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Design and Construction of Ag₃PO₄-based Composite Photocatalysts for Environmental Purification
(環境浄化のためのAg₃PO₄を基盤とする複合光触媒の設計と構築)

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2013
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ABSTRACT

Photocatalytic degradation of organic pollutants has attracted increasing attention because it’s a promising, environmental, and cost-effective technology. For the better utilization of visible light accounting for about 43% of solar energy, visible-light-sensitive photocatalysts are urgently anticipated. Silver orthophosphate (Ag₃PO₄) as a novel photocatalyst exhibits surprisingly high efficiency under visible light irradiation. The quantum yield of the generation of O₂ gas by water oxidation using Ag₃PO₄ is nearly 90% at wavelength around 420 nm. It has a promising future in photocatalytic applications. However, pure Ag₃PO₄ exhibits low efficiency in photocatalytic degradation of gaseous pollutants and superior activity in photodecomposition of organic dyes is still anticipated. The recombination of photo-generated electron-hole pairs, the redox potential of generated electron, and the surface status of Ag₃PO₄ are considered as factors that affect its photocatalytic performances. In this regard, the research target of this work is to understand the effect of electronic structures and surface properties on photocatalysis and to improve the generation and separation of photo-generated electron-hole pairs towards developing highly efficient Ag₃PO₄–based photocatalysts for environmental purifications. To achieve this target, three novel composite photocatalysts based on Ag₃PO₄ were successfully synthesized and investigations of the relationships among electronic structures, surface properties and photocatalytic performances were carried out. This dissertation is divided into five chapters:

In chapter 1, an overview of the photocatalysis and the semiconductor
photocatalysts was introduced firstly. As followed, the synthesis and utilization of composite photocatalysts were summarized with details to provide useful information for developing efficient composite photocatalysts for environmental purification. More importantly, the synthesis of $\text{Ag}_3\text{PO}_4$ and $\text{Ag}_3\text{PO}_4$-based composite photocatalysts, and strategies of achieving high photocatalytic activities were also summarized.

In chapter 2, a novel composite photocatalyst $\text{Ag}_3\text{PO}_4/\text{In(OH)}_3$ with adjustable surface-electric property for efficient photodegradation of organic dyes was obtained via an in-situ precipitation method. Moreover, the surface-electric property of the composite photocatalyst was continually adjusted by changing the content of $\text{In(OH)}_3$ and introduced into the photocatalytic degradation of Rhodamine B (Rh B) in water. It was found that more negative-charged surface of the composite photocatalysts is advantageous for adsorption of organic dyes. Therefore, the surface-electric property is closely related to the photocatalytic activity. The apparent rate constant of the $\text{Ag}_3\text{PO}_4/\text{In(OH)}_3$ (molar ratio=1.65:1) is 5 times higher than that of pure $\text{Ag}_3\text{PO}_4$. Moreover, the photosensitization and the intrinsic photocatalytic degradation of Rh B were also investigated under 540 ± 13nm and 420 ± 13nm monochromatic irradiations, respectively. It was revealed that the intrinsic photocatalytic pathway dominates the whole degradation process. Here, the composite photocatalyst with adjustable surface-electric property and suitable band structure reveals a novel material design-concept of exploiting a new photocatalyst based on the reaction kinetics and thermodynamics.
In chapter 3, a new heterojunction Ag₃PO₄/Cr-SrTiO₃ photocatalyst towards efficient elimination of gaseous organic pollutants under visible light irradiation was successfully synthesized. Iso-propanol (IPA) photodegradation over the heterojunctions under visible-light irradiation was employed for evaluating their photocatalytic properties. The highest activity was observed in the Ag₃PO₄/Cr-SrTiO₃ heterojunction with the mass ratio of 1:4 (Ag₃PO₄: Cr-SrTiO₃) sintered at 500 °C. The evolution rate of CO₂ over the composite is about 33 times higher than that of pure Ag₃PO₄. Moreover, the valence-band state of Ag₃PO₄ and Cr doped SrTiO₃ were analyzed by X-ray photoelectron spectroscopy (XPS) to deduce the band structures, which is helpful for understanding the transfer of photocarriers between the two semiconductors. Results reveal that electronic structures of composite photocatalyst promote the generation and separation of photo-generated electron-hole pairs and the multi-electron reactions. Therefore, composite photocatalyst showed much higher activity than the individual materials.

In chapter 4, another new composite photocatalyst Ag₃PO₄/Sr₂Nb₂O₇₋ₓNx with adjustable band structures towards efficient elimination of gaseous organic pollutants under visible light irradiation was obtained. The N 2p orbitals have higher potential energies than that of O 2p orbitals, and their hybridization lifts up the top of the valence band of Sr₂Nb₂O₇. Therefore, the N-doped Sr₂Nb₂O₇ can absorb visible light. More importantly, the electronic structure of Sr₂Nb₂O₇₋ₓNx could be adjusted continually by nitridation with NH₃ under different temperatures. The relationship between electronic structure and photocatalytic activity was also systematically
investigated. The best activity was obtained over the \( \text{Ag}_3\text{PO}_4/\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x \) (\( x = 0.82 \)) nitrided at 750°C with band gap is about 2.15 eV. The evolution rate of \( \text{CO}_2 \) over the composite is about 40 times higher than that of pure \( \text{Ag}_3\text{PO}_4 \). Investigations of energy-band structure via valence-band X-ray photoelectron spectrum (VB-XPS) were also carried out for understanding the separation and transfer of photogenerated electrons and holes between the two photocatalysts. It was found that band-gap narrowing can enlarge the visible light absorption, but lower the redox potential of generated electrons and holes. Therefore, an optimal band structure for best photocatalytic activity can be obtained by continually adjusting the electronic structures.

In chapter 5, an overall summary and conclusions of achievements of this dissertation work were provided. This thesis provided three new \( \text{Ag}_3\text{PO}_4 \)-based composite photocatalysts with high efficiency for environmental purifications and revealed that the surface-electric property, electric structure, and multi-electron reaction are closely related to the photocatalytic activity. More importantly, a novel material design-concept of exploiting a new photocatalyst based on the reaction kinetics and thermodynamics was provided in this work. The prospects for further work were also presented in this chapter.
Chapter 1 Introduction

1.2 photocatalysis

Nowadays, steadily worsening environmental pollution has raised awareness of a potential global crisis [1-2]. Pollutants that are emitted from various sources pose severe ecological problem as the most conventional methods for removal of these pollutants are mostly ineffective and not environmentally compatible. Therefore, finding new pollution-free technologies for environmental remediation with high efficiency is an urgent task.

Compared with other treatments, semiconductor photocatalysis for environmental purification has attracted increasing attention because of it’s advantages, such as: (i) cost-effective, (ii) no need of secondary energy source, (iii) environmental friendly, (v) deep decomposition or degradation of pollutants, (vi) strong stability and (vii) capable of extended use without substantial loss of photocatalytic activity[3]. In this regard, semiconductor photocatalyst has a promising potential in photocatalytic purification of environmental pollutants [4–7].

Since Fujishima and Honda successfully realized the photocatalytic water splitting based on TiO₂ materials in 1972[8], lots of researches have been performed on the fundamental processes and enhancements of photocatalytic efficiency over various semiconductors. Besides of applications in environmental purification, the potential applications of photocatalysis are found as follows: (i) photolysis of water to yield hydrogen; (ii) photocatalytic reduction of CO₂ to hydrogen fuel; (iii) photo-induced super-hydrophilicity; and (iv) photoelectrochemical conversion, etc [9-10].
1.1.1 General principles of photocatalysis

In photocatalysis, two reactions are occurring simultaneously, in which one is oxidation by photogenerated holes, and the other one is reduction by photogenerated electrons [11-13]. As shown in Fig.1.1, the electronic energy structure within a semiconductor consists of distinguished regimes, i.e., the conduction band (CB), and the valence band (VB). In terms of energy, the difference between the upper edge of the valence band and the lower edge of the conduction band is called the band gap (E_g) of the semiconductor. If the two levels can be described with the same wave vector, the semiconductor is considered to have a direct band gap; otherwise it has an indirect band gap. The band gap is one of the most critical parameters defining the optical properties of semiconductors [14-16].

The scheme for the basic mechanism of a semiconductor photocatalytic process is shown in Fig.1.1. In photocatalysis processes, when the energy of the incident photons from the light irradiation matches or exceeds that of the band gap, the light absorption and the consequent photoexcitation of electron-hole pairs would take place. Initially, the energy of the incident photons is stored in the semiconductor by photoexcitation, and then it is converted into chemical form by a series of electronic processes and surface/interface reactions. Therefore, these steps are included in a semiconductor photocatalytic cycle [17], as illuminated in Fig.1.1. Firstly, the excited electrons are transferred from the VB to the CB, leaving an equal number of vacant sites (generated holes). Secondly, the generated electrons and holes migrate to the surface of the photocatalyst. It is worth noting that the recombination of a large
proportion of electron-hole pairs occurs during the migration, dissipating the input energy in the form of heat or emitted light. Thirdly, electrons and holes react with absorbed electron accepters and electron donors, respectively. The involving oxidation and reduction occur in this step.

**Figure.1.1** The scheme for the basic mechanism of a semiconductor photocatalytic process.

Moreover, co-catalysts such as some noble metals and oxides (e.g. Pt, Pd, Au, Ag, NiO, and RuO₂) are loaded on the surface of photocatalysts to prevent the recombination of electron-hole pairs and amplify the photocatalytic activity. The reasons can be explained as followings: one is that the hetero-junctions, formed between the host semiconductor and the co-catalyst, provide an internal electric field that inhibits the recombination of the electron-hole pairs and facilitates the charge carrier migration; another one is that co-catalysts take the roles as the active-sites for photocatalytic reaction because their better conductivity, lower overpotential and higher catalytic activity than the host semiconductor [17].
1.1.2 A historical overview of photocatalysis

The earliest work about photocatalysis was able to find in 1921 by Bauer et al. The authors found that titania is partially reduced during illumination with sunlight in the presence of an organic compound (such as glycerol) [18]. After that, in 1924, the photocatalytic deposition of a silver salt on zinc oxide to produce metallic silver was reported by Baur and Perret [19]. A few years later, Renz reported the photocatalytic reduction of silver nitride to metallic silver and gold chloride to metallic gold on a number of illuminated oxides, such as TiO$_2$ and Nb$_2$O$_5$, in 1932 [20]. In 1938, Goodeve and Kitchener were inspired by the phenomena of “chalking” on the paints and carried out an excellent study on the photocatalytic decomposition of a dye on titania powder in air. The authors proposed that titania acts as a catalyst to accelerate the photochemical oxidation and also studied a number of other oxides and speculated on the precise mechanism[21]. In 1949, Jacobsen proposed a cyclic redox process in which the titania was reduced while the organic components were oxidized, followed by re-oxidation of the titania by oxygen from the air [18]. During the 1950s, some researches about zinc oxide as photocatalysts were reported [22-23]. It is worth noting that Kennedy investigated the photo-adsorption of O$_2$ on the surface of TiO$_2$ which is very important for understanding the photocatalytic process in 1958 [24]. In 1966, Lohmann published a highly detailed study of the photoelectrochemical (PEC) behavior of ZnO, both in the presence and absence of redox couples. The results showed that the overall current at the ZnO electrode under illumination is the sum of anodic and cathodic currents [25, 26]. In 1972, Fujishima and Honda reported the
possibility of photocatalytic water splitting over the TiO$_2$ electrode (see Fig. 1.2) [8].

**Figure. 1.2** Photoelectrochemical cell used in the photolysis of water [8].

From then, the investigation of photonic energy conversion by photocatalytic methods started to receive much wider attention. Intense research has been carried out on TiO$_2$ photocatalysis, which has been focused on understanding the fundamental principles, enhancement of photocatalytic efficiency, and the photocatalytic applications. In 1973, R.I. Bickley and co-workers reported the photoadsorption and photocatalytic oxidation of isopropanol over TiO$_2$. It has been shown that when TiO$_2$ (rutile) is illuminated with light of wavelength $\lambda > 300$ nm in the presence of isopropanol vapor and oxygen at 300 K, the primary organic oxidation product is acetone[27a]. After that, heterogeneous photocatalysis of other organics, such as methylbutanols [27b], isobutene [27c], 2-methylbutane [27d] and et al, were investigated in 1970s. In 1980s, investigations about the photochemical reactions and applications were developed. For instance, Enrico Borgarello and co-workers
published their results about photochemical cleavage of water by photocatalysis in Nature, which attracted wide attention in 1981[28]. Although there were some reports about photocatalysis in 1980’s and 1990’s, the investigation on the photocatalyst experienced a period of lower research activity [17]. After that, with the development of nanotechnology, as well as advanced characterization techniques for materials (e.g. SEM, TEM, and XPS), the research on the photocatalysis has grown exponentially.

During the following years, many efforts have been devoted to modifying TiO₂, such as element doping with N, C or S [29-33], the construction of hetero-junctions with metals (Pt or Pd) or other semiconductors (NiO, RuO₂, WO₃ or CdS) [34-37], and the light sensitization with quantum dots or dyes. Simultaneously, some possible alternatives to TiO₂, such as SrTiO₃ [38-40], CaTiO₃, KTaO₃, Ta₂O₅, and ZrO₂ were also investigated [41-43]. In recent years, great efforts have been made to develop new photocatalysts. Complex metal oxides, including niobates, tantalates, vandates, germanates, and so on, have been exploited as new photocatalysts [44-55]. In 2001, Zou and Ye firstly reported a new photocatalyst NiOₓ/In₁₋ₓNiₓTaO₄ for overall splitting water under visible-light irradiation [55]. This discovery brought a new concept in producing of clean hydrogen fuel from water. In 2006, the solid solution of gallium and zinc nitrogen oxide (Ga₁₋ₓZnₓN₁₋ₓOₓ) was reported by Domen and co-workers with high photocatalytic activity for splitting water under the irradiation of visible light [56]. Simultaneously, a number of sulfides, nitrides, and oxynitrides, such as CdS, ZnS, ZnIn₂S₄, Ta₃N₅, TaON, C₃N₄ and etc., have been investigated as alternative materials for visible light or solar photocatalysis [57-64]. In 2010, Ye’s
group reported that silver orthophosphate (Ag$_3$PO$_4$) as a novel photocatalyst with promising efficiency in water oxidation and photodecomposition of organic dyes. More specifically, the quantum yield of the generation of O$_2$ gas by water splitting using Ag$_3$PO$_4$ is nearly 90% under visible light, which is significantly higher than that of most photocatalysts (nearly \( \sim 20\% \))[65]. Since then, a series of efforts have been focused on morphology modification [66-68], electronic-structure calculation [69] and composite construction [70-71]. Recently, some composite photocatalysts based on Ag$_3$PO$_4$, such as AgX/Ag$_3$PO$_4$ (X = Cl, Br, I) [72], Ag$_3$PO$_4$/TiO$_2$ [73], Fe$_3$O$_4$/Ag$_3$PO$_4$ [74], Ag$_3$PO$_4$/SnO$_2$ [75], and Graphene oxide/Ag$_3$PO$_4$ [76] have been successfully synthesized and exhibited enhanced photocatalytic activities.

Nowadays, extensive researches have been carried out on exploration of novel photocatalysts, understanding the fundamental principles, enhancing the photocatalytic efficiency, and expanding the scope of applications. Some commercial products related to the photocatalysis have already been applied in our life. However, efficient photocatalysts for the purification of environmental pollutants are still needed in the future.

1.1.3 Functional photocatalysis in environmental purification

1.1.3.1 Photocatalytic degradation of organic dyes from water

Nowadays, over 0.7 million tons of organic synthetic dyes are manufactured each year mainly for the use in the textile, leather goods, industrial painting, food, plastics, cosmetics, and consumer electronic sectors [77]. Dyes can be classified on the basis
of structure, function, or both. Fig. 1.3 contains a representative listing of dyes grouped according to their chemical structure.

**Figure. 1.3** Several representative dyes with different functional groups [78].

Compared with other treatments, the photocatalytic degradations of organic pollutants have attracted increasing attention because it is a promising, environmental, and cost-effective technology for the treatment of contaminated groundwater and wastewater. In photocatalytic degradation of organic dyes, there are two possible pathways: intrinsic photocatalysis and photosensitization.
Figure 1.4 (a) Schematic processes of photocatalytic pathway and (b) photosensitization pathway of dyes degradation.

As shown in Fig. 1.4(a), the intrinsic photocatalysis pathway is mainly considered to be controlled by the following processes: (1) the light absorption of the semiconductor catalyst, (2) the generation of photogenerated electrons and holes, (3) the transfer of charge carriers, and (4) the utilization of the charge carriers by the reactants. In details, the energy of the absorbed photon should be larger than that of band gap of the semiconductor which is necessary for generation of the reductive conduction band electrons ($e_{cb}^-$) and oxidative valence band holes ($h_{vb}^+$) (Eq.1). The holes can react with surface adsorbed H$_2$O to produce •OH radicals (Eq.2) or oxidize the organic substrates into their radicals (Eq.3). Meanwhile, the electrons are always used to yield superoxide radical anions O$_2$$^•$ through reaction with adsorbed O$_2$ (Eq.4). The subsequent radical reactions usually have low- or non- barriers, resulting in the facile oxidative degradation of dyes (Eq.5-7) [79].

\[
\text{Photocatalyst} + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \quad (1) \\
\text{H}_2\text{O} + h_{vb}^+ \rightarrow \cdot\text{OH} + \text{H}^+ \quad (2) \\
\text{R–H (Rh B)} + h_{vb}^+ \rightarrow \text{RH}^+ \leftrightarrow \text{R}^+ + \text{H}^+ \rightarrow \rightarrow \quad (3) \\
\text{O}_2 + e_{cb}^- \rightarrow \text{O}_2^•^- \quad (4)
\]
R–H + •OH → R• + H2O  \hspace{1cm} (5)

R• + O2 → ROO• \xrightarrow{O_2/H_2O}\text{Degradation}  \hspace{1cm} (6)

H-R + •OH → HROH• \xrightarrow{O_2/H_2O}\text{Degradation}  \hspace{1cm} (7)

On the other hand, for some self-sensitive dyes, such as Rh B, the photosensitization pathway is also available for degradation of dyes. As shown in Fig.1.4.b, adsorbed dye is excited by the visible light (Eq. 8) on the photocatalyst surface and then injects electrons into the conduction band of the semiconductor to form cationic radicals of dye (Eq. 9). The electrons in the conduction band of the semiconductor undergo the transformation to Eq. 10~13. Finally, dye is degraded to the end products (Eq. 14) [79-82].

