranes [119,209,210] and multi-wall carbon nanotubes/Ag3PO4/polyacrylonitrile ternary composite fiber membranes [211] were also been studied in detail.

Compare to nanosized powder-like photocatalysts, we believe that immobilized photocatalysts are the main direction of development of photocatalysis due to it recycle capability is much better than the nanosized powder-like photocatalysts. Researchers should put more strength to create immobilized photocatalysts with high photocatalytic performance. Except the innovation of Ag3PO4-based photocatalyst, designing suitable photoreactor for the pollutant treatment also is a vital aspect that worthy of attention. Researchers should design photo reactors which suitable for the real-world situation as well as combine the characteristics of photocatalysts for better photocatalytic performance. It is interesting to note that most researchers are focused on the study of the innovation of Ag3PO4-based photocatalyst to restrain its photocorrosion, and very few researchers have to keep an eye on the rejuvenation of Ag3PO4-based photocatalyst. The photocorrosion phenomenon is inevitable for any of Ag3PO4-based photocatalyst participated photocatalytic reaction. Until now, we only know that H2O2 could served as the chemical oxidation to reinsert the Ag0 into the Ag3PO4 photocatalyst (6Ag + 3H2O2 + 2H2O2•−→2Ag3PO4 + 2H2O + 4OH −), and controlled the morphology of the regenerated photocatalyst owing to its pH variation ability which influences nucleation and growth. We hope that researchers could pay great attention to this field, and report novel rejuvenation methods for Ag3PO4-based photocatalyst.

For the better photocatalytic performance, combine photocatalysis with other pollutant treatment methods seems to be a valid way. For instance, Almomani et al. [212] proved that combining solar photocatalytic oxidation process with ozonation could significantly enhanced the removal performance of non-biodegradable pharmaceuticals, increased the degree of mineralization, reduce the chemical requirements, and reduced the demand for ozone and energy through the tested performance of a pilot plant for the treatment of wastewater containing emerging contaminates. The photogenerated electrons accumulate on the conduction band of Ag3PO4 could react with O2 and H+ to form H2O2 (0.68V vs NHE). However, the generated H2O2 can hardly be used in the photocatalysis process. Even more, at a low concentration, the H2O2 could consuming the photoinduced holes, which has been demonstrated as the main active specials in the pollutant photocatalysis process of Ag3PO4. Hence, how to turn the disadvantages into advantages of Ag3PO4 is a big challenge for researchers. Huang et al. [206] fabricated a Z-scheme-like Ag3PO4@NiFe2O4 composite photocatalyst combined photocatalysis and Fenton process for the better degradation efficiency of MO, bisphenol A and Escherichia coli. The H2O2 produced by Ag3PO4 could be catalytically decomposed into ‘-O2′ and ‘OH radicals by the NiFe2O4 nanoparticles decorated on the surface of Ag3PO4 via a photo-Fenton process (Fe3++H2O2→Fe2++O2 + H+; Fe2++3OH−→Fe(OH)3↓), and concomitantly generated H2O2 for the regeneration of Ag3PO4. The photocatalytic reaction of this composite are demonstrated to be the h+ (produced by Ag3PO4), ‘-O2′ and ‘OH radicals, and it is reasonable to conjecture that the enhanced photocatalytic activities are attributed to the conversion of H2O2 (produced by Ag3PO4) by NiFe2O4 through a photo-Fenton reaction. Combining photocatalysis with adsorption-desorption also is an interesting research direction. Generally, adsorption is a spontaneous process, while desorption usually need chemical or energy input. Using light as the energy source seems to be an ideal choice because it is finely tunable with high spatial and temporal accuracy, no transport limitations, available everywhere, no by-product, and non-invasive to the environment on demand. For example, recently, Xu et al. [213] prepared UiO-66-NH2/Ag3PO4 nanoparticle composites for the adsorption of sulfamethoxazole (SMX). The authors declared that the light-sensitive Ag3PO4 nanoparticles of the composites is benefit for the desorption of SMX due to the transformation from Ag3PO4 to Ag0. Accordingly, 200 mg/g SMX could be adsorbed by UiO-66-NH2/Ag3PO4 composites, and 134/146 mg/g SMX can be desorbed. This work opened new opportunities for adsorption-desorption of targeted organic materials using visible light. However, up to now, discussion of
deposition of Ag₃PO₄ is really rare, which need researchers pay more attention in this field.

9. Conclusions and outlook

As a photocatalyst, silver phosphate has gained tremendous attention ever since its photocatalysis application was discovered back in 2010. Without doubt, it is one of the most promising photocatalyst even though some challenges still need to be conquered for industrialization and commercialization. In this regard, it is necessary to make a comprehensive understanding of the deep mechanism of its remarkable photocatalytic performance as well as the shortcoming while using it as a photocatalyst in real-world situation. This review has discussed and summarized the recent progress in the field where Ag₃PO₄ was used as photocatalysts as well as some novel photoreactors for better photocatalytic activity. We briefly summarized the fundamental understanding of Ag₃PO₄ as photocatalyst by using computational techniques, and the difference of synthesis methods for fabricating terrific Ag₃PO₄ photocatalyst was also discussed. The obstacles that hinder its practical applications and the solutions to remove these obstacles were also presented in this review. Metal deposition could effectively suppress the photocorrosion phenomenon of Ag₃PO₄, thereby improving its photocatalytic activity, and protect it from dissolution in aqueous solution. By combining it with other materials, the composites could easily break the limitation such as limited light absorption range and high recombination rate of photogenerated charge carriers for a single component. Doping is also a feasible way to remove some obstacles that hinder the practical application of Ag₃PO₄. It could modify the surface structure, adjust the band gap energy, and influence the kinetic state of photoexcited charge carriers of Ag₃PO₄. Through subtly designing the synthetic process, we could achieve both elements doping and morphology control at the same time. However, it should be noted that not all elements doping are thermodynamically feasible. We need to put more efforts to study the feasibility of specific element doping, and the position of the dopant atoms in the lattice of host material. Excessive doping concentration could act as recombination centers, which should not be ignored. The development of photoreactors is another vital aspect for the practical application of photocatalysis. Never forget that we need highly efficient photoreactors which gear to actual circumstances to achieve the goal of practical application. In addition, the following items should be also addressed prior to practical application.

