1	Application of silver phosphate-based photocatalysts: Barriers and solutions
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## 44 Abstract:

45 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 46 47 environmental problems. Ag<sub>3</sub>PO<sub>4</sub> 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, 48 due to the uncontrollable photocorrosion phenomenon, the Ag<sub>3</sub>PO<sub>4</sub>-based photocatalysis is still at laboratory 49 otocatalytic performance, scale. To remove the obstacles for practical application and to further improv 50 this review summarized the achievements that have been made in this field 51 an with an effort to introduce 52 the reasons for Ag<sub>3</sub>PO<sub>4</sub> exhibiting excellent photocatalytic performance. ance. Subsequently, the different synthesis s that hindered the practical application of methods of Ag<sub>3</sub>PO<sub>4</sub> were discussed. Finally, we outlined the 53 Ag<sub>3</sub>PO<sub>4</sub> and proposed the ways to remove these barriers. This review also underlined the crucial problems that 54 should be addressed prior to practical appli 55 Keywords: Synthesis method; Barrie; Meyel deposition; Hybrid composite; Doping; Photoreactor. 56 57 58 59 60 61 62 63 64

Facing the increasingly serious environmental issues, many methods have been developed to solve these 66 67 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 68 way to take advantage of solar energy and it could be abundantly available everywhere in the world [18-24]. It 69 is undoubted that the semiconductor photocatalysis is an extremely promising technology to handle the far-70 reaching issues faced by us, e.g., the growing renewable-energy shortage crisis and environmental problems 71 [23]. The photocatalytic industry has ushered in an era of flourishing ever und 72 Sujishima and Honda [25] reported that TiO<sub>2</sub> could be used as an electrode under ultra-violet rade 73 photoelectrochemical water splitting back in 1970s. 74 Give the credit to the properties of  $TiO_2$  (e.g., electronic ture, chemical stability, and low cost), it is 75 76 unquestionable that TiO<sub>2</sub> is an extremely promising photocatalyst. However, restrained by its wide band gap ra violet irradiation, suggesting that it could only utilize energy ( $E_g = 3.23 \text{ eV}$ ), TiO<sub>2</sub> is mainly excit 77 o promote the efficiency of solar energy utilization, extending the 4% of solar energy at most [26]. 78 79 corresponding region to visa practicable solution. To achieve this goal, there are generally two ways: -li¢ One is the combination of TiO with other materials such as non-metal ions (e.g., N, C, and S) [27-29], halogen 80 [30, 31], transition metal ions (e.g., Fe, Cr, Mn, and V) [32, 33], noble metal ions [34], graphene [35-37], and 81 semiconductor (e.g., CdS-TiO<sub>2</sub> [38], CdSe-TiO<sub>2</sub> [39], Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> [40], WO<sub>3</sub>-TiO<sub>2</sub> [41], Cu<sub>2</sub>O-TiO<sub>2</sub> [42], and 82 SnO<sub>2</sub>-TiO<sub>2</sub>[43]) or doping other elements into the crystal of TiO<sub>2</sub> [44-47]; another is the development of some 83 novel semiconductor photocatalysts such as tungsten-containing photocatalyst [48], bismuth-based 84 85 photocatalyst [49, 50], g-C<sub>3</sub>N<sub>4</sub> [51], and Ag<sub>3</sub>PO<sub>4</sub> [52]. Among them, Ag<sub>3</sub>PO<sub>4</sub> was demonstrated to have a superior performance in the field of oxygen rate and dye degradation. Thus, Ag<sub>3</sub>PO<sub>4</sub> has attracted great attention 86

ever since Ye and co-workers [52] discovered its photocatalytic application in 2010.

Ag<sub>3</sub>PO<sub>4</sub> is a photocatalyst which can be excited by visible light. Its band gap energy is approximately 2.43 88 89 eV [52]. Generally, pure Ag<sub>3</sub>PO<sub>4</sub> photocatalyst could absorb solar energy with a wavelength shorter than 530 nm. The valence band of  $Ag_3PO_4$  is approximately +2.9 V vs. normal hydrogen electrode (NHE, pH = 0), 90 91 suggesting that it possesses strong oxidizing property. Moreover, quantum efficiency of Ag<sub>3</sub>PO<sub>4</sub> could reach approximately 90% in water oxidation (while using AgNO<sub>3</sub> as scavenger). This is greater than the widely known 92 photocatalysts such as N-doped TiO<sub>2</sub> and BiVO<sub>4</sub> [52]. Ag<sub>3</sub>PO<sub>4</sub> could serve as an efficient photocatalyst for the 93 treatment of environmental contaminants, such as phenol and phenol derivatives [ 94 **6**], humic acid [57], Cr(VI) [58], dyes [15, 59, 60], endocrine disrupting compounds [61], pharmaced 95 d personal care products [21, 62-64]. Despite these benefits, practical application of Ag<sub>3</sub>PO<sub>4</sub>-b d photocatalysis has not been achieved to 96 date, due to several key barriers such as the high cost of taw enals, the slightly soluble in water, and the 97 self-photocorrosion phenomenon [65, 66]. Herein, 98 this review, we aim to offer a systematically to remove the obstacles that impede the practical summarization and reasonable suggestion 99 application of Ag<sub>3</sub>PO<sub>4</sub> in a full-scale s uatio 100

# 101 2. Why does Ag<sub>3</sub>PO<sub>4</sub> show excellen photocatalytic performances?

The crystal structure of  $A_{3}PO_{4}$  is a body-centered cubic (BBC) which is composed of several isolated, regular PO<sub>4</sub> tetrahedral unit cells, with its P-O bonds distance being about 1.539 Å. The space group of Ag<sub>3</sub>PO<sub>4</sub> is P4-3n with a lattice parameter of approximately 6.004 Å (inset of Figure 1). The location of its valence band is much lower than the O<sub>2</sub>/H<sub>2</sub>O potential (+1.23 V vs. NHE), meaning that it has extraordinary oxidation capability (Figure 1). Owing to the position of the conduction band of Ag<sub>3</sub>PO<sub>4</sub> (+0.45 V vs. NHE, pH = 0), the photogenerated electrons would be more likely to react with oxygen to produce H<sub>2</sub>O<sub>2</sub> (2e<sup>-</sup> + 2H<sup>+</sup> + O<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O<sub>2</sub>) instead of producing O<sub>2</sub><sup>-</sup> or HO<sub>2</sub><sup>-</sup> active oxygen species. In the mean time, photogenerated holes would directly

participate in the oxidation reaction (pollutant +  $h^+ \rightarrow CO_2 + H_2O$  + other products;  $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ ) 109 despite of the valence band of Ag<sub>3</sub>PO<sub>4</sub> is positive enough to react with H<sub>2</sub>O to produce OH. Direct hole 110 111 oxidation is overmatched the traditional free radical oxidation. According to Fu et al. [67], although the potential of holes generated by Bi<sub>2</sub>WO<sub>6</sub> is insufficient to form OH radicals, Bi<sub>2</sub>WO<sub>6</sub> still is able to dechlorine of 4-112 113 chlorophenol, to oxidize CHCl<sub>3</sub> and CH<sub>3</sub>CHO [68], or to split water for oxygen evolution [69]. Ag<sub>3</sub>PO<sub>4</sub> has strong oxidation capability and high thermal stability. For instance, Teng et al. [65] announced that Rh B could 114 be thoroughly degraded by Ag<sub>3</sub>PO<sub>4</sub> polypods after 36 h under natural indoor weak light irradiation, while only 115 18% for N-doped TiO<sub>2</sub> after 120 h under the same condition. Zhang et al. [70] dee 116 ed that Ag<sub>3</sub>PO<sub>4</sub> could keep a good structure and thermal stability below 540 °C, and Ag<sub>3</sub>PO<sub>4</sub> same 117 annealing process (100 and 400 °C) shows better photocatalytic activity to Rh B than that f Ag<sub>3</sub>PO<sub>4</sub> samples without sintering. The 118 structure of Ag<sub>3</sub>PO<sub>4</sub> still remains even after sintering at 400 min, and only a few thin Ag nanoparticles 119 °C





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12	2

Figure 1. Schematic diagram of photocatalytic redox process of Ag<sub>3</sub>PO<sub>4</sub>. Inset: ball and stick

123 configuration of  $Ag_3PO_4$  (the inset is cited from ref. [71]).

124 Plenty of researchers have demonstrated that Ag<sub>3</sub>PO<sub>4</sub> exhibited extremely high photocatalytic capability in

both oxygen production by water splitting and photodegradation of organic contaminant. To understand why

Ag<sub>3</sub>PO<sub>4</sub> shows an outstanding photocatalytic performance, we briefly summarized the articles available, and 126 attributed the outperformed photocatalytic activities of Ag<sub>3</sub>PO<sub>4</sub> to the following reasons. First, the constitution 127 128 and distribution of the conduction band minimum (CBM) of  $Ag_3PO_4$  are useful to the electron transfer [72]. The 129 formation of a rigid tetrahedral unit of PO<sub>4</sub> makes the CBM mainly be constituted by Ag s states in Ag<sub>3</sub>PO<sub>4</sub> as 130 well as a fully occupied d state in the valence band maximum (VBM). The CBM of Ag<sub>3</sub>PO<sub>4</sub> is well dispersed without the so-called "contaminant" of d states, which decreased the effective mass of electrons of Ag<sub>3</sub>PO<sub>4</sub>, and 131 favors its transfer (Figure 2). Besides, Ag<sub>3</sub>PO<sub>4</sub> has a very isotropic distribution of CBM, which makes the chance 132 of meeting photoinduced holes decreases compare to the semiconductors with an opic distribution. Second, 133 the inductive effect of PO<sub>4</sub><sup>3-</sup> is favors for the separation of electron-hole 134 ]. The large electron clouds overlapping of PO<sub>4</sub><sup>3-</sup> ions makes it more likely to draw hole and reject electrons, which reduced the 135 photocatalytic activity. Third, native defects recombination of photogenerated charge carriers, and enhanced 136 such as Ag vacancies are favorable for the photocatalytic crivity [73]. Ag vacancies are inevitably yield due to 137 cceptor (since the outer electron of Ag atoms is easier to the photocorrosion of Ag<sub>3</sub>PO<sub>4</sub>. It behaves a 138 s a figh concentration in Ag<sub>3</sub>PO<sub>4</sub>. By acting as capture traps for escape than that of P atoms) and h 139 140 photogenerated holes, it can recombination of charge carriers, thus promoting the photocatalytic nhi capability of Ag<sub>3</sub>PO<sub>4</sub>. In brief the excellent photocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub> could be credited to the 141 separation efficiency of photogenerated electron-hole pairs. Besides, there might be some other reasons for 142 superb photocatalytic capacity of Ag<sub>3</sub>PO<sub>4</sub> that have not been identified yet, and further work requires to be 143 144 carried in the future. out