Dye (Rh B)+ hv → Dye* ; - 1.09 V  \hspace{1cm} (8)

Dye* + Sem. → Dye+ + Sem.(e−)  \hspace{1cm} (9)

O2 + 2H2O + 2e− ↔ H2O2 + 2OH−  \hspace{1cm} (10)

O2 + H2O + 2e− ↔ HO2− + OH−  \hspace{1cm} (11)

O2 + e− ↔ O2•−  \hspace{1cm} (12)

O2 + H+ + e− ↔ HO2  \hspace{1cm} (13)

Dye+ {O2; O2•−; HO2•−... or other active oxygen species} → peroxyl or hydroxylated intermediates → degraded or mineralized products (14)

1.1.3.2 Photocatalytic decomposition of organic pollutants in air

As pollutants in water, the air pollutants also become a world-wide crisis and threaten to the human healthy. In general, the air pollutants include the acetic acid,
toluene, xylene, ethanol, undecane, acetone, and acetaldehyde. In many research about photocatalytic oxidation reactions, 2-propanol (IPA) is always chosen as a model reactant, because this is one of most frequently utilized VOCs in the industry and more importantly is that the mechanism of IPA-decomposition has been investigated and clarified. The kinetic model of the photocatalytic degradation of IPA includes steps as follows [83-85]:

(1) Photocatalytic degradation of IPA to actone [85a,b]:

\[
\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \quad (15)
\]

\[
h^+ + \text{OH}^-(s) \rightarrow \cdot \text{OH}, \text{or } h^+ + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ \quad (16)
\]

\[
e^- + \text{O}_2(s) \rightarrow \text{O}_2^- \quad (17)
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \quad (18)
\]

The generated \cdot \text{OH} radical reacts with IPA to form a radical:

\[
\text{CH}_3\text{CH(OH)CH}_3 + \cdot \text{OH} \rightarrow \text{CH}_3\cdot \text{(OH)CH}_3 + \text{H}_2\text{O} \quad (19)
\]

After that, the radical could be decomposed to acetone through several reaction pathways:

\[
\text{CH}_3\cdot \text{(OH)CH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}^+ + e_{cb}^- \quad (20)
\]

\[
\text{CH}_3\cdot \text{(OH)CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{COO}^- \cdot \text{(OH)CH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}^+ + \text{O}_2^- \quad (21)
\]

\[
\text{CH}_3\cdot \text{(OH)CH}_3 + \cdot \text{O}_2\text{H} \rightarrow \text{CH}_3\text{COOH(OH)CH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}_2 \quad (22)
\]

As above analysis, the photocatalytic degradation of IPA to acetone is kind of single-photon reaction.

(2) Photocatalytic degradation of IPA to CO\textsubscript{2}:

For the photocatalytic oxidation of IPA, there is an agreement to consider that (a)
the main gaseous products are acetone, CO₂, and H₂O [85c,d], and (b) acetone is the main route to the CO₂ formation for the deep oxidation of IPA.

The overall reaction of the deep photocatalytic oxidation of IPA is [85a-d]:

\[ \text{CH}_3\text{CHOHCH}_3 + 5\text{H}_2\text{O} + 18\text{h}^+ \rightarrow 3\text{CO}_2 + 18\text{H}^+ \]  (23)

In such reaction, IPA can be deep oxidized into CO₂ and H₂O with consumption of multi-photons. In detailed reaction-process, J. M. Herrmann and co-workers declared that the IPA species are oxidized in the absence and in the presence of O₂ into acetone that is the single route to the deep photocatalytic oxidation of IPA [85a,b]. On the other hand, Weizong Xu and co-worker reported that there are two possible ways for the deep photocatalytic oxidation of IPA into CO₂ (as shown in Scheme 1) such as [85e]:

**Scheme 1:** Illustration of the reaction mechanism for deep photocatalytic oxidation of IPA on TiO₂ powder [85e].

As analyzed in part (1) and (2), it can be concluded that the mechanism for the oxidation of IPA to acetone has been investigated and clarified. For the deep oxidation of IPA to CO₂, although the reaction-process has not been clarified, there is no doubt that it belongs to multi-electron reaction.
1.1.4 Approaches for improving the photocatalytic activity

1.1.4.1 Engineering on the electronic structure

As the primary and the crucial step in the overall photocatalytic reaction, the absorption of light is determined by the electronic structure of semiconductor. As shown in the spectrum of solar irradiation in Fig.1.5, the UV light occupies about 4% and visible light occupies about 43% in the solar energy. Wide band gap semiconductors, such as TiO₂, ZnO, and et al., only absorb UV light, which limits their practical applications to reach the final aim of efficient utilization of solar energy. From the view of effectively utilizing solar energy, developing highly efficient visible-light-sensitive photocatalysts with narrowed band gap is highly anticipated and thus has attracted extensive attention.

![Solar Radiation Spectrum](image)

**Figure.1.5** The spectrum of solar irradiation.

The energy band configuration of a semiconductor plays a significant role in the absorption of light and in determining the redox potentials. To sensitize the optical absorption into the visible region, the band gaps of the photocatalysts could be narrowed by lowering the level of the conduction band, lifting the level of the valence band, or both.
1. Lowering the conduction band

In photocatalytic reaction, photogenerated electrons in the CB can reduce $H^+$ to produce $H_2$ for water splitting or combine with $O_2$ to form the superoxide radical for the elimination of organic pollutant. Therefore, the level of the CB could determine both whether these reactions can proceed and how efficient these processes are. In general, lowering the CB is achieved by the substitution of alkali metal or alkaline-earth elements and the p-block cations with a $d^{10}$ electronic configuration. This method has been utilized in band modification of some indates and antimonates such as $\text{AInO}_2$ ($\text{A} = \text{Li, Na}$), $\text{NaSbO}_3$, $\text{MIIn}_2\text{O}_4$ ($\text{M} = \text{Ca, Sr}$), $\text{M}_2\text{Sb}_2\text{O}_7$ ($\text{M} = \text{Ca, Sr}$), and $\text{CaSb}_2\text{O}_6$ [86-89].

![Figure 1.6](image)

**Figure. 1.6** (A) Electronic structures of $\alpha$-$\text{AgMO}_2$ ($\text{M} = \text{Al, Ga, In}$). (B) Photocatalytic degradation of isopropanol using $\alpha$-$\text{AgGaO}_2$ and $\alpha$-$\text{AgInO}_2$, under visible light irradiation ($400 \text{ nm} < \lambda < 520 \text{ nm}$) [45-46].

As successful examples, polycrystalline samples $\alpha$- and $\beta$-$\text{AgMO}_2$ ($\text{M} = \text{Al, Ga, In}$) with lowering CBs were successfully synthesized by Ouyang and co-workers [45]. As shown in Fig.1.6a, the calculation of electronic structure indicates that when $\text{M}$ is varied in the order Al, Ga, and In, the CBs of these samples are mainly constructed from the $\text{Ag} 5s5p$ and $\text{M} sp$ states, and all the VBs are comprised of the $\text{Ag} 4d$ and $\text{O}$
2\textit{p} states. The potential levels of these VBs are quite stable, but these CBs are varied with M. Compared with others, \textit{\textalpha}-\textit{AgGaO}_2 exhibits the highest activity for the photodegradation of isopropanol (IPA) (Fig.1.6b)

In another way, the CB minimum also can be lowered based on substitution with \textit{d}-block cations that have a \textit{d}^{10} electronic configuration. For example, the group Vb elements V, Nb and Ta can lower the CB minimums of InMO\textsubscript{4} (M=V, Nb, Ta) and BiMO\textsubscript{4} (M=Nb, Ta) for water splitting [90-92].

(2) Lifting the valence band

Beside the modification of CB, adjustment of VB is another approach to narrow the band structure of semiconductor. In past decades, extensive studies were carried out to adjusting the level of the VB.

Based on previous reports, there are three approaches, including doping with \textit{3d}-transition elements, cations with \textit{d}^{10} or \textit{d}^{10}\textit{s}^{2} configurations, and non-metal elements. A typical example is the \textit{3d}-transition elements doped TiO\textsubscript{2} which attracted wide attention. Theoretical studies reveal that the localized \textit{3d} levels shift to lower energy with increasing atomic number of the dopants[93-94]. Zou and co-workers reported on In\textsubscript{1-x}Ni\textsubscript{x}TaO\textsubscript{4} (x = 0-0.2) with doping a \textit{3d}-transition elements, which exhibits high activity for overall water splitting under visible light irradiation [95].

In another way, the cations with \textit{d}^{10} or \textit{d}^{10}\textit{s}^{2} electronic configurations can introduce occupied \textit{d} or \textit{s} -states into the VB. The reason is that hybridization of these \textit{d} or \textit{s} –states with O 2\textit{p} states contributes to an up-shift of the top of the VB. The
successful examples such as AgNbO₃, CaBi₂O₄, and Pb₃MgNb₂O₉ have been reported. Based on the same strategy, a number of new visible-light-sensitive photocatalysts containing Cu⁺ and Sn²⁺ have also been developed. [45, 46, 96-98].

The other approach for lifting up the level of VB is to introduce non-metal anions on the O sites. For example, N, C, B and S doped TiO₂ have been extensively investigated. Recently, Li et al reported that layered structure HNb₃O₈ was able to be N-doped without destroying of its layered structure (see Fig.1.7A) [99]. As shown in Fig.1.7 (B, C), the band gap was narrowed from 3.5 eV to 2.7 eV and the onset of absorption edge was a red-shift by ~80 nm. Under visible light irradiation, N-doped HNb₃O₈ exhibited superior activity to commercial TiO₂, N-doped Nb₂O₅ and N-doped TiO₂ samples (see Fig.1.7d). Moreover, oxynitrides such as LaTiON, oxysulfides such as Sm₂Ti₂S₂O₅, and oxyhalides such as BiOX (X = Br, I) [100-103] can also effectively absorb visible light and exhibit higher photocatalytic activity.

**Figure. 1.7** (A) Schematic picture of N-doping in the lamellar solid acid (HNb₃O₈) using urea as the N-source. (B) Schematic band structures of HNb₃O₈ and N-doped HNb₃O₈. (C) UV-visible diffuse reflectance spectra of N-doped and undoped HNb₃O₈ and Nb₂O₅ samples; the insets show pictures of the HNb₃O₈ and N-doped
HNb$_3$O$_8$ samples. (D) Photocatalytic degradation of Rhodamine B (RhB) under visible light irradiation (\( \lambda > 400 \) nm), using no catalyst (a), N-doped Nb$_2$O$_5$ (b), Degussa P25 (c), N-doped TiO$_2$ (d), and N-doped HNb$_3$O$_8$ (e)[99].

1.1.4.2 Engineering on the physicochemical properties

Other than the intrinsic band structures, the physicochemical properties, e.g., the crystallinity, the particle size, and the surface area of semiconductors can also significantly influence their photocatalytic activities [95,104,105].

(1) Increasing the surface area

In general, the photocatalytic reactions are carried out between generated electron-hole and absorbed electron donors/acceptors on the surface of photocatalysts. Therefore, the large surface area is advantageous for surface-dependent photocatalysis because it provides more reactive sites and stronger adsorption. In nowadays, novel preparation techniques, such as sono chemical, sol-gel, and deposition-precipitation methods, have been proposed and applied to achieve high-surface-area products [106-109]. Moreover, most of the currently employed preparation methods are also able to deliver highly crystalline products. Li and Ye prepared Pb$_3$Nb$_4$O$_{13}$/fumed silica composite photocatalysts via a deposition-precipitation method [109]. The photocatalysts exhibited notably improved activities in the degradation of Rhodamine B, as compared with that of unsupported Pb$_3$Nb$_4$O$_{13}$. Due to the high surface area of the fumed silica, the adsorption uptake of Rhodamine B onto the composite catalysts was found to be more than 5 times higher than that of bare Pb$_3$Nb$_4$O$_{13}$. Zhang and
co-workers synthesized the mesoporous Zn$_2$GeO$_4$ by a simple ions-exchange method between colloidal suspension of Na$_2$GeO$_3$ and Zn$^{2+}$ at room temperature [110]. Due to the large surface areas (163 ~ 54 m$^2$ g$^{-1}$), the activity of the mesoporous Zn$_2$GeO$_4$ in producing CH$_4$ is about 2.5 times higher than that of Zn$_2$GeO$_4$ prepared by solid state reaction in CO$_2$ photoreduction. Besides these, the nanostructures or mesoporous structures of WO$_3$, TiO$_2$, Zn$_2$GeO$_4$, NaNbO$_3$, and SrTiO$_3$ etc, exhibited much enhanced activity compared with corresponding bulk materials [111-117]. Furthermore, the sheet-like crystallites of molecular thickness and extremely high two-dimensional anisotropy can provide more active sites, and they also exhibit interesting charge-bearing properties due to the large-area. A series of photocatalysts belong to this category, such as KCa$_2$Nb$_3$O$_{10}$ [118] and Ba$_5$Ta$_4$O$_{15}$ [119].

(2) Exploiting the special crystal facets

As the photocatalytic reaction belongs to a kind of surface-dependent reaction which takes place on the surfaces of semiconductors, the exposed crystal facets play a critical role in determining the photocatalytic activity [120]. The synthesis of single crystals with exposed active facets may represent a promising and efficient method for the further improvement of photocatalytic performance. One of the most important discoveries is that high surface energy {001} facets in anatase TiO$_2$ exhibit superior photocatalytic properties than the most common {101} facets [121a]. Besides the TiO$_2$ nanoplates with exposed {001}, Xi and co-workers reported the well-defined m-BiVO$_4$ nanoplates with exposed {001} facets exhibited superior photocatalytic
activity. Moreover, the single-crystalline BiVO$_4$ was synthesized by a straightforward hydrothermal route in which no template or organic surfactant was used (Fig.1.8)[121b].

Figure 1.8 (A) SEM image and (B) high-magnification HRTEM image of m-BiVO$_4$ nanoplates [121b].

(3) Improving the separation of electrons/holes pairs

In photocatalysis, the separation of excited electrons/holes and the recombination of the electrons/holes are both influence factors to the photocatalytic activity[17]. Composite photocatalysts with heterostructured electronic structure has been designed to alleviate the charge carrier recombination then to improve the photocatalytic efficiency. A good matching of their CB and VB levels can realize a vectorial transfer of photogenerated charge carriers from one to the other as illustrated in Fig. 1.9, where the relative positions of the energy bands of the two particles are shown in terms of energetic rather than spatial levels. After coupling, the energy gap between corresponding band levels drives the charge carriers from one particle to its neighbor to form a special separation between electrons and holes.
Figure 1.9 Coupling two different semiconductor particles and charge carrier separation.

Up to now, numerous heterostructured photocatalysts, such as TiO$_2$[122], SrTiO$_3$ [123], and ZnO [124] coupled with different photocatalysts, have been successfully synthesized and exhibit higher photocatalytic activity than individual photocatalyst.

1.3 Composite photocatalyst

1.3.1 Advantages of composite photocatalyst

The composite photocatalysts based on two semiconductors with suitable band structure can inhibit the recombination of electrons and holes. The advantageous of the composite photocatalyst can be summarized as follows:

i) Enhanced vectorial transfer of photogenerated charge carriers.

ii) Inhibited recombination of photogenerated charge carriers.

iii) More aggregated electrons and holes.

In the past decades, many efforts have been explored into the development of composite photocatalysts. Based on previous reports, the composite photocatalysts can be synthesized by following methods.
1.3.2 Synthesis methods of composite photocatalyst

Synthesis method of photocatalyst is closely related to the morphology, crystal structure and the photocatalytic activity. For synthesis of composite photocatalysts, abundant methods have been reported. In general, those methods are carried out in: 1) low temperature, and 2) high temperature. For the first one, it is always utilized in liquid phase and smaller particle sized of the photocatalysts can be obtained more easily. On the other hand, the high-temperature treatment in gaseous phase is benefit for the interfacial connection but the particle size may be much larger.

1.3.2.1 Synthesis in low temperature

Composite photocatalysts can be synthesized in low/room temperature in liquid phase. It is a facile way to obtain adjustable and functional morphologies for enhanced activity.

Chu et al. reported a Cu$_2$O@TiO$_2$ core–shell heterojunction photocatalyst prepared by an in-situ hydrolysis and crystallization method [125], as illustrated in Fig.1.10. On the surface of fresh prepared Cu$_2$O, a great deal of water molecules are adsorbed through hydrogen bonds with surface hydroxyl groups. Ti(Obu)$_4$ are prehydrolyzed in situ by the adsorbed water, then further hydrolyzed and condensed after addition of water/ethanol solution, and finally crystallized in situ around Cu$_2$O during the calcination treatment. Since many metal oxides (TiO$_2$, WO$_3$, and SnO$_2$, etc.) have surface hydroxyl groups to adsorb water molecules, the in situ synthetic method can thus be applied to prepare other core–shell structured heterojunction materials.
Moreover, Yao et al. reported an in-situ precipitation method for the synthesis of Ag$_3$PO$_4$/TiO$_2$ [126]. In typical, positively charged silver ions (Ag$^+$) are adsorbed on the surface of TiO$_2$ due to the existence of O$^-$ anions, and then the reaction of Ag$^+(ad)$ and PO$_4^{3-}$ takes place on the surface of TiO$_2$ forming an Ag$_3$PO$_4$/TiO$_2$ heterostructure.

Besides these, there are some other heterojunctions synthesized by in-situ synthesis method, such as ZnO/magadiite [127], SnO$_2$/Fe$_2$O$_3$ [128], WO$_3$/Fe$_3$O$_4$ [129], PbS/CdS [130] and et al. The in-situ synthesis method in lower temperature is a facile way to help us obtain the heterojunction with special morphologies which is advantageous for high photocatalytic activity.

1.3.2.2 Synthesis in high temperature

Compared with low-temperature method, the calcination treatment in high temperature is a direct way to obtain composite photocatalysts.