1) The mechanism of Ag₃PO₄ photocorrosion should be in-depth studied. Researchers demonstrated that metallic Ag could appear in both the synthesis process and photocatalysis process. Appropriate metallic Ag loading is conducive to its photocatalytic activity and stability. However, few researchers have discussed the exact amount of silver dissolving out from the lattice of Ag₃PO₄ in photocatalysis process. A quantizable Ag⁰ generated by photocorrosion is favorable for the evaluation of modification effect. Extensive agglomeration of Ag nanoparticles would decrease the adsorption rate and capacity of Ag₃PO₄. Besides, the loading position of Ag on the surface of Ag₃PO₄ was rarely studied. Non-uniform diameters Ag nanoparticles randomly loading is undesirable for scientific studies. These two aspects are important for the further enhancement of photocatalytic performance of Ag₃PO₄.

2) The control of morphology, particle diameter, and surface states is important for the enhancement of photocatalytic performance of Ag₃PO₄-based materials. A short distance of the charges transferred from core to surface is beneficial to the decreases in the recombination of carriers. Besides, the surface of photocatalysts is the place where photocatalytic reactions occur. Different morphology, particle diameters, and surface states show different photo-degradation capability towards pollutants. The relationship of these three factors needs to be further elaborated. In addition, synthesis methods have great influence on these factors. Thus, developing simple and green methods are needed to meet the requirements of practical application in the future.

3) Design of small amount Ag₃PO₄ loaded hybrid composite is an important subject for the practical application of Ag₃PO₄ owing to the high cost of pure Ag₃PO₄. However, there is a big controversy in distinguishing whether it is type II heterojunction or Z-scheme-like photocatalytic mechanism while the band gap of the two semiconductors are staggered. Thus, we need to develop a clear and direct technology to distinguish these two photocatalytic mechanisms. Besides, barely any researchers have studied the combination of doped Ag₃PO₄ with other semiconductor materials for the enhancement of photocatalytic performance, which we hope that some researchers would put strength to study this aspect in the future. Furthermore, theoretical simulation is a powerful technique for the design of photocatalyst, which should be abundantly using in the design stage. To experimentally prove the designed photocatalysts available is a low efficiency “try-error” methodology. Using theoretical simulation could give us a clear view whether the designed photocatalyst is theoretically feasible, and guide us to select the proper parameters for the optimal photocatalytic performance.

4) In order to turn laboratory-scale academic research into full-scale practical application to efficiently utilize solar energy as well as environmental purification, development of efficient pilot-scale treatment system is indispensable to provide useful information for further large-scale application. In addition, characteristics of Ag₃PO₄-based photocatalysts should be taken into consideration in the design of suitable photoreactors. Besides, there are mainly two ways to use the photocatalysts in reactors, i.e., using nanosized powder-like photocatalysts and using immobilized photocatalysts. Generally, nanosized powder-like Ag₃PO₄ hybrid composite photocatalyst possess higher photocatalytic activity than the immobilized ones. However, the separation of the nanosized powder-like Ag₃PO₄ hybrid composite photocatalyst in dispersion system and recycling of it is difficult, which needs further efforts to balance the superior photocatalytic activity (smaller particle size usually means higher photocatalytic activity) and recycling efficiency. We believe that an immobilized Ag₃PO₄-based photocatalyst with high photostability and photocatalytic activity is a feasible way for practical applications, which should researchers put more strength in this aspect. Besides, although some researchers have studied coupling Ag₃PO₄ with some recyclable support materials such as aerogels, magnetic materials, small balls, and membranes, further efforts to develop recyclable Ag₃PO₄ based composite photocatalysts with excellent photocatalytic performance could not be ignored. Moreover, the rejuvenation of Ag₃PO₄-based photocatalyst is of great importance for the practical application. We expect researchers could pay more attention to this aspect, and hopefully designed a self-rejuvenated Ag₃PO₄-based hybrid composite to solve the photocorrosion problem.

5) To date, most studies have only tested the photocatalytic performance of Ag₃PO₄ under ideal conditions and focused on the degradation of single pollutant such as MO, Rh B, and phenol. However, in real-world situation, the circumstance of aqueous solution is much more complicated. Researchers should put more energy to discuss the outcomes while using modified Ag₃PO₄ photocatalysts to deal with the pollutants in real wastewater. The combination of physical, chemical, and microbiological means with photocatalytic treatment are required to get a desirable level of water quality.

6) Other than the aforementioned aspect, health concern of using Ag₃PO₄ as a photocatalyst should also put into consideration. With the using of Ag₃PO₄ as a photocatalyst, it is inevitable released some of it into the environment after the photocatalytic process. In consideration of its anti-bacterial property, the risk of leak of Ag₃PO₄ in environment to flora, fauna and human being health need to be carefully assessed. However, adverse effects of released Ag₃PO₄ in
the environment are still unknown. To the best of our knowledge, no research articles have been reported in this subject, and we hope some researchers could pay attention to this problem of Ag$_3$PO$_4$ in the future.

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