Method	Morphology	Synthesis procedure	Experimental conditions	Photocatalytic activity	Ref.
Ion-exchange method	1D hollow porous microrod	Under vigorous magnetic stirring, 0.01 M Na <sub>2</sub> WO <sub>4</sub> aqueous solution was added into 0.05 g AgNO <sub>3</sub> aqueous solution, then 0.05 M Na <sub>2</sub> HPO <sub>4</sub> aqueous solution was added drop by drop into the above solution.	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.	Rh B was completely degrade within 60 s; MO was completely degrade in 60 s.	[74]
	porous nanotube	40 mL 0.05 M NaHCO <sub>3</sub> was added slowly into 1 mmol AgNO <sub>3</sub> 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 0.13 mmol Na HPQ4 solution drop by drop(5 s/d) into the above solution under sig room stirring for 3 h, collect the precipitates and dried at 60°C.	30 mg photocatallyts were added into 50 mL Rh B (N0 mg/L) and phenol 20 mg/L) solution, p spectively.	Rh B was completely degrade in 8 min;87% phenol was degrade in 80 min.	[80]
Precipitation method	particle	Under magnetic stirring at room temperature, an appropriate amount of $Ca_{10}(PO_4)_6(OH)_2$ were added into AgNO <sub>3</sub> solution (the Ag/P atomic ratio was 3.0).	0.02 g photocatalysts were added into 10 mg/L HA solution. Light source: 300 W Xe lamp	95% DOC was removed after 2 h.	[57]

Table 1. The synthesized parameters of Ag<sub>3</sub>PO<sub>4</sub> with different preparation methods

	cubic enclosed completely by six perfect {100} facets	0.1 M ammonia aqueous solution was added drop by drop into 0.2 g AgNO <sub>3</sub> aqueous solution to form a transparent solution, then added 0.15 M Na <sub>2</sub> HPO <sub>4</sub> aqueous solution into the above solution.	0.2 g photocatalysts were added into 100 mL 8 mg/L MB solution. Light source: 300 W Xe lamp.	MB was completely degrade in 3 min.	[78]
	rhombic dodecahedral	0.15 M Na <sub>2</sub> HPO <sub>4</sub> aqueous solution was added drop by drop into 0.2 g CH <sub>3</sub> COOAg aqueous solution.	0.2 g photocatalysts were added into MO and Rh B solution, respectively. Light source: 500 W Xe an Jano	MO was completely degrade in 4 min; Rh B was completely degrade within 4 min.	[79]
Hydrothermal method	tetrapod	2.5 mmol AgNO <sub>3</sub> were added in 3 mmol 85% H <sub>3</sub> PO <sub>4</sub> aqueous solution, then added 37.5 mmol urea into the above solution. Transferred the resulting preducers into a Teflon-line stabless steel automate and montained at 80 °C for 24	0.1 g protocatalysts werendded into 1.0 rL 8 mg/L Rh h solution. Light source: 300 W Xe arc lamp.	98% Rh B was degrade after 18 min.	[75]
	P				

	irregularly spherical	0.25 M Na <sub>3</sub> PO <sub>4</sub> solution was added into 0.75 M AgNO <sub>3</sub> solution with vigorous stirring for 10 min, and adjust the pH value by 1 M H <sub>3</sub> PO <sub>4</sub> 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, 0.00375 M for AgNO <sub>3</sub> ), and reaction time (2 h, 6 h, 12 h, 24 b)	0.15 g photocatalysts were added into 180 mL 0.02 M AgNO <sub>3</sub> solution, and purged with helium gas to eliminate air before light irradiation. Kept the temperature of the system around 30 °C by thermostatic circulating wher. Light sourth: 500 W Xe at lan o	The initial rate of $O_2$ evolution determined to be 1156 µmolg <sup>-1</sup> h <sup>-1</sup> and apparent quantum yield at 420 nm amounted to 3.69%.	[81]
Colloidal method	colloidal	0.02 M AgNo3 there added into 0.02 M Na <sub>2</sub> HPD <sub>4</sub> aqueous solution, and collect the analyst and dried at 700C for 12 h.	0.125 g photocatalysts were added into 125 mL EY (0.042mM) and MB (0.05mM) solution, respectively. Light source: 500 W halogen linear lamp.	EY was completely degrade after 10 min; 90% MB was degrade after 15 min.	[76]
Heteroepitaxial growth	concave trisoctahedral	Ammonia solution was added into 0.2 g AgNO <sub>3</sub> aqueous solution, then, the Au@Ag nanorods with high aspect ratio and 0.15 M Na <sub>2</sub> HPO <sub>4</sub> aqueous solution was added in order.	0.2 g photocatalysts were added in 100 mL 8 mg/L Rh B solution. Light source: 300 W Xe arc lamp.	Rh B was completely degrade within 3 min.	[77]

159 Note: Rh B (rhodamine B); MO (methyl orange); PVP (poly vinyl pyrrolidone); HA (humic acid); dissolved

160 organic carbon (DOC); EY (Eosin Y); MB (methylene blue).

#### 161 **3.1 Ion-exchange method**

162 Ion-exchange method is the mostly used method for the fabrication of Ag<sub>3</sub>PO<sub>4</sub>. It takes advantage of the different solubility of raw materials such as AgM and NPO<sub>4</sub> (M and N are the ions or ionic group except for 163 Ag<sup>+</sup> and PO<sub>4</sub><sup>3-</sup>, respectively), to replace M<sup>-</sup> or N<sup>3+</sup> by PO<sub>4</sub><sup>3-</sup> or Ag<sup>+</sup>, thereby forming Ag<sub>3</sub>PO<sub>4</sub> particles. The 164 operation condition is simple, and the cost is low. It synthesizes  $Ag_3PO_4$  samples at room temperature without 165 special equipment. The choice of raw material is the key technology in this method. Yu et al. [74] recently 166 synthesized a one-dimensional Ag<sub>3</sub>PO<sub>4</sub> hollow microrods with extremely high pb catalytic performance and 167 self-stability through anion exchange method. Ag<sub>2</sub>WO<sub>4</sub> was utilized as 168 sources instead of AgNO<sub>3</sub> or CH<sub>3</sub>COOAg. Ag<sub>3</sub>PO<sub>4</sub> has lower solubility compared to Ag<sub>2</sub>WO and thus Ag<sub>2</sub>WO<sub>4</sub> could react with HPO<sub>4</sub><sup>2-</sup> 169 ions to form Ag<sub>3</sub>PO<sub>4</sub> in a thermodynamically favored direct on in this reaction procedure, the released Ag<sup>+</sup> ions 170 are really close to the Ag<sub>2</sub>WO<sub>4</sub>. The inward HPO<sub>4</sub><sup>2-</sup> is some compare to the outward Ag<sup>+</sup>, which favors the 171 ned Ag<sub>3</sub>PO<sub>4</sub> has perfect and regular 1D structure with 2 formation of a hollow interior (Figure 3). T 172 μm in diameter and 2 μm in length, which is similar to the Ag<sub>2</sub>WO<sub>4</sub> microrods precursor. The Ag<sub>3</sub>PO<sub>4</sub> samples 173 botc legrade Rh B within 60 s and MO in 60 s, whilst spherical particles as synthesized could thoroughly 174 needed 14 min and 28 min, respectively. In addition, the 5-cycle run test demonstrated that this structure could 175 serve as a viable way to enhance the stability of Ag<sub>3</sub>PO<sub>4</sub>. 176



 $3Ag_2WO_4 + 2HPO_4^{2-} = 2Ag_3PO_4 + H_2WO_4 + WO_4^{2-}$ 

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**Figure 3.** Schematic illustration of the ion exchange method: the transfer of Ag<sub>2</sub>WO<sub>4</sub> solid microrod to

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Ag<sub>3</sub>PO<sub>4</sub> porous hollow microrod (adapted from ref. [74]).

## 180 **3.2 Precipitation method**

The precipitation method is also frequently used for Ag<sub>3</sub>PO<sub>4</sub> fabrication. Keisuke et al. [57] demonstrated 181 182 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 183 and crystalline size) are almost the same, it was calculated that the specific surface area of the synthesized 184 Ag<sub>3</sub>PO<sub>4</sub> fabricated through precipitation method is nearly 7 times larger than t through the ion-exchange 185 method (8.7  $m^2/g$  and 1.2  $m^2/g$  for precipitation method prepared 186 exchange method prepared, respectively). In addition, the particle size of the former one is man v centered on  $0.3 \sim 0.4 \,\mu\text{m}$ , while the latter 187 one is predominantly ranging from 6 to 10  $\mu$ m. It was report d t t the Ag<sub>3</sub>PO<sub>4</sub> samples prepared by precipitation 188 method showed 95% DOC removal rate for humic act degradation after 2 h visible light ( $\lambda = 451$  nm) 189 irradiation. 190

# 191 **3.3 Hydrothermal method**

Using hydrothermal met e Ag<sub>3</sub>PO<sub>4</sub> photocatalyst is also a noteworthy approach. Hydrothermal 192 method is utilizing the chemical reaction between the reagents at a particular temperature and pressure [82-84]. 193 Owing to the specific condition of this method, it could replace solid-phase reaction, which is difficult to occur. 194 By controlling the basic synthesis parameter such as hydrothermal temperature and intensity of pressure, 195 Ag<sub>3</sub>PO<sub>4</sub> products with few defects, good direction, regular morphology, and high purity could be obtained [75, 196 81, 85, 86]. The products have superior crystalline and the size is easy to control. Meanwhile, this method is 197 198 beneficial to the generation of intermediate and special valence state compounds, and could equably realize the doping process, because the atmosphere of surronding under hydrothermal condition is liable to control. Wang 199

et al. [75] first used this method with the assistance of urea to prepare a highly uniformed Ag<sub>3</sub>PO<sub>4</sub> with tetrapod 200 morphology at 2012. Production of tetrapod Ag<sub>3</sub>PO<sub>4</sub> undergoes three steps. (i) precipitation process: the addition 201 202 of urea could neutralize the phosphoric acid to form  $H_2PO_4^-$  to react with Ag<sup>+</sup> produce A<sub>g3</sub>PO<sub>4</sub> microrod; (ii) the 203 dissolution process: with the reaction time increase, microrod Ag<sub>3</sub>PO<sub>4</sub> would dissolve by the ammonia released 204 from urea hydrolysis; (iii) recrystallization process; through the reaction between dissolved Ag( $NH_{3}$ )<sub>2</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>, the tetrapod Ag<sub>3</sub>PO<sub>4</sub> was shaped up. The uniform tetrapod Ag<sub>3</sub>PO<sub>4</sub> possess four cylindrical microrods arms 205 grow along the [110] direction with an average diameter of 5  $\mu$ m and a length of 15-30  $\mu$ m, and its specific 206 surface areas is 38.0 m<sup>2</sup>/g. The degradation rate of Rh B by as-obtained Ag<sub>3</sub>PC 207 eles was more than 2 times higher than the Ag<sub>3</sub>PO<sub>4</sub> samples prepared by ion-exchange method. Re 208 onditions have been of great influence on the morphology and facets of as-prepared samples. Finistance, Cui et al. [87] have discussed the 209 effect of temperature in hydrothermal synthesis procedure rO<sub>4</sub>. The authors found out that with the 210 temperature increased from 20 °C to 120 °C, the intensity of (110) peaks becomes sharper and stronger, which 211 Generally, more exposed {110} facets means higher means an increased ratio of exposed {1 212 photocatalytic activity of Ag<sub>3</sub>PO<sub>4</sub>, which is onducive to the photocatalytic performance. 213