Zhang and co-workers reported a Bi$_2$O$_3$/SrTiO$_3$ composite photocatalyst with enhanced photocatalytic activity under visible light irradiation was synthesized via calcination method (see Fig. 1.11a) [131]. The effects of the calcination temperatures on the photocatalytic activities of the composite powders were also investigated.
Figure 1.11 SEM image of Bi$_2$O$_3$/SrTiO$_3$ (a) and the band structure diagram and TEM images of NaNbO$_3$/In$_2$O$_3$ composite (b) [131-132].

Moreover, Jun Lv and co-workers reported that NaNbO$_3$ rods modified by In$_2$O$_3$ nanoparticles (NaNbO$_3$/In$_2$O$_3$) were successfully synthesized by an improved coprecipitation method, in which the precursors of NaNbO$_3$/In$_2$O$_3$ were obtained from the anhydrous ethanol solution and then were calcined at 773 K for 12h [132]. The characterization results confirm that formation of composite could promote the transfer of photoexcited holes and thus restrict their recombination with electrons, leading to the enhancement of photocatalytic activity (see Fig. 1.11b). Besides these, other composite photocatalysts based on TiO$_2$, and SrTiO$_3$ are also synthesized via calcination method.

In summary, the synthesis method in low temperature can help us to obtain the composite photocatalysts with special morphology which is benefit for the exposure of special crystal facets or increasing the surface areas; the synthesis method in high temperature is a facile and direct way to obtain the composite photocatalysts with strong interfacial connection which is advantageous for the transfer of photon carriers.
1.3.3 Applications of composite photocatalysts

1.3.3.1 Photocatalytic water-splitting

Since the discovery of photocatalytic decomposition from H\textsubscript{2}O to H\textsubscript{2} over TiO\textsubscript{2}, converting solar energy to green energy hydrogen by photocatalytic splitting water is an important research topic in photoatalysis. Up to now, some composite photocatalysts are also developed for this target. As above mentioned, composite NaNbO\textsubscript{3}/In\textsubscript{2}O\textsubscript{3} was found to be advantageous for photocatalytic H\textsubscript{2} evolution under visible light irradiation and pure water splitting under ultraviolet light irradiation (see Fig.1.12). The quantum yield was about 1.45\% in H\textsubscript{2} evolution under visible light irradiation.

Another In\textsubscript{2}O\textsubscript{3}-based composite photocatalyst In\textsubscript{2}O\textsubscript{3}/N–InNbO\textsubscript{4} was reported by Jun Lv et al. for H\textsubscript{2} evolution from water splitting [133]. The photocatalytic experiments indicated the H\textsubscript{2} evolution rate of In\textsubscript{2}O\textsubscript{3}/N–InNbO\textsubscript{4} composite was 27.3 µmol h\textsuperscript{-1} g\textsuperscript{-1} under visible light irradiation (λ> 420 nm), which was 18.6 times the rate of In\textsubscript{2}O\textsubscript{3} and 2.3 times the rate of N–InNbO\textsubscript{4}. The band structure of In\textsubscript{2}O\textsubscript{3}/N–InNbO\textsubscript{4} composite was considered to be advantageous for the transportation and separation of photoexcited electron/hole pairs, as shown in Fig.1.12. Jang et al. prepared a coupled CdS/TiO\textsubscript{2} photocatalyst by coupling CdS nanoparticles with TiO\textsubscript{2} nanosheets to maximize the contact between the two phases [134]. The thus-coupled photocatalyst showed higher activity for hydrogen production. This coupling mode has been found to be highly favorable to the vectorial electron transfer between the co-axial CdS and TiO\textsubscript{2}
1.3.3.2 Photocatalytic elimination of organic dyes from water

Up to now, lots of composite photocatalysts have been utilized in purification of organic dyes in water. For instance, Vinodgopal and Kamat [135] reported very rapid decolorization of Acid Orange 7 using a coupled SnO$_2$/TiO$_2$ photoelectrode under a bias potential. The enhanced photocatalytic activity was ascribed to the improved charge separation which due to good matching in the energy levels ($E_{CB}$ for SnO$_2$ = 0 V vs. NHE at pH 7, while for TiO$_2$, $E_{CB}$ = 0.5 V vs. NHE at pH 7). Other TiO$_2$-based composite photocatalysts, such as TiO$_2$/WO$_3$ [136], TiO$_2$/CdS [137], TiO$_2$/Cu$_2$O [125], TiO$_2$/Ag$_3$PO$_4$ [126], also exhibit high efficiency in photocatalytic degradation of organic dyes. Xi and co-workers reported a recyclable Fe$_3$O$_4$/WO$_3$ core–shell photocatalyst which possess large surface-exposure area, high visible-light-absorption efficiency, stable recyclability, and efficient charge-separation properties. The visible-light photocatalytic ability of the Fe$_3$O$_4$/WO$_3$ has been significantly enhanced.
activity in the photodegradation of organic-dye materials (see Fig. 1.13) [129].

Figure. 1.13 TEM images of the Fe$_3$O$_4$/WO$_3$ core–shell structures (a), and the charge-transfer process in the Fe$_3$O$_4$/WO$_3$ core–shell structures. After photon excitation by visible light, photogenerated electrons (e$^-$) and holes (h$^+$) migrate to Fe$_3$O$_4$ and WO$_3$, respectively, and react with the adsorbed species [129].

Besides these, some composite photocatalysts based on Ag$_3$PO$_4$, such as AgX / Ag$_3$PO$_4$ (X = Cl, Br, I) [138], Fe$_3$O$_4$/ Ag$_3$PO$_4$ [139], Ag$_3$PO$_4$/SnO$_2$ [140], and Graphene oxide/Ag$_3$PO$_4$ [141] had been successfully synthesized and exhibited enhanced photocatalytic activities in dye degradation.

1.3.3.3 Photocatalytic elimination of organic pollutants in air

Photocatalytic degradation of organic pollutants in air also has attracted lots of attention. As a typical pollutant in air, Isopropyl alcohol (IPA) is always chosen as the model of photocatalytic degradation. Up to now, some TiO$_2$-based composite photocatalysts have been explored with enhanced activities. For instance, TiO$_2$/short MWNTs was reported by Luo and co-workers [142]. The short MWNTs can be considered as a good electron acceptor, which can impress the e$^-$/h$^+$ pairs recombination and increase the photon efficiency. Moreover, Sher Bahadur Rawal
reported that Ag$_3$PO$_4$/TiO$_2$ [143] composites revealed the highest photocatalytic activity in decomposing IPA and evolving CO$_2$. It is deduced that the remarkable visible-light photocatalytic activity of Ag$_3$PO$_4$/TiO$_2$ composite originates from the unique relative band positions of the two semiconductors. Since the VB level of Ag$_3$PO$_4$ (+2.9 V vs. NHE) is located lower than that of TiO$_2$ (+2.7 V vs. NHE), the visible-light sensitization of Ag$_3$PO$_4$ induces the hole-transfer from Ag$_3$PO$_4$ to TiO$_2$. As a result, the holes generated in the VB of TiO$_2$ can induce the complete decomposition of IPA.

1.4 Ag$_3$PO$_4$ – based composite photocatalysts

Silver orthophosphate (Ag$_3$PO$_4$) as a novel photocatalyst with promising efficiency in water oxidation and photodecomposition of organic dyes was reported by Ye’s group [65]. The quantum yield of the generation of O$_2$ gas by water oxidation using Ag$_3$PO$_4$ is nearly 90% around 420 nm. It has a promising future in photocatalytic applications. Since then, a series of efforts have been focused on morphology modification, electronic-structure calculation and composite construction of Ag$_3$PO$_4$.

1.3.1 Calculation of Electronic structure of Ag$_3$PO$_4$

Ye’s group reported that Ag$_3$PO$_4$ belongs to body-centered cubic structure type with a lattice parameter of ~6.004 Å [65]. The structure consists of isolated, and regular PO$_4$ tetrahedra (P-O distance of ~1.539 Å) forming a body- centered cubic
lattice. Six Ag ions are distributed among twelve sites of two-fold symmetry. Furthermore, a comparative calculation of the electronic structures of Ag₃PO₄, Ag₂O, and AgNbO₃ by first principles provided possible explanations for the high performance of Ag₃PO₄ [144]. As shown in Figure 1.14, the wave function at the conduction band minimum (CBM) of Ag₃PO₄ is significantly delocalized because it mainly consists of Ag s states. A large degree of hybridization between Ag s states occurs on adjacent atoms in Ag₃PO₄, which is advantageous for a dispersive band structure at the CBM without the ‘contamination’ of d-states, and contributes to a decreased effective electron mass. Moreover, the CBM of Ag₃PO₄ has a very isotropic distribution, which is advantageous for electron transfer (Figure 1.14 A). In contrast, the CBM of Ag₂O possesses the character of Ag d-O p derived anti-bonding states, which are localized at atomic sites and are disadvantageous for electron transfer. Moreover, the authors reported that the CBM of AgNbO₃ mainly consists of dₓz and dᵧz states, which result in an anisotropic charge distribution (Figure 1.14 C) and allowing electron transfer only along the z-direction. It has to note that the band structure of AgNbO₃ is not suitable for photocatalysis because the limited directionality of the electron pathway increases the probability of carrier recombination. Based on above analysis, it can be concluded that the excellent photocatalytic performance of Ag₃PO₄ is partly due to the highly dispersive band structure at the CBM, which results from Ag s –Ag s hybridization without localized d -states. Similar calculations for Ag₃PO₄ were subsequently reported by another group [200].
1.3.2 Engineering on the morphology of Ag$_3$PO$_4$

In order to investigate the effects of the shapes and facets of particular photocatalysts on their photocatalytic properties, single-crystals of Ag$_3$PO$_4$ with different morphologies were synthesized. Ye’s group reported two types of Ag$_3$PO$_4$. One is rhombic dodecahedron shape with exposed \{110\} facets, and another one is cube bounded by \{100\} facets. These crystals were grown using CH$_3$COOAg and a [Ag(NH$_3$)$_2$]$^+$ complex as the silver ion precursors, respectively [68]. The Ag$_3$PO$_4$ dodecahedrons were formed by 12 well-defined \{110\} planes with cubic crystal symmetry (Figure 1.15 A), whereas the Ag$_3$PO$_4$ cubes displayed sharp corners, edges, and smooth surfaces (Figure 1.15B). Moreover, their application performance studies indicate that the Ag$_3$PO$_4$ cubic crystals exhibit much higher catalytic activities and photoelectric properties than spherical particles for the organic contaminants.
degradation and photoelectric conversion under visible-light irradiation, which may be due to their novel cubic structure and exposed \{100\} facets. The dodecahedrons exhibited higher photocatalytic activity for the degradation of methyl orange (MO) and Rh B dyes than the cubes (Figures 1.15C and D). This result reveals that the \{110\} facet is more reactive than the \{100\} facet, which is according with the higher surface energy of 1.31 Jm\(^{-2}\) for the \{110\} facet compared to 1.12 Jm\(^{-2}\) for the \{100\} facet.

![Figure 1.15 SEM images of Ag\(_3\)PO\(_4\) sub-microcrystals with different morphologies: (A) rhombic dodecahedrons and (B) cubes. The photocatalytic activities of Ag\(_3\)PO\(_4\) rhombic dodecahedrons, cubes, spheres, and N-doped TiO\(_2\) are shown for the degradation of (C) MO and (D) RhB under visible light irradiation (\(\lambda > 400\) nm) [68].](image)

Recently, Ye’s group reported two-dimensional dendritic Ag\(_3\)PO\(_4\) and investigated the photocatalytic activity (as shown in Fig.1.16). The novel Ag\(_3\)PO\(_4\) nanostructures exhibited much higher activities than irregular Ag\(_3\)PO\(_4\) nanocrystals and N-doped TiO\(_2\) for the organic contaminant degradation under visible-light irradiation. Moreover, it is clearly reveals that the rational fabrication of 2D semiconductor
nanostructure may be an effective technique for development of highly efficient visible-light sensitive photocatalysts.

**Figure. 1.16** SEM images of two-dimensional dendritic Ag₃PO₄ (a), and the Schematic illustration of the possible oxidation process of Ag nanowires to dendritic Ag₃PO₄ nanostructures (b) [146].

Wang et al. [147] reported a facile method to obtain the rejuvenate Ag₃PO₄ after photocatalytic reaction in dyes degradation. More interesting, the rejuvenated Ag₃PO₄ is composed of a novel type of regular tetrahedron nanocrystals exposed entirely with {111} facets (as shown in Fig.1.17). The rejuvenated Ag₃PO₄ still has excellent photocatalytic performance in photodegradation of Rh B, albeit a little inferior to the fresh Ag₃PO₄.

**Figure. 1.17** SEM images of the rejuvenated Ag₃PO₄ (a); The schematic models of Ag₃PO₄ (111) surface that contain several atom steps (b) [147].
1.3.3 Constructing of Ag$_3$PO$_4$-based composite photocatalysts

Recently, some composite photocatalysts based on Ag$_3$PO$_4$, such as AgX/Ag$_3$PO$_4$ (X = Cl, Br, I) [138], Fe$_3$O$_4$/Ag$_3$PO$_4$ [139], Ag$_3$PO$_4$/SnO$_2$ [140], Ag$_3$PO$_4$/ScPO$_4$ [145], Bi$_2$MoO$_6$/Ag$_3$PO$_4$ [148], BiOCl/Ag$_3$PO$_4$ [149], and Graphene oxide/Ag$_3$PO$_4$ [141] have been successfully synthesized and exhibited enhanced photocatalytic activities. Ye’s group reported a serials of rhombic dodecahedral AgX/Ag$_3$PO$_4$ (X = Cl, Br, I) heterocrystals with enhanced photocatalytic properties and stabilities.

![Figure 1.18](image)

**Figure. 1.18** (A) SEM images of the AgCl/Ag$_3$PO$_4$ heterocrystals, (B) SEM images of the AgBr/Ag$_3$PO$_4$ heterocrystals, (C) SEM images of the AgI/Ag$_3$PO$_4$ heterocrystals and (D) XRD patterns of the heterocrystals [138].

As shown in Fig. 1.18, novel core–shell heterocrystals have been obtained by this simple anion exchange process between Ag$_3$PO$_4$ rhombic and NaCl, NaBr and NaI aqueous solutions at room temperature. Due to the lower solubility and the higher
resistance to corrosion of the AgX (X = Cl, Br, I), the novel core–shell heterocrystals exhibit enhanced structural stabilities during the photocatalytic process. Moreover, due to the band structure of the heterocrystals, separation of photoexcited electron–hole pairs was enhanced and the probability of electron–hole recombination was decreased, which resulted in enhanced photocatalytic activity.

Subsequently, a serials of composite based on Ag3PO4 and mental oxides were explored by other researchers. Yao et al. [129], reported Ag3PO4/TiO2 heterojunction with enhanced photocatalytic activity and stability in rhodamine B (Rh B) degradation. Yang-Sen Xu and Wei-De Zhang synthesized Bi2MoO6/Ag3PO4 via a facile deposition–precipitation method [1148]. The photocatalytic tests display that the Bi2MoO6/Ag3PO4 nanocomposites possess a much higher rate for degradation of rhodamine B and methylene blue than the pure Ag3PO4 nanoparticles and Bi2MoO6 under visible light. Cao et al. deposited Ag3PO4 particles on the surface of plates of BiOCl and applied it into degradation of methylene blue (MB)[149]. The BiOCl/Ag3PO4 composites not only show highly enhanced visible light photocatalytic activity but also exhibit highly improved UV photocatalytic activity.

Besides the metal oxides composites, metal/semiconductor hetero-photocatalysts were also introduced due to the unique plasmonic effects and rapid photoexcited charge separation. A novel necklace-like heterostructures Ag/Ag3PO4 was successfully prepared by our group recently [150]. As shown in Fig.1.19, selective growth of Ag3PO4 submicro-cubes on Ag nanowires constructs necklace-like heterostructures Ag/Ag3PO4 which exhibits much higher activities than both pure
Ag₃PO₄ cubes and Ag nanowires for degradation of organic contaminants under visible light irradiation. The reason may be primarily ascribed to highly efficient charge separation at the contact interfaces as well as rapid electron export through Ag nanowires.

![Figure 1.19 SEM images of the Ag nanowire/Ag₃PO₄ cube necklace-like heterostructure (a); Photocatalytic activities of Ag nanowire/Ag₃PO₄ cube necklace-like heterostructures, Ag nanowires, and pure Ag₃PO₄ cubes for MO degradation under visible-light irradiation (λ > 420 nm)(b) [150].](image)

All in all, these previous reports about Ag₃PO₄-based composite photocatalysts indicate that constructing composite photocatalyst is a feasible and favorable way to improve the photocatalytic activity of Ag₃PO₄ and enlarge its practical applications.

### 1.4 Research motivation and thesis organization

In nowadays, steadily worsening environmental pollution has raised awareness of a potential global crisis. The photocatalytic degradations of organic pollutants have attracted increasing attention because it’s a promising, environmental, and cost-effective technology. As the most efficient photocatalyst, silver orthophosphate (Ag₃PO₄) exhibits extremely high activity under visible light irradiation. Especially,
the quantum yield of the generation of O₂ gas by water oxidation using Ag₃PO₄ is nearly 90%. However, pure Ag₃PO₄ exhibits low efficiency in photocatalytic degradation of gaseous pollutants and superior activity for Ag₃PO₄ in photodecomposition of organic dyes is still anticipated. The recombination of photo-generated electron-hole pairs, the redox potential of generated electron, and the surface status of Ag₃PO₄ are considered as factors that affect its photocatalytic performances.

The motivation of this work is to try to design and construct new photocatalysts based on Ag₃PO₄ with high efficient in environmental purification. In this regard, the research targets are included as: 1) successfully construct new composite photocatalysts based on Ag₃PO₄ for elimination of air pollutants, 2) construct new composite photocatalysts based on Ag₃PO₄ for photocatalytic degradation of organic pollutants in water, 3) figure out the influence mechanism of the electronic structures and surface properties on photocatalysis and 4) find optimal electronic structure and surface properties to improve the generation and separation of electron/hole pairs and to improve the adsorption capacity towards the best activity of Ag₃PO₄–based composite photocatalysts.

To achieve these targets, the research work of this dissertation is arranged as follows:

In chapter 2, a novel composite photocatalyst Ag₃PO₄/In(OH)₃ is obtained via an in-situ precipitation method. The phase compositions, optical properties, and morphologies of the heterojunction photocatalysts are systematically investigated via
powder X-ray diffraction, UV-Visible absorption spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy, and transmission electron microscopy. In order to investigate the influence mechanism of surface properties on photocatalysis, the surface-electric property of the composite photocatalyst is adjusted by using the In(OH)$_3$. The photodegradation of Rhodamine B (Rh B) is carried out to test the photocatalytic activity of the heterojunction. Moreover, the photosensitization and the intrinsic photocatalytic degradation of Rh B are also investigated under 540 ± 13nm and 420 ± 13nm monochromatic irradiations, respectively, to clarify the intrinsic photocatalytic degradation and photosensitization.

In order to introduce the Ag$_3$PO$_4$ into air purification, a new heterojunction Ag$_3$PO$_4$/Cr-SrTiO$_3$ photocatalyst is successfully synthesized in chapter 3. Iso-propanol (IPA) photodegradation over the heterojunctions under visible-light irradiation is employed for evaluating their photocatalytic properties. The effects of different mass ratio and calcination temperature on photocatalytic activity are systematically investigated. In particular, the valence-band states of Ag$_3$PO$_4$ and Cr doped SrTiO$_3$ are analyzed by X-ray photoelectron spectroscopy (XPS) to deduce the band structures, which helps understand the transfer of photocarriers between the two semiconductors.

The N 2p orbitals have higher potential energies than that of O 2p orbitals, and their hybridization has the possibility to lifts up the top of the valence band of Sr$_2$Nb$_2$O$_7$, which make the photocatalyst respond to visible light. Therefore, another new composite photocatalyst Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ with adjustable band structures
towards efficient elimination of gaseous organic pollutants under visible light irradiation is obtained in chapter 4. In order to figure out the influence mechanism of the electronic structure on photocatalysis and find optimal composite band structures, the Sr$_2$Nb$_2$O$_{7-x}$N$_x$ with adjustable band gaps are obtained from Sr$_2$Nb$_2$O$_7$ precursors by nitridation with NH$_3$ under different temperatures. Detailed calculations on the band structures of photocatalysts are carried out. The valence-band states of Ag$_3$PO$_4$ and Sr$_2$Nb$_2$O$_{7-x}$N$_x$ were analyzed by X-ray photoelectron spectroscopy (XPS), which helps understand the optimal band structure for the best photocatalytic activity.

In chapter 5, an overall summary and conclusions of achievements of this dissertation work was provided. The prospects for further work were also presented in this chapter.

Reference:


Chapter 1


148, 65.


Commun., 2011, 47, 2041.


Chapter 2 Ag₃PO₄/In(OH)₃ composite photocatalysts with adjustable surface-electric property for efficient photodegradation of organic dyes

Abstract

A new composite photocatalyst Ag₃PO₄/In(OH)₃ was successfully synthesized via in-situ precipitation method and applied to eliminate Rhodamine B under the irradiation of solar simulator. The composite photocatalysts exhibited higher activity than that of individual Ag₃PO₄ and In(OH)₃, and the highest activity (the rate constant $k_{app} = 1.75 \text{ min}^{-1}$) was observed over the Ag₃PO₄/In(OH)₃ with a molar ratio of 1.65:1.0. The further mechanism study and material characterizations indicated that the photocatalytic activity is closely related to the surface-electric property of the composite photocatalyst. Moreover, the surface-electric property could be continually adjusted by changing the content of In(OH)₃. The photosensitization and the intrinsic photocatalytic degradation of Rh B were investigated under 540 ± 12 nm and 420 ± 12 nm monochromatic irradiations, respectively. The results indicated that the intrinsic photocatalytic degradation of Rh B dominated the overall degradation under the solar light irradiation. The energy-band structure of the composite photocatalyst was also investigated and considered as a reason for the enhanced multi-electron reactions. Here, the composite photocatalyst with adjustable surface-electric property and suitable band structure reveals a novel material design-concept of exploiting a new photocatalyst based on the reaction kinetics and thermodynamics.
2.3 Introduction

The photocatalytic degradations of organic pollutants have attracted increasing interesting because it’s a promising, environmental, and cost-effective technology for the treatment of contaminated groundwater and wastewater [1-4]. For the better utilize visible light accounting for about 43% of solar energy, great efforts have been made to exploit visible-light-sensitive photocatalysts. Besides some conventional methods such as cation ion or anion ion doping [5], heterojunctions [6], band engineering [7], dye sensitization [8-9] and so forth, some multiple-metal oxides, such as Ag-based [10-11], Bi-based [12-16], In-based semiconductors [17-18] have been fabricated. Among these photocatalysts, silver orthophosphate ($Ag_3PO_4$) as a novel photocatalyst with promising efficiency in water oxidation and photodecomposition of organic dyes was reported recently [19]. The quantum yield of the generation of O$_2$ gas by water splitting using $Ag_3PO_4$ is nearly 90% around 420 nm, which is significantly higher than that of most photocatalysts (< 20%) [2, 19]. Since then, a series of efforts have been focused on improvement of $Ag_3PO_4$ physical properties by using morphology modification [20-22], electronic-structure calculation [23] and composite construction [24-25]. Recently, some composite photocatalysts based on $Ag_3PO_4$, such as $AgX/Ag_3PO_4$ (X = Cl, Br, I) [26], $Ag_3PO_4/TiO_2$ [27], $Fe_3O_4/Ag_3PO_4$ [28], $Ag_3PO_4/SnO_2$ [29], and Graphene oxide/$Ag_3PO_4$ [30] have been successfully synthesized and exhibited enhanced photocatalytic activities. However, the efficiency of $Ag_3PO_4$ in photodecomposition of gaseous organic contaminants still need be improved.
In most cases, the band structure in composite photocatalyst is considered as the primary reason for the enhanced activity. As illustrated in Scheme A, separation of electrons/holes pairs can be enhanced which contributes to the higher photocatalytic activity. Besides the band gap structure, the surface-electric property of the semiconductor is also an important factor for photocatalytic activity because of its influence on the adsorption of organic dyes, which is relevant to the reaction dynamics. According to previously reports [31-32], the surface charge characteristic can be adjusted in two ways: one is adjusting of the pH values of the photocatalyst suspension, and another one is composing with other materials as a composite. For instance, K. Bourikas and co-workers [31] reported that more positively charged surfaces could adsorb more AO7 molecule, which is closely related to the photocatalytic activity. Therefore, they used HNO₃ to adjust the pH values of the TiO₂ suspension and found that the highest adsorption of AO7 on the TiO₂ was obtained when pH value was 2.0. Besides the pH adjusting, Jungwon Kim and co-workers [32]
used phosphate to adjust the surface charge characteristic of TiO$_2$ and obtained enhanced photoactivity in dye degradation. To the best of our knowledge, there is no report on the surface-electric property of the Ag$_3$PO$_4$. And unfortunately, Ag$_3$PO$_4$ cannot be stable neither in acid or alkaline solution due to the hydrolyzation of Ag$^+$ and PO$_4^{3-}$ ions, which means it’s unavailable to adjust the surface-electric property of the Ag$_3$PO$_4$ via pH adjusting. Therefore, composing Ag$_3$PO$_4$ with suitable materials is a promising strategy to obtain adjustable surface-electric property for enhanced photocatalytic efficiency.

In(OH)$_3$ with a wide band gap of 5.15 eV has attracted increasing attention because of its higher hole oxidation potential to decompose benzene and stronger redox ability of conduction band (CB) electrons for H$_2$ evolution under UV-light irradiation compared to TiO$_2$ [33]. Moreover, the photocatalytic reduction of CO$_2$ to hydrocarbons was realized over mesoporous In(OH)$_3$, which is the evidence that In(OH)$_3$ has great redox ability for photocatalytic applications. More details are discussed in 2.3.3. Besides these, due to its unique physical and chemical properties, it also has potential applications in various fields such as nonlinear optics [34a], nanoelectronics [34b], and gas sensing [34c]. Herein, a new composite photocatalyst based on Ag$_3$PO$_4$ and In(OH)$_3$ was designed to attain the efficient elimination of Rhodamine B under solar-light simulated irradiation. Surface-electric properties of the composite photocatalysts with different molar ratios were investigated via zeta-potential characterization. Moreover, the photosensitization and the intrinsic photocatalytic degradation of Rh B were investigated under 542 ± 12 nm and 420± 12
nm monochromatic irradiations respectively, to confirm the dominated pathway of Rh B degradation. The energy-band structure of the Ag₃PO₄/In(OH)₃ composite was also investigated to help understand the transfer of photoelectrons between the two semiconductors. The enhanced photoactivity of Ag₃PO₄/In(OH)₃ could be attributed to the collaborated effects of the surface-electric property and the suitable band structure of the composite photocatalyst.

2.4 Experimental

2.2.1 Synthesis of In(OH)₃ nanorods

Nanorods of In(OH)₃ were synthesized via a hydrothermal treatment method. Typically, 0.3 g of InCl₃ · 4H₂O was dissolved in 100 mL of distilled water with stirring for 30 min. Then, 3 g of Urea was added into the solution and kept stirring for 30 min. After that, 100.0 mL of the mixture was poured into a Teflon-lined stainless steel autoclave and heated up to 130 °C for 13 h. The obtained precipitates were washed several times with distilled water till neutral pH solution and dried at room temperature overnight.

2.2.2 Synthesis of Ag₃PO₄/In(OH)₃ composite photocatalyst

Deposition of Ag₃PO₄ nanoparticles onto the In(OH)₃ was carried out by an in-situ precipitation method. Typically, as-prepared In(OH)₃ was dispersed in 100 mL of distilled water and sonicated for 10 min. Meanwhile, some amount of Ag(NO)₃ was dissolved in 50 ml of distilled water and stirred for 10 min. Then, a 10 % ammonia
solution was added into above solution to obtain silver-ammine complex. After that, the silver-ammine solution was mixed with the suspension of In(OH)$_3$ nanorods and stirred for several hours. Finally, a 5.0 mmol/L of Na$_2$HPO$_4$ was added into the mixture drop by drop and kept stirring for 20 h. The obtained precipitates were washed several times with distilled water and then dried at 60°C for 12h. The Ag$_3$PO$_4$/In(OH)$_3$ (the molar ratios of Ag$_3$PO$_4$ to In(OH)$_3$ are 3.0:1.0, 1.65:1.0, 0.65:1.0, 0.3:1.0, and 0.15:1.0) were synthesized by the same method. For comparison, pure Ag$_3$PO$_4$ particles were also prepared under the same conditions without the In(OH)$_3$ nanorods.

### 2.2.3 Photocatalyst characterization

X-ray diffraction patterns were characterized with a Rigaku Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-K$_\alpha$ radiation ($\lambda=1.54178$ Å). SEM images were recorded with a JEOL 6700F field emission scanning electron microscope. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV-2500 Spectrophotometer and converted to absorption spectra by the standard Kubelka-Munk method. The surface area measurements were carried out on a Surface Area Analyzer (BeL Japan Corp.). Light intensity in the photocatalytic reaction was monitored using a spectroradiometer (USR-40; Ushio Inc., Japan). The surface electronegativity was characterized via Zeta potential measurement (Delsa$^\text{TM}$Nano C, Beckman,Co.).
2.2.4 Photocatalytic reaction

In all photocatalytic experiments, 0.2g of the as-prepared Ag$_3$PO$_4$, In(OH)$_3$, and Ag$_3$PO$_4$/In(OH)$_3$ samples were dispersed in 100 mL of 8.0 mg/L Rhodamine B (RhB) solution. The light source was a solar light simulation lamp with 30.5 mWcm$^{-2}$ illumination intensity. The photodegradations of organic dyes were monitored by measuring the changes of UV-vis absorption spectra as a function of irradiation time. For the contrast experiments under monochromatic irradiation, a 300 W Xe arc lamp (7 A imported current, focused through a 45 × 45 mm shutter window) equipped with a band-pass filter (540nm ± 13nm and 420nm ± 13nm, HOYA.CO., Japan) and a water filter was used as the light source. The spectra of the light sources are shown in Fig. 2.1.

![Figure 2.1](image_url)

**Figure 2.1.** The spectra of the light sources: (a) solar-light simulator (b,c) the Xe lamp equipped a band-pass filter (540nm ± 13nm and 420nm ± 13nm).
Changes in total organic carbon (TOC) were determined by using a total organic carbon analyzer (Model TOC-V CPH). The concentration of H_2O_2 that obtained during the photocatalytic reaction was determined by a photometric method [45].

2.3 Results and discussion

2.3.1 The formation mechanism of Ag_3PO_4/In(OH)_3

Ag_3PO_4/In(OH)_3 was synthesized by an in-situ precipitation method in the silver-ammine solution with pH of about 12.0. The surface-electric property of In(OH)_3 nanorods was characterized via zeta potential measurement. The growth process of Ag_3PO_4 onto In(OH)_3 is illustrated in Fig.2.2.

![Figure 2.2](image)

**Figure 2.2** The schematic diagram of growth process of Ag_3PO_4/In(OH)_3.

When In(OH)_3 was suspended in a solution with pH higher than 10.7, the surfaces of In(OH)_3 nanorods were negatively charged (see Fig.2.3). As a result, positively
charged silver ions \((\text{Ag(NH}_3)^+\) could be adsorbed onto the surfaces of \(\text{In(OH)}_3\). After the \(\text{Na}_2\text{HPO}_4\) solution was dropped into the mixture, the \(\text{Ag}^+\) (ad) would react with the \(\text{HPO}_4^{2-}\) on the surface of \(\text{In(OH)}_3\) to form the composite \(\text{Ag}_3\text{PO}_4/\text{In(OH)}_3\). The synthetic process of the \(\text{Ag}_3\text{PO}_4/\text{In(OH)}_3\) composite photocatalyst can be summarized as follows:

\[
\text{In(OH)}_3\text{(s)} + \text{Ag(NH}_3)^+(\text{aq}) \rightarrow \text{In(OH)}_3\text{-Ag(NH}_3)^+(\text{ad}) \quad \text{pH}= 11.0–12.0
\]

\[
\text{In(OH)}_3\text{-Ag(NH}_3)^+(\text{ad})+ \frac{1}{3}\text{HPO}_4^{2-}(\text{aq}) + \frac{1}{3}\text{OH}^- + \frac{2}{3}\text{H}_2\text{O} \rightarrow \text{Ag}_3\text{PO}_4/\text{In(OH)}_3 + \text{NH}_4\text{OH}
\]

**Figure 2.3** The zeta potentials of \(\text{In(OH)}_3\) suspension with different pH values.

### 2.3.2 Characteristics of the \(\text{In(OH)}_3/\text{Ag}_3\text{PO}_4\) composite photocatalyst

Fig. 2.4 shows the X-ray diffraction patterns of as-prepared \(\text{In(OH)}_3\), \(\text{Ag}_3\text{PO}_4\), and \(\text{Ag}_3\text{PO}_4/\text{In(OH)}_3\) (molar ratio = 0.15:1). The indexed diffraction peaks can be ascribed as \(\text{Ag}_3\text{PO}_4\) and \(\text{In(OH)}_3\), respectively. Peaks related to other materials cannot be detected in the synthesized samples, indicating that the \(\text{Ag}_3\text{PO}_4\) did not react with the
In(OH)$_3$. Morphologies of the as-prepared samples were observed with SEM.

**Figure 2.4.** XRD patterns of the prepared In(OH)$_3$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst (molar ratio, 0.15:1).

**Figure 2.5** SEM and TEM images of (a) Ag$_3$PO$_4$, (b) In(OH)$_3$ and (c~d) Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst (molar ratio, 0.15:1).
The Ag₃PO₄ contains rhombic dodecahedral and cubic with sizes from several hundred nanometers to several micrometers (see Fig. 2.5a). In contrast, the In(OH)₃ consists of microrods with uniform size of about 1 µm in length and 100 nm in diameter (see Fig. 2.5b,c). Furthermore, the morphology of the composite (Ag₃PO₄/In(OH)₃ = 0.15:1, molar ratio) is shown in Fig. 2.5(c,d). For this sample, Ag₃PO₄ was synthesized on the surface of In(OH)₃ nanorods as illustrated in Fig. 2.2. As shown in Fig. 2.5(d), the TEM image indicates that the Ag₃PO₄ and In(OH)₃ are well connected, which promotes the electron transfer between them.

Fig. 2.6a shows the UV-vis absorption spectra of Ag₃PO₄, In(OH)₃, and In(OH)₃ composite photocatalyst Ag₃PO₄ (molar ratio, 1.65:1). The absorption spectrum of Ag₃PO₄ indicates that it can absorb solar energy with a wavelength shorter than ~530 nm, corresponding to 2.5 eV of band-gap energy. This result coincides with our previous report [19]. Meanwhile, the absorption spectrum of In(OH)₃ shows that the optical absorbance edge is about 240 nm and the band gap is 5.17 eV, which are in agreement with previous work [35a]. Thus, in the absorption spectra of the Ag₃PO₄/In(OH)₃ composite, besides the absorption band edge (around 500~530 nm) in the visible light range, another band edge for pure In(OH)₃ appears in the deep UV light range. Moreover, the UV-Vis light absorptions of the heterojuctions are related with the molar ratios between Ag₃PO₄ and In(OH)₃ (See Fig. 2.6b), such as more content of In(OH)₃ in composite results in lower absorption of light.
Figure 2.6. (a) UV-Vis absorption spectra of Ag₃PO₄, Ag₃PO₄/In(OH)₃ (molar ratio = 1.65:1), and In(OH)₃. (b) UV-Vis absorption spectra of (a) Ag₃PO₄, (b) Ag₃PO₄/In(OH)₃ (molar ratio = 3:1), (c) 1.65:1, (d) 1:1, (e) 0.65:1, (f) 0.3:1, (g) 0.15:1, and (h) In(OH)₃.
2.3.3 Photocatalytic activities of Ag$_3$PO$_4$, In(OH)$_3$, and Ag$_3$PO$_4$/In(OH)$_3$

2.3.3.1 Photocatalytic activity of In(OH)$_3$ in CO$_2$ photoreduction.

As mentioned in introduction, because of the higher potential of conduction band and the lower potential of valance band, In(OH)$_3$ exhibits high efficiency in decomposition of benzene and H$_2$ evolution under UV-light irradiation. In this work, the redox ability of generated electron/holes of In(OH)$_3$ was further identified via CO$_2$ photoreduction under full arc Xe lamp irradiation.

The samples were prepared by a sol-gel hydrothermal synthesis 5 mmol of In(NO$_3$)$_3$·4.5H$_2$O was mixed with 30 mL of ethylene glycol (EG) (99%, Wako Co., Japan). After stirring for 10 min, 20 mL of isopropanol (Wako, 99%) was dropped into the solution and then the solution was heated it at 80°C until totally volatilized to obtain a white gel. After milling the gel completely, the obtained powders were mixed with 80 mL distilled water, and then the mixture was poured into 120 mL of Teflon-lined stainless steel autoclave. This autoclave was heated up to 180°C and kept for 36 hours. The obtained precipitate was washed with distilled water for several times and dried at room temperature overnight.

The scanning electron microscope (SEM) image (Fig.2.7a) shows that the particles of In(OH)$_3$ with cubic and rectangular shapes were about several hundred nanometers in size. The microstructure was further investigated by transmission electron microscopy (TEM). A representative high-resolution TEM (HRTEM) image (Fig.2.7b) of a small crystallite (inset of Fig.2.7b) reveals that the crystallite is single crystal with a lattice space measured about 0.37 nm, which corresponds to the spacing
of (200) lattice plane of In(OH)$_3$. With a lower magnification, the TEM image of a nanocube (Fig. 2.7c) shows the contrast between dark edge and light center indicates the existence of pores. Furthermore, the Nitrogen adsorption-desorption isotherms (Fig. 2.7d) indicates that the hysteresis loop is approximately in accord with a type H$_3$ loop which is always observed with aggregates of plate-like particles giving rise to slit-shaped pores [35b]. The distribution of pore sizes (inset of Fig.2d) calculated through the Barrett-Joyner-Halenda (BJH) method shows the presence of pores with average pore size of 9.5 nm. The surface area of the sample calculated from the linear region of the plot is about 64.5 m$^2$g$^{-1}$.

**Figure 2.7** (a) SEM image; (b,c) High and low magnification of HRTEM image of mesoporous In(OH)$_3$; (d) nitrogen adsorption-desorption isotherms and pore size distribution (inset);
Figure 2.8 DFT calculation of In(OH)₃: (a) energy band dispersion and (b) density of states.

The theoretical calculation of the band structure was carried out for understanding its photophysical and photocatalytic properties. As shown in Fig. 2.8a, the energy-band structure indicates that In(OH)₃ is a direct band-gap semiconductor. The dispersion of the density of states is advantageous for the electrons generation and transmission. The density of states (Fig. 2.8b) reveals that the conduction band minimum and the valence band maximum are dominated by In 5s and O 2p, respectively. The band edge of valence band (E_{VB}) of In(OH)₃ is estimated to be 4.24 eV (vs NHE) [35a]. The potential of VB of In(OH)₃ is more positive than that of E₀(O₂/H₂O) [2H₂O→ O₂+ 4H⁺ + 4e⁻ E₀(O₂/H₂O) 0.93 V, vs. NHE, pH = 5] [35c].

The conduction band (CB) position can be deduced by E_{CB} = E_{VB} – E_g. Therefore, the band edge of conduction band (E_{CB}) position is -0.93 eV (vs NHE), which is more negative than that of E₀(CO₂/CH₄) [CO₂ + 8e⁻ + 8H⁺→ CH₄ + 2H₂O E₀(CO₂/CH₄) -0.24 V, vs. NHE, pH = 5]. Therefore, the photogenerated electrons and holes can
react with the adsorbed CO₂ and H₂O to produce CH₄.

Fig. 2.9 shows the CH₄ evolution over mesoporous In(OH)₃ under full arc Xe lamp irradiation. In order to investigate the effects of porous structure, the activity of sample with non-mesoporous structure (named as n-In(OH)₃), which was synthesized via hydrothermal treatment in aqueous solution of ammonia, was also characterized. The evolution rate of CH₄ over the mesoporous In(OH)₃ is about 0.8 µmol(g h)⁻¹, which is 20 times higher than that of n-In(OH)₃ (0.04 µmol(g h)⁻¹). The reason may be due to the mesoporous structure that can enlarge the surface area and enhance the gas adsorption of the sample. The results reveal that the redox potentials of conduction band and valance band of In(OH)₃ is suitable for CO₂ photocatalytic reduction.

![Figure 2.9. CH₄ evolution over In(OH)₃ with various co-catalysts under full-arc Xe lamp irradiation. (co-catalysts: Pt, 0.5 wt%);](image-url)
2.3.3.2 Photocatalytic ability of Ag$_3$PO$_4$, In(OH)$_3$, and Ag$_3$PO$_4$/In(OH)$_3$ in dyes photodegradation

In this study, Rhodamine B (RhB) solution was chosen as a model pollutant for the evaluation of photocatalytic activities of the Ag$_3$PO$_4$, In(OH)$_3$, and Ag$_3$PO$_4$/In(OH)$_3$. The photocatalytic degradation of RhB was carried out under the simulation solar irradiation (30.5 mWcm$^{-2}$ illumination intensity). Fig. 2.10 depicts the photocatalytic degradation of Rh B based on its concentration changes. It could be observed that 98.0% of the Rh B was degraded within 1.5 minutes of irradiation (see Fig. 2.10a) over the composite photocatalyst Ag$_3$PO$_4$/In(OH)$_3$. In contrast, the photoactivities of the Ag$_3$PO$_4$ and In(OH)$_3$ were extremely lower than that of Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst. The Ag$_3$PO$_4$ spent 9 minutes to decolorize 95% of the Rh B solution, while the In(OH)$_3$ exhibited even negligible activity. The kinetics of these photocatalytic reactions can be described using the first order reaction for low concentrations of Rh B solutions (see Fig. 2.10 b). The apparent rate constant ($K_{app}$, min$^{-1}$) determined from regression curves of $-\ln(C/C_0)$ versus irradiation time is 1.75 min$^{-1}$ for Rh B degradation over the Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst (molar ratio=1.65:1). In comparison, the apparent rate constant of Ag$_3$PO$_4$ is about 0.35 min$^{-1}$. In a word, the Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst has notably enhanced activity in photocatalytic degradation of Rh B. Moreover, in the absence of photocatalyst, only 6.7% of the Rh B was degraded after 2h of irradiation (see Fig. 2.10 c).
Figure 2.10 (b) The regression curves of $-\ln(C/C_0)$ versus irradiation time. (c) Self-photocatalysis solution of Rh B under solar simulating irradiation.
Measurements of total organic carbon (TOC) concentrations were adopted to assess the completed decomposition extent of an organic substrate during the irradiation period. As shown in Fig. 2.11, TOC concentrations of both the irradiated Rh B/Ag$_3$PO$_4$ suspensions (curve a) and the irradiated Rh B/composite photocatalyst suspensions (curve b) decrease with increasing irradiation time. The initial TOC concentrations of curve b is lower than that of curve a which may be due to the higher adsorption of Rh B molecular over the Ag$_3$PO$_4$/In(OH)$_3$ (to be discussed later). The TOC concentrations of the Rh B/Ag$_3$PO$_4$ suspensions (curve a) are greater than those of the Rh B/composite photocatalyst suspensions (curve b), indicating that the degree of mineralization of the organic substrate in the Rh B/Ag$_3$PO$_4$ suspensions ($\Delta$% TOC = 29.4%) is much lower than that in the Rh B/composite photocatalyst suspensions ($\Delta$% TOC = 40.0%). Moreover, the TOC decreased quickly in the first 4 min reaction for the Rh B/composite photocatalyst suspensions and in the first 10 min
reaction for the Rh B/Ag₃PO₄ suspensions, respectively. However, the TOC values almost did not change anymore in another 2 h of irradiation, indicating that completed decomposition of the dye proceeded very slowly.

Table 1 The apparent rate constants of photocatalysts under different irradiations.

<table>
<thead>
<tr>
<th></th>
<th>Ag₃PO₄</th>
<th>In(OH)₃</th>
<th>Ag₃PO₄/In(OH)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under 540 nm monochromatic irradiation (light intensity: 5.106 mW cm⁻²)</td>
<td>$k_{app}=0.011 \text{ min}^{-1}$</td>
<td>$k_{app}=0.0012 \text{ min}^{-1}$</td>
<td>$k_{app}=0.071 \text{ min}^{-1}$</td>
</tr>
<tr>
<td>Under 420 nm monochromatic irradiation (light intensity: 5.292 mW cm⁻²)</td>
<td>$k_{app}=0.15 \text{ min}^{-1}$</td>
<td>---</td>
<td>$k_{app}=0.42 \text{ min}^{-1}$</td>
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</table>

In order to investigate the photosensitization of Rh B and the intrinsic photocatalytic degradation of Rh B respectively, the photoactivities of Ag₃PO₄, In(OH)₃, and Ag₃PO₄/In(OH)₃ under monochromatic irradiations (540 ± 13 nm, and 420 ± 13 nm) were also evaluated. The light intensity and the apparent rate constant of samples are listed in the table 1. Under 540 nm monochromatic irradiation, the intrinsic photocatalytic degradation of Rh B could be excluded because of the Ag₃PO₄ or the In(OH)₃ cannot be excited by 540 nm monochromatic light. As shown in Fig.2.12 (a,b), all of the samples exhibited activities. In particular, the highest efficiency was obtained on the composite photocatalyst Ag₃PO₄/In(OH)₃ (molar ratio: 1.65:1). More than 98.0% of the Rh B was degraded within 40 min irradiation and the apparent rate constant is about $K_{app} = 0.071 \text{ min}^{-1}$. In comparison, the photoactivities of the Ag₃PO₄ and the In(OH)₃ were much lower than that of Ag₃PO₄/In(OH)₃. There was about 70% of Rh B degraded after 120 min irradiation over the Ag₃PO₄ photocatalyst. For the In(OH)₃, it took 14 h to degrade 80% of the Rh
B solution. As listed in Table 1, the apparent rate constants of the Ag$_3$PO$_4$ and the In(OH)$_3$ are $K_{app} = 0.011$ min$^{-1}$ and $K_{app} = 0.0012$ min$^{-1}$, respectively. Meanwhile, under 420 nm monochromatic irradiation, the photosensitization of Rh B could be inhibited because of the Rh B molecular cannot be sensitized by 420 nm monochromatic light.

![Figure 2.12](image)

**Figure 2.12.** (a,b) Photocatalytic degradation of Rhodamine B (Rh B) solution over Ag$_3$PO$_4$, In(OH)$_3$, and Ag$_3$PO$_4$/In(OH)$_3$ (molar ratio = 1.65:1) under monochromatic irradiation 540 nm.
As shown in Fig. 2.12 (c), more than 98.0% of the Rh B was decolorized within 7 min irradiation over the Ag₃PO₄/In(OH)₃ composite photocatalyst and the apparent rate constant is about $K_{app} = 0.42 \text{ min}^{-1}$. For the individual photocatalysts, the Ag₃PO₄ needs more than 20 min to degrade the Rh B completely, while the In(OH)₃ exhibits even negligible activity. Compared with the results under 540 nm monochromatic irradiation, the samples exhibited higher activity under 420 nm monochromatic irradiation. In particular, the Ag₃PO₄/In(OH)₃ composite photocatalyst shows 5.9 times higher in the apparent rate constant under 420 nm irradiation than that of composite photocatalysts under 540 nm irradiation; the Ag₃PO₄ exhibits 13.6 times higher in the apparent rate constant under 420 nm than that of Ag₃PO₄ under 540 nm irradiation. Since mechanism of Rh B degradation is very complicated, the Rh B degradation is considered as one-electron reaction for convenience of Q.E calculation. Therefore, the AQE can be calculated by using this equation:

Figure 2.12. (c) Photocatalytic degradation of Rhodamine B (Rh B) solution over Ag₃PO₄ and Ag₃PO₄/In(OH)₃ (molar ratio = 1.65:1) under monochromatic irradiation 420 nm.
\[ \text{AQE} = \frac{[\text{N(Rh B)}]}{[\text{N (photons)}]} \times 100 \% \]

In which, \([\text{N(Rh B)}]\) signify the mole number of decolorized Rh B; \([\text{N (photons)}]\) signify the number of incident photons in unite time;

In this work, the AQE of the composite photocatalyst under irradiation with 420 nm was calculated as 10.7%.

Contrast experiment without photocatalyst was carried out under the same condition to exclude the self-photocatalysis of Rh B. After 20h irradiation, the degree of degradation of Rh B were about only 4.8 % under 542 nm monochromatic irradiation and 1.7% of the Rh B under 420 nm monochromatic irradiation, respectively. That difference of degradation may be due to the sensitization of Rh B.

### 2.3.4 Mechanism of the photodegradation over the Ag₃PO₄/In(OH)₃ composite photocatalyst

#### 2.3.4.1 Two possible pathways of degradation of Rh B

Degradation of the Rh B in solution undergoes two possible pathways: intrinsic photocatalysis and photosensitization [36]. As shown in Scheme B1, the
photocatalysis pathway is mainly considered to be controlled by the following processes: (1) the light absorption of the semiconductor catalyst, (2) the generation of photogenerated electron and hole, (3) the transfer of charge carriers, and (4) the utilization of the charge carriers by the reactants. Meanwhile, Scheme B2 summarizes some of the accepted features of the photosensitization pathway. [36]: Rh B adsorbed on the photocatalyst surface is excited by the visible light (Eq.1) and injects electrons into the conduction band of the semiconductor to form Rh B cationic radicals (Eq. 2). The electrons in the conduction band of the semiconductor undergo the similar transformation to Eq. 3~6. Finally, Rh B is photocatalytic degraded to end products (Eq. 7) [36-39].

\[
\begin{align*}
\text{Rh B} + h\nu & \rightarrow \text{Rh B}^*; - 1.09 \text{ V (vs NHE)} \quad (1) \\
\text{Rh B}^* + \text{Sem.} & \rightarrow \text{Rh B}^+ + \text{Sem.}(e^-) \quad (2) \\
2e^- + O_2 + 2H^+ & \rightarrow H_2O_2, 0.695 \text{ V} \quad (3) \\
O_2 + H_2O + 2e^- & \leftrightarrow HO_2^- + OH^-; -0.076 \text{ V} \quad (4) \\
O_2 + e^- & \leftrightarrow O_2^-; -0.33 \text{ V} \quad (5) \\
O_2 + H^+ + e^- & \leftrightarrow HO_2^-; -0.046 \text{ V} \quad (6) \\
\text{Rh B}^+ + h^+ + \cdot OH + \cdot O_2^- & \rightarrow CO_2 + H_2O + \text{mineral acids} \quad (7)
\end{align*}
\]

The intrinsic photocatalytic pathway of Rh B degradation was confirmed over the Ag₃PO₄ under monochromatic irradiation at 420 nm. The UV-vis light absorption spectrum indicates that this dye exhibits negligible absorption around 420 nm, but the Ag₃PO₄ could be excited by the light shorter than 500 nm. Thus, the photocatalytic degradation of Rh B was attributed to the intrinsic photocatalysis of the Ag₃PO₄. The
photosensitization of Rh B was detected under 540 nm monochromatic irradiation. The UV-Vis light adsorption spectrum of Rh B solution indicates that Rh B molecular can be excited by 540 nm irradiation. Moreover, the potentials of the conduction bands of Ag$_3$PO$_4$ and In(OH)$_3$ are +0.45 eV and -0.93 eV, respectively, which are more positive than the redox potential of $E^0$ (Rh B*/Rh B$^{•+}$) (-1.09 V) [37]. It leads to electron injection from the adsorbed Rh B* species to the conduction bands of photocatalysts. The electrons injected from excited dyes were primarily used in the formation of H$_2$O$_2$ via 2-electron reduction of dioxygen adsorbed on the photocatalysts [41]. Accordingly, the photosensitization pathway of Rh B should be responsible for the activity under monochromatic irradiation with 540 nm. Under the irradiation of solar simulator, both Ag$_3$PO$_4$ and Rh B molecular could be excited, therefore, two pathways were included in the overall photocatalytic degradation.

As above results shown, both the Ag$_3$PO$_4$ and the Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalysts exhibited higher activity under 420 nm monochromatic irradiation. Moreover, the intensities of monochromatic lights were almost the same. All in all, the intrinsic photocatalytic degradation of Rh B is much stronger than the photosensitization of Rh B, which means the intrinsic photocatalytic degradation of Rh B dominated the overall degradation under the solar light irradiation.

2.3.4.2 Effects of surface-electric property on the enhanced activity

Since the photocatalytic degradation of organic dyes requires technologies both to capture dyes from the solution and to convert it into end products, the adsorption of
dyes onto the surface of photocatalyst is the crucial process [31,32]. Since the Rh B molecule is positively charged in solution (see Fig. 2.13), more negative zeta-potential promote the adsorption of Rh B on the surface of photocatalyst.

![Molecular structure of Rh B in solution.](image)

**Figure 2.13** Molecular structure of Rh B in solution.

As listed in Table 2, the surface-electric properties of photocatalysts were evaluated by zeta-potentials at pH 7.5~8.0. The zeta-potential of the composite photocatalyst Ag₃PO₄/In(OH)₃ is about -60.2 mV which is more negative than that of Ag₃PO₄ (-1.78 mV) and In(OH)₃ (+17.4 mV).

<table>
<thead>
<tr>
<th>Molar ratio: (Ag₃PO₄ to In(OH)₃)</th>
<th>Zeta Potential (mV)</th>
<th>Adsorption of Rh B (mg/g)</th>
<th>Degradation of Rh B (K_{app}/min)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>17.4</td>
<td>0.40</td>
<td>1.1×10⁻⁴</td>
<td>24.2</td>
</tr>
<tr>
<td>0.15:1</td>
<td>-41.4</td>
<td>0.59</td>
<td>1.12</td>
<td>13.4</td>
</tr>
<tr>
<td>0.3:1</td>
<td>-45.2</td>
<td>0.63</td>
<td>1.24</td>
<td>8.3</td>
</tr>
<tr>
<td>0.65:1</td>
<td>-51.4</td>
<td>0.64</td>
<td>1.71</td>
<td>4.8</td>
</tr>
<tr>
<td>1.65:1</td>
<td>-60.2</td>
<td>0.68</td>
<td>1.75</td>
<td>4.56</td>
</tr>
<tr>
<td>3:1</td>
<td>-44.5</td>
<td>0.61</td>
<td>1.73</td>
<td>4.1</td>
</tr>
<tr>
<td>1:0</td>
<td>-1.78</td>
<td>0.26</td>
<td>0.35</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Therefore, the composite photocatalyst Ag₃PO₄/In(OH)₃ can adsorb the Rh B molecule more efficiently, which has been confirmed by contrast experiments carried out in dark. As shown in Table 2, the adsorption amount of Rh B over the composite Ag₃PO₄/In(OH)₃ is about 0.68 mg/g, which is much higher than that of Ag₃PO₄ (0.40 mg/g) and In(OH)₃ (0.26 mg/g). The reason for the different surface-electric
properties may be attributed to the hydrolyzation of In$^{3+}$ and PO$_4^{3-}$ ions as follows:

$$\text{In}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{In(OH)}_3 + 3\text{H}^+ \quad (8)$$

$$\text{PO}_4^{3-} + \text{H}_2\text{O} \leftrightarrow \text{HPO}_4^{2-} + \text{OH}^- \quad (9)$$

or \( \text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O} \quad (10) \)

The hydrolyzation of In$^{3+}$ in solution results in more H$^+$ adsorbed on the surface of In(OH)$_3$, which made the photocatalyst positively charged (as shown in reaction 5). As the same reason, the individual Ag$_3$PO$_4$ was negatively charged because of the hydrolyzation of PO$_4^{3-}$ (as shown in reaction 9). After constructing composite photocatalysts, the HPO$_4^{2-}$ or OH$^-$ could be consumed by H$^+$, which would promote the reaction 9 to produce more OH$^-$ and result in more negative surface-electric property.

As above analysis, the adsorption of Rh B is related to the surface-electric property of the photocatalyst. Therefore, continuously adjusting the surface-electric property of photocatalyst would help us to find the optimal point. Herein, we successfully adjusted the surface-electric properties of the Ag$_3$PO$_4$/In(OH)$_3$ composite by changing the content of In(OH)$_3$. As shown in Table 2, all of zeta potentials of composite samples with different molar ratios are more negative than that of individual Ag$_3$PO$_4$ and individual In(OH)$_3$. In particular, the most negatively charged surface was obtained when the molar ratio of Ag$_3$PO$_4$ to In(OH)$_3$ is 1.65:1.0. Moreover, the best activity was also obtained at the molar ratio 1.65:1.0 (Ag$_3$PO$_4$ to In(OH)$_3$) with a rate constant $k_{app}=1.75 \text{ min}^{-1}$, which is significantly higher than that of individual Ag$_3$PO$_4$ and individual In(OH)$_3$. 

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Figure 2.14 (a) Adsorption of Rh B over Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalysts with different zeta potentials. (b) Photocatalytic activity of Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalysts with different zeta potentials.

For more directly observation, the variation tendencies of the degradation and adsorption of Rh B, and the zeta potential of the photocatalysts are shown in Fig.2.14. It’s found that the variation tendencies of the adsorption and degradation of Rh B are in accordance with that of zeta potential, which indicates that the surface-electric property of the Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst is closely related to the adsorption and photocatalytic degradation of Rh B. Moreover, the surface area of
sample was also investigated. The results reveal that there is no obvious relationship between the surface area and the photocatalytic activity.

2.3.4.3 Effects of composite band structures on enhanced activity

As previous reports reported, the band structure of the composite photocatalysts is also responsible for the enhanced photocatalytic activity. As mentioned, the potential of conduction band of Ag$_3$PO$_4$ cannot match the redox potentials of the active oxygen species [39-40], which are necessary in the degradation of various organic substrates [42-43]. Therefore, the multi-electron reaction ($2e^- + O_2 + 2H^+ \rightarrow H_2O_2$, 0.695 V vs NHE) over Ag$_3$PO$_4$ is a more important way to obtain the oxygen species for Rh B photocatalytic degradation [44]. Moreover, as simulated in Scheme B3, the generated electrons could be injected to the In(OH)$_3$ and partly of them could be even transferred to Ag$_3$PO$_4$ due to the relatively positions of the conduction bands of Ag$_3$PO$_4$ (+0.45 eV) [19], In(OH)$_3$ (-0.93 eV) [33] and the redox potential of $E^0$ (Rh B*/Rh B•). For this view, the In(OH)$_3$ particles plays an important role as the electron carriers between excited Rh B* and Ag$_3$PO$_4$ or electron acceptors adsorbed on the particles.

In order to confirm this point, the contrast experiment over mixture of Ag$_3$PO$_4$ and In(OH)$_3$ without calcination was carried out under the same condition (see Fig. 2.15). The apparent rate constants of the mixture is about 0.29 min$^{-1}$ which is much lower than that of composite is ($k_{app}$=1.75 min$^{-1}$). All in all, beside the surface-electric property, the band structure of the Ag$_3$PO$_4$/In(OH)$_3$ composite is also advantageous
for the multi-electron reaction over Ag₃PO₄ (2e⁻ + O₂ + 2H⁺ → H₂O₂, 0.695 V vs NHE).

![Figure 2.15](image)

**Figure 2.15** Potodegradation of Rh B over mixture of Ag₃PO₄ and In(OH)₃ (1.7g: 0.3g) under solar simulating irradiation. (a) UV-vis adsorption spectra and (b) the change of concentration of Rh B.

### 2.3.4.4 Concentration of Hydrogen peroxide (H₂O₂)

In order to prove the multi-electron reaction was really realized, the hydrogen peroxide (H₂O₂) as product should be confirmed. Fortunately, hydrogen peroxide
(H₂O₂) can be detected by a photometric method, which is based on the horsedish peroxides (POD)-catalyzed oxidation by H₂O₂ of N, N-diethyl-p-phenylenediamine (DPD)[45]. In typical, two molecules of DPD could be oxidized by H₂O₂ with POD as catalyst turn to the radical cation, DPD⁺. The reaction is shown as follow:

![Chemical Reaction Diagram]

The radical cation DPD⁺ can be stabilized by resonance and forms a stable colour, with one absorption maxima at 510 nm and one at 551 nm. In general, the absorption at 551 nm is used for subsequent calculation.

The concentration of H₂O₂ in a sample of water can be calculated from the absorbance at 551 nm by considering the following relationship [45]:

\[
[H₂O₂]_{\text{sample}} = \frac{(A^{551}V_{\text{final}})\,el\,V_{\text{sample}}}{\text{cm}^2}
\]

Where the \( A^{551} \) is the absorbance at 551 nm, \( V_{\text{final}} \) is the final volume after addition of all regents and buffer, 16 mL, \( V_{\text{sample}} \) is the volume of original sample, 12 mL, \( e \) is the constant, \( l \) is the pathlength of optical cell, 1 cm.

The constant \( e \) at 551 nm can be calibrated with oxidation by iodine (i.e. two oxidation equivalents), as shown in Fig. 2.16. The value of constant \( e \) at 551 nm is about 5360 M⁻¹cm⁻¹.
Figure 2.16 Absorption spectra of the DPD/POD reagent after reaction with I$_2$ in water solution with concentration of 20 $\mu$M, 28 $\mu$M, 40 $\mu$M, and 51 $\mu$M.

Figure 2.17 Absorption spectra of the DPD/POD reagent after reaction with H$_2$O$_2$. (a) Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst and (b) Ag$_3$PO$_4$ in water solution without Rh B; (c) Ag$_3$PO$_4$/In(OH)$_3$ composite photocatalyst and (d) Ag$_3$PO$_4$ in water solution without Rh B.
solution with Rh B after 15 min irradiation of light irradiation (300nm< \( \lambda \) <800nm).

Fig. 2.17 shows the spectra of the reagent solution after its reaction with different concentration of H\(_2\)O\(_2\). As mentioned, the oxidized DPD exhibits two absorption peaks, one at 510 nm and the other around 551nm. The base lines were taken from the darkness experiments in 15 min which indicates the negatively evolution of H\(_2\)O\(_2\) without light irradiation.

Based on calculation, the concentration of H\(_2\)O\(_2\) in the suspension of Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)/In(OH)\(_3\) with irradiation time were shown in Fig.2.18 (a). As it shown, both Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)/In(OH)\(_3\) composite photocatalyst can continually generate H\(_2\)O\(_2\) under light irradiation (300nm< \( \lambda \) <800nm), which means the multi-electron reaction is really realized. Moreover, after 15 min irradiation, the concentration of H\(_2\)O\(_2\) in Ag\(_3\)PO\(_4\) water suspension is about 71.6 \( \mu \)M and that of Ag\(_3\)PO\(_4\)/In(OH)\(_3\) is about 86.8 \( \mu \)M, which means the composite photocatalyst is more advantageous for the multi-electron reaction which maybe attributed to the enhanced stability of composite photocatalyst. Moreover, with addition of Rh B, the reagent solution would generate more H\(_2\)O\(_2\) under the same experimental conditions. As shown in Fig.2.18 (b), after 15 min light irradiation when the dyes have been decolorized completely, the concentrations of H\(_2\)O\(_2\) over Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)/In(OH)\(_3\) composite photocatalyst were increased with 34.7 % and 65.3 %, respectively. For the Ag\(_3\)PO\(_4\) suspension, the concentration of H\(_2\)O\(_2\) is about 96.5 \( \mu \)M, and that of the Ag\(_3\)PO\(_4\)/In(OH)\(_3\) composite photocatalyst is about 143.5 \( \mu \)M. The reason may be due to the photosensitization of Rh B. As above analysis, the photosensitized Rh B could inject electrons to the
photocatalysts which participated in the multi-electron reactions. Therefore, the photosensitization of Rh B over the photocatalyst would enhance the multi-electron reaction.

Figure 2.18 The concentration of H₂O₂ in the water suspension (a) and in the dyes solution with Ag₃PO₄ and Ag₃PO₄/In(OH)₃ composite photocatalysts under light irradiation (300nm < λ < 800nm).
2.4 Conclusions

A new composite photocatalyst $\text{Ag}_3\text{PO}_4/\text{In(OH)}_3$ was successfully synthesized via an in-situ precipitation method in the silver-ammine solution. The results of photocatalytic degradation prove that the composite photocatalyst $\text{Ag}_3\text{PO}_4/\text{In(OH)}_3$ is more efficient than the individual materials. More particularly, the best activity was obtained at molar ratio 1.65:1.0 ($\text{Ag}_3\text{PO}_4$ to $\text{In(OH)}_3$) with the rate constant $k_{\text{app}}=1.75$ min$^{-1}$, which is significantly higher than that of the individual $\text{Ag}_3\text{PO}_4$ ($k_{\text{app}}=0.35$ min$^{-1}$). The surface-electric properties of the $\text{Ag}_3\text{PO}_4/\text{In(OH)}_3$ composite photocatalysts could be continually adjusted by the $\text{In(OH)}_3$ and the variation tendency of zeta potentials was in accordance with that of photocatalytic activities, which indicates that surface-electric property was mainly responsible for the enhanced photoactivity. The composite photocatalysts with adjustable surface-electric property reveals a novel material design concept of exploiting a new photocatalyst based on considering both the reaction kinetics and thermodynamics. The results and discussions herein supply useful information for the further developments of other composite photocatalysts.

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22432.


2012, 36,1541.


Chapter 3 A new heterojunction $\text{Ag}_3\text{PO}_4$/Cr-$\text{SrTiO}_3$ photocatalyst towards efficient elimination of gaseous organic pollutants under visible light irradiation

Abstract:

A new heterojunction $\text{Ag}_3\text{PO}_4$/Cr-$\text{SrTiO}_3$ was designed to eliminate the gaseous pollutants under visible light irradiation. The phase compositions, optical properties, and morphologies of the heterojunction photocatalysts were systematically investigated via powder X-ray diffraction, UV-Visible absorption spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy, and transmission electron microscopy. The photodegradation of Isopropyl alcohol (IPA) was carried out to test the photocatalytic activity of the heterojunction. The results revealed that the heterojunction exhibited considerably improved efficiency in IPA photodegradation (CO$_2$, 13.2 ppmh$^{-1}$) in comparison with pure $\text{Ag}_3\text{PO}_4$ (CO$_2$, 0.4 ppmh$^{-1}$) and Cr-$\text{SrTiO}_3$ (CO$_2$, 1.9 ppmh$^{-1}$) under visible light irradiation. In addition, the effects of mixing ratio and calcination temperature of the heterojunction were studied. The highest activity was observed in the $\text{Ag}_3\text{PO}_4$/Cr-$\text{SrTiO}_3$ heterojunction with the mass ratio of 1:4 ($\text{Ag}_3\text{PO}_4$: Cr-$\text{SrTiO}_3$) sintered at 500°C. An investigation of energy-band structure via valence-band X-ray photoelectron spectrum indicates that the conduction band (CB) and valence band (VB) of $\text{Ag}_3\text{PO}_4$ are both more positive than that of Cr-$\text{SrTiO}_3$, which facilitates the separation and transfer of photogenerated electrons and holes between the two photocatalysts.
3.1 Introduction

Semiconductor-based photocatalysts have attracted worldwide attention, because they can eliminate environmental pollutants and produce clean H₂ energy by utilizing solar energy efficiently [1~5]. During the past decades, TiO₂ [6~8] has been widely investigated as a classic photocatalyst. However, its band gap is so wide that it can only absorb the UV light which occupies about 4% in solar light. Therefore, in recent years, much effort has been focused on searching for other efficient photocatalysts that are active under visible-light irradiation. On this theme, various semiconductors have been developed, such as modified-TiO₂ [9~13], multimental oxides [14~16], sulfides [17, 18], oxynitrides [19~21] and heterojunctions [22~24].

Among these photocatalysts, silver orthophosphate (Ag₃PO₄) as a novel photocatalyst with promising efficiency in water oxidation and photodecomposition of organic dyes was reported recently [25a]. More specifically, Ag₃PO₄ can achieve a quantum efficiency of about 90% at wavelength around 420 nm in water oxidation, which is significantly higher than that of other previously reported semiconductors. Moreover, further investigations about the photoelectric/photocatalytic properties, morphology controlling, and facet effect of Ag₃PO₄ were carried out, and enhanced performances were obtained [25b,c,d,e]. However, the efficiency of Ag₃PO₄ in photodecomposition of gaseous organic contaminants is still needed to improved. One reason is that its potential of the conduction band (CB) is more positive than the reduction potential of O₂ (e⁻ + O₂ + H⁺ → HO₂, -0.046 V vs NHE) [26, 27]. As a result, the generated electrons cannot be consumed by combining with O₂ which is
very important for the photooxidization of the gaseous organic compound [5]. Another reason is that the decomposition of IPA to CO₂ is a complex multiphoton-involved process ($\text{CH}_3\text{CHOHCH}_3 + 5\text{H}_2\text{O} + 18\text{h}^+ \rightarrow 3\text{CO}_2 + 18\text{H}^+$)[44], which cannot easily be realized on pure Ag₃PO₄. Moreover, as the electrode potential of Ag₃PO₄/Ag (around 0.45 V vs. NHE) is more positive than that of H⁺/H₂ (0 V vs. NHE) [27], Ag₃PO₄ can easily be reduced to Ag⁰ during in the photocatalytic reactions. Constructing a heterojunction between Ag₃PO₄ and another semiconductor with proper band structure can induce multi-electron reaction ($2\text{e}^- + \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$, 0.695 V vs NHE), and can accumulate holes on the valence band of Cr-SrTiO₃ for the multiphoton-involved process, which will effectively solve the above-mentioned problems.

In previous studies, numerous heterostructured photocatalysts, such as TiO₂ [28,29], SrTiO₃ [30,31], and ZnO [32, 33] coupled with different photocatalysts, have been designed and tested for photodegradation of the pollutants. However, there are few examples of heterostructured photocatalysts based on Ag₃PO₄ [25e, 34]. Compared with above mentioned semiconductors, Cr-doped SrTiO₃ is a semiconductor photocatalyst with narrower band gap (about 1.9 eV), which can adsorb the visible light with wavelength as long as 600 nm and exhibit remarkable efficiency in H₂ evolution [35]. Furthermore, the band gap of Ag₃PO₄ is 2.45 eV, and its conduction band (CB) and valence band (VB) positions are +0.45 eV and +2.90 eV, respectively [25a]. In view of the chemical potential, the CB and VB levels of Cr doped SrTiO₃ are appreciably more negative than that of Ag₃PO₄. Thus, Cr-doped
SrTiO$_3$ and Ag$_3$PO$_4$ are two appropriate candidates to construct a heterostructured photocatalyst to work under visible-light irradiation. Hence, in this work, we synthesized a novel heterostructured photocatalyst based on Ag$_3$PO$_4$ and Cr doped SrTiO$_3$ via a solid calcination method. Iso-propanol (IPA) photodegradation over the heterojunctions under visible-light irradiation was employed for evaluating their photocatalytic properties. The effects of different mass ratio and calcination temperature on photocatalytic activity were systematically investigated. In particular, the valence-band state of Ag$_3$PO$_4$ and Cr doped SrTiO$_3$ were analyzed by X-ray photoelectron spectroscopy (XPS) to deduce the band structures, which helps understand the transfer of photocarriers between the two semiconductors.

3.2 Experiments

3.2.1 Photocatalysts preparation. All of the reagents were analytical grade and used without further purification. The Cr doped SrTiO$_3$ (Cr-SrTiO$_3$) was synthesized similar to our previous reports [36]. As shown in Fig.3.1, stoichiometric titanium isopropylate ([($\text{CH}_3$)$_2\text{CHO}$]$_4\text{Ti}$), strontium acetate (Sr(Ac)$_2$$\cdot$0.5H$_2$O), and Cr(NO$_3$)$_3$$\cdot$9H$_2$O were mixed thoroughly in ethylene glycol (dehydrated) with a molar ratio of 1:0.95:0.05, respectively. The mixed solution was heated at 70°C until the reagents totally volatilized to obtain a gel. After grinding the gel completely, the obtained powders were added into 80 ml of aqueous NaOH aqueous solution (5 molL$^{-1}$), and then the mixture was poured into 120 ml of a Teflon-lined stainless steel autoclave. This autoclave was heated up to 180°C and kept for 36 h. The obtained
precipitate was washed several times with distilled water for several times and dried at room temperature overnight.

Figure 3.1 Flowchart of the preparation of Cr-doped SrTiO₃ powders.

Moreover, the diffraction peak positions of the (110) plane in the range of \(2\theta=31\sim34\) was characterized to confirm the position of doped Cr. As shown in Fig. 3.2, due to the ionic radius of Cr\(^{3+}\) (0.0615 nm) or Cr\(^{6+}\) (0.044 nm) is smaller than that of Sr\(^{2+}\) (0.118 nm) but is close to that of Ti\(^{4+}\) (0.0605 nm) [36], the peak position of Cr-SrTiO\(_3\) shifted slightly toward a higher 2\(\theta\) value, that means the Cr\(^{3+}\) or Cr\(^{6+}\) were doped into the site of Sr\(^{2+}\) but not doped in to the site of Ti\(^{4+}\).
Figure 3.2 Diffraction peak positions of the (110) plane in the range of $2\theta = 31\sim 34$.

![XRD spectrum of SrTiO$_3$ and Cr-SrTiO$_3$](image)

Figure 3.3 Flowchart of the preparation of Ag$_3$PO$_4$ powders.

The Ag$_3$PO$_4$ was synthesized by the ion-exchange method as described in our former report [25]. Appropriate amounts of AgNO$_3$ and Na$_2$HPO$_4$ were mixed and milled thoroughly until the initial color changed to yellow. The obtained precipitate
was washed with distilled water for several times and dried at room temperature overnight. The Ag$_3$PO$_4$/Cr-SrTiO$_3$ heterojunctions with different mass ratios were prepared by grinding and mixing individual solids thoroughly in ethanol in an agate mortar. After that, the prepared samples were dried at 60°C overnight and then calcined at different temperatures for 5h in an oven, respectively.

### 3.2.2 Photocatalysts characterization.

The physical property and photocatalytic activity of Ag$_3$PO$_4$ and Cr-SrTiO$_3$ were systematically investigated. X-ray diffraction patterns were characterized with a Rigaku Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda=1.54178$ Å). Scanning electron microscopy images and energy-dispersive X-ray spectroscopy patterns were recorded with a JEOL 6700F field emission scanning electron microscopy. Transmission electron microscope and high-resolution images were performed with a JEOL 2100F field emission transmission electron microscopy operated at 200 kV. UV-visible diffuse reflectance spectrum was recorded with a Shimadzu UV-2500 Spectrophotometer and converted to absorption spectra by the standard Kubelka-Munk method. The surface area measurements were carried out in a Surface Area Analyzer (BELSORP II). The valence state of Cr was analyzed on an X-ray photoelectron spectroscopy (PHI Quantera SXM). Light intensity in the photocatalytic reaction was monitored using a spectroradiometer (USR-40; Ushio Inc., Japan).
3.2.3 Photocatalytic reaction.

In the photocatalytic measurement, a 300 W Xe arc lamp (7 A imported current, focused through a 45 × 45 mm shutter window) equipped with a set of glass filters (L42 + HA30, 420 nm < λ < 800 nm, HOYA.CO., Japan) and a water filter was used as the light source. Under such condition, the illumination intensity was 30 mWcm\(^{-2}\) (see Fig.3.4). The 0.2 g of sample was evenly spread over a dish with an area of 8.5 cm\(^2\) in a 500 mL of a borosilicate glass vessel. Then the inside atmosphere of the vessel was exchanged by artificial air [V(N\(_2\)) : V(O\(_2\)) = 4 : 1] for 10 min to remove gaseous impurities. After the sample was sealed in the vessel, gaseous isopropyl of Isopropyl alcohol (IPA) was injected into the vessel (the initial concentration of IPA was about 1250 ppm ~ 1500 ppm). Before irradiation, the sample was kept in the dark to ensure an adsorption-desorption equilibrium of IPA on the sample. The final products of the photocatalytic oxidation of IPA were CO\(_2\) and H\(_2\)O. To evaluate the photocatalytic activity, the IPA and CO\(_2\) were measured by using a gas chromatography (GC-2014, Shimadzu Corp., Japan) equipped with a methanizer and a flame ionization detector (FID).

![Figure 3.4](image_url) The spectrum of the Xe lamp equipped with a UV cutoff and a heating absorbing filter
3.3 Results and Discussion

3.3.1 Characteristics of Ag₃PO₄/Cr-SrTiO₃ composite photocatalysts

Fig. 3.5 shows the X-ray diffraction (XRD) pattern of the as-prepared Ag₃PO₄/Cr-SrTiO₃ composite calcined at 500°C. The indexed diffraction peaks can be ascribed as Ag₃PO₄ and Cr-SrTiO₃, respectively. Peaks related to other titanates were not observed in the synthesized samples, indicating that the Ag₃PO₄ did not react with the Cr-SrTiO₃. With the increasing the content of the Cr-SrTiO₃, the intensities of the Cr-SrTiO₃ peaks were increased.

![Figure 3.5 A comparison of XRD patterns of Cr-SrTiO₃, Ag₃PO₄, and Ag₃PO₄/Cr-SrTiO₃ composite powders.](image)

Morphologies of the prepared samples were characterized using SEM and TEM. The Ag₃PO₄ phase is composed of particles with sizes from several hundred nanometers to 1 micrometer (See Fig. 3.6a). In contrast, the Cr-SrTiO₃ consists of spherical aggregates (~200 nm in diameter) of nanoparticles 30-40 nm in diameter (See Fig. 3.6b). Next, the morphology of the composite (Ag₃PO₄: Cr-SrTiO₃= 1:4) was
investigated by SEM-EDX, as shown in Fig. 3.6c. For this sample, sub-micropowder particles are partially covered with aggregated nano-particles.

Figure 3.6 SEM image of $\text{Ag}_3\text{PO}_4$ (a), Cr-SrTiO$_3$ (b) and $\text{Ag}_3\text{PO}_4$/ Cr-SrTiO$_3$ (1:4) composite (c); TEM image of $\text{Ag}_3\text{PO}_4$/ Cr-SrTiO$_3$ (1:4) composite (d) and the energy dispersive spectra (EDS) pattern of $\text{Ag}_3\text{PO}_4$/ Cr-SrTiO$_3$ (1:4) composite. The result showed that the composite was composed of $\text{Ag}_3\text{PO}_4$ (square 1) and Cr-SrTiO$_3$ (square 2).

Further EDX analysis indicates that former powder and latter particle are $\text{Ag}_3\text{PO}_4$
and Cr-SrTiO$_3$, respectively (See Fig. 3.6 square (1) and (2)), which reveals that the Cr-SrTiO$_3$ partially covers on the Ag$_3$PO$_4$ surface. To further understand the contact between Ag$_3$PO$_4$ and Cr-SrTiO$_3$, TEM observation was applied, as shown in Fig. 3.6d. The TEM image indicates that the Ag$_3$PO$_4$ and Cr-SrTiO$_3$ are well connected, which is advantageous for the inter-particle photocarrier transfer between Ag$_3$PO$_4$ and Cr-SrTiO$_3$. Furthermore, as expected from the particle sizes, the BET surface area of Cr-SrTiO$_3$ is larger than that of Ag$_3$PO$_4$ (See Table 1). With an increase in the ratio of Cr-SrTiO$_3$, the BET surface area of the composites also increases.

Table 1 Surface area and pore volume of heterojunctions with different mass ratio

<table>
<thead>
<tr>
<th>Mass ratio: (Ag$_3$PO$_4$/Cr-SrTiO$_3$)</th>
<th>Surface area ($\text{m}^2\text{g}^{-1}$)</th>
<th>Pore volume ($\text{cm}^3\text{g}^{-1}$)</th>
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</table>

3.3.2 Optical properties of photocatalysts.

Fig. 3.7 shows the UV-Vis absorption spectra of Ag$_3$PO$_4$, Cr-SrTiO$_3$, and Ag$_3$PO$_4$/Cr-SrTiO$_3$ composite. The absorption spectrum of Ag$_3$PO$_4$ indicates that it can absorb solar energy with a wavelength shorter than ~530 nm. Moreover, the two absorption edges reveal an indirect band gap of 2.36 eV and a direct transition of 2.45 eV, which are generally in agreement with our previous work [25].
Meanwhile, after doping with Cr, the absorption edge of Cr-SrTiO$_3$ is around 650 nm, which is red-shifted in comparison with that of SrTiO$_3$[35], as shown in 3.8a. Fig. 3.8b shows the calculation diagram of the band gaps of SrTiO$_3$ and Cr-SrTiO$_3$. For a crystalline semiconductor, the optical absorption near the band edge can be described by the equation [4]:

\[(\alpha h\nu)^n = A(h\nu-E_g)\]

Where $\alpha$, $\nu$, $A$, and $E_g$ represent the absorption coefficient, light frequency, proportionality constant, and band gap, respectively. In the equation, $n$ depends on the transition characteristic of the photocatalyst. For an indirect semiconductor, $n$ equals 0.5, while $n$ is 2 for a direct semiconductor. Herein, the values of $n$ are 2 for the SrTiO$_3$ and Cr-SrTiO$_3$ [36]. Therefore, the band gaps of photocatalysts are shown like in Fig. 3.8b.
Figure 3.8 (a). UV-Vis diffuse reflectance spectrum of SrTiO$_3$, and Cr-SrTiO$_3$. (b).

The calculation diagram of the band gaps.

In comparison, the visible-light absorption of Cr-SrTiO$_3$ is obviously weaker than that of Ag$_3$PO$_4$. Therefore, the light absorption of the heterojunction is between that of Ag$_3$PO$_4$ and Cr-SrTiO$_3$ under 500 nm. On the other hand, the heterojunction exhibits stronger absorption over 500 nm than that of Ag$_3$PO$_4$ and Cr-SrTiO$_3$. This absorption could be attributed to the metallic Ag nanoparticles [37–38], which is obtained after
the calcination process. For further confirmation, Ag-deposited Cr-SrTiO$_3$ and Ag-deposited Ag$_3$PO$_4$ were prepared and characterized.

![UV-Vis diffuse reflectance spectrum](image)

**Figure 3.9** (a) UV-Vis diffuse reflectance spectrum of Cr-SrTiO$_3$, Ag-deposited Cr-SrTiO$_3$, and (b)Ag$_3$PO$_4$ and Ag-deposited Ag$_3$PO$_4$.

Ag-deposited Cr-SrTiO$_3$ and Ag-deposited Ag$_3$PO$_4$ were prepared by calcination method (500 °C, 3h), respectively. In details, 1.0 g of Cr-SrTiO$_3$ and 0.015g of AgNO$_3$ were mixed and grounded thoroughly. Then, the mixture was heated under 500 °C for 3h, which is the same as the treatment of the heterojunction. Ag-deposited Ag$_3$PO$_4$
was obtained by heating Ag₃PO₄ under the same procedure. As shown in Fig. 3.9, both of the Ag-deposited samples exhibit stronger light absorption over 500 nm than that of pure photocatalysts.

With changing mass ratios, the absorptions of the heterojunctions were changed but not quite different, and all of the heterojunctions can absorb the light up to 800 nm (see Fig.3.10).

**Figure 3.10** UV-Vis diffuse reflectance spectrum of Cr-SrTiO₃, Ag₃PO₄, and Ag₃PO₄/Cr-SrTiO₃ composite powders. (a) Ag₃PO₄, (b) Ag₃PO₄/Cr-SrTiO₃(4:1), (c) Ag₃PO₄/Cr-SrTiO₃(2:1), (d) Ag₃PO₄/Cr-SrTiO₃(1:2), (e) Ag₃PO₄/Cr-SrTiO₃(1:4), (f) Ag₃PO₄/Cr-SrTiO₃(1:6), (g) Ag₃PO₄/Cr-SrTiO₃(1:10), and (h) Cr-SrTiO₃.

### 3.3.3 Visible light photocatalytic activities of Ag₃PO₄, Cr-SrTiO₃ and Ag₃PO₄/Cr-SrTiO₃ heterojunctions

The photocatalytic conversions of IPA to CO₂ over different photocatalysts were carried out under visible light irradiation (420 nm< \( \lambda \) <800 nm). As shown in Fig.
3.11 (a), all of the heterostructured samples exhibit different efficiencies with changing the mass ratios. The best activity is obtained at the mass ratio 1:4. To investigate the activity in more details, the degradation of IPA over time for Ag$_3$PO$_4$/Cr-SrTiO$_3$ (mass ratio, 1:4) and pure photocatalysts were analyzed (Fig. 3.11b). In the presence of Ag$_3$PO$_4$/Cr-SrTiO$_3$ (mass ratio, 1:4) sample, 97% of the IPA is degraded within 3.8 h of irradiation. In contrast, the IPA decomposition ratios are only 33% and 11% over pure Ag$_3$PO$_4$ and Cr-SrTiO$_3$ after 15 h of irradiation respectively. Moreover, as shown in Fig. 3.11(c), the rate of CO$_2$ evolution over Ag$_3$PO$_4$/Cr-SrTiO$_3$ (mass ratio, 1:4) is much higher than that of pure Cr-SrTiO$_3$ and Ag$_3$PO$_4$ respectively. There is 291.2 ppm of CO$_2$ obtained by Ag$_3$PO$_4$/Cr-SrTiO$_3$ (mass ratio, 1:4) in comparison with 8.2 ppm and 58.3 ppm achieved by Ag$_3$PO$_4$ and Cr-SrTiO$_3$, respectively.

The AQE of the photocatalyst in IPA photodecomposition could be calculated by the equation:

\[
AQE = \frac{[N(CO_2) \times 6 + N(\text{acetone})]}{N(\text{photons})} \times 100 \%
\]

In which, \([N(CO_2)]\) and \(N(\text{acetone})\) signify the mole number of generated CO$_2$ and generated acetone in unit time; \([N(\text{photons})]\) signify the number of incident photons in unite time;

In this work, the AQE of the Ag$_3$PO$_4$/Cr-SrTiO$_3$ was calculated as 0.17%.
Figure 3.11. (a) The photocatalytic conversion activities of Cr-SrTiO$_3$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/Cr-SrTiO$_3$ composite powders (mass ratio, Ag$_3$PO$_4$/Cr-SrTiO$_3$) (b) The...
concentration change of IPA and (c) the evolution of CO$_2$ over Cr-SrTiO$_3$, Ag$_3$PO$_4$, and Ag$_3$PO$_4$/Cr-SrTiO$_3$ (1:4) composite powders under visible light irradiation (420 nm < $\lambda$ < 800 nm).

Furthermore, recycling reactions for decomposition of IPA over heterojunction samples were carried out under the same conditions. As shown in Fig. 3.12, decomposition rate of IPA and evolution rates of acetone or CO$_2$ did not change obviously during the three recycling reactions which indicate that the heterojunction is quite stable during the recycling reactions.
Figure 3.12 Recycling reactions of IPA photodecomposition over heterojunction Ag₃PO₄/Cr-SrTiO₃ (mass ratio 1:4). (a) concentration of IPA; (b) actone evolution; (c) CO₂ evolution

Figure 3.13 Comparison of XPS spectra of Cr 2p in samples: Cr-SrTiO₃, heterojunctions before and after photodegradation of IPA.

The XPS spectra of heterojunctions before and after photocatalytic degradation of IPA were also detected to confirm the stable of Cr-SrTiO₃. Fig. 3.13 shows the comparison of XPS spectra of heterojunctions before and after photodegradation of
IPA with that of the pure Cr-SrTiO$_3$. The state of Cr 2p didn't change after coupling to heterojunction or after photodegradation of IPA. It also indicates that the heterojunction is quite stable and the reaction can be classified as a catalytic reaction.

### 3.3.4 Band structures of the photocatalyst

Since photocatalytic activity is largely dependent on the band structure, the investigations of conduction band (CB) and the valence band (VB) are necessary for understanding the enhanced photocatalytic activity [39–40]. First of all, from our former report [25, 26], the band gap of Ag$_3$PO$_4$ is 2.45 eV, and its CB and VB positions are +0.45 eV and +2.90 eV, respectively. Moreover, the band gap of Cr-SrTiO$_3$ is about 2.5 eV (see Fig. 3.8b). As previously reported [49–53], in the electronic structure of SrTiO$_3$, the valence band top is made up predominately of the O 2p states, and the conduction band bottom is determined by the Ti 3d states. In this work, the XPS results indicate that only a sharp peak was observed at 576 eV, which could be assigned to the trivalent chromium (Cr$^{3+}$) as that in the standard Cr$_2$O$_3$[54] (see Fig. 3.14). As a consequence, its valence band bottom was lifted up by the occupied Cr$^{3+}$ level, while the original conduction band bottom of SrTiO$_3$ determined by Ti 3d is not affected (see Fig. 3.15). This is similar to the case of Cr-doped TiO$_2$, in which the occupied Cr$^{3+}$ level has previously been calculated to be ~2.2 eV lower than the conduction band bottom formed by Ti 3d (e.g.) or ~1.0 eV higher than the valence band top formed by O 2p [55].
For heterostructured photocatalysts, a good matching of their CB and VB levels can realize the vectorial transfer of photogenerated charge carriers from one to the other, which can contribute to improving the photocatalytic efficiency [41]. The relative positions of the VB tops of Ag$_3$PO$_4$ and Cr-SrTiO$_3$ were investigated by comparing their VB x-ray photoelectron spectroscopy (XPS) spectra. As shown in Fig.

**Figure 3.14** XPS spectra of Cr 2p in Cr-SrTiO$_3$.

**Figure 3.15** Schematic band structures of SrTiO$_3$ and Cr-SrTiO$_3$. 
Chapter 3

3.14 the VB top of Ag₃PO₄ is 0.85 eV higher than that of Cr-SrTiO₃. From our former report [25, 26], the band gap of Ag₃PO₄ is 2.45 eV, and its CB and VB positions are +0.45 eV and +2.90 eV, respectively. Moreover, the band gap of Cr-SrTiO₃ is about 2.5 eV (see Fig. 3.8b). the potentials of VB and CB are thus +2.05 eV and -0.45 eV, respectively. The schematic band structure of Ag₃PO₄/Cr-SrTiO₃ heterojunction is plotted in Fig.3.16. The potential difference between corresponding band levels can drive the charge carriers from one material to its neighbor to form a spatial separation between electrons and holes.

Figure 3.16 The Schematic band structure of Ag₃PO₄/Cr-SrTiO₃ heterojunction.

In order to confirm the electron transfer between Ag₃PO₄ and Cr-SrTiO₃ was really occurred, photocatalytic water splitting over Ag₃PO₄ (0.1g), Cr-SrTiO₃ (0.4g) and Ag₃PO₄/Cr-SrTiO₃ heterojunction (0.5g, mass ratio, 1:4) were carried out (see Fig.3.17). The evolution rate of O₂ over Ag₃PO₄ (0.1g) is about 103.8 µmol h⁻¹ and the evolution rate of H₂ over Cr-SrTiO₃ is 42.2 µmol h⁻¹. In contrast, the evolution rate of
O₂ over Ag₃PO₄/Cr-SrTiO₃ heterojunction is only 4.7 µmolh⁻¹ and no H₂ been detected over Ag₃PO₄/Cr-SrTiO₃ heterojunction. The decreased evolution of O₂ provides a strong evidence to prove that heterostructure has been synthesized between Ag₃PO₄ and Cr-SrTiO₃ and generated holes can transfer from Ag₃PO₄ to Cr-SrTiO₃ efficiently.

Figure 3.17 The O₂ evolution over (a) Ag₃PO₄/Cr-SrTiO₃ (1:4, mass ratio, 0.5g) and (b) Ag₃PO₄ (0.1g); The H₂ evolution over (c) Cr-SrTiO₃ (0.4g) and (d) Ag₃PO₄/Cr-SrTiO₃ (1:4, mass ratio, 0.5g).

Although constructing the heterojunction reduces the redox potentials, the aggregation of electrons and holes over different parts of the heterojunction orients the photochemical reaction to an alternative way which is very advantageous for deeply photodecomposition of IPA to CO₂. The IPA photooxidization undergoes two kinds of typical reaction processes as belows [42, 43]:

(i) one-electron reaction

\[
\text{CH}_3\text{CHOHCH}_3 + e^- + O_2 + H^+ \rightarrow \text{CH}_3\text{COCH}_3 + \text{HO}^- + \text{H}_2\text{O}
\]
or $\text{CH}_3\text{CHOHCH}_3 + h^+ \rightarrow \text{CH}_3\text{COCH}_3 + 2H^+ + e^-$

(ii) multi-electron reaction

$\text{CH}_3\text{CHOHCH}_3 + 5\text{H}_2\text{O} + 18h^+ \rightarrow 3\text{CO}_2 + 18H^+$

Since the generation of each acetone molecule from IPA usually requires one hole, while the reaction of acetone to $\text{CO}_2$ is a more complex multiphoton-involved process, it’s understandable that the photocatalytic decomposition of IPA to acetone is easier than the mineralization of acetone to $\text{CO}_2$ [44]. As shown in Fig. 3.18, the amount of acetone over pure $\text{Ag}_3\text{PO}_4$ is much higher than that of $\text{CO}_2$, which indicates that one-photon reaction take predominance role over $\text{Ag}_3\text{PO}_4$. In contrast, due to the aggregated holes of the $\text{Ag}_3\text{PO}_4$/Cr-$\text{SrTiO}_3$ heterojunction, multiphoton reaction is more easily realized which is signifies the advantage for conversion of IPA to $\text{CO}_2$ (see Fig.4c). Meanwhile, the aggregated electrons of the $\text{Ag}_3\text{PO}_4$/Cr-$\text{SrTiO}_3$ heterojunction are also beneficial for the reduction of oxygen which plays an important role in the photocatalytic degradation of IPA to $\text{CO}_2$.

Figure 3.18. Photodegradation of IPA: acetone evolution and $\text{CO}_2$ evolution over $\text{Ag}_3\text{PO}_4$ under visible light irradiation.
3.3.5 Effects of the calcination temperature and mass ratio on the photocatalytic activity.

The effect of the calcination temperature on the photocatalytic activity was also investigated. Fig. 3.19 (a) shows the XRD patterns of the Ag₃PO₄/Cr-SrTiO₃ (mass ratio, 1:4) composite powders calcined at 300°C, 500°C, and 700°C. For the sample calcined at 300°C, there are only Ag₃PO₄ and Cr-SrTiO₃ confirmed. With increasing temperature, the Ag₃PO₄ begins to decompose to produce metallic Ag and completely decomposes by 700°C. By comparing the TEM images of the samples synthesized at 300°C and 500°C (see Fig. 3.19(b) and (c)), we can find silver particles apparently dispersed on the surface of Ag₃PO₄ (heating at 500°C). With higher magnification, the inset of Fig. 3.19(c) shows that the size of nano-silver particle is about 5 nm. As previous research indicated, Ag/silver halide structures, including Ag/AgCl [45], Ag/AgBr [46], and Ag/AgI [47,48], exhibited higher efficiency in organic dye decomposition due to the Ag⁰ species that formed during synthesis and irradiation processes could trap the generated electrons. In this work, the metallic silver particles separated out from the surface of Ag₃PO₄ also serve as photogenerated electrons trappers, which is advantageous for the electron transfers and aggregation (as plotted in Fig. 3.16). Therefore, the multiphoton reaction of IPA photodegradation can be realized more easily. As exhibited in Fig. 3.19(d), the samples calcined at 500°C exhibits the best photocatalytic activity. For the sample calcined at 300°C, there was little metallic silver produced and the contact between the Ag₃PO₄ and the Cr-SrTiO₃ particles may be weaker, which make the electron transfer between the two
semiconductors difficult. With increasing calcination temperature to 700°C, the photocatalytic efficiency decreased obviously because of the Ag$_3$PO$_4$ completely decomposed. The experiment results reveal that an optimum calcination temperature is an important factor in the preparation of the composite powders with high photocatalytic activity.

Figure 3.19 (a) The XRD patterns and (d) the evolution rate of CO$_2$ under visible light irradiation of the Ag$_3$PO$_4$/ Cr-SrTiO$_3$ (1:4) composite powders calcined at different temperature over (420 nm<λ< 800 nm) (i) 300°C, (ii)500°C, and (iii)700°C; TEM images of the Ag$_3$PO$_4$/ Cr-SrTiO$_3$ heterojunction calcined at 300°C (b) and that of sample calcined at 500°C (c), inset is the HRTEM image of metallic silver particle and at different temperature.
The effect of the mass ratio on the photocatalytic activity was also investigated. As exhibited in Fig. 3.11(a), the photocatalytic activities of the heterostructured samples are closely dependent on the mass ratio of Ag$_3$PO$_4$/Cr-SrTiO$_3$. When mass ratio $> 1:4$, the photocatalytic activity increases; however, when the mass ratio $< 1:4$, the photocatalytic efficiency decreases. This variation tendency can be explained by the following reasons. One is that Cr-SrTiO$_3$, which is consists of spherical aggregates ($\sim$200 nm in diameter) of nanoparticles 30-40 nm in diameter, has high surface area and pore volume (see table 1). Therefore, increasing the content of Cr-SrTiO$_3$ in the heterojunctions could provide more reactive sites and stronger gas adsorption ability. However, visible-light absorption of Cr-SrTiO$_3$ is obviously weaker than that of Ag$_3$PO$_4$, which results in the more content of Cr-SrTiO$_3$ (as shown in Fig.3.7), the less visible-light absorption of the heterojunctions.

**Table. 2** Intensity ratios of metallic Ag to Ag$_3$PO$_4$ and Cr-SrTiO$_3$

<table>
<thead>
<tr>
<th>Mass ratio</th>
<th>Intensity of Ag$_3$PO$_4$ [210]</th>
<th>Intensity of Cr-SrTiO$_3$ [110]</th>
<th>Intensity of Ag [111]</th>
<th>Intensity ratio (Ag/Ag$_3$PO$_4$)</th>
<th>Intensity ratio (Ag/Cr-SrTiO$_3$)</th>
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Another reason is that the metallic Ag nanoparticles on the surfaces of Ag$_3$PO$_4$ are beneficial for the aggregation of electrons. Moreover, according to the intensity ratios between Ag and the photocatalysts, the amounts of metallic Ag are different in each sample (as shown in Fig. 3.20(a), Table. 2). Therefore, the variation tendency of the intensity ratio between Ag and Ag$_3$PO$_4$ is correlated to that of the photocatalytic
efficiency (see Fig. 3.20(b)). The highest activity was observed on the sample (mass ratio is 1:4, Ag$_3$PO$_4$/Cr-SrTiO$_3$) with the intensity ratio (Ag to Ag$_3$PO$_4$) is about 0.61.

Figure 3.20 (a) XRD pattern of heterojunction with mass ratio (1:4) and (b) comparison of intensity ratios and CO$_2$ evolution rates
The contrast experiments over Ag/Ag$_3$PO$_4$ and Ag/Cr-SrTiO$_3$ were also carried out. As shown in table 3 and table 4, different intensity ratios of metallic Ag to Ag$_3$PO$_4$ and Ag to Cr-SrTiO$_3$ were synthesized and the photocatalytic activities over the sample with intensity ratio of Ag to Ag$_3$PO$_4$ (0.61) and Ag to Cr-SrTiO$_3$ (0.204) were compared with that of Ag$_3$PO$_4$/Cr-SrTiO$_3$.

**Table. 3** Intensity ratios of metallic Ag to Ag$_3$PO$_4$ and photocatalytic activities

<table>
<thead>
<tr>
<th>Mass of AgNO$_3$ (g)</th>
<th>Intensity of Ag$_3$PO$_4$ [210]</th>
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<th>Intensity ratio (Ag/Ag$_3$PO$_4$)</th>
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<th>Acetone evolution rate (ppmh$^{-1}$)</th>
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**Table. 4** Intensity ratios of metallic Ag to Cr-SrTiO$_3$ and photocatalytic activities

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<th>Mass of AgNO$_3$ (g)</th>
<th>Intensity of Cr-SrTiO$_3$ [210]</th>
<th>Intensity of Ag [111]</th>
<th>Intensity ratio (Ag/ Cr-SrTiO$_3$)</th>
<th>CO$_2$ evolution rate (ppmh$^{-1}$)</th>
<th>Acetone evolution rate (ppmh$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>8763</td>
<td>565</td>
<td>0.064</td>
<td>1.144</td>
<td>19.93</td>
</tr>
<tr>
<td>0.03</td>
<td>7201</td>
<td>1871</td>
<td>0.260</td>
<td>2.615</td>
<td>23.60</td>
</tr>
<tr>
<td>0.045</td>
<td>7932</td>
<td>3864</td>
<td>0.487</td>
<td>2.382</td>
<td>23.63</td>
</tr>
<tr>
<td>0.06</td>
<td>6232</td>
<td>4481</td>
<td>0.719</td>
<td>2.406</td>
<td>21.97</td>
</tr>
</tbody>
</table>
As shown in Fig. 3.21, both of the evolution of acetone and CO$_2$ over the heterojunction are higher than that of the individual photocatalysts, which provides evidence that metallic Ag between Ag$_3$PO$_4$ and Cr-SrTiO$_3$ take the role as mediator for electrons transfer.

**Figure. 3.21** (a) Acetone evolution and (b) CO$_2$ evolution of Ag/Ag$_3$PO$_4$, Ag/Cr-SrTiO$_3$, and Ag$_3$PO$_4$/Cr-SrTiO$_3$. 

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3.4. Conclusions

A new heterojunction based on Ag$_3$PO$_4$ and Cr-SrTiO$_3$ was designed to attain the efficient elimination of gaseous IPA under visible light irradiation. The study of energy-band potentials via valence-band XPS demonstrated that the potentials of the conduction band (-0.45 eV) and the valence band (+2.05 eV) of the Cr-SrTiO$_3$ are more negative than that of Ag$_3$PO$_4$ (+0.45 eV and +2.90 eV, respectively), which is advantageous for the separation and transfer of electrons/holes pairs between these two photocatalysts. The photocatalytic characterizations indicated that the calcination temperature and mass ratio of the Ag$_3$PO$_4$/Cr-SrTiO$_3$ dominate the photocatalytic activity of the heterojunctions. All of these heterojunctions could degrade IPA under visible light-irradiation; in particular, the Ag$_3$PO$_4$/Cr-SrTiO$_3$ (mass ratio, 1:4, 500°C) sample showed the highest catalytic performance (CO$_2$ evolution rate, 13.2 ppmh$^{-1}$), which was about 33 times higher than that of pure Ag$_3$PO$_4$. The present work is evidences that fabricating heterojunctions with proper hand structure to establish a new chemical reaction process is an effective strategy to enhance photocatalytic efficiency or attain new photocatalytic application. The results and discussions herein supply useful informations for further developing the other heterojunction photocatalysts.
Reference


Chapter 4 Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ composite photocatalyst with adjustable band structures for efficient elimination of gaseous organic pollutants under visible light irradiation

Abstract:

A new heterojunction Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ (x= 0–2.07) was designed to eliminate the gaseous pollutants under visible light irradiation. The phase compositions, optical properties, and morphologies of the heterojunction photocatalysts were systematically investigated via powder X-ray diffraction, UV-Visible absorption spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy, and transmission electron microscopy. The calculation of electronic structure indicates that the top of the valance band of Sr$_2$Nb$_2$O$_7$ could be lifted up by nitrogen doping. Therefore, the electronic structure of Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ composite photocatalysts could be continually adjusted with different content of nitrogen in Sr$_2$Nb$_2$O$_{7-x}$N$_x$. The photocatalytic degradation of Isopropyl alcohol (IPA) was carried out to test the photocatalytic activity of the heterojunction. The results indicated that the highest activity (CO$_2$ evolution rate, 10.32 ppmh$^{-1}$) was observed over the Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ heterojunction when the Sr$_2$Nb$_2$O$_7$ was nitrided under 1023K, which is about 40 times higher than that of the pure Ag$_3$PO$_4$ (CO$_2$ evolution rate, 0.26 ppmh$^{-1}$) under visible light irradiation. An investigation of energy-band structure via valence-band X-ray photoelectron spectrum indicates that the conduction band (CB) and valence band (VB) of Ag$_3$PO$_4$ are both more positive than that of Sr$_2$Nb$_2$O$_{7-x}$N$_x$, which facilitates the separation and transfer of photogenerated electrons and holes.
between the two photocatalysts. By continually adjusted the electronic structures, the optimal band gap of the Sr$_2$Nb$_2$O$_{7-x}$N$_x$ is proved as about 2.15 eV and the potential of valance band is +1.88 eV.

4.1 Introduction

As mentioned in chapter 3, the air pollution has become the most crucial issue around the world especially in the developing country. The photocatalytic degradation of the organic pollutants in the air has attracted increasing interests because it’s a promising, environmental, and cost-effective technology [1-4]. During the past decades, great efforts have been made to exploit the efficient photocatalysts, such as TiO$_2$ and N-doped TiO$_{2-x}$N$_x$ [5-10], AgNbO$_{3(1-x)}$SrTiO$_{3(x)}$[11,12], Na-based materials [13,14], Ag-based materials [15-18], WO$_3$[19], PbSnO$_3$[20] and etc[21]. Compared with the wide band gap photocatalyts, the visible-light sensitive photocatalysts can absorb more solar energy because of the narrower band structure. As one of the most efficient visible-light-sensitive photocatalysts, Ag$_3$PO$_4$ has been reported with a quantum efficiency of ~90% around 420 nm in water oxidation which indicates it has great potential in photocatalytic applications [22a]. Moreover, further investigations about the photoelectric/photocatalytic properties, morphology controlling, and facet effect of Ag$_3$PO$_4$ were carried out, and enhanced performances were obtained [22b,c,d,e]. However, the photoactivity of Ag$_3$PO$_4$ in photodecomposition of gaseous organic contaminants still has room for improving. One reason is that its potential of the conduction band (CB) is more positive than the reduction potential of O$_2$ (e$^{-}$ + O$_2$
+ H⁺ → HO₂, -0.046 V vs NHE) [23, 24]. As a result, the generated electrons cannot be consumed by combining with O₂ which is very important for the photooxidization of the gaseous organic compound [25]. Another reason is that the decomposition of IPA to CO₂ is a complex multielectron-involved process (CH₃CHOHCH₃ + 5H₂O + 18h⁺ → 3CO₂ + 18H⁺) [26], which is difficult to be realized on pure Ag₃PO₄. Moreover, as the electrode potential of Ag₃PO₄/Ag (around 0.45 V vs. NHE) is more positive than that of H⁺/H₂ (0 V vs. NHE) [27], Ag₃PO₄ can easily be reduced to Ag⁰ during in the photocatalytic reactions.

As mentioned in chapter 3, a new composite photocatalysts based on Ag₃PO₄ and Cr doped SrTiO₃ has been successfully synthesized with enhanced photoactivity. It was found that electronic structures of composite photocatalyst promote the generation and separation of photo-generated electron-hole pairs and the multi-electron reactions. As a result, the composite photocatalyst exhibited much higher activity than the individual Ag₃PO₄ and SrTiO₃. However, there is a remained problem that the redox potential of the holes would be lowered after transferring. Therefore, find an optimal point between the transfer of electron/holes pairs and the redox potentials is an important issue for improving the photocatalytic activity of composite photocatalysts.

Herein, another Sr-based semiconductor (N-doped Sr₂Nb₂O₇) with adjustable band gaps was chosen as the candidate for a new composite photocatalyst Ag₃PO₄/Sr₂Nb₂O₇-xNx for efficient photodegradation of organic pollutants. Sr₂Nb₂O₇ as a wide band-gap semiconductor has attracted wide interest because of its high
quantum yields for the overall photocatalytic water splitting [28-35]. Moreover, doping of foreign elements is a strategy to develop visible-light efficient photocatalysts. Recently, nitrogen doