

Review Article

Ag₃PO₄ Semiconductor Photocatalyst: Possibilities and Challenges

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Ag₃PO₄ as a photocatalyst has attracted enormous attention in recent years due to its great potential in harvesting solar energy for environmental purification and fuel production. The photocatalytic performance of Ag₃PO₄ strongly depends on its morphology, exposed facets, and particle size. The effects of morphology and orientation of Ag₃PO₄ on the catalytic performance and the efforts on the stability improvement of Ag₃PO₄ are reviewed here. This paper also discusses the current theoretical understanding of photocatalytic mechanism of Ag₃PO₄, together with the recent progress towards developing Ag₃PO₄ composite photocatalysts. The crucial issues that should be addressed in future research activities are finally highlighted.

1. Introduction

The development of efficient photocatalysts is very important and desirable in environmental pollution mediation and solar energy conversion [1–6]. Over the past decades, fundamental progress has been made in developing novel photocatalysts, particularly visible light response catalysts for the efficient utilization of solar energy. A great deal of photocatalysts, including inorganic, molecular, and hybrid organic/inorganic materials, have been explored to meet specific requirements such as a light-absorbing wavelength modification, photoinduced charge separation, and a faster photocatalytic reaction. Among the various photocatalysts developed, TiO₂ is undoubtedly the most popular and widely used photocatalyst since it is of low cost, high photocatalytic activity, chemical and photochemical stability [7, 8]. However, TiO₂ is not ideal for all purposes and performs rather poorly in processes associated with solar photocatalysis due to its wide band gap (3–3.2 eV), thus making impractical overall technological process based on TiO₂. To design visible-light-driven photocatalysts, two strategies have been proposed. One is to modify the wide band gap photocatalysts (such as TiO₂, ZnS) by doping or by producing

hetero-junctions between them and other materials [4, 7–12], and the other involves exploration of novel semiconductor materials capable of absorbing visible light. Various compounds, such as BiVO₄ [13], Bi₂WO₆ [1, 14], CaBi₂O₄ [15], PbBi₂Nb₂O₉ [16], Bi₄Ti₃O₁₂ [17], and Ag@AgCl [18], and others have been reported to be promising photocatalysts under visible light irradiation [19–22]. Despite many of these photocatalysts being effective for the degradation of organic pollutants and water splitting, up to date, the present achievements are still far from the ideal goal.

Yi and his coworkers [23] have recently presented the pioneering work on exploring the photocatalytic properties of Ag₃PO₄ that exhibit extremely high photooxidative capabilities for the O₂ evolution from water and the decomposition of organic dyes under visible-light irradiation. Actually, the photodegradation rate of organic dyes over Ag₃PO₄ is dozens of times faster than the rate over BiVO₄ and commercial TiO_{2-x}N_x [23, 24]. Moreover, the most interesting is that this novel photocatalyst can achieve a quantum efficiency of up to 90% at wavelengths greater than 420 nm, which is significantly higher than the previous reported values. This finding potentially opens an avenue for solving current energy crisis and environment problems with abundant solar light, and the

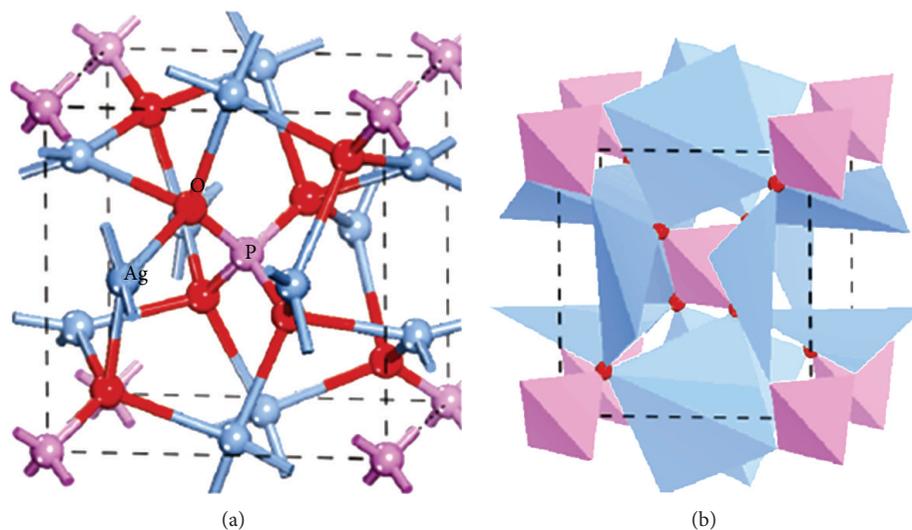


FIGURE 1: Unit-cell structure of cubic Ag_3PO_4 , showing (a) ball and stick and (b) polyhedron configurations. Red, purple, and blue spheres represent O, P, and Ag atoms, respectively [24].