214 **3.4 Other methods** 

Apart from the three methods discussed above, there are still several approaches to prepare the  $Ag_3PO_4$ photocatalyst. For example, Khan et al. [76] synthesized highly active  $Ag_3PO_4$  by the colloidal method. According to their reports, the prepared sample was uniformly spherical-like, and homogeneously in distribution compared to the samples fabricated by precipitation method. The colloidal method created a less concentrated surrounding compared to the precipitation method. In the colloidal method, the reaction limited aggregation played a dominant role, and the cluster-cluster repulsion phenomenon could be conquered by thermal activation process. In precipitation method process (concentrated environment), however, diffusion-limited aggregation

results within a short time and the clusters are easier to get close. Samples prepared by colloidal method show 222 2.6 times higher photocatalytic capacity than that prepared by precipitation method under the same conditions. 223 224 Surface of photocatalysts is the place where photocatalytic reaction occurred. The more reactive surface, the 225 higher the surface energy. Hence, the facet of  $Ag_3PO_4$  should also be taken into consideration in the synthesis procedure. Jiao et al. [77] firstly fabricated a concave trisoctahedral Ag<sub>3</sub>PO<sub>4</sub> microcrystals surrounded by {221} 226 and {332} facets through heteroepitaxial growth method. Compared with low-index facets, high-index facets 227 usually equipped with extraordinary density of atomic steps, ledges, kinks, dangling bonds, and higher chemical 228 reaction activities [88]. The samples prepared by this method could thoroughly move Rh B within 3 min, 229 which is extremely higher than N-doped TiO<sub>2</sub>. However, stability of Ag high-index facets remains is 230 a problem, which needs further research to remove this roadblo 231

## 232 3.5 Facet control

 $\mathbf{PO}_4$  (i.e., {100}, {110}, and {111}), which show 233 There are generally three low-index facets of A tter stability compared to high-index facets. The main comparable photocatalytic performance bu 234 difference between these three low-index facts of Ag<sub>3</sub>PO<sub>4</sub> is the surface states such as the concentration of Ag<sup>+</sup> 235 cancies, and the concentration of dangling phosphorus-oxygen bonds. 236 cations, the concentration For {100} facets, the proportion of P atoms and  $Ag^+$  cations is 1:2, without any  $O^{2-}$  anions in the planes. The 237 enriched Ag<sup>+</sup> cations could be converted to Ag by the photoexcited electrons, which could enhance the 238 separation of photogenerated carries, thereby improving their photocatalytic performance [78]. Additionally, 239 240 the  $\{100\}$  facets of Ag<sub>3</sub>PO<sub>4</sub> possess a metal-like electronic property, which might be conducive to the promoted harvesting efficiency of photons. Compare to {100} facets, regular rhombic dodecahedral shaped {110} facets 241 242 Ag<sub>3</sub>PO<sub>4</sub> 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 {110} planes contained threefold-243

coordinated with one dangling bond and two-coordinated with two dangling bonds, whilst in the {100} planes, 244 245 all the Ag atoms were coordinative saturated, which explained the reason for {110} facets exhibiting the higher 246 reactivity than the {100} facets. As for tetrahedron Ag<sub>3</sub>PO<sub>4</sub> with {111} facets, the planes consisted of overabundance of dangling phosphorus-oxygen bonds, which could act as oxidation sites for a better reactivity. 247 Besides, the hole mass along [111] is smaller than other directions in Ag<sub>3</sub>PO<sub>4</sub> crystals [89]. That would improve 248 the hole mobility of the tetrahedrons samples, and enhance the separation efficiency, thus improving the 249 photocatalytic activity. It is generally recognized that Ag<sub>3</sub>PO<sub>4</sub> exposed with one more of these three facets have 250 great photocatalytic activity, and tetrahedral Ag<sub>3</sub>PO<sub>4</sub> with exposed {111] 251 more photocatalytically active than rhombic dodecahedrals with {110} facets and cubes with {1 252 . However. Hsieh et al. [90] demonstrate that there might be controversies about this recognition. The authors tested the photodecomposition 253 capability of MO solution of Ag<sub>3</sub>PO<sub>4</sub> with different morpholog cubes, rhombic dodecahedra and tetrahedrons). 254 Interestingly, the results show that the Ag<sub>3</sub>PO<sub>4</sub> cubes show the best photodecomposition capability of MO, 255 of that, and Ag<sub>3</sub>PO<sub>4</sub> tetrahedrons are completely inactive Ag<sub>3</sub>PO<sub>4</sub> rhombic dodecahedra shows a little 256 onclude that this is because {111} surface have the highest barrier for after 90 min of reaction. The authors 257 e most steep upward band bending among these three facets), hence there 258 electron transport to the sur may no photogenerated electrons and holes arrived in the {111} faces of Ag<sub>3</sub>PO<sub>4</sub> to participate in the 259 photocatalysis. On the contrary, {100} facet have the least degree of upward band bending, which indicate its 260 have the best electron transmission capacity among these three facets, and the upward bending degree of {110} 261 262 facet is between {111} and {100} facet, signify less efficiency of photogenerated electron transfer than that of {100} facet. In addition, Kim et al. [91] exhibit that tetrahedron Ag<sub>3</sub>PO<sub>4</sub> have the fastest oxidation capability of 263 264 amplex red compare to  $Ag_3PO_4$  with mixed facet and cube. The authors state that this is owing to the {100} facets have coordinatively saturated Ag atoms, whereas the Ag atoms on {111} facets are located at three-265

coordinated sites with one dangling bond. Once the  $[Ag_2 = O - Ag]_{surface}$  combined with h<sup>+</sup>, the (111) surface would be less stable than that of (100) surface, leading to higher recombination rate of photoexcited electrons and holes. To date, there was no consistent recognition of which the crystal structure of Ag<sub>3</sub>PO<sub>4</sub> is better for the photocatalytic degradation of pollutants or water splitting, which need researchers put more strength in this aspect in the future study.

## 271 3.6 Summary

The synthesis method plays a significant role in determining the morphology of photocatalysts and its 272 photocatalytic performance. The growth procedure of Ag<sub>3</sub>PO<sub>4</sub> was largely th the Ag<sup>+</sup> source in ion-273 exchange method, while in precipitation method was dependent on the P 274 unce. Thus, the selection of raw material in these methods needs to be carefully considered. As for hydrothermal method, the temperature and 275 n mat hydrothermal method could generate time are the key factors that affect the products. It is we key 276 materials with high crystallinity, few defects, and regular d morphology [84]. However, the particle size of as-277 obtained samples was larger than that of pr om temperature, the surface area could greatly decrease 278 at hydrothermal temperature, and the yield of this method is quite low. Besides, the operation sequence of this 279 hat f other two methods. In this section, we only briefly introduced some 280 method is more complicated than specific features of these methods. In the synthesis process, other influential factors such as the additives and 281 pH should be also taken into consideration. For instance, Sulaeman et al. [92] proved that the content of ethanol 282 as the solvent could influence the Ag/P atomic ratio of Ag<sub>3</sub>PO<sub>4</sub>, thus influence the formation of Ag vacancies 283 on the surface of  $Ag_3PO_4$ . Hsieh et al. [90] confirmed that the formation of  $[Ag(NH_3)_2]^+$  complex has great 284 influence for morphology precipitation 285 the control of method. The molar ratio of 286 NH<sub>4</sub>NO<sub>3</sub>/NaOH/AgNO<sub>3</sub>/K<sub>2</sub>HPO<sub>4</sub> was controlled at 2 : 1.8 : 1 : 2 in a sequence adding order to synthesis Ag<sub>3</sub>PO<sub>4</sub> cubes. By adjusting the molar ratio of NH<sub>4</sub>NO<sub>4</sub> and AgNO<sub>3</sub>, the authors successfully fabricate Ag<sub>3</sub>PO<sub>4</sub> particles 287

with different morphology (e.g., rhombic dodecahedra, {100}-truncated rhombic dodecahedra, tetrahedra, and 288 tetrapods). Forming  $[Ag(NH_3)_2]^+$  complexes before adding phosphate could strikingly reduce the driving force 289 290 toward Ag<sub>3</sub>PO<sub>4</sub> production, thus efficiently controlled the shape of products. Besides, different morphology of Ag<sub>3</sub>PO<sub>4</sub> also was a significant parameter for the photocatalytic activity needs to carefully considered. The porous 291 292 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 293 carefully take all these influence parameters into consideration, choose a specific method for a specific purpose. 294 In addition, researchers also should make unremitting efforts to develop simple 295 green synthesis methods for the full-scale fabrication of Ag<sub>3</sub>PO<sub>4</sub> photocatalyst with high photocata 296 formance in the future.

## 297 4. What hinder the practical application of Ag<sub>3</sub>PO<sub>4</sub>?

Ag<sub>3</sub>PO<sub>4</sub> is an excellent photocatalyst because it ca ited by visible light and possess strong 298 photooxidation capability. However, to date, application £Ag<sub>3</sub>PO<sub>4</sub> in treating organic pollutants in real-world 299 want to know what hinders the practical application of scenarios has not yet been achieved. Thus 300 Ag<sub>3</sub>PO<sub>4</sub>. There are indeed several bariers that need to be removed. One big challenge is the severe self-301 is cyclic utilization. The photocorrosion phenomenon gives rise to a uts) 302 photocorrosion, which strend series of severe issues. Firstly, in large-scale applications, consumption of bare Ag<sub>3</sub>PO<sub>4</sub> photocatalyst is high 303 because silver is a noble metal. Price of TiO<sub>2</sub> (CODE # 51026962. Sinopharm Chemical Reagent Co., Ltd.) is 304 almost ¥3.75 per gram. However, the price of AgNO<sub>3</sub> (CODE # 81012360. Sinopharm Chemical Reagent Co., 305 Ltd.) is approximately 10.24 per gram, which means that the price of Ag<sub>3</sub>PO<sub>4</sub> is 30.72 per gram at least 306 (without considering the cost of  $PO_4^{3-}$  source and other additives), which is 8 times more expensive than TiO<sub>2</sub> 307 (CODE # 51026962. Sinopharm Chemical Reagent Co., Ltd.). That makes using bare Ag<sub>3</sub>PO<sub>4</sub> as photocatalyst 308 for water purification impracticable. Secondly,  $Ag_3PO_4$  is slightly soluble in water (Ksp = 1.6 \* 10<sup>-16</sup>), and 309

dissolved in nitric acid or ammonia solution, thus its reclamation in real-world situation is difficult. Lastly, the 310 photogenerated electrons under light irradiation could be absorbed by the Ag<sup>+</sup> released from Ag<sub>3</sub>PO<sub>4</sub>, and 311 consequently reduced to metallic silver, which would deposit on the surface of  $Ag_3PO_4$  ( $4Ag_3PO_4 + 6H_2O +$ 312  $12h^+ + 12e^- \rightarrow 12Ag + 4H_3PO_4 + 3O_2$ ). This is owing to the position of conduction band of Ag<sub>3</sub>PO<sub>4</sub> is +0.45 V, 313 314 which is much more positive than the potential of  $H_2O/H_2$  and more negative than that of Ag/Ag<sup>+</sup>, thus the photoinduced electrons would be adopted by Ag<sup>+</sup> released from the lattice of Ag<sub>3</sub>PO<sub>4</sub> instead of H<sub>2</sub>O if there 315 were no scavengers exist. As a result, the structure of  $Ag_3PO_4$  could be destroyed, and thus the photocatalytic 316 activity would decrease after several photocatalysis reactions, which greatly ind 317 d its practical application. According to the high-resolution Ag 3d XPS spectra of pure Ag<sub>3</sub>PO<sub>4</sub> 318 run of degradation of Rh B (Figure 4), Chang et al. [66] calculated that more than 27% of mallic Ag would be formed on the surface of 319 ed by Ag<sub>3</sub>PO<sub>4</sub> within 4 min under Xe lamp Ag<sub>3</sub>PO<sub>4</sub>. Teng et al. [65] reported that Rh B was completel ( dr 320 irradiation. After three cyclic experiments, however, only 34% of Rh B was degraded under the same situation. 321



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- 323
- Figure 4. The high-resolution Ag 3d XPS spectra of pure Ag<sub>3</sub>PO<sub>4</sub> after one run of degradation of Rh B
- 324

(cited from ref. [66]).

- 325 5. How to remove these barriers?
- 326 **5.1 Surface modification**

#### 5.1.1 Plasmonic effect

328 Metal deposition is a commonly used method for the enhancement of photocatalytic performance. There 329 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 330 331 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 332 matched work functions and were stuck together intimately, a metal-semiconductor Schottky junction was 333 formed, which can facilitate the separation of electron-hole pairs for charge th etween these components 334 [93, 94]. However, improved separation efficiency was cost of the re-335 ty of carriers. Owing to the difference of Fermi levels of metal and the conduction band of ne semiconductor or valence band of p-type 336 semiconductor, the energy of carriers was inevitably lost dur the transfer process from semiconductor to 337 metal [95]. Normally, the plasmonic metals were defined as Au, Ag and Cu, and the others were generally 338 tic research field [95]. The localized surface plasmon considered as non-plasmonic metals in the 339 resonance (LSPR) effects could result in collective oscillation of the free electrons, which can induce strong 340 ner y, hence enhancing the absorption and photocatalytic performances of 341 absorption of the electrom etic the semiconductor [96]. For netal/Ag<sub>3</sub>PO<sub>4</sub> composites, generally, the electrons would flow into metal from 342 Ag<sub>3</sub>PO<sub>4</sub> crystal until it came to the equilibrium of the two systems and formed a new Fermi level as long as the 343 heterostructures were formed. Meanwhile, bands of Ag<sub>3</sub>PO<sub>4</sub> bend upward to the surface and an internal electric 344 345 field directed from Ag<sub>3</sub>PO<sub>4</sub> to metal were established. The electrons would accumulate on the metal instead of the surface of  $Ag_3PO_4$ , thereby mitigating its photocorrosion. These electrons could merge with the trapped 346 347 surface oxygen molecules to generate  $O_2$ : reactive species for photooxidation reaction. Moreover, insoluble metal deposited on Ag<sub>3</sub>PO<sub>4</sub> could guard the Ag<sub>3</sub>PO<sub>4</sub> from dissolution in aqueous solution. 348

Ag nanoparticles could be generated in both production and photocatalysis processes. In Ag/Ag<sub>3</sub>PO<sub>4</sub> 349 composites system, the photogenerated electrons would be transferred to Ag, and the holes remain on the 350 Ag<sub>3</sub>PO<sub>4</sub> lattice surface during the irradiation, owing to the existence of PO<sub>4</sub><sup>3-</sup> ions, thereby boosting the 351 separation efficiency of photoexcited electron/hole pairs and achieving high stability [97]. The main function 352 353 of Ag in this system is to accelerate the transfer of photoexcited electrons from Ag<sub>3</sub>PO<sub>4</sub> conduction band to the Ag nanoparticles and forming  $O_2^-$  or  $O_2^-$  reactive species by trapping  $O_2$  and  $H_2O$  for degradation of organic 354 contaminants [98]. Ag/Ag<sub>3</sub>PO<sub>4</sub> showed a more efficient and stable photocatalytic performance compared to pure 355 Ag<sub>3</sub>PO<sub>4</sub> even after five cycles [99]. The XRD patterns of Ag/Ag<sub>3</sub>PO<sub>4</sub> ycling photodegradation 356 experiments (Figure 5) showed that the change of the phase structure 357 preciable (the content of Ag nanoparticles were 5.73% and 5.84% before and after cycling expe ments), and no more Ag nanoparticles were 358 generated. The reduction ability of Ag<sub>3</sub>PO<sub>4</sub> could also be p om by Ag deposition. Patil et al. [100] reported 359 that Ag/Ag<sub>3</sub>PO<sub>4</sub> glass nanocomposites could be used for H<sub>2</sub> production from H<sub>2</sub>S, with maximum H<sub>2</sub> output 360 being 3920.4 µmol·h<sup>-1</sup> g<sup>-1</sup>. The overvoltage of Ag metal is -0.22 V vs. NHE, which is more negative 361 compared to pristine Ag<sub>3</sub>PO<sub>4</sub> (+0.285 V vs NHE), which makes the H<sub>2</sub> yield over Ag seems profitable and 362 provite system, the stability issue was still not fully solved, because some 363 reasonable. However, in st photogenerated electrons inevtably stayed in the conduction band of Ag<sub>3</sub>PO<sub>4</sub>, which could reduce Ag<sup>+</sup> of 364 Ag<sub>3</sub>PO<sub>4</sub> to form metallic Ag. 365



radical. Besides, photoexcited electrons in the conduction band of  $Ag_3PO_4$  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  $O_2^-$  and h<sup>+</sup> radicals. In addition, under a 300 W Xe lamp with a cutoff light filter of 645 nm, the as-prepared Au/Ag<sub>3</sub>PO<sub>4</sub> samples still show efficient degradation rate of Rh B, which further verified the light absorption range is amplified to 800 nm.

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## 386 **5.1.2 Constructing multiple semiconductor composites heterojunction**

Coupling semiconductor with other is a valid way for the enhancement of photocatalytic performance. The 387 hybrid photocatalysts may have complementary features and have optimal perform es than single component. 388 The separation and transportation of photogenerated charges could be imp 389 d semiconductors with larger band gaps could be sensitized through introducing semicondue s with smaller band gaps. Moreover, the 390 stability of semiconductors could be increased by with some semiconductors with superb 391 electrochemical/photochemical stability. During the past legades, numerous studies of semiconductor coupled 392 paration efficiency of photoinduced charge carriers, with Ag<sub>3</sub>PO<sub>4</sub> were reported, showing in 393 strengthened photostability of Ag<sub>3</sub>FD<sub>4</sub>, chanced photoreduction ability, and simultaneously increased 394 similified present the two types of connection mechanism between 395 photocatalytic performants semiconductors and Ag<sub>3</sub>PO<sub>4</sub> (type II and Z-scheme-like), carbon materials or polymers coupled Ag<sub>3</sub>PO<sub>4</sub>, and 396 397 some novel ternary or multi-component Ag<sub>3</sub>PO<sub>4</sub> 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) (Figure 6). The former two types are more commonly used in practical heterostructure divices. 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 (Figure 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 403 [104, 105]. As for Type II heterojunction, photogenerated electrons in the conduction band of PC I could transfer 404 405 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 (Figure 6B). Similar to the Schottky junction of 406 metal/semiconductor composites, in the interface of two semiconductors, a built-in field would be generated, 407 which is conducive to the separation of photoexcited electron-hole pairs in this region, leading to the 408 enhancement of photocatalytic performance. The elevated photocatalytic capability could also be attributed to 409 the augmented surface area and enhanced absorption of reactants. Charge transfer 410 ctions were depending on the position of the conduction band and valence band of the two semicon 411 In this heterojunction system, we preferred that Ag<sub>3</sub>PO<sub>4</sub> to act as PC II to transfer the photoind ed electrons to other semiconductor, which 412 may show a better inhibition capability for the photocorros on the type II heterojunction where Ag<sub>3</sub>PO<sub>4</sub> act 413 as the PC I. It should be noted that metallic Ag could be till generated in the photocatalysis process, reducing 414 the cyclic utilization capability of Ag<sub>3</sub>PO<sub>4</sub>. 06] reported that the type II heterojunction Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> 415 composites showed 90% degradation te of he methylene blue (MB) after 6 min under irradiation, which was 416 Tbs composite system reduced the loading of metallic Ag from 77 wt% to 417 higher than that of Ag<sub>3</sub>PO<sub>4</sub> nnle 47 wt%, which could be regarded as significant progress for reducing photocorrosion phenomenon. 418



Type I

Туре П

Type III

Figure 6. (A) Type I (straddling), (B) type II (staggered), and (C) 420 oken) heterostructure. Although the recombination of photoinduced electron-hole pairs is re-421 by the type II heterojunctions, the redox ability of the charges in this system is weakened. The Z heme-like photocatalytic system may be an 422 leterojunction photocatalytic systems, the ideal candidate to solve this problem [107]. Similar to 423 yp separation of photoexcited electron/hole pairs could be also enhanced in the Z-scheme-like photocatalytic 424 system. Photogenerated electrons in the con d of PC I could encounter with the photogenerated holes 425 in the valence band of PC II through ei her a conductor or a direct contact (Figure 7 A and B). The photoinduced 426 tive conduction band of PC II for photoreduction process, while the 427 electrons still remain in th leg nor photoexcited holes remain in the more positive valence band of PC I for photooxidation reaction. The driving 428 force energy needed for this system is reduced which could make the hybrid photocatalyst utilize visible-light 429 more efficiently. 430



Figure 7. (A) With conductor and (B) mediator free Z-scheme like heterostructure.

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Transition metal sulfides (e.g. MoS<sub>2</sub> and WS<sub>2</sub>) recently attract 433 more and more attention from researchers.  $g_3PO_4$ , it is reasonable to believe that the Considering the band gap energy of transition metal sulfi es 434 composition of these semiconductors could construcing a Z-scheme-like heterojunction, which could 435 fides and the reduction of Ag<sub>3</sub>PO<sub>4</sub>, hence improve both effectively restrain the oxidation of transiti 436 The two dimensional graphene-like materials MoS<sub>2</sub> have a suitable band the photocatalytic activity and stability 437 which is well matched with Ag<sub>3</sub>PO<sub>4</sub> to form Z-scheme-like photocatalytic 438 edges (E<sub>CB</sub>=-0.12 V, E<sub>VB</sub>= system [108, 109]. Zhu et al. [110] reported that Ag<sub>3</sub>PO<sub>4</sub>/MoS<sub>2</sub> composite photocatalyst exhibited excellent 439 photocatalytic degradation rate of organic contaminants and ascendant stability according to the recycling 440 experiments. MoS<sub>2</sub> could effectively accept electrons and form strong interaction with Ag<sub>3</sub>PO<sub>4</sub>. Photogenerated 441 electrons of Ag<sub>3</sub>PO<sub>4</sub> could recombine with the photoinduced hole of MoS<sub>2</sub> in Ag particles which were formed 442 by the photocorrosion of Ag<sub>3</sub>PO<sub>4</sub>. The Ag particles serve as charge recombination center and are favorable to 443 the development of the Z-scheme-like system. The holes remaining in Ag<sub>3</sub>PO<sub>4</sub> and electrons in MoS<sub>2</sub> could 444 simultaneously be utilized for the redox reactions. The separation efficiency was improved and the 445

446 photocatalytic performance was also enhanced.

Metal-free graphitic carbon nitride  $(g-C_3N_4)$  is a material with stable, abundant, responsive to visible-light, 447 448 and exhibits splendid electronic properties. The band gap width of g-C<sub>3</sub>N<sub>4</sub> is about 2.7 eV (the conduction band position of g-C<sub>3</sub>N<sub>4</sub> is -1.12 V and the valence band position of it is 1.57 V) [18, 111-114]. He et al. [115] reported 449 450 that the Z-scheme-like Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> composite could transfer CO<sub>2</sub> to fuel. Photoinduced holes in g-C<sub>3</sub>N<sub>4</sub> and the photoexcited electrons in Ag<sub>3</sub>PO<sub>4</sub> would combine in Ag nanoparticles. The photogenerated electrons in g-451  $C_3N_4$  could reduce H<sup>+</sup> or CO<sub>2</sub> while the photogenerated holes in Ag<sub>3</sub>PO<sub>4</sub> could be used to oxidize H<sub>2</sub>O to O<sub>2</sub> or 452 degrade pollutants. The biggest CO<sub>2</sub> conversion rate of Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatal 57.5  $\mu$ mol·h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, which 453 was almost 6.1 and 10.4 times higher than that of  $g-C_3N_4$  and P25 under 454 conditions, respectively. Besides the two kinds of hybrid mechanisms introduced abo e, other materials such as carbon materials 455 (e.g., fullerene and graphene) [116, 117], polymers [118-11] and metal-organic frameworks [122-124] could 456 be used as the conductor for the improvement of photoca dytic performance. Given credit to the good electron 457 most appropriate material to combine with Ag<sub>3</sub>PO<sub>4</sub> [125transport of carbon compounds, it may be a 458 127]. In the carbon-based materials, gaphy give with  $\pi$ -conjugated structure of sp- and sp<sup>2</sup>-hybridized carbon 459 tten on. Its electron and hole mobility is about  $2 * 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  [128] and atoms have attracted tremendous 460 10<sup>4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> [129] order of magnitude, respectively, and the conductivity of graphdiyne is measured as 2.516 461 \* 10<sup>-4</sup> S/m [130]. The graphydiyne has uniformly distributed pores and a tunable band gap in the range of 0.46 462 - 1.22 eV [131]. Guo et al. [132] studied the promoted photocatalytic acitivity of graphydiyne/Ag<sub>3</sub>PO<sub>4</sub> pickering 463 emulsion. The abundant butadiyne bonds (  $-C \equiv C - C \equiv C$  ) makes graphydiyne works as an excellent 464 acceptor (formed a large  $\pi$ -conjugated system) for the photoexctited electrons of Ag<sub>3</sub>PO<sub>4</sub>, and an appropriate 465 amount of the precursor  $Ag^+$  could be reduced to  $Ag^0$  by the introduction of graphydiyne due to the low work 466 function of it. According to the authors, MB solution could be completely photodegraded within 10 min by this 467

468 graphydiyne/ $Ag_3PO_4$  emulsion system under visible light irradiation, while only 75% MB were photodegraded 469 by carbon nanotube/ $Ag_3PO_4$  or graphene/ $Ag_3PO_4$  photocatalyst under the same condition.

470 Coupling  $Ag_3PO_4$  with polymers may be an efficient way to restrain the photocorrosion of  $Ag_3PO_4$ , because it could function as a passivation layer to cut down the number of surface recombination sites and prevents the 471 photocorrosion of semiconductor [133]. For instance, Yue et al. [121] synthesized a core-shell structure 472 Ag<sub>3</sub>PO<sub>4</sub>@benzoxazine soft gel nanocomposite for the improvement of interface properties and stability of 473 Ag<sub>3</sub>PO<sub>4</sub>. The silver amine complex ion formed through the amino group of benzoxazine and Ag<sup>+</sup> ions on the 474 surface of Ag<sub>3</sub>PO<sub>4</sub> could consuming the photogenerated electrons of Ag<sub>3</sub>PO<sub>4</sub> with  $O_2$  molecule absorbed on 475 it surface to produce  $O_2^-$  radicals, thus restrain the photocorrosion of Ag<sub>3</sub> 476 des, the shell of benzoxazine could efficiently inhibit the dissolution of Ag<sub>3</sub>PO<sub>4</sub> in aqueous solution on, hence promoted the structural stability. 477 With the development of photocatalysis technology, hers are no longer satisfied study the binary 478 ese complex photocatalyst, more and more researchers put their strength on the study of ternary or multi-component 479 nced that using some intermedium such as noble metal hybrid composites. To date, lots of research 480 [134-139], carbon materials [14, 140-12], or polymers [143-145] to accelerate the charge carrier transformation 481 hybrid composite photocatalyst. For instance, Cai et al. [140] recently is an efficient way to constru 482 at synthesized Ag<sub>3</sub>PO<sub>4</sub>@RGO@h<sub>2</sub>,Cr:SrTiO<sub>3</sub> photocatalysts which showed an excellent anti-photocorrosion and 483 photocatalytic performance. The enwrapped RGO is avail for the transfer of charge carriers, and could prolong 484 485 its lifetime. In addition, it could behavior as sheltering layer to prevent photocorrosion. The as-obtained sample 486 could completely degrade Rh B after 5 min sunlight irradiation, and no loss was detected in the photocatalytic process after 5 cycles. Si et al. [146] reported a Z-scheme-like Ag<sub>3</sub>PO<sub>4</sub>/graphdiyne/g-C<sub>3</sub>N<sub>4</sub> photocatalyst for 487 488 oxygen evolution. The graphdyne could boost the oxygen generation by acting as conductive electron mediator bridge as well as to stabilize  $Ag_3PO_4$  as a promising substrate. The  $O_2$  evolution of this composite could reach 489

490 753.1  $\mu$ molg<sup>-1</sup>h<sup>-1</sup>, which is 12.2 times higher than that of pure Ag<sub>3</sub>PO<sub>4</sub> photocatalyst.

Shao et al. [143] improved the photocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub>@benzoxazine by synthesizing 491 492 Ag<sub>3</sub>PO<sub>4</sub> tetrapods with more exposure of  $\{110\}$  facet and decorated of carbon quantum dots (CQDs) on the surface of Ag<sub>3</sub>PO<sub>4</sub>. The CQDs could act as an "exciter" by expanding light absorption and strengthening energy 493 494 conversion via up-conversion photoluminescence effect, thus activate more photogenerated charge carriers from the {110} facet of Ag<sub>3</sub>PO<sub>4</sub> tetrapod. Simultaneously, it could facilitate the electron transfer from the conduction 495 band of Ag<sub>3</sub>PO<sub>4</sub> to the conduction band of itself. The silver amine complex formed between Ag<sub>3</sub>PO<sub>4</sub> and 496 benzoxazine is beneficial for the free radical chain reaction. This 3D core-shell structure 497 re decreased the solubility of Ag<sub>3</sub>PO<sub>4</sub>. The photocatalytic activity of this composite still remains 9 498 al rates of sulfamethoxazole with 10 min even after 9 cycles. 499 Except the abovementioned ternary Ag<sub>3</sub>PO<sub>4</sub> hybrid s system, other multi-component Ag<sub>3</sub>PO<sub>4</sub> 500 hybrid composites were also been studied by researchers. For example, Pan et al. [147] introduced TiO<sub>2</sub> into the 501 on photocatalyst to prevent the aggregation. Comparing laminar Ag<sub>3</sub>PO<sub>4</sub>/Ag/MoS<sub>2</sub> Z-scheme-like h 502 rt of Ag<sub>3</sub>PO<sub>4</sub>/Ag/MoS<sub>2</sub> in this composite still forms a Z-scheme-like with traditional heterojunctions, the 503 lar ellar structure, the conduction band of  $MoS_2$  may be higher than that of 504 structure. Additionally, cret to f TiO<sub>2</sub>, which could lead the photogenerated electrons from MoS<sub>2</sub> transferred into the conduction band of TiO<sub>2</sub>, 505 further promote the separation efficiency of photoinduced charge carriers. The photoluminescence of 506 Ag<sub>3</sub>PO<sub>4</sub>/Ag/MoS<sub>2</sub>/TiO<sub>2</sub> is obvious weaker than others (Figure 8), which proved this conjecture. Direct Z-507 508 scheme-like photocatalysts for water splitting suffer from charge separation and photocatalytic backward reaction issues [148, 149]. Li et al. [150] announced that the synergistic effect of a type II heterostructure could 509 510 efficiently suppress the backward reaction. The authors deposit Ag<sub>3</sub>PO<sub>4</sub> nanoparticles on CeO<sub>2</sub>/TiO<sub>2</sub> hierarchical branched nanowires, and speculated that the cascade energy level alignment in CeO<sub>2</sub>/TiO<sub>2</sub> hierarchical branched 511

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  $Ag@Ag_3PO_4/g-C_3N_4/NiFe$  layered double hydroxide (LDH) nanocomposites [151] and dual Zscheme-like g-C\_3N\_4/Ag\_3PO\_4/Ag\_2MoO\_4 [152] composites were also been investigated by researchers, and their proposed mechanism for charge transfer pathways (including the abovementioned  $Ag_3PO_4/Ag/MoS_2/TiO_2$  and  $Ag_3PO_4/CeO_2/TiO_2$ ) were show in figure 9.



518

520

519 **Figure 8.** The photoluminescence of the semple, with different excitation wavelenghth, (A) 325 nm, (B)



526 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 527 a physical or chemical method, which introduces ions into the internal of host material lattice. It could efficiently 528 modify the surface structure of host material, form some defects (acting as capture centers to inhibit the 529 recombination of photoinduced electron/hole pairs), increase some spectral response, cause significant changes 530 in the band gap (introducing levels), influence the kinetic state of photoinduced charge carriers (causing linear 531

expansion of the transition of charge carriers, and prolong the life time of photoinduced charges), hence is conduced 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 element n the original crystal. For 539 instance, an impurity energy band would be formed in the doping proc 540 -doped  $Ag_3PO_4$  [158]. The additional Ni<sup>2+</sup> could facilitate the utilization of photons as well the separation efficiency of photoinduced 541 charge carriers. The photodegradation rate of methyl oran, e 0 mg/L) could be reached at 89% by Ni<sup>2+</sup>-542 doped Ag<sub>3</sub>PO<sub>4</sub> after 4 min under visible light irradiation, whereas 12% of MO (40 mg/L) was only degraded by 543 ation. Five cycling experiments showed that the pure Ag<sub>3</sub>PO<sub>4</sub> photocatalyst under the 544 photodegradation rate of MO (20 mg/L) was still up to 92%. The introduction of copper atoms could substitute 545 ce f Ag<sub>3</sub>PO<sub>4</sub>, thus create defects that influence the structural ordering, silver atoms in the crystal 546 stabilize the cubic structure, and prevent the reduction of Ag<sup>+</sup> by acting as recombination centers to trap 547 photogenerated electrons [159]. Introducing  $Bi^{3+}$  ions could replace the  $P^{5+}$  ions of Ag<sub>3</sub>PO<sub>4</sub> [160]. The valance 548 band level of Ag<sub>3</sub>PO<sub>4</sub> could be decreased by bismuth doping, and the band gap energy of Bi<sup>3+</sup>-Ag<sub>3</sub>PO<sub>4</sub> could be 549 reduced to 1.954 eV. Doping Bi<sup>3+</sup> ions in Ag<sub>3</sub>PO<sub>4</sub> suppressed the formation of excess OH defects. High-550 concentration OH defect is not good for the electronic transitions, and could destroy Ag-O bonds in Ag<sub>3</sub>PO<sub>4</sub> to 551 552 accelerate electronic recombination. Notably, in an aqueous solution, MO molecules carry a negative charge while the Bi<sup>3+</sup> ions carry a positive charge in doped Ag<sub>3</sub>PO<sub>4</sub>. Hence, adsorption capability could be accelerated 553

because of the internal attraction between these two groups, which facilitated the photocatalytic reaction. P (V) 554 of Ag<sub>3</sub>PO<sub>4</sub> could be substituted by Mo (VI) cations, and new intermediate levels in the forbidden band would 555 556 be formed after doping procedure of molybdenum [161]. Electronic repulsion capability of  $Ag_3PO_4$  could be improved by Mo doping due to the Mo (VI) cations are more positive than the P (V) cations. Mo doping could 557 558 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 559 could serve as traps to delay the recombination of charge carriers, and forming intermediate states in the 560 forbidden band to lower the  $E_g$ . The  $E_g$  could be reduced to 2.07 eV for 0.5d Ag<sub>3</sub>PO<sub>4</sub>, and shows two 561 time faster degradation rates than pure Ag<sub>3</sub>PO<sub>4</sub> microcrystals toward Rh 562 Lanthanides doped semiconductors could form crystall defects, which could enhance visible 563 rated electron-hole pairs [156]. The surface wavelengths emission and inhibit the recombination of photor. 564 structure of Ag<sub>3</sub>PO<sub>4</sub> could be affected by La doping [162] As the concentration of La dopant increased, more 565 ced photocatalytic capability of La-doped Ag<sub>3</sub>PO<sub>4</sub> was surface defects and pores would be genera 566 aided by the increased porosity, surface defects, and surface area. Other lanthanides like Dy or Er doped Ag<sub>3</sub>PO<sub>4</sub> 567 G-dolinium cations could replace  $Ag^+$  ions for the Gd-doped  $Ag_3PO_4$ 568 were also be reported [1 164 photocatalysts [164]. The  $M^{3+}$  M = Gd, Dy, and Er) ions in this system combined with an electron to form  $M^{2+}$ , 569 570 which would further react with  $O_2$  to increase the formation of  $O_2^-$ .

Ba-doped Ag<sub>3</sub>PO<sub>4</sub> 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<sub>3</sub>PO<sub>4</sub> 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<sub>3</sub>PO<sub>4</sub> particles. After five cycling runs, the time for complete degradation was in the range of 5 to 7 min for Rh B, and 2.5 to 4 min 576 for MO. Ba doping might greatly increase the amount of oxygen defects, which could inhibit the recombination 577 of the photoinduced charge carriers. An alternative explanation was that doping Ba in the  $Ag_3PO_4$  created a 578 charge imbalance, which caused more OH<sup>-</sup> to trap more holes, thereby restraining the recombination of charge 579 pairs and generating more OH.

To date, some cationic metal (e.g. Ni, Bi, Ba, Cu, Mo, La) has been successfully doped into Ag<sub>3</sub>PO<sub>4</sub> lattice, 580 and effectively enhanced the photocatalytic performance. However, the metal doping generally introduce 581 localized energy levels in the band gap to modification host material, which may also bring the risk of impairing 582 charge separation and transport by acting as a recombination center. In this re, and e might want to know the 583 anionic nonmetal doping behavior in Ag<sub>3</sub>PO<sub>4</sub> since there are plenty of 584 le research paper proved the anionic nonmetal doping in TiO<sub>2</sub> and other photocatalytic could obtain a better photocatalytic performance [166-585 168]. Recently, a fluorine-doped Ag<sub>3</sub>PO<sub>4</sub> photocatalyst with ing activity and stability by a facile in-situ 586 fluorination was reported by Li et al. [169]. Doping F expents with moderate amount have no effect on the 587 roduce impurity phases. Besides, the average crystallite basic crystal structure of cubic Ag<sub>3</sub>PO<sub>4</sub> and 588 size and crystallinity was improved when the fluoride ions was introduced into Ag<sub>3</sub>PO<sub>4</sub>, which is benefit for the 589 es. Higher crystallinity degree in conducive to the suppressing of bulk 590 dissolution and recrystallize on p charge recombination, and prohoting charge separation and transportation. Most of F<sup>-</sup> ions would substitute O<sup>2-</sup> 591 ions in Ag<sub>3</sub>PO<sub>4</sub> lattice, and forming a stronger P-F bond compare to the P-O bond. The Fermi level of F-doped 592 Ag<sub>3</sub>PO<sub>4</sub> would move toward the conduction band, which is in favor of the charge separation. Small amount of 593 594 fluorine would adsorbed on the surface of Ag<sub>3</sub>PO<sub>4</sub>, and absorb more H<sub>2</sub>O owing to the fluorine induced -F...(H-OH)<sub>x</sub> group involving hydrogen-bonding interactions. F doping would induce more surface defects such as 595 596 oxygen vacancies, which enhance the capture of surface O<sub>2</sub> as well as the activation of O<sub>2</sub> by photoinduced electrons. In addition, the band gap of F-doped  $Ag_3PO_4$  was raised. Accordingly, the band gap of  $Ag_3PO_4$  and 597

F-doped  $Ag_3PO_4$  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  $Ag_3PO_4$ .

600 Owing to the strong P-O bond, incorporating S into Ag<sub>3</sub>PO<sub>4</sub> lattice is difficult, which need much energy input to inset those dopants into PO<sub>4</sub> matrix. Therefore, some researchers proposed using oxoanion groups to 601 602 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  $Ag_3PO_4$  lattice by a precipitation method. It was feasible to replace 603  $PO_4^{3-}$  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 604 0.230 nm for PO<sub>4</sub><sup>3-</sup>). The S element in SO<sub>4</sub><sup>2-</sup> had strong electronic interactions with g, P and O elements. Give 605 credit to the higher electronegative of S compared to the P atom, the addition 606 would decrease the electron densities around Ag and P elements. Doped SO<sub>4</sub><sup>2-</sup> created impurituates were mainly distributed in the valence 607 band region, and no impurity state appeared in the forbidde tord ap. The Fermi level of SO<sub>4</sub><sup>2-</sup>-doped Ag<sub>3</sub>PO<sub>4</sub> 608 was significantly shifted towards the conduction band. As the concentration of dopant increased, both the VBM 609 regions, which were conduced to the enhancement of and the CBM gradually shifted towards lo 610 oxidative capability of photoexcited bles and suppressed the reduction capability of photoexcited electrons. 611 so ation of SO42-doped Ag3PO4 was 4.5 times higher compared to Bi3+-612 The photodegradation rates £ Rh doped Ag<sub>3</sub>PO<sub>4</sub>. Although the photodegradation rate slightly decreased after two cycling runs, the degradation 613 of Rh B solution is still up to 98% after six cyclic runs. Luo et al. [173] proposed a doughnut-like carbonate-614 doped Ag<sub>3</sub>PO<sub>4</sub> with high photocatalytic activity through an ion-exchange method. Similar to the Ba-doped 615 Ag<sub>3</sub>PO<sub>4</sub> aforementioned, the authors took advantage of the lower solubility of Ag<sub>3</sub>PO<sub>4</sub> ( $K_{sp} = 1.4 \times 10^{-16}$ ) 616 compared to Ag<sub>2</sub>CO<sub>3</sub> ( $K_{sp} = 8.45 * 10^{-12}$ ) to get a hollow hexagon doughnut-like structure. The CO<sub>3</sub><sup>2-</sup> doping 617 introduced impurity levels which could narrow the energy gap of Ag<sub>3</sub>PO<sub>4</sub> and enhanced its photocatalytic 618 activity. Photoexcited electrons and holes can be efficiently separated and migrated through  $CO_3^{2-}$  doped 619

doughnut-like Ag<sub>3</sub>PO<sub>4</sub>. The photodegradation rate of Rh B solution still maintained 85% of its original activity
 after five cyclic running.

622 5.3 Summary

In this section, we systematically discussed various strategies to enhance photocatalytic performance of 623 Ag<sub>3</sub>PO<sub>4</sub>, including the deposition of metals, combination with other semiconductors, and doping specific 624 amount of elements into the lattice of Ag<sub>3</sub>PO<sub>4</sub>. The main purpose of these methods was to boost the 625 separation/transition efficiency of photoexcited electron-hole pairs, and inhibit its recombination. These 626 methods provide efficient ways to overcome the photo instability and improve the 627 hotocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub>, as well as prevents the dissolution of Ag<sub>3</sub>PO<sub>4</sub>. Metal/Ag<sub>3</sub>PO 628 photocatalyst provide a solid way to enhance the photostability of Ag<sub>3</sub>PO<sub>4</sub>. To date, however, past of the researches published only focused 629 on the plasmonic effect of Ag/Ag<sub>3</sub>PO<sub>4</sub> composite, other not playhour metals were barely studied. We hope that 630 researchers would put more strength in that aspect, 631 nd put forward some other metal/Ag<sub>3</sub>PO<sub>4</sub> hybrid activity for practical application. Besides, for the photocatalyst with high photostability 632 metal/semiconductor system, the particle size, shape, and surrounding environment has a large influence of the 633 which also need researchers spend time on the study of the aspect in 634 plasmonic bands of metal 635 the future.

Constructing enhanced photocatalytic performance of  $Ag_3PO_4$  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  $Ag_3PO_4$ , decorated small number of  $Ag_3PO_4$  with other inexpensive materials could efficiently cut down the cost, which seems to be a promising way for the industrial application of  $Ag_3PO_4$ . However, studies of semiconductor/ $Ag_3PO_4$  were still in its primary stage, only few researchers have put

attention on the combination of metal or semiconductor with a specific facet of Ag<sub>3</sub>PO<sub>4</sub>, as well as the 642 643 homojunction of Ag<sub>3</sub>PO<sub>4</sub>. For instance, researchers demonstrated that TiO<sub>2</sub> with well-defined  $\{101\}/\{001\}$  facet 644 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 645 enhancement of photoactivity and stability of Ag<sub>3</sub>PO<sub>4</sub>. Recently, Xie et al. [174] constructed an Ag<sub>3</sub>PO<sub>4</sub> 646 morphological homojunction with enhanced photocatalytic activity. The Ag<sub>3</sub>PO<sub>4</sub> homojunction consist of 647 submicron spherical and rhombic dodecahedron particles, introduce an internal field between them, which 648 facilitates the transfer of charge carriers and separation of photoinduced elect 649 hole pairs. However, the authors were using a simple physical combination process to synthesiz 650 <sup>3</sup>PO<sub>4</sub> homojunction, a more sophisticated method and explanation for the homojunction of  $A^{2}PO_{4}$  should be further studied. In addition, 651 a vital parameter for the photocatalytic the structures of metal or semiconductor modified  $Ag_3PO_4$ 652 653 performance. Numerous structures were proposed to further enhance the photocatalytic activity. For instance, cubes were fabricated by Bi et al. [175] in 2012. The one-dimensional necklace-like Ag nanowi 654 authors compared the photocatalytic active y of this composite with core-shell coaxial hetero-nanowires 655 de radation of Rh B. The degradation results shows that the necklace-like 656  $Ag/Ag_3PO_4$  and pure  $Ag_3PO_4$ Ag nanowires/Ag<sub>3</sub>PO<sub>4</sub> cubes only need 2 min for the complete degradation of Rh B, while the core-shell coaxial 657 hetero-nanowires Ag/Ag<sub>3</sub>PO<sub>4</sub> and pure Ag<sub>3</sub>PO<sub>4</sub> need 6 and 8 min, respectively. Improved photocatalytic activity 658 could attribute to the effectively export of enriched electrons on the Ag nanowires and the remained high 659 660 concentration of holes on Ag<sub>3</sub>PO<sub>4</sub> cubes. The position and number of Ag<sub>3</sub>PO<sub>4</sub> cubes could be easily controlled in this composite. Novel collective photocatalytic properties could be achieved by the necklace-like structure. 661 662 Research on novel structure such as isolated structure, multi-segmented heterojunction structure, porous core-663 shell structure half core-shell stack structure of Ag<sub>3</sub>PO<sub>4</sub> 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] 664 successfully synthesized P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composites. The authors declared that the photogenerated 665 666 electrons of Ag<sub>3</sub>PO<sub>4</sub> and Ag<sub>2</sub>O in this composite could flow to the Fermi level of Ag, while the photoexcited holes of TiO<sub>2</sub> and Ag<sub>3</sub>PO<sub>4</sub> could transfer to the valence band of Ag<sub>2</sub>O under sunlight irradiation. In addition, the 667 SPR effect of Ag could lead to generation of energetic electrons, and injected to the TiO<sub>2</sub> to produce superoxide 668 anion radicals and holes for the improved photocatalytic activity of this composite. Thus, the recombination rate 669 of electron-hole pairs was largely decreased, and the photocatalytic activity and stability were largely enhanced. 670 There is no doubt that doping is an efficient way for the modification of PO<sub>4</sub>. Doping appropriate 671 amount of dopants into Ag<sub>3</sub>PO<sub>4</sub> could efficiently affect the light absor 672 vell as the charge dynamics. However, there are still some shortcomings in this method. For example, it is hardly to obtain a high doping 673 level owing to the difference of ionic radii of doped and hos for opants could serve as recombination centers, 674 and decrease the redox capability while the use of doparts is introducing electronic states under the CBM or 675 method like the aforementioned Ba-doped Ag<sub>3</sub>PO<sub>4</sub> and above the VBM. It is worth mentioning the 676 CO<sub>3</sub><sup>2-</sup>-doped Ag<sub>3</sub>PO<sub>4</sub> represents a simple and effective way for the full-scale fabrication of photocatalysts with 677 poing. In addition, the selectivity of modified Ag<sub>3</sub>PO<sub>4</sub> also needs to be taken 678 morphology control and elem nts into consideration. For instance, the CO<sub>3</sub><sup>2-</sup>-doped Ag<sub>3</sub>PO<sub>4</sub> could completely degrade Rh B solution within 8 min 679 and MO within 14 min [173]. This is also important for the practical application of Ag<sub>3</sub>PO<sub>4</sub>. Moreover, to date, 680 researches about element doped Ag<sub>3</sub>PO<sub>4</sub> are really lacking, especially for the nonmetal doped Ag<sub>3</sub>PO<sub>4</sub> and co-681 682 doping effect, which needs researchers investigated more at this side, and hopefully researchers could summarize general rules for the doping effect of Ag<sub>3</sub>PO<sub>4</sub>. Furthermore, combined Ag<sub>3</sub>PO<sub>4</sub> with other doped 683 684 materials were abundant studied in the past decade. However, combined doped Ag<sub>3</sub>PO<sub>4</sub> with other materials 685 were barely reported, which seems to be a notable aspect for the modification of  $Ag_3PO_4$  photocatalyst.

Another critical issue in the application of photocatalysis is the designing of photoreactors with satisfactory 687 688 performances at full-scale. Undoubtedly, photocatalysis is a potential pollutant treatment technology. Subramanism et al. [177] calculated that up to 23000 dollars could be saved by using a submerged membrane 689 690 photoreactor with flux of 4000 L/m<sup>2</sup> 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 691 have been developed, which all exhibit excellent photocatalysis performance. The first solar photoreactor 692 10A) which installed in designed for photocatalytic applications is parabolic trough reactor (PTR, Fig 693 Albuquerque (New Mexico, USA) back in 1989 which could concentrat 694 nlight about 50 times on the photoreactor, and was used to treat polluted water containing chlor ated solvents and heavy metals [178, 179]. 695 Accordingly, chromium (IV) [180], dichloroacetic and phenol [182], 4-chlorophenol [183], 696 dichlorophenol [184], pentachlorophenol [185], atrazine [83], and industrial wastewater [186] was successfully 697 avoid possible photocatalyst sedimentation problems. degraded by PTR. It favors mass transfer 698 Besides, PTR is a sealing system, and that heans no evaporation of volatile compounds. However, there are 699 ctor First, PTR can only make use of direct solar radiation, suggesting that 700 certain disadvantages about it is practically useless on cloudy days. Second, the need of tracking system makes it usually expensive to install. 701 702 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 703 photocatalytic decomposition of pollutants [187-189]. 704

Non-concentrating reactors (NCRs, Figure 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.

713 Compound parabolic collecting reactors (CPCRs, Figure 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 714 concentrating system without solar tracking system, which significantly decr 715 e costs and complexity of this system. The reflective surface could reflect indirect light onto the re-716 es, thus make it capture both direct and diffuse sunlight, as well as makes the reactor volumes caller. The sanitary landfill leachate [192], 717 olive mill waste [193], urban wastewater [194], toxic compound ich as pathogenic organisms [195], pesticides 718 [196], chlorinated solvents [197], and biorecalcitrant concounds [198, 199] could be removed from water by 719

this photoreactor.

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Figure 10. Schematic drawing of (A) parabolic trough reactor, (B) non-concentrating reactor, and (C)

С

compound parabolic collecting reactor.

В

Except the abovementioned three photoreactors, several kinds of pilot photoreactors have been developed, 724 which exhibit satisfactory photocatalysis performances at bench-scale. For instance, Abdel-Maksoud et al. [200] 725 726 designed a tray photoreactor (Figure 11A) based on using the sand supported  $TiO_2$  as photocatalysts for the 727 degradation of phenol. The reactor is operated in a recirculating batch mode. The liquid could be recirculation 728 pumped into the central vertical feeder which passes through the tray center. The inverted nozzle makes sure a 729 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 730 the efficient light penetration. After the photocatalytic treatment, the liquid wuld 731 down to the tank bottom ensuring water oxygenation, participate in the loop until the it hit th 732 quality standards. This tray photoreactor is suitable for scale-up and commercialization owing it modular design, integrated storage, and 733 applied Ag<sub>3</sub>PO<sub>4</sub>/AgBr/Ag-HKUST-1-MOF ease of continuous mode operation. Mosleh et al. [122] suc ess 734 photocatalysts in a continuous flow photocatalytic roating packed bed (Figure 11B) for mixture dyes 735 todegradation under blue LED light irradiation. The (methylene blue, auramine-O, and erythr 736 degradation efficiency of these three dues is 2.01%, 89.96%, and 89.57%, respectively. The optimum operating 737 of ir adiation time, 15 mg/L of each dye, 0.4 g/L of photocatalyst, 100 rpm 738 parameters are as follows: min of rotational speed, 0.3 L/min of solution flow rate and 25 L/min of aeration rate. The composite photocatalyst 739 shows high stability under repeated photocatalytic reaction for 5 times. Besides, this photocatalytic reactor has 740 less physical size and volume than conventional photocatalytic reactor because of the higher interfacial surface 741 created by the device and highly efficient photocatalyst. The packed catalyst saves the cost of the filtration stage 742 and avoids emission of Ag<sub>3</sub>PO<sub>4</sub>/AgBr/Ag-HKUST-1-MOF photocatalysts. 743



Figure 11. (A) The tray photoreactor (cited from ref. [200]) and (B) the rotating packed bed 745 photocatalytic rector (cited from ref. 746 There are mainly two ways to use the photocatalysts in these reactors, i.e., using nanosized powder-like 747 photocatalysts and using immobilized photocatalysts. The nanosized powder-like photocatalysts were often 748 d tl utilized in laboratory experiments, and was generally mov rough precipitation or filtration methods. The 749 750 reactors with dispersed photocatalysts have low preure drop, large contact surface area for adsorption and 751 reaction, and effective mass transfer of nina hts nanosized powder-like photocatalysts [201]. However, the stirring of treated water and s parati f nanosized powder-like catalysts from it after each run is difficult 752 desits practical application in real-world wastewater situations. Lee et al. [202] 753 to be achieved, which greatly successfully separated nanosized powder-like TiO<sub>2</sub> photocatalysts dispersing in water by an optimal coagulant 754 755 dose, proper flocculation, and sand filtration measurements. However, these methods are complicated, costly, 756 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 757 758 through filtration materials and block filter membranes. Combined Ag<sub>3</sub>PO<sub>4</sub> with magnetic materials such as 759 Fe<sub>3</sub>O<sub>4</sub> [203, 204], MnFe<sub>2</sub>O<sub>4</sub> [205], and NiFe<sub>2</sub>O<sub>4</sub> [206] appears to be an efficient way for the recycling of Ag<sub>3</sub>PO<sub>4</sub> 760 based composite photocatalysts. The magnetic composite could be totally separated from the solution by an 761 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, 762 763 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 764 765 vital to develop novel immobilized photocatalysts with enough photocatalytic activity for the pollutant treatment. 766 Chen et al. [134] synthesized 3D graphene aerogels/Ag/Ag@Ag<sub>3</sub>PO<sub>4</sub> heterostructure photocatalysts for the efficient adsorption-photocatalysis of different dyes in water. Graphene is an ideal supporting material for the 767 construction of Ag<sub>3</sub>PO<sub>4</sub> based composite photocatalysts. The macroscopic or structure of 3D graphene 768 aerogels makes it an easy and convenient recycling support for semicon 769 botocatalysts. At the end of a photocatalytic cycle, workers could simply use tweezers to take the photocatalyst, and could be employed 770 into another phtocatalytic cycle after rinsing. Zhu et al. innesized a novel P/Ag/Ag<sub>2</sub>O/Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> 771 76 composite film on the inner-surface of glass tube for circulatory water purification and antibacterial application 772 under solar light irradiation. The degradation h B of this composite could reach 99.9% after 60 min, 773 and showed no attenuation of degradation rate even after five recycling runs. Qu et al. [144] fabricated sandwich 774 amine/Al<sub>2</sub>O<sub>3</sub> porous small balls with excellent photocatalytic activity 775 structural Ag<sub>3</sub>PO<sub>4</sub> nanopain le/n under natural irradiation. The rele of polydopamine in this composite is to adhere between Al<sub>2</sub>O<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub>, 776 777 and reduce a small part of Ag<sub>3</sub>PO<sub>4</sub> to metallic Ag nanosphere for increased specific surface area and enhanced photocatalytic activity. The porous Al<sub>2</sub>O<sub>3</sub> plays the role of the substrate for the Ag<sub>3</sub>PO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> heterojunction, 778 and increase the specific surface area of this composite. The authors calculated the natural light intensity in an 779 ordinary sunny day was 220 lx, which is 1/5 than that of 90 mW/cm<sup>2</sup> Xe lamp and 1/9 than that of 180 mW/cm<sup>2</sup> 780 Xe lamp. In the natural irradiation, 5 ppm of MB, Rh B, and orange II could be completely degraded in 40, 60 781 and 30 min, respectively. Besides, the superhydrophilic surface of this composite provide an excellent antioil 782

property, which greatly reduces secondary pollution, and a small ball structure photocatalyst is much more easy 783 to use and recycle. In addition, membrane is a monolithic material, which is easy to recycle in aqueous solution. 784 The photocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub> based composite photocatalyst membranes such as 785 Ag<sub>3</sub>PO<sub>4</sub>/polyacrylonitrile composite electrospun fiber membranes [119, 209, 210] and multi-wall carbon 786 787 nanotubes/Ag<sub>3</sub>PO<sub>4</sub>/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 788 direction of development of photocatalysis due to it recycle capability is much better than the nanosized powder-789 like photocatalysts. Researchers should put more strength to create immovili 790 photocatalysts with high photocatalytic performance. Except the innovation of Ag<sub>3</sub>PO<sub>4</sub>-base 791 catalyst, designing suitable photoreactor for the pollutant treatment also is a vital aspect that thy of attention. Researchers should design 792 photoreactors which suitable for the real-world situation as vel as combine the characteristics of photocatalysts 793 for better photocatalytic performance. It is interesting to ote that most researchers are focused on the study of 794 in its photocorrosion, and very few researchers have to the innovation of Ag<sub>3</sub>PO<sub>4</sub>-based photocatal 795 keep an eye on the rejuvenation of Ag PO<sub>4</sub>-based photocatalyst. The photocorrosion phenomenon is inevitable 796 ocate vst participated photocatalytic reaction. Until now, we only know that  $H_2O_2$ for any of Ag<sub>3</sub>PO<sub>4</sub>-based pho-797 could served as the chemical xidation to reinsert the  $Ag^0$  into the  $Ag_3PO_4$  photocatalyst ( $6Ag + 3H_2O_2 +$ 798  $2H_PO_4^{2-} \rightarrow 2Ag_3PO_4 + 2H_2O + 4OH^{-}$ ), and controlled the morphology of the regenerated photocatalyst owing 799 to its pH variation ability which influences nucleation and growth. We hope that researchers could pay great 800 801 attention to this field, and report novel rejuvenation methods for Ag<sub>3</sub>PO<sub>4</sub>-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 805 demand for ozone and energy through the tested performance of a pilot plant for the treatment of wastewater 806 807 containing emerging contaminates. The photogenerated electrons accumulate on the conduction band of Ag<sub>3</sub>PO<sub>4</sub> could react with  $O_2$  and  $H^+$  to form  $H_2O_2$  (0.68 V vs NHE). However, the generated  $H_2O_2$  can hardly be used in 808 809 the photocatalysis process. Even more, at a low concentration, the  $H_2O_2$  could consuming the photoinduced holes, which has been demonstrated as the main active specials in the pollutant photocatalysis process of Ag<sub>3</sub>PO<sub>4</sub>. 810 Hence, how to turn the disadvantages into advantages of  $Ag_3PO_4$  is a big challenge for researchers. Huang et al. 811 [206] fabricated a Z-scheme-like Ag<sub>3</sub>PO<sub>4</sub>@NiFe<sub>2</sub>O<sub>4</sub> composite photocatal st 812 bined photocatalysis and Fenton process for the better degradation efficiency of MO, bispheno 813 Escherichia coli. The H<sub>2</sub>O<sub>2</sub> produced by Ag<sub>3</sub>PO<sub>4</sub> could be catalytically decomposed into  $O_2^{-2}$  OH radicals by the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles 814 +  $e^-$  (produced by NiFe<sub>2</sub>O<sub>4</sub>)  $\rightarrow$  Fe<sup>2+</sup>; decorated on the surface of Ag<sub>3</sub>PO<sub>4</sub> via a photo-Fenton proc 815  $Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH; Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-; Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH + H^+).$  The main 816 active specials in the photocatalysis proce composite are demonstrated to be the  $h^+$  (produced by 817 Ag<sub>3</sub>PO<sub>4</sub>),  $O_2^-$  and OH radicals, and it is reaconable to conjecture that the enhanced photocatalytic activities are 818  $Q_2$  produced by Ag<sub>3</sub>PO<sub>4</sub>) by NiFe<sub>2</sub>O<sub>4</sub> through a photo-Fenton reaction. attributed to the conversion 819 of F Combining photocatalysis with adsorption-desorption also is an interesting research direction. Generally, 820 adsorption is a spontaneous process, while desorption usually need chemical or energy input. Using light as the 821 energy source seems to be an ideal choice because it is finely tunable with high spatial and temporal accuracy, 822 823 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-NH<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> nanoparticle composites for the adsorption 824 825 of sulfamethoxazole (SMX). The authors declared that the light-sensitive Ag<sub>3</sub>PO<sub>4</sub> nanoparticles of the composites is benefit for the desorption of SMX due to the transformation from Ag<sup>+</sup> to Ag<sup>0</sup>. Accordingly, 826

200mg/g SMX could be adsorbed by UIO-66-NH<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> 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 Ag<sub>3</sub>PO<sub>4</sub> is really rare, which need researchers pay more attention in this field.

## 831 **7.** Conclusions and outlook

As a photocatalyst, silver phosphate has gained tremendous attention ever since its photocatalysis 832 application was discovered back in 2010. Without doubt, it is one of the most promising photocatalyst even 833 though some challenges still need to be conquered for industrialization and comm alization. In this regard, it 834 is necessary to make a comprehensive understanding of the deep mecha 835 ts remarkable photocatalytic performance as well as the shortcoming while using it as photocathyst in real-world situation. This review has 836 discussed and summarized the recent progress in the field  $_{3}PO_{4}$  was used as photocatalysts as well as 837 the some novel photoreactors for better photocatalytic 838 ctivity. We briefly summarized the fundamental mputational techniques, and the difference of synthesis understanding of Ag<sub>3</sub>PO<sub>4</sub> as photocatalyst 839 methods for fabricating terrific Ag<sub>3</sub>PO photecatalyst was also discussed. The obstacles that hinder its practical 840 more these obstacles were also presented in this review. Metal deposition 841 applications and the solution to could effectively suppress the photocorrosion phenomenon of Ag<sub>3</sub>PO<sub>4</sub>, thereby improving its photocatalytic 842 activity, and protect it from dissolution in aqueous solution. By combining it with other materials, the composites 843 could easily break the limitation such as limited light absorption range and high recombination rate of 844 845 photogenerated charge carriers for a single component. Doping is also a feasible way to remove some obstacles that hinder the practical application of Ag<sub>3</sub>PO<sub>4</sub>. It could modify the surface structure, adjust the band gap energy, 846 847 and influence the kinetic state of photoexcited charge carriers of Ag<sub>3</sub>PO<sub>4</sub>. Through subtly designing the synthetic process, we could achieve both elements doping and morphology control at the same time. However, it should 848

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 are 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 Ag<sub>3</sub>PO<sub>4</sub> photocorrosion should be in-depth studied. Researchers demonstrated that 855 metallic Ag could appear in both the synthesis process and photoc sis process. Appropriate 856 metallic Ag loading is conducive to its photocatalytic activity and 857 ty. However, few researchers have discussed the exact amount of silver dissolving out com the lattice of  $Ag_3PO_4$  in photocatalysis 858 process. A quantizable Ag<sup>0</sup> generated by photocor bsi avorable for the evaluation of modification 859 effect. Extensive agglomeration of Ag nanopart sees would decrease the adsorption rate and capacity 860 Ag on the surface of Ag<sub>3</sub>PO<sub>4</sub> was rarely studied. Nonof Ag<sub>3</sub>PO<sub>4</sub>. Besides, the loading 861 uniform diameters Ag nanoparticle randomly loading is undesirable for scientific studies. These two 862 rther enhancement of photocatalytic performance of Ag<sub>3</sub>PO<sub>4</sub>. 863 aspects are impor for

2) The control of morphology, particle diameter, and surface states is important for the enhancement of photocatalytic performance of  $Ag_3PO_4$ -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 photodegradation 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 Ag<sub>3</sub>PO<sub>4</sub> loaded hybrid composite is an important subject for the practical 872 application of Ag<sub>3</sub>PO<sub>4</sub> owing to the high cost of pure Ag<sub>3</sub>PO<sub>4</sub>. However, there is a big controversy in 873 distinguishing whether it is type II heterojunction or Z-scheme-like photocatalytic mechanism while 874 875 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 no researchers have 876 studied the combination of doped Ag<sub>3</sub>PO<sub>4</sub> with other semiconductor materials for the enhancement of 877 photocatalytic performance, which we hope that some researchers vo 878 put strength to study this aspect in the future. Furthermore, theoretical simulation is a 879 technique for the design of photocatalyst, which should be abundantly using in the lesign stage. To experimentally prove the 880 degsined photocatalysts available is a low effi y-error" methodology. Using theoretical 881 ier 882 simulation could give us a clear view whether the designed photocatalyst is theoretically feasible, and e optimal photocatalytic performance. guide us to select the proper parar 883 le ac demic research into full-scale practical application to efficiently 4) In order to turn laboratory-se 884 ell) as environmental purification, development of efficient pilot-scale 885 utilize solar ene treatment system is indispensable to provide useful information for further large-scale application. In 886 addition, characteristics of Ag<sub>3</sub>PO<sub>4</sub>-based photocatalysts should be taken into consideration in the 887 design of suitable photoreactors. Besides, there are mainly two ways to use the photocatalysts in 888 reactors, i.e., using nanosized powder-like photocatalysts and using immobilized photocatalysts. 889 Generally, nanosized powder-like Ag<sub>3</sub>PO<sub>4</sub> hybrid composite photocatalyst possess higher 890 891 photocatalytic activity than the immobilized ones. However, the separation of the nanosized powderlike Ag<sub>3</sub>PO<sub>4</sub> hybrid composite photocatalyst in dispersion system and recycling of it are difficult, which 892

893		needs further efforts to balance the superior photocatalytic activity (smaller particle size usually means
894		higher photocatalytic activity) and recycling efficiency. We believe that an immobilized Ag <sub>3</sub> PO <sub>4</sub> -based
895		photocatalyst with high photostability and photocatalytic activity is a feasible way for practical
896		application, which should researchers put more strength in this aspect. Besides, although some
897		researchers have studied coupling Ag <sub>3</sub> PO <sub>4</sub> with some recyclable support materials such as aerogels,
898		magnetic materials, small balls, and membranes, further efforts to develop recyclable Ag <sub>3</sub> PO <sub>4</sub> based
899		composite photocatalysts with excellent photocatalytic performance could not be ignored. Moreover,
900		the rejuvenation of Ag <sub>3</sub> PO <sub>4</sub> -based photocatalyst is of great importance for the practical application. We
901		expect researchers could pay more attention to this aspect, and hereiuny designed a self-rejuvenated
902		$Ag_3PO_4$ -based hybrid composite to solve the photocorror in problem.
903	5)	To date, most studies have only tested the photocatalyte performance of Ag <sub>3</sub> PO <sub>4</sub> under ideal conditions
904		and focused on the degradation of single pollutert such as MO, Rh B, and phenol. However, in real-
905		world situation, the circumstance character solution is much more complicated. Researchers should
906		put more energy to discuss the outcomes while using modified Ag <sub>3</sub> PO <sub>4</sub> photocatalysts to deal with the
907		pollutants in real externation of physical, chemical, and microbiological means with
908		photocatalytic treatment are required to get a desirable level of water quality.
909	6)	Other than the aforementioned aspect, health concern of using Ag <sub>3</sub> PO <sub>4</sub> as a photocatalyst should also
910		put into consideration. With the using of $Ag_3PO_4$ as a photocatalyst, it is inevitable released some of it
911		into the environment after the photocatalytic process. In consideration of its anti-bacterial property, the
912		risk of leak of Ag <sub>3</sub> PO <sub>4</sub> in environment to flora, fauna and human being health need to be carefully
913		assessed. However, adverse effects of released Ag <sub>3</sub> PO <sub>4</sub> in the environment are still unknown. To the

914 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<sub>3</sub>PO<sub>4</sub> in the future.

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