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Minireview

Recent progress in Ag_3PO_4 -based all-solid-state Z-scheme photocatalytic systems

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ABSTRACT

Heterogeneous semiconductor photocatalysis is a promising green technology solution to energy and environmental problems. Traditional photocatalyst TiO_2 , with a wide band gap of 3.2 eV, can only be excited by UV light and utilizes less than 4% of solar energy. Silver phosphate (Ag_3PO_4) is among the most active visible-light-driven photocatalysts reported. Unfortunately, unwanted photocorrosion is the main obstacle to the practical application of Ag_3PO_4 . Much effort has been made in recent years to address this issue and further enhance the photocatalytic performance of Ag_3PO_4 . The construction of Z-scheme photocatalytic systems that mimic natural photosynthesis is a promising strategy to improve the photocatalytic activity and stability of Ag_3PO_4 . This brief review concisely summarizes and highlights recent research progress in Ag_3PO_4 -based all-solid-state Z-scheme photocatalytic systems with or without a solid-state electron mediator, focusing on their construction, application, and reaction mechanism. Furthermore, the challenges and future prospects of Ag_3PO_4 -based Z-scheme photocatalytic systems are discussed.

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1. Introduction

Heterogeneous semiconductor photocatalysis is considered a promising technology due to its great potential to solve energy and environmental problems [1,2]. Traditional photocatalyst TiO_2 is low cost, highly photocatalytically active, and shows excellent chemical and photochemical stabilities [3,4]. However, the wide band gap of TiO_2 renders it responsive to only UV light, which accounts for only 4% of solar light. Meanwhile, the visible light region comprises 43% of the entire solar spectrum. Accordingly, much research is currently focused on the manufacture of efficient visible-light-response photocatalysts for the utilization of solar energy [5–8].

Among well-known visible-light-driven photocatalysts, sil-

ver orthophosphate (Ag_3PO_4), has attracted increasing attention since first being reported by Ye et al. [9] in 2010. Ag_3PO_4 has a body-centered cubic structure with space group $P4_3n$ [10]. As shown in Fig. 1, all atoms are in four-coordinate environments, with the Ag atom coordinated by four O atoms, the P atoms coordinated by four O atoms, and the O atoms coordinated by three Ag atoms and one P atom [11]. Ag_3PO_4 has an indirect band gap of 2.36 eV and direct transition of 2.43 eV, and is considered a promising visible-light-driven photocatalyst [10]. Under visible light illumination, Ag_3PO_4 can achieve a quantum efficiency of ~90% for water oxidation using AgNO_3 as the electron acceptor [9], which is much higher than that of the other reported visible-light-driven photocatalysts [12]. In our previous work, under simulated solar light or visible LED

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Fig. 1. Crystal structure of Ag_3PO_4 with (a) ball-stick and (b) polyhedron representations (red, purple, and blue spheres represent O, P, and Ag atoms, respectively) [11].

light, Ag_3PO_4 drastically degraded dye pollutants in a short time [13,14]. Ag_3PO_4 has excellent photocatalytic activity due to its superior electronic structure characteristics [10]. Using density-functional-theory-based calculations, Umezawa et al. [15] concluded that the excellent photocatalytic performance of Ag_3PO_4 was partly attributed to the highly dispersive band structure of the conduction-band minimum (CBM), which results from Ag s /Ag s hybridization without localized d states. Zhu et al. [11] employed first-principles density functional theory incorporating the LDA+ U formalism to investigate the origin of Ag_3PO_4 photocatalytic activation. They demonstrated that Ag_3PO_4 has a highly disperse conduction band and the PO_4^{3-} inductive effect, which helps separate electron/hole pairs. Furthermore, the defect states of Ag vacancies act as capture traps for photoexcited holes, which promotes the separation of electron/hole pairs excited by visible-light irradiation.

Although Ag_3PO_4 possesses outstanding visible-light-driven photocatalytic performance, the photocorrosion of Ag_3PO_4 is the main obstacle to its practical application [10,12]. The conduction band (CB) of Ag_3PO_4 is located at +0.45 V vs. NHE (normal hydrogen electrode, pH = 0), indicating that H_2O cannot be reduced to H_2 by Ag_3PO_4 . Therefore, the electrons in the

Ag_3PO_4 CB can reduce Ag^+ ions released from the crystal lattice of Ag_3PO_4 to Ag. This phenomenon destroys the Ag_3PO_4 structure and decreases its photocatalytic performance [10]. To meet industrial requirements, much effort has been devoted to further enhance the photocatalytic performance and stability of Ag_3PO_4 , including metal deposition [16,17], assembly with carbon materials [18–20], immobilization on support materials [21,22], and combination with other semiconductors to form type-II heterojunctions or Z-scheme systems [10,12,23]. In particular, mimicking natural photosynthesis in Ag_3PO_4 -based all-solid-state Z-scheme systems could produce a wide absorption range, high charge-separation efficiency, strong redox ability, and long-term stability [23]. In this brief review, we provide an overview of the main achievements in Ag_3PO_4 -based Z-scheme photocatalytic systems, focusing on their construction, application, and reaction mechanism, followed by a brief discussion of the future development of this class of photocatalytic system.

2. Derivation and mechanism of all-solid-state Z-scheme photocatalytic system

Photocatalytic reaction processes mostly involve three steps. (i) Generation of electrons and holes through the absorption of light with higher energy than the band gap of the semiconductor photocatalyst; (ii) charge separation and migration onto the photocatalyst surface; and (iii) reduction/oxidation reactions on the photocatalyst surface [24,25]. To utilize solar light, the band gap of the photocatalyst must be narrow. However, a narrow band gap allows photogenerated electrons and holes to easily recombine. Therefore, it is difficult for a single photocatalyst to simultaneously utilize solar light and possess high photocatalytic activity. This problem can be overcome by constructing heterogeneous photocatalytic systems (usually type-II heterojunctions) [26]. In a type-II heterostructured photocatalyst system (Fig. 2(a)) under visible light irradiation, photoinduced electrons (e^-) in the CB of photocatalyst I (PC I)

Fig. 2. (a) Charge transfer in a type-II heterojunction; (b) Charge separation mechanism in natural photosynthesis [28]; (c) Schematic diagram of a Z-scheme system with shuttle redox mediators.

can transfer to the CB of photocatalyst II (PC II), while holes (h^+) in the valence band (VB) of PC II can migrate to the VB of PC I, which promotes the effective separation of electrons and holes, resulting in enhanced photocatalytic performance [26]. Although the recombination of electrons and holes is inhibited in type-II heterostructured photocatalytic systems, the redox ability of photogenerated electrons and holes on reaction sites is decreased after migration (Fig. 2(a)) [23,27]. Therefore, it is necessary to design and explore new photocatalytic systems to solve these problems. By mimicking natural photosynthesis, a newly-developed Z-scheme photocatalytic system can satisfy the aforementioned requirements [23,27].

In nature, H_2O and CO_2 are converted into O_2 and carbohydrate through photosynthesis in green plants (Fig. 2(b)). This photosynthetic process, which looks like the letter “Z”, is known as the Z-scheme system. As shown in Fig. 2(b), photosystems I (PS I) and II (PS II) are excited by solar light irradiation, and the photogenerated electrons jump to a higher electronic state (excitation), which is connected to an electron transfer chain (electron mediator). The electrons in PS I flow from the electron transport chain, leading to the reduction of coenzyme $NADP^+$ into $NADP$, which reduces CO_2 to carbohydrate, while water oxidation occurs in PS II [28,29]. Mimicking the natural photosynthesis of green plants, the artificial Z-scheme photocatalytic system has been explored, and was first used for water splitting, with an electron acceptor/donor (A/D) usually serving as the electron mediator [30–32]. As shown in Fig. 2(c), two different narrow-bandgap semiconductor photocatalysts are selected as PS I and PS II. Under visible light irradiation, photoinduced electron transfer from the CB of PS II to the VB of PS I is dependent on the redox reactions of the A/D pair. Therefore, the electron in the CB of PS I and the hole in the VB of PS II participate in water splitting. Commonly used A/D pairs are IO_3^-/I^- , Fe^{3+}/Fe^{2+} , and NO_3^-/NO_2^- [23]. These redox mediators can strongly absorb visible light, decreasing the light absorption of the photocatalysts (PS I and PS II), making it difficult to maintain long-term stability and active states of these A/D pairs. Furthermore, this Z-scheme system (Fig. 2(c)) cannot be used to degrade pollutants in solution because the pollutants can hinder the redox reaction of the A/D pair. Accordingly, all-solid-state Z-scheme photocatalytic systems have been developed.

As shown in Fig. 3(a), two different narrow band gap photocatalysts were used as PS I and PS II. A solid conductor between the two photocatalysts forming the ohmic contact was employed as a solid-state electron mediator [23]. Under visible light, the electrons can be simultaneously excited from the VB of both PS I and PS II to the CB, leaving holes in the VB. The electrons from the CB of PS II can directly recombine with the holes from the VB of PS I through the ohmic contact [23,32]. Therefore, the recombination of electrons and holes is inhibited within PS I or PS II, such that electrons in the CB of PS I and holes in the VB of PS II can be mostly reserved for forward reduction and oxidation reactions (Fig. 3(a)), respectively. Moreover, in this system, the shielding effect of irradiated incident light caused by the A/D pair can be eliminated. Without this limitation, all-solid-state Z-scheme systems can be used in both

Fig. 3. (a) Schematic illustration of an all-solid-state Z-scheme system with a conductor as the electron mediator. (b) Schematic illustration of a direct Z-scheme system.

the gas and liquid phase.

As many defects can aggregate at the solid/solid contact interface, the energy levels of the solid/solid contact interface are quasicontinuous, which is similar to in a conductor. This indicates that the solid/solid contact interface has some properties similar to conductors. Therefore, the solid/solid contact interface can also form the ohmic contact [23]. Without a conductor as the electron mediator, a direct Z-scheme photocatalytic system can be formed when PS I directly contacts PS II (Fig. 3(b)). Similarly, the direct Z-scheme photocatalytic system can also retain oxidative holes and reductive electrons in different counterparts (Fig. 3(b)), resulting in enhanced photocatalytic activity. Evidently, all-solid-state Z-scheme photocatalytic systems can solve the problems of single photocatalyst and type-II heterostructured photocatalytic systems (Fig. 3).

Ag_3PO_4 has a very deep valence band, located at approximately +2.9 V vs. NHE (pH = 0), making it well aligned for oxidation reactions [12]. Ag_3PO_4 is used as PS II and coupled with a suitable visible-light-driven photocatalyst (PS I) to form the Z-scheme system. Therefore, the photogenerated electrons in the CB of Ag_3PO_4 can recombine with the holes from PS I, resulting in the improved photostability of Ag_3PO_4 . Furthermore, the leaving holes in the VB of Ag_3PO_4 can retain the strong oxidizability, allowing the photocatalytic oxidation of water and organic pollutants [10,12]. Therefore, Ag_3PO_4 -based Z-scheme photocatalytic systems show great potential for solving energy and environmental problems in the future.

3. Ag_3PO_4 -based Z-scheme photocatalytic systems with a conductor as electron mediator

In Ag_3PO_4 -based Z-scheme photocatalytic systems, metal Ag conductor has always been used as the electron mediator because Ag nanoparticles can be generated *in situ* during preparation or produced by the photoreduction of Ag_3PO_4 in the photocatalytic process. Recent progress in Ag_3PO_4 -based Z-scheme photocatalytic systems with solid state electron mediators are summarized in Table 1.

In recent years, graphitic C_3N_4 (g- C_3N_4), a novel metal-free inorganic semiconductor, has attracted much attention in the photocatalysis of water splitting, CO_2 reduction, and environmental purification [33]. The band gap of g- C_3N_4 is about 2.7 eV, meaning that it can absorb visible light up to 460 nm. Furthermore, the CB minimum of g- C_3N_4 is extremely negative, so photogenerated electrons in the CB of g- C_3N_4 should have a

Table 1Recent work on Ag₃PO₄-based Z-scheme photocatalytic systems with solid state electron mediators.

PS I	PS II	Electron mediator	Synthesis method	Light source	Reactant	Application	Activity	Ref.
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	<i>in situ</i> precipitation	300 W Xe lamp with a UV cut filter	30 mL of MO (10 mg/L)	degradation	DE = 100% (5 min)	[35]
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	solvent evaporation	300 W Xe lamp ($\lambda > 400$ nm)	50 mL of MB (10 mg/L) 600 ppm NO	degradation	DE _{MB} = 99% (14 min) DE _{NO} = 49% (15 min)	[37]
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	precipitation route	300 W Xe lamp ($\lambda > 400$ nm)	100 mL of SMX (1 mg/L)	degradation	DE = 100% (90 min)	[38]
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	deposition method	500 W Xe lamp ($\lambda > 420$ nm)	0.4 MPa CO ₂	CO ₂ reduction	57.5 μ mol/(h·g _{cat})	[39]
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	electrostatic assembly and precipitation	white LED light	AgNO ₃ aqueous solution (100 mL, 10 g/L)	O ₂ production	19 μ mol/L of O ₂ (14 min)	[40]
g-C ₃ N ₄	Ag ₃ PO ₄	Ag	<i>in-situ</i> precipitation	300 W Xe lamp ($\lambda > 420$ nm)	40 mL of 0.02 mol/L AgNO ₃ solution	O ₂ production	520 μ mol/(h·g)	[41]
AgI	Ag ₃ PO ₄	Ag	<i>in-situ</i> anion-exchange	500 W Xe lamp ($\lambda > 420$ nm)	MO or PhOH solution (50 mL, 20 mg/L)	degradation	DE _{MO} = 97% (18min) DE _{PhOH} = 90%(18min)	[43]
AgBr	Ag ₃ PO ₄	Ag	<i>in-situ</i> anion-exchange	500 W Xe lamp with a UV cut filter	A07 solution (30 mL, 20 mg/L)	degradation	DE = 92% (15 min)	[44]
Ag ₂ S	Ag ₃ PO ₄	Ag	<i>in-situ</i> anion-exchange	300 W Xe lamp ($\lambda > 400$ nm)	80 mL of MO (10 mg/L)	degradation	DE = 100% (120 min)	[45]
SiC	Ag ₃ PO ₄	Ag	precipitation and photoreduction	300 W Xe lamp ($\lambda > 420$ nm)	MO or PhOH solution (100 mL, 10 mg/L)	degradation	DE _{MO} = 97% (15min) DE _{PhOH} = 95%(30min)	[46]
In ₂ O ₃	Ag ₃ PO ₄	Ag	precipitation and photoreduction	300 W Xe lamp ($\lambda > 420$ nm)	C ₂ H ₄ (200 ppm)	degradation	DE = 100% (2 h)	[47]
CuBi ₂ O ₄	Ag ₃ PO ₄	Ag	<i>in situ</i> precipitation	300 W Xe lamp ($\lambda > 420$ nm)	Tetracycline (10 mg/L, 100mL)	degradation	DE = 75% (60min)	[48]
SrTiO ₃	Ag ₃ PO ₄	Ag	deposition method	300 W Xe lamp	RhB (20 mg/L, 50mL), MB (20 mg/L, 50mL), PhOH(10 mg/L, 50mL)	degradation	DE _{RhB} = 100% (16min) DE _{MB} = 100% (12min) DE _{PhOH} = 100%(16min)	[49]
Ag ₃ PO ₄	WO _{2.72}	Ag	deposition method	300 W Xe lamp ($\lambda > 420$ nm)	RhB, MB and MO (10 mg/L, 100mL)	degradation	DE _{RhB} = 100% (3min) DE _{MB} = 100% (2min) DE _{MO} = 100%(20min)	[50]
MoS ₂	Ag ₃ PO ₄	Ag	ethanol-water mixed solvents precipitation	35 W Xe lamp ($\lambda > 420$ nm)	MB(20 mg/L, 30mL) RhB(20 mg/L, 30mL) MO(10 mg/L, 30mL) PhOH (5 mg/L, 30mL)	degradation	DE _{MB} = 100% (60min) DE _{RhB} = 100% (80min) DE _{MO} = 100%(120min) DE _{PhOH} = 95%(200min)	[51]
Ag ₂ MoO ₄	Ag ₃ PO ₄	Ag	solution phase reaction	350 W Xe lamp ($\lambda > 420$ nm)	MB, RhB, MO and PhOH (2×10 ⁻⁵ mol/L, 100mL)	degradation	DE _{MB} = 97% (5min) DE _{RhB} = 95% (5min) DE _{MO} = 90%(5min) DE _{PhOH} = 60%(30min)	[53]
La,Cr:SrTiO ₃	Ag ₃ PO ₄	RGO	precipitation and mixed method	300 W Xe lamp ($\lambda > 420$ nm)	RhB and 2,4-DNP (10 mg/L, 50mL)	degradation	DE _{RhB} = 100% (10min) DE _{2,4-DNP} = 85% (60min)	[56]

MO—methyl orange; DE—degradation efficiency; MB—methylene blue; SMX—sulfamethoxazole; PhOH—phenol; A07—acid orange 7; RhB—rhodamine B; RGO—reduced graphene oxide; 2,4-DNP—2,4-dinitrophenol.

high reduction ability [33,34]. As described above, holes in the VB of Ag₃PO₄ have excellent oxidation abilities; therefore, combining Ag₃PO₄ with g-C₃N₄ to construct a Z-scheme photocatalytic system was expected to achieve enhanced photocatalytic performance. Katsumata et al. [35] synthesized a g-C₃N₄/Ag₃PO₄ hybrid photocatalyst using a facile *in situ* precipitation route, confirming that a small amount of Ag was formed on the g-C₃N₄/Ag₃PO₄ surface from the electron-rich structure of g-C₃N₄ donating electrons to Ag₃PO₄. The as-prepared g-C₃N₄/Ag₃PO₄ containing 25 wt% g-C₃N₄ exhibited the highest photocatalytic performance for methyl orange (MO) degradation, and its activity and stability were better than that of pure Ag₃PO₄. The higher photoluminescence (PL) intensity of g-C₃N₄/Ag₃PO₄ compared to pure Ag₃PO₄ was attributed to the higher recombination rate between electrons in the CB of Ag₃PO₄ and holes in the VB of g-C₃N₄. Furthermore, superoxide radicals (O₂^{•-}) and holes were found to be the main reactive

species for g-C₃N₄/Ag₃PO₄ in MO degradation. If photogenerated charge carrier transfer in g-C₃N₄ and Ag₃PO₄ occurs via a type-II heterojunction mechanism, the photogenerated electrons in the CB of g-C₃N₄ would migrate to the CB of Ag₃PO₄. Due to the positive E_{CB} (+0.45 V vs. NHE) of Ag₃PO₄, the electrons in the CB of Ag₃PO₄ could not reduce O₂ to O₂^{•-} with a redox potential of −0.046 V, which was not in agreement with the radical capture experiments. The CB potential of g-C₃N₄ is −1.15 V, and electrons in the CB of g-C₃N₄ can reduce O₂ to O₂^{•-}. Therefore, g-C₃N₄/Ag₃PO₄ was confirmed as a typical Z-scheme photocatalyst with Ag as the electron mediator, and the photocatalytic mechanism for MO degradation by g-C₃N₄/Ag₃PO₄ is shown in Fig. 4(a). Under visible light irradiation, both Ag₃PO₄ and g-C₃N₄ are excited, leading to the formation of photogenerated electrons in the CB and holes in the VB. Electrons in the CB of Ag₃PO₄ shifted into Ag nanoparticles due to the more positive Fermi energy of Ag compared to the CB level of Ag₃PO₄.

Fig. 4. (a) The Z-scheme photocatalytic mechanism of g-C₃N₄/Ag₃PO₄ for MO degradation under visible light [35]; (b) Photocatalytic mechanism of the g-C₃N₄/Ag₃PO₄ composite [39]; (c) Charge separation and transfer in the solar-driven Z-scheme Ag₃PO₄/Ag/g-C₃N₄ photocatalytic system [40].

Simultaneously, the holes in the VB of g-C₃N₄ can move to Ag and combine with the electrons from Ag₃PO₄. However, the highly reducing electrons in the CB of g-C₃N₄ could react with O₂ to form O₂⁻, which would lead to MO degradation. The holes with strong oxidative abilities in the VB of Ag₃PO₄ would degrade MO directly (Fig. 4(a)). As previously reported, Ag₃PO₄ with (111) facets exhibited the best photocatalytic activity due to the (111) facet possessing the highest surface energy [36]. Fan et al. [37] developed a facile solvent evaporation method for the synthesis of g-C₃N₄/Ag₃PO₄(111) hybrid photocatalyst, during which metallic Ag was also formed. Under visible light irradiation ($\lambda > 400$ nm), the as-obtained g-C₃N₄/Ag₃PO₄(111) containing 10 wt% of g-C₃N₄ exhibited the highest photocatalytic activity in the degradation of methylene blue (MB) and NO gas, and possessed stable photocatalytic ability compared with pure Ag₃PO₄. The detection of reactive species confirmed that the enhanced photocatalytic activity of g-C₃N₄/Ag₃PO₄(111) composite was due to the efficient separation of electron/hole pairs through a Z-scheme system composed of Ag₃PO₄, Ag, and g-C₃N₄, in which Ag acted as the electron mediator. In another study, a facile precipitation method was employed to synthesize the Ag₃PO₄/g-C₃N₄ Z-scheme photocatalyst, which was used to degrade sulfamethoxazole in water. Under visible light irradiation, the sulfamethoxazole removal efficiency using Ag₃PO₄/g-C₃N₄ ($m/m = 98/2$) was higher than that of pure Ag₃PO₄ and g-C₃N₄. In the photodegradation process, *in situ* generated metallic Ag acted as an electron mediator between Ag₃PO₄ and g-C₃N₄ [38].

In addition to its application in photodegradation, the Ag₃PO₄/g-C₃N₄ Z-scheme system has also been used to convert CO₂ to fuels and oxidize H₂O to O₂. Fan et al. [39] prepared Ag₃PO₄/g-C₃N₄ composite using a simple deposition method, and then formed metallic Ag *in situ* by irradiating the Ag₃PO₄/g-C₃N₄ composite with a 500 W Xe lamp. Under simulated sunlight irradiation, the optimal Ag₃PO₄/g-C₃N₄ showed a CO₂ conversion rate of 57.5 $\mu\text{mol}/(\text{h}\cdot\text{g}_{\text{cat}})$, which was 6.1 times higher than that of g-C₃N₄, and found that the main reduction product was CO. The results of CO₂ photoreduction and reactive species scavenging confirmed that the transfer of electrons and holes in Ag₃PO₄/g-C₃N₄ composite obeyed the Z-scheme photocatalytic mechanism, as shown in Fig. 4(b). Under simulated sunlight, the photogenerated electrons in the CB of Ag₃PO₄ shift to metallic Ag and then combine with holes from g-C₃N₄. The leaving electrons in the CB of g-C₃N₄ can reduce CO₂ to fuels. Using an electrostatic assembly and solution-based precipitation method, Yang et al. [40] reported a Z-scheme system of Ag₃PO₄/g-C₃N₄ for water photooxidation using AgNO₃ as the electron acceptor. The authors demonstrated that the morphology of g-C₃N₄ in the composite material can influence photoactivity in the O₂ evolution reaction. After exposure to white LED light, the evolved O₂ efficiency over the optimal Ag₃PO₄/g-C₃N₄ composite was higher than that over pure Ag₃PO₄. Electronic spin resonance (ESR) results indicated that hydroxyl radicals (OH[•]) were formed in the oxygen evolution process. If the photocatalytic mechanism for oxygen evolution reaction was a type-II heterojunction, the photogenerated holes

in the VB of Ag_3PO_4 could migrate to the VB of g- C_3N_4 , meaning that $\text{OH}^\bullet$ could not be generated. This confirmed that an *in situ* Z-scheme system was obtained by the generation of metallic Ag nanoparticles, which acted as a recombination center for photogenerated electrons from Ag_3PO_4 and holes from g- C_3N_4 , maintaining active holes in the VB of Ag_3PO_4 for water oxidation (Fig. 4(c)). Using a facile *in situ* precipitation method, g- C_3N_4 /tetrahedral Ag_3PO_4 hybrid photocatalysts with different mass ratios of g- C_3N_4 were prepared by Ktsumata et al. [41], in which the g- C_3N_4 content had a large influence on the photocatalytic performance. The 20 wt% g- C_3N_4 /tetrahedral Ag_3PO_4 photocatalyst exhibited the highest photocatalytic activity for O_2 evolution from water because a Z-scheme system composed of Ag_3PO_4 , Ag, and g- C_3N_4 was formed.

In addition to g- C_3N_4 , researchers have coupled other photocatalysts with Ag_3PO_4 to construct Z-scheme photocatalytic systems with enhanced activity and stability. The solubility of Ag_nX ($\text{X} = \text{Br}, \text{I}, \text{S}$) is lower than that of Ag_3PO_4 , allowing $\text{Ag}_3\text{PO}_4/\text{Ag}_n\text{X}$ ($\text{X} = \text{Br}, \text{I}, \text{S}$) hybrids to be obtained via an *in situ* ion-exchange route [42]. $\text{Ag}_3\text{PO}_4/\text{AgI}$ composite was fabricated using an *in situ* anion-exchange method by Fang et al. [43] and showed enhanced visible-light-driven photocatalytic performance for MO and phenol degradation compared to pure Ag_3PO_4 and AgI. XPS and TEM analysis confirmed that Ag nanoparticles formed in the early stage of the photocatalytic process, which could act as the charge transmission bridge between Ag_3PO_4 and AgI to construct the Z-scheme system, resulting in enhanced activity and stability. Similarly, other Z-scheme photocatalysts, such as $\text{AgBr}/\text{Ag}_3\text{PO}_4$ [44] and $\text{Ag}_2\text{S}/\text{Ag}_3\text{PO}_4$ [45], have been synthesized via anion-exchange methods with *in situ* generated metallic Ag acting as the electron mediator in the photocatalytic process. Furthermore, other Ag_3PO_4 -based Z-scheme systems using Ag as the electron mediator, including $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{SiC}$ [46], $\text{In}_2\text{O}_3/\text{Ag}/\text{Ag}_3\text{PO}_4$ [47], $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{CuBi}_2\text{O}_4$ [48], $\text{SrTiO}_3/\text{Ag}/\text{Ag}_3\text{PO}_4$ [49], $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{WO}_{2.72}$ [50], and $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{MoS}_2$ [51], have been prepared via liquid phase synthesis (see Table 1). In the $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{WO}_{2.72}$ Z-scheme system, Ag_3PO_4 and $\text{WO}_{2.72}$ were used as PS I and PS II, respectively, due to the VB of $\text{WO}_{2.72}$ being located at a more positive position than that of Ag_3PO_4 and the CB of Ag_3PO_4 being located at a more negative position than that of $\text{WO}_{2.72}$.

Recently, a novel plasmonic Z-scheme system was developed due to the response of noble-metal nanoparticles (such as Ag) to visible light through the surface plasmon resonance (SPR) effect [52]. Tang et al. [53] prepared binary $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid materials using a facile solution phase reaction. XRD analysis showed that Ag nanoparticles were formed on the surface of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composites in the initial stage of photocatalytic process, leading to the generation of the $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ photocatalyst, which exhibited enhanced photocatalytic activity and photostability toward the remediation of organic dye compared with pure Ag_3PO_4 . This result was due to the plasmonic Z-scheme photocatalytic mechanism, which was confirmed by reactive species trapping experiments and band structure analysis of Ag_3PO_4 and Ag_2MoO_4 . As shown in Fig. 5, under visible light irradiation,

Fig. 5. Plasmonic Z-scheme photocatalytic mechanism in the $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ photocatalyst under visible light irradiation [53].

Ag_3PO_4 can absorb photons to produce photogenerated electrons and holes. The surface plasmonic resonance effect and dipolar character of metallic Ag allows Ag to also absorb visible light, with each absorbed photon inducing the efficient separation of an electron and hole. Plasmon-induced electrons in Ag nanoparticles are transported to the CB of Ag_2MoO_4 to react with O_2 , forming $\text{O}_2^{\bullet-}$ active species, which can degrade organic pollutants. Simultaneously, photogenerated electrons in the CB of Ag_3PO_4 transfer to the Ag nanoparticles to recombine with holes produced by plasmonic absorption in the Ag nanoparticles, while the photogenerated holes in the VB of Ag_3PO_4 can directly oxidize the dye molecules.

In addition to Ag, some nonmetal materials with excellent conductivity can be employed as solid state electron mediators. Recent studies have confirmed that reduced graphene oxide (RGO) can be used as the electron mediator to promote charge transfer between PS I and PS II in the Z-scheme system [54,55]. Liu et al. [56] reported a $\text{Ag}_3\text{PO}_4/\text{RGO}/\text{La,Cr:SrTiO}_3$ composite photocatalyst that showed superior anti-photocorrosion and photocatalytic activities in the degradation of both RhB and 2,4-DNP. Reactive species trapping experiments and ESR results indicated that $\text{O}_2^{\bullet-}$ and holes played significant roles in the photocatalytic degradation processes. If charge carrier transfer between Ag_3PO_4 and La,Cr:SrTiO_3 occurred via a type-II heterojunction mechanism, namely, the photogenerated electrons in the CB of La,Cr:SrTiO_3 migrate to the CB of Ag_3PO_4 with holes in the VB of Ag_3PO_4 simultaneously transferring to the VB of La,Cr:SrTiO_3 , then the photogenerated electrons would accumulate in the CB of Ag_3PO_4 and be unable to reduce O_2 into $\text{O}_2^{\bullet-}$, which would contradict the above experimental results. Therefore, charge transfer in $\text{Ag}_3\text{PO}_4/\text{RGO}/\text{La,Cr:SrTiO}_3$ composite was shown to obey the Z-scheme photocatalytic mechanism. Under visible light irradiation, photogenerated electrons in the CB of Ag_3PO_4 could transfer to the donor levels of La,Cr:SrTiO_3 via RGO and recombine with photogenerated holes. Meanwhile, the excited electrons in the CB of La,Cr:SrTiO_3 with a high reduction ability could react with O_2 to produce $\text{O}_2^{\bullet-}$, and holes in Ag_3PO_4 with excellent oxidation power could react with H_2O to produce $\text{OH}^\bullet$, thereby achieving the highly efficient degradation of RhB and 2,4-DNP. Further-

more, RGO could be used as a sheltering layer to protect Ag_3PO_4 from photocorrosion.

4. Direct Ag_3PO_4 -based Z-scheme photocatalytic systems without an electron mediator

A schematic of a direct Z-scheme photocatalytic system is shown in Fig. 3(b). As discussed above, without an electron mediator, the direct Z-scheme photocatalytic system could also retain a high redox ability. Recent studies on direct Ag_3PO_4 -based Z-scheme photocatalytic systems are summarized in Table 2.

As described above, combining Ag_3PO_4 with g- C_3N_4 can form Z-scheme photocatalytic systems with Ag as the electron mediator [35–41]. However, direct $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ Z-scheme systems have also been reported. Yi et al. [57] synthesized g- $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ composite by mixing g- C_3N_4 and Ag_3PO_4 in water with stirring, finding that both the C_2H_4 photo-oxidative activity and stability of Ag_3PO_4 were enhanced by fabrication of the composite. According to the C_2H_4 degradation results and band structure analysis of g- C_3N_4 and Ag_3PO_4 , it was concluded that charge transfer in the g- $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ composite did not follow a conventional type-II heterojunction, and a direct Z-scheme photocatalytic mechanism was suggested. Chen et al. [58] used a facile *in situ* precipitation method to prepare $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ nanocomposites with different molar ratios of Ag_3PO_4 to g- C_3N_4 that exhibited enhanced photocatalytic performance for methylene blue degradation compared to pure Ag_3PO_4 and g- C_3N_4 under visible light. Furthermore, XPS results showed no metallic Ag on the surface of the fresh and used $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ nanocomposites. The results of electron spin resonance (ESR), the photoluminescence (PL), and reactive species determination confirmed that the migration of photo-generated electrons/holes exhibited a direct Z-scheme mechanism in the $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ nanocomposite.

Other direct Z-scheme composites, such as $\text{Ag}_3\text{PO}_4/\text{ZnO}$ [59], $\text{Ag}_3\text{PO}_4/\text{SnSe}_2$ [60], $\text{Ag}_3\text{PO}_4/\text{SnSe}_2$ [61], $\text{Ag}_3\text{PO}_4/\text{Bi}_2\text{MoO}_6$ [62], $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ [63], and $\text{Ag}_3\text{PO}_4/\text{WO}_3$ [64], have also been synthesized using liquid-phase methods, including precipitation/deposition, hydrothermal treatment, and an organic phase *in situ* growth strategy.

In a Z-scheme system of $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ reported previously [51], Ag_3PO_4 nanoparticles were loaded on the surface of MoS_2 nanoslices. Inevitably, metallic Ag could be *in situ* produced in the initial stage of the photocatalytic process and act as the electron mediator. However, Fan et al. [63] reported the direct Z-scheme system of a $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ core-shell heterostructure, which was constructed because the MoS_2 shell can protect Ag_3PO_4 from dissolution and photocorrosion during the photocatalytic process. The $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ photocatalyst showed excellent photocatalytic activity and stability in the photodegradation of RhB and the photocatalytic selective oxidation of benzyl alcohols (BA) to benzaldehyde compared with Ag_3PO_4 . The energy band structure and quenching effects of different scavengers showed that the superior photocatalytic activity of the as-synthesized $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ composite originated from the direct Z-scheme charge carrier migration mechanism, as shown in Fig. 6(a). Under visible light irradiation, both Ag_3PO_4 and MoS_2 were excited. Subsequently, electrons in the CB of Ag_3PO_4 could recombine with holes in the VB of MoS_2 through the solid/solid contact interface. As a result, abundant electrons on the CB of MoS_2 and holes on the VB of Ag_3PO_4 participated in the reduction reaction of dissolved O_2 and the oxidation of RhB and BA, respectively.

Notably, in the direct Z-scheme system of $\text{Ag}_3\text{PO}_4/\text{WO}_3$ composite, WO_3 operates as PS II rather than Ag_3PO_4 due to the VB of WO_3 lying at a more positive position than that of VB of Ag_3PO_4 . The enhanced photocatalytic performance was mainly attributed to the improved separation of photogenerated charge carriers between Ag_3PO_4 and WO_3 via the direct Z-scheme mechanism (Fig. 6(b)). Under visible light irradiation, Ag_3PO_4 and WO_3 can be excited to produce electrons and holes, simultaneously, electrons in the CB of WO_3 transfer to the VB of Ag_3PO_4 to combine with holes. The holes retained in the VB of WO_3 can directly degrade the adsorbed organic dyes or oxidize OH^- to $\text{OH}^\bullet$ radicals, triggering a series of degradation reactions. The electrons left in the CB of Ag_3PO_4 can be consumed through a multi-electron reaction with oxygen and finally produce $\text{OH}^\bullet$ radicals, which accelerate the organic dye degradation [64].

5. Conclusions and prospect

Table 2

Recent studies on direct Ag_3PO_4 -based Z-scheme photocatalytic systems.

PS I	PS II	Synthesis method	Light source	Reactant	Application	Activity	Ref.
g- C_3N_4	Ag_3PO_4	mixed method	300 W Xe lamp	C_2H_4 (200 ppm)	degradation	DE = 100% (3 h)	[57]
g- C_3N_4	Ag_3PO_4	<i>in situ</i> precipitation	300 W Xe lamp ($\lambda > 420$ nm)	MB (0.9×10^{-5} mol/L, 100 mL)	degradation	DE = 99% (30 min)	[58]
ZnO	Ag_3PO_4	deposition method	300 W Xe lamp	RhB (60 mL, 5 mg/L)	degradation	DE = 32% (240 min)	[59]
SnS_2	Ag_3PO_4	hydrothermal and pre- cipitation	500 W Xe lamp ($\lambda > 420$ nm)	MO (150 mL, 10 mg/L)	degradation	DE = 50% (60 min)	[60]
SnSe_2	Ag_3PO_4	<i>in situ</i> precipitation	300 W Xe lamp ($\lambda > 400$ nm)	RhB (15 mL, 10 mg/L)	degradation	DE = 100% (50 min)	[61]
Bi_2MoO_6	Ag_3PO_4	<i>in situ</i> chemical method	50 W 410 nm LED light	MB (30 mL, 8 mg/L)	degradation	DE = 96.8% (90 s)	[62]
MoS_2	Ag_3PO_4	an organic phase <i>in situ</i> growth strategy	300 W Xe lamp ($\lambda > 420$ nm)	RhB (50 mL, 10 mg/L) BA (50 mL, 4 mmol/L)	degradation and selective oxidation	$\text{DE}_{\text{RhB}} = 100\%$ (16 min) $\text{CE}_{\text{BA}} = 92\%$ (3 h)	[63]
Ag_3PO_4	WO_3	hydrothermal method	300 W Xe lamp ($\lambda > 420$ nm)	MB (10 mg/L, 100 mL) MO (10 mg/L, 100 mL)	degradation	$\text{DE}_{\text{MB}} = 95\%$ (60 min) $\text{DE}_{\text{MO}} = 90\%$ (180 min)	[64]

BA—benzyl alcohols; CE—conversion efficiency.

Fig. 6. (a) Schematic illustration of the photocatalytic mechanism of the $\text{Ag}_3\text{PO}_4/\text{MoS}_2$ core-shell heterostructure under visible light [63]; (b) Proposed mechanism for the direct Z-scheme charge-carrier transfer process in the $\text{Ag}_3\text{PO}_4/\text{WO}_3$ composite [64].

Photocatalysis is a promising technology for solving the environmental and energy problems in the future. Traditional photocatalyst TiO_2 has a wide band gap that limits its practical application. Silver phosphate (Ag_3PO_4) is among the most active visible-light-driven photocatalysts reported, with the excellent photocatalytic performance ascribed to its superior electronic structure characteristics. However, photocatalyst stability remains a major problem of Ag_3PO_4 in both water oxidation and organic decomposition. To meet industrial requirements, much effort has been devoted to further improving the photocatalytic performance and stability of Ag_3PO_4 , including metal deposition, assembly with carbon materials, immobilization on support materials, and combination with other semiconductors to construct type-II heterojunctions or Z-scheme systems. In particular, Ag_3PO_4 -based all-solid-state Z-scheme photocatalytic systems could effectively improve the separation/transportation of charge carriers and substantially enhance the photocatalytic activity and stability of Ag_3PO_4 . Although great progress has been made, some remaining problems must be solved to further advance the use of Ag_3PO_4 -based Z-scheme photocatalytic systems.

(1) As shown in Figs. 2(a) and 3(b), when the band gaps of the two semiconductors are staggered, there is much controversy regarding whether the type-II heterojunction photocatalytic mechanism or the indirect Z-scheme photocatalytic mechanism occurs. Using $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ composite as an example, some reports have confirmed that the migration of photogenerated electrons and holes in $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ exhibits the direct Z-scheme mechanism [57,58], while other studies have shown that $\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$ composite followed a type-II heterojunction mechanism [65–67]. Therefore, an *in situ* detection technique should be developed to clearly distinguish these photocatalytic mechanisms.

(2) Recently, graphene, which has excellent electrical conductivity, has attracted great interest in photocatalysis [68]. Therefore, the graphene could be used as the electron mediator in the Ag_3PO_4 -based Z-scheme photocatalysts to improve photocatalytic activity. Previous reports also showed that the size and morphology of Ag_3PO_4 can greatly influence its photocata-

lytic performance [12]. Therefore, the size and morphology of Ag_3PO_4 should be adjusted to design more efficient Ag_3PO_4 -based Z-scheme photocatalytic systems.

(3) Previous reports of Ag_3PO_4 -based Z-scheme photocatalysts have mainly focused on the photodegradation of organic pollutants in water (Tables 1 and 2), while their application to photocatalytic H_2 generation and CO_2 reduction require future development. Ag_3PO_4 -based Z-scheme systems have been applied to treat harmful gases (ethylene and nitric oxide), and could, therefore, be extended to degrade other harmful gases, such as formaldehyde and toluene.

(4) Separation and reuse of the photocatalysts in a solution dispersion system must be considered. Combining Ag_3PO_4 and magnetic semiconductor materials to form Z-scheme photocatalytic systems could address this issue.

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Graphical Abstract

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Recent progress in Ag_3PO_4 -based all-solid-state Z-scheme photocatalytic systems

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This brief review summarizes recent research progress in Ag_3PO_4 -based all-solid-state Z-scheme photocatalytic systems and discusses their challenges and future development prospects.

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基于 Ag_3PO_4 的全固态Z型光催化体系研究进展

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摘要: 随着现代工业的迅猛发展, 人类面临的能源危机和环境污染问题日益严重. 光催化剂技术有望利用太阳能同时解决这两大问题, 其关键在于设计高效的光催化体系. 传统光催化材料 TiO_2 具有价廉、活性高及稳定性好等优点, 然而其带隙宽($E_g = 3.2 \text{ eV}$), 仅能利用占太阳光谱约4%的紫外光, 从而限制其利用太阳能. 可见光占太阳光谱的40%以上, 因此开发可见光响应的光催化材料成为光催化领域研究焦点.

2010年, 叶金花课题组报道了 Ag_3PO_4 在可见光照射下可高效分解水产氧及降解水体中有机污染物, 从而使其迅速成为研究热点. Ag_3PO_4 是目前为止报道的光量子效率最高的可见光响应的催化材料, 带隙能在2.3~2.5 eV范围内, 其高效的光催化活性归结于其独特的电子结构利于光生电荷的分离及转移. 然而, 由于 Ag_3PO_4 本身易光蚀, 稳定性差, 必然限制其实际应用. 近年来, 为在进一步提升 Ag_3PO_4 活性的基础上增强稳定性, 研究者通过多种方法对其进行修饰, 包括贵金属沉积、碳材料修饰、负载及半导体异质复合等. 相对于前面几种修饰方法, 半导体复合相对高效且成本低. 半导体复合主要构成II型异质结构和Z型光催化体系. II型异质结构由于内建电场的存在可以促进光生电荷的定向转移, 从而提高光生电荷的分离效率, 进而提高光催化活性. 然而, 这种电荷的定向迁移会降低光生电荷的氧化还原能力.

模拟绿色植物的光合作用过程, 一种全固态Z型光催化体系应运而生, 其是将两种导带和价带位置匹配的可见光驱动的催化剂分别作为光催化系统I (PS I)和光催化系统II (PS II), 同时选用导电性能优良的材料(Ag, Au和RGO等)作为电子介体. 可见光照条件下, PS I和PS II均被激发产生电子和空穴, PS II导带上的电子通过电子介质与PS I价带空穴复合, 一方面抑制了PS I和PS II本身电子和空穴的复合, 另一方面保留了PS I导带电子的强还原性和PS II价带空穴的强氧化性. 另外, PS I和PS II紧密结合形成具有准连续能级的固-固接触界面, PS II导带上的电子直接与PS I价带空穴复合, 形成无电子介体的直接Z型光催化体系.

Ag_3PO_4 价带顶相对靠下, 氧化能力强, 往往作为PS II组分, 其与导带顶相对靠上的催化剂(PS I)构成Z型体系, 这样 Ag_3PO_4 导带电子可与PS I的价带空穴复合, 减弱电子对 Ag_3PO_4 本身的还原, 提高其稳定性; 另一方面, Ag_3PO_4 价带空穴可参与氧化反应. 基于 Ag_3PO_4 的Z型体系主要以Ag作为电子介体, 归因于在制备及光催化过程中原位产生的少量Ag可直接作为电子介体. 此外, 还原氧化石墨烯(RGO)也可作为电子介体, 并且其存在可进一步提高 Ag_3PO_4 的稳定性. 需要指出的是, 基于Ag的等离子体共振效应, Ag_3PO_4 基等离子体Z型光催化体系也受到关注.

目前, Z型光催化体系处在发展阶段, 必然存在一些问题, 比如, II型异质光催化体系与直接Z型光催化体系如何区分, 有待进一步研究. 另外, 报道的基于 Ag_3PO_4 的Z型体系主要用来光催化降解水体中的有机污染物, 催化剂的回收再利用受到限制, 今后可开发磁性 Ag_3PO_4 基Z型体系, 解决回收再利用的问题; 另外, 通过能带调控, 可将基于 Ag_3PO_4 的Z型体系多用于光催化产氢、还原 CO_2 及处理有害气体.

关键词: 磷酸银; 光催化; Z型体系; 应用; 机理

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