research of Ag_3PO_4 is thus attracting considerable interest. Since then, many efforts have been devoted to further improving and optimizing their photoelectric and photocatalytic properties. Despite the fact that Ag_3PO_4 is a promising candidate for environmental remediation and renewable energy, the consumption of a large amount of noble metal and the low structural stability of pure Ag_3PO_4 strongly limits its practical environmental applications. Therefore, it is a highly crucial task to improve the photocatalytic stability of Ag_3PO_4 while maintaining its high photocatalytic activity. In this paper, the effects of morphology and orientation of Ag_3PO_4 on the catalytic performance and the current theoretical understanding of key aspects of Ag_3PO_4 photocatalysts are presented. Also reviewed is the effort on the photocatalytic stability of Ag_3PO_4 and Ag_3PO_4 composite photocatalyst.

2. The Structure of Ag_3PO_4

Ag_3PO_4 is of body-centred cubic structure type with space group $P4-3n$ and a lattice parameter of $\sim 6.004 \text{ \AA}$. The structure consists of isolated, regular PO_4 tetrahedra (P–O distance of $\sim 1.539 \text{ \AA}$) forming a body-centred-cubic lattice. The six Ag^+ ions are distributed among twelve sites of twofold symmetry [25]. This indicates that each Ag atom at $(0.25, 0, 0.50)$ actually occupies one of the two sites at $(x, 0, 0.50)$ and $(0.5 - x, 0, 0.50)$ on the 2-fold axis. The unit-cell structure of cubic Ag_3PO_4 is shown in Figure 1, in which the Ag atom experiences 4-fold coordination by four O atoms [24]. The P atoms have 4-fold coordination surrounded by four O atoms, while the O atoms have 4-fold coordination surrounded by three Ag atoms and one P atom.

3. Morphology Control and Catalytic Properties of Ag_3PO_4

Since Ag_3PO_4 was first reported as visible light response photocatalyst by Yi and his coworkers [23], much research

has been devoted to investigate this active photocatalyst [26–29], and different methods have been developed to synthesize various Ag_3PO_4 and its composites [28, 30–32]. The investigation of photocatalytic activity shows that all of the prepared Ag_3PO_4 exhibit excellent photocatalytic activity under UV light irradiation or visible-light illumination, which is much more excellent than that of commercial P25 TiO_2 [33, 34] or N-doped TiO_2 [30, 35, 36] as shown in Figure 2.

It is well known that the morphology of materials is closely related to the exposed facets of the crystals, which directly affect the properties of the catalysts. Various Ag_3PO_4 nanostructures including spherical morphology [33, 34], rhombic dodecahedrons [30], concave trisoctahedrons [37], cubes [26, 30], and tetrapods [38] with controlling particle size [39] have been designed and synthesized to further improve or optimize the photocatalytic properties. The investigations revealed that the rhombic dodecahedrons exhibit much higher photocatalytic activity in comparison with spheres and cubes for the degradation of organic contaminants [23, 30], and the enhanced photocatalytic activity of Ag_3PO_4 rhombic dodecahedrons is primarily ascribed to the higher surface energy of $\{110\}$ facets (1.31 J/m^2). The highly exposed $\{110\}$ facets also lead to the higher visible light activity of Ag_3PO_4 tetrapods than that of the polyhedrons for the degradation of toxic organic compounds [38]. The concave trisoctahedral Ag_3PO_4 microcrystals with high-index facets have also been reported to show much higher photocatalytic properties than cubic Ag_3PO_4 and commercial N-doped TiO_2 [37].

The synthetic parameters, such as reaction component, temperature, and reaction time, usually serve as effective routes for tailoring the morphology and structure of Ag_3PO_4 crystals. By directly reacting AgNO_3 and Na_2HPO_4 , only Ag_3PO_4 particles with irregular spherical structures can be obtained, while the single crystalline Ag_3PO_4 submicrocubes with sharp corners, edges, and smooth surfaces can be

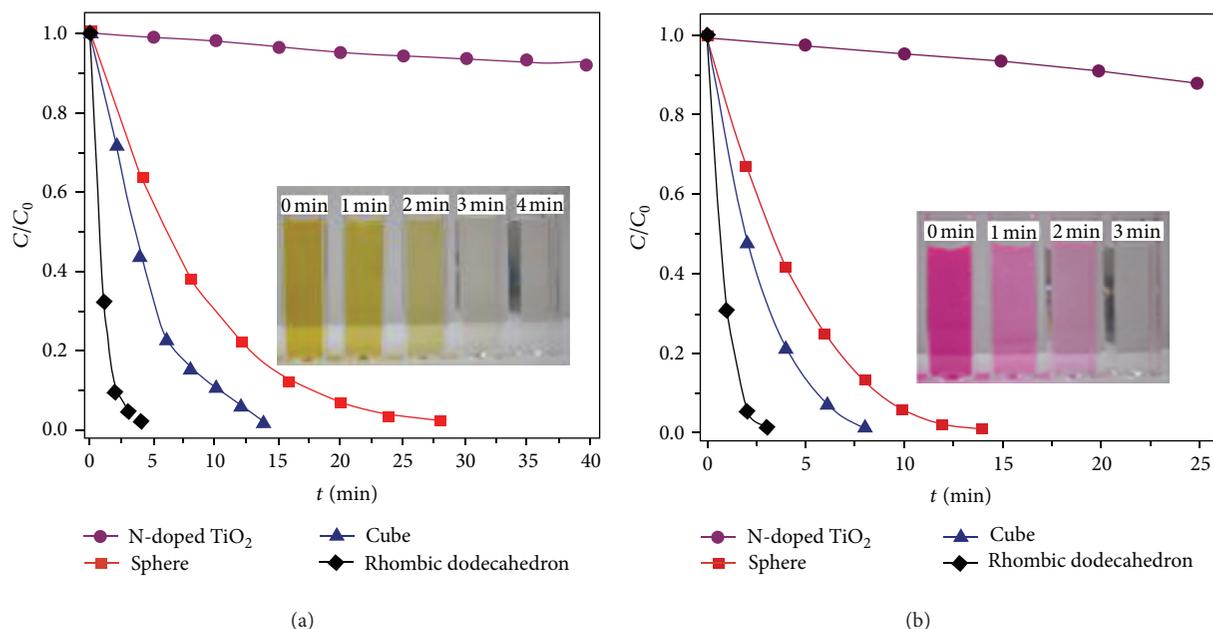


FIGURE 2: Photocatalytic activities of Ag₃PO₄ rhombic dodecahedrons, cubes, and spheres and N-doped TiO₂ for (a) MO and (b) RhB degradation under visible-light irradiation ($\lambda > 420$ nm) [30].

fabricated with $[\text{Ag}(\text{NH}_3)_2]^+$ as precursors under the same conditions, which therefore exhibit higher photocatalytic activity than spherical nanoparticles [35]. Moreover, the morphologies and structures of the as-prepared Ag₃PO₄ crystals could be further tailored by changing the aging time of the $[\text{Ag}(\text{NH}_3)_2]^+$ complex due to the ammonia volatility. For example, when $[\text{Ag}(\text{NH}_3)_2]^+$ complex solution was aged at room temperature for 1 h, the as-prepared Ag₃PO₄ crystals possess irregular cubic morphology and six rhombic planes. Upon further increasing the aging time up to 2 h, the Ag₃PO₄ crystals transform into irregular structure with concave surfaces. Interestingly, when the aging time has been prolonged to 4 h, the corresponding Ag₃PO₄ products with four symmetrically arrowheaded morphologies have been fabricated (shown in Figure 3), and no cubes have been observed. The variation of morphologies and structures of the as-prepared Ag₃PO₄ crystals leads to the variation of optical properties (Figure 3(d)). Similar morphology variation of Ag₃PO₄ particles prepared by a pyridine-assisted hydrothermal method is found to change regularly from spherical to particles with the corners and edges then to rhombic dodecahedrons with an increase in pyridine concentration [27].

4. Theoretical Study of the Electronic Structure and Photocatalytic Performance

To elucidate its mechanism of the extremely high photooxidative under visible light irradiation of Ag₃PO₄, theoretical works have been carried out by using first-principle method. Photocatalysis reactions are determined primarily by three processes: (1) the photoexcitation of electron-hole pairs due to light harvesting, (2) the transfer of carriers to the surface,

and (3) chemical reactions on the surface. So far, theoretical investigations are mainly focused on the first process, which is relevant to energy band configuration because photoexcited carriers are generated only when the incident photon energy is higher than the bandgap of the photocatalyst. Alignment between the band edges and the redox potentials of the target molecules is also crucial, considering that photoexcited carriers can only be transferred to the adsorbed molecules when there is a sufficiently large negative offset of the conduction band minimum (CBM) and a sufficiently large positive offset of the valence band maximum (VBM) with respect to the redox potentials. Ma et al. investigated the electronic properties and photocatalytic activation of Ag₃PO₄ using first principles density functional theory (DFT) incorporating the local density approximation (LDA) + U formalism [24]. It is found that one PO₄ tetrahedron and three tetrahedral AgO₄ are combined with each other through the corner oxygen. The tetrahedral AgO₄ is heavily distorted to have a dipole moment of 2.2 D (D = debye), which should be closely attributed to a specific nonmetal salt of the oxyacid structure of Ag₃PO₄. In addition, PO₄³⁻ ions have a large negative charge which maintains a large dipole in the Ag₃PO₄, resulting in the distortion of tetrahedral AgO₄. As a consequence, a correlation between the photocatalytic activity and the distortion of AgO₄ tetrahedron is true for a specific phosphate structure. Meanwhile, PO₄³⁻ possessing a large electron cloud overlapping prefers to attract holes and repel electrons, which helps the e⁻/h⁺ separation. The calculated results show that Ag₃PO₄ is an indirect band gap semiconductor; the direct band gap is 2.61 eV and the indirect band gap is 2.43 eV having the character of σ or π bonding states in the VB and the corresponding σ^* or π^* antibonding states in the CB. The effective mass of electrons is far smaller

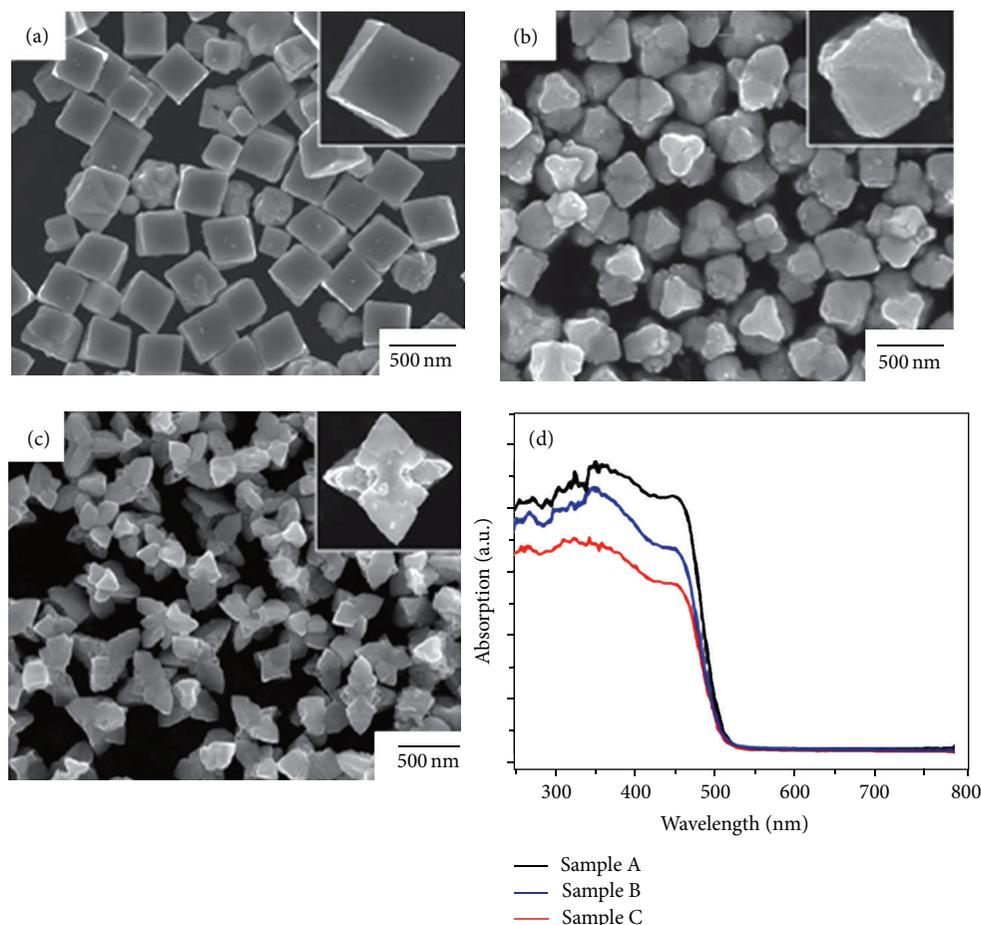


FIGURE 3: SEM images of Ag_3PO_4 products prepared with different aging time: (a) 1 h, (b) 2 h, and (c) 4 h; (d) their ultraviolet-visible diffusive absorption spectrums [35].

than that of holes, which consequently results in a striking difference of the mobility between photoexcited electrons and holes. This is beneficial for decreasing the recombination of electron-hole pairs in Ag_3PO_4 . In addition, Ag vacancies in Ag_3PO_4 with high concentration have a significant effect on the separation of electron-hole pairs and optical absorbance in the visible-light region. To explore the mechanism of the high performance of Ag_3PO_4 , Umezawa et al. have conducted a comparative study of the electronic structures of Ag_3PO_4 , Ag_2O , and AgNbO_3 by first principles calculations [32]. The CBM consisting of Ag s states in Ag_3PO_4 and Ag d states in Ag_2O is the main difference between Ag_3PO_4 and Ag_2O , which is due to the rigid PO_4 tetrahedral unit; partial charge density originating from O sp and P sp derived bonding states is evident in the local density of states (DOS). This increases the ionic character of Ag^+ and $(\text{PO}_4)^{3-}$, making the covalent Ag–O bonds weaker. Thus, the hybridization of Ag d and O p states is negligible in Ag_3PO_4 , rendering fully occupied d states at the VBM. On the contrary, covalent Ag–O bonds, that is, antibonding states of Ag d–O p lying at the CBM are formed in Ag_2O . In AgNbO_3 , the majority of the CBM is composed of Nb d states and the nature of the Ag–O bonding does not significantly affect the characteristics of the CBM.

In Figure 4, the band structures of Ag_3PO_4 , Ag_2O , and AgNbO_3 are illustrated, accompanied by the wave function corresponding to the CBM. In Ag_3PO_4 , the wave function at the CBM is dramatically delocalized due to mainly consisting of Ag s states. In contrast, the CBM of Ag_2O possesses the character of Ag d–O p antibonding states, which are unfavorable for electron transfer due to their localization. In Ag_3PO_4 , a large amount of hybridization between Ag s states on adjacent atoms leads to a dispersive band structure at the CBM without the “contamination” of d states, resulting in a decreased effective electron mass. In AgNbO_3 , the CBM mainly composes of d_{xz} and d_{yz} states, causing an anisotropic charge distribution (Figure 4(c)) and allowing electron transfer only along the z-direction. This anisotropy can also be found in the band structure, where the dispersion of the CBM is very dispersive along X-S-Y and flat along S- Γ indicating the high dependence of the directions. This is undesirable for photocatalysis process because the limited directionality of the electron transfer leads to higher probability of carrier recombination. The CBM of Ag_3PO_4 has, on the contrary, a very isotropic distribution and is hence favorable for electron transfer (Figure 4(a)). The effective mass of the electron is relatively small in every direction in Ag_3PO_4 , which is

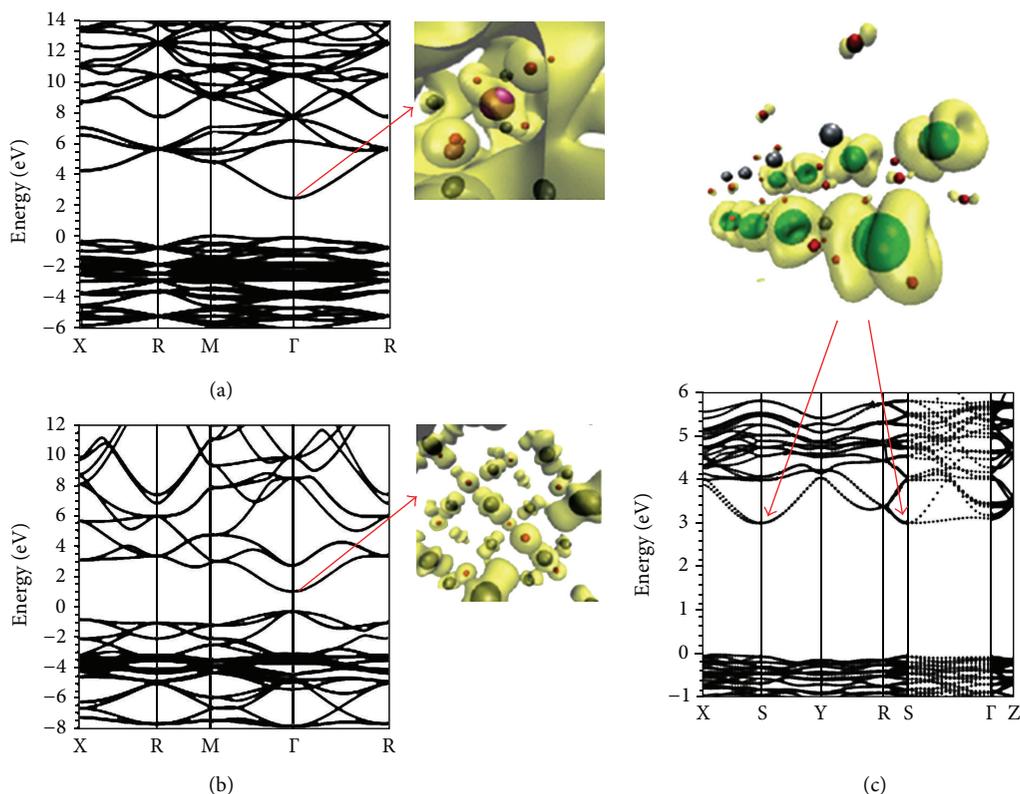


FIGURE 4: (Color) band structures for (a) Ag_3PO_4 , (b) Ag_2O , and (c) AgNbO_3 . The square of the wave function (yellow surface) corresponding to the CBM is also shown in each case, where silver, red, mauve, and green particles represent the positions of Ag, O, P, and Nb atoms, respectively. The isosurfaces are at $0.01 e/\text{\AA}^3$ [32].

also advantageous for electron transfer. Thus, the excellent photocatalytic performance of Ag_3PO_4 is partly due to the highly dispersive band structure at the CBM, which results from Ag s–Ag s hybridization without localized d states.

Using the local density approximation (LDA) and LDA+U approaches, the calculated band gaps of 0.36 and 1.30 eV are far less than the experimental value of 2.45 eV due to the missing discontinuity in the exchange–correlation potential and the self–interaction error within the LDA. To effectively remedy the drawbacks of LDA and understand the photocatalytic mechanism, hybrid density functional theory (DFT) using PBE0 formalism, was used to calculate the band structure, density of state (DOS), and optical properties of Ag_3PO_4 [40]. The hybrid–DFT method gives a direct band gap, $E_{\text{gdir}} = 2.61$ eV, and an indirect one, $E_{\text{gindir}} = 2.43$ eV, which agrees well with the experimental value (2.45 eV). Compared with the top of valence band (VB), the bottom of conduction band (CB) is well dispersive, which indicates that the photogenerated electrons possess smaller effective mass and, therefore, higher migration ability. The redox ability of Ag_3PO_4 is evaluated by determining the energy positions of valence and conduction bands using Mulliken electronegativity and the band gap value calculated accurately. Figure 5 renders the valence and conduction band edge potentials of Ag_3PO_4 . The VBM potential of Ag_3PO_4 is 2.67 V, more positive than $\text{O}_2/\text{H}_2\text{O}$ (1.23 V), indicating that Ag_3PO_4 has the ability to oxidize H_2O to produce O_2 or

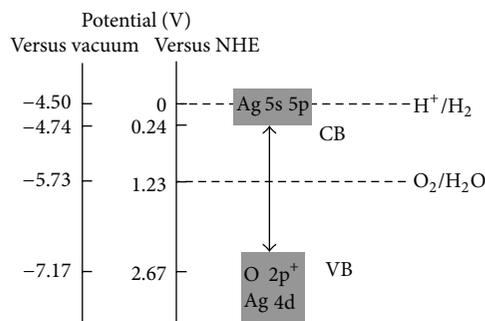


FIGURE 5: Calculated VBM and CBM potentials of Ag_3PO_4 [40].

oxidation pollutants. Whereas the CBM potential of Ag_3PO_4 is 0.24 V, which is lesser than H^+/H_2 (0 V) and cannot reduce H^+ to H_2 [40]. More recently, Ma et al. investigated the electronic and photocatalytic properties of Ag_3PC_4 (C = O, S, Se) by the hybrid density functional method. Similar results for Ag_3PO_4 are obtained [41].

5. Visible Light Response Ag_3PO_4 Based Composite Photocatalyst

To harvest photons in visible region, many narrow bandgap metal oxides or chalcogenides have been coupled with TiO_2

to fabricate visible-light photocatalysts, which exhibit visible-light photocatalytic activity to a certain extent. Such a strategy is also applied to modify Ag_3PO_4 photocatalyst to enhance its photocatalytic activity and/or improve its stability. The previous investigations showed that the photocatalytic activity of Ag_3PO_4 can be enhanced as Ag nanoparticles deposited on Ag_3PO_4 because the Ag_3PO_4 decomposition could capture the photogenerated electrons and thus prevent the recombination of electron-hole pairs within the Ag_3PO_4 samples at the initial stage of photocatalytic reactions. However, the photoactivity decreases with increasing Ag contents due to the formation of Ag layers on the surface of Ag_3PO_4 that shield light absorption, inhibit the transfer of holes from the valance band of Ag_3PO_4 to the interface between photocatalyst, and solution and also hinder the contact of dye molecules with Ag_3PO_4 , and, accordingly, the photocatalytic activity deteriorates gradually [34]. This deterioration of the Ag_3PO_4 photocatalytic activity due to photocorrosion largely limits its practical application as a recyclable highly efficient photocatalyst. It is found that the Ag/ Ag_3PO_4 heterocubes synthesized by reacting Ag_3PO_4 cubes with glucose in an aqueous ammonia solution exhibit higher photocatalytic activities than pure Ag_3PO_4 cubes for the organic contaminants degradation under visible-light irradiation [26]. The stability improvement of Ag_3PO_4 by covering Ag^0 nanoparticles on the surface of Ag_3PO_4 is attributed to the localized surface plasmon resonance (LSPR) effects of silver nanoparticles and a large negative charge of PO_4^{3-} ions [2, 27], which effectively inhibit the reducibility of Ag^+ ions in the Ag_3PO_4 lattice. Ag_3PO_4 can also be rejuvenated from weak photocatalytically active Ag as a recyclable highly efficient photocatalyst by oxidizing Ag with H_2O_2 under a PO_4^{3-} ion atmosphere [29]. However, these strategies are not ideal from the practical application perspective. Thus, the fabrication of Ag_3PO_4 based composite photocatalysts with high photocatalytic activity and excellent stability as well as lower Ag usage for their large scale applications is desirable.

Yao et al. synthesized $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ visible light photocatalyst by depositing of Ag_3PO_4 nanoparticles onto the TiO_2 (P25) surface photocatalyst [42]. Their results show that the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ heterostructured photocatalyst shows enhanced activity and is much more stable than unsupported Ag_3PO_4 . The enhanced activity is attributed to the electron-hole effective separation and the larger surface area of the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite, while the enhanced stability is ascribed to the chemical adsorption of Ag^+ cations in Ag_3PO_4 and O^- anions in TiO_2 . Moreover, the silver weight percentage of the photocatalyst decreases from 77% to 47%, significantly reducing the cost of Ag_3PO_4 based photocatalysts for the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite [42].

The UV photocatalytic activity of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite heterostructures was comparable to that of Ag_3PO_4 nanoparticles surfaces. While the stability and hence reusability of the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ heterostructure catalysts was substantially enhanced as compared with that of Ag_3PO_4 nanoparticles or TiO_2 nanobelts alone. These results were attributed to the improved charge separation of the photogenerated electrons and holes under UV light at the

$\text{Ag}_3\text{PO}_4/\text{TiO}_2$ interface and/or surfactant-like function of the nanobelts in stabilizing the Ag_3PO_4 nanoparticles. $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite heterostructures appear to be more desirable in long-term applications because of their photocatalytic activity as well as the enhanced chemical stability [33].

Considering that the VB level of Ag_3PO_4 is appreciably lower than that of TiO_2 with +2.7 V (versus NHE) and Ag_3PO_4 can be severed as an appropriate sensitizer for TiO_2 , Lee et al. fabricated the novel heterojunction structures of Ag_3PO_4 -core/ TiO_2 -shell by covering the Ag_3PO_4 nanoparticles with polycrystalline TiO_2 by sol-gel method. The prepared $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composites show notably enhanced photocatalytic activity in decomposing gaseous 2-propanol and evolving CO_2 compared to bare Ag_3PO_4 and TiO_2 . It is inferred that the unusually high visible-light photocatalytic activity of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite originates from the unique relative band positions of the two semiconductors [43].

Besides $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite heterostructures, $\text{AgX}/\text{Ag}_3\text{PO}_4$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) heterocrystals have also attracted much attention due to the excellent photocatalytic activity. Bi and coworkers [44] have reported that the $\text{AgX}/\text{Ag}_3\text{PO}_4$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) heterocrystals prepared by in situ ionexchange method embodied some advantages compared to the single Ag_3PO_4 , and it is a more promising and fascinating visible-light-driven photocatalyst than pure Ag_3PO_4 [45]. The $\text{AgBr}/\text{Ag}_3\text{PO}_4$ hybrid synthesized using an in situ anion-exchange method displayed much higher photocatalytic activity than single AgBr or Ag_3PO_4 , as well as high stability under visible light irradiation. The high stability was attributed to the formed $\text{Ag}@\text{AgBr}/\text{Ag}_3\text{PO}_4@/\text{Ag}$ plasmonic system, which effectively retains its activity due to the efficient transfer of photoinduced electrons [45].

6. Conclusion and Perspectives

In this paper, we have summarized the survey of efforts on Ag_3PO_4 photocatalysts. As a quintessence, for example, Ag_3PO_4 photocatalysts have excellent photocatalytic activity and yield a high quantum yield of nearly 90% under visible light ($\lambda = 420 \text{ nm}$) found for the evolution of O_2 in water photolysis [23]. All of the developments show that Ag_3PO_4 and/or its heterogeneous composites have the potential as excellent visible-light-active candidates with high photocatalytic activity. However, to comply with the challenging requirements of economically viable industrial production, many issues are still yet to be addressed, including long-term stability of Ag_3PO_4 in photocatalytic processes. New methods for fabrication Ag_3PO_4 with exposed high-energy facets and novel heterogeneous Ag_3PO_4 cocatalysts are highly desirable. To date, there have been relatively few quantitative studies in the charge carrier dynamics in Ag_3PO_4 and/or its cocatalysts systems, how these dynamics are related to material design, and how they impact the photocatalytic processes. In heterogeneous systems, a particular challenge is that electron-hole recombination is a bimolecular process, which its dynamics often depend nonlinearly on the charge carrier density and so cannot be described using a single time constant. Therefore, obtaining a substantial

breakthrough in efficiency requires an exact understanding of the surface/interface processes at the atomic scale. A true picture of photocatalyst surfaces in action, including such recombination dynamics, needs to be studied by in situ observations using transient optical spectroscopy techniques. A further challenge is translating laboratory-scale academic research into scalable, manufacturable technologies to meet the demands of the efficient utilization of solar energy in the areas of renewable energy and environmental purification.

Acknowledgments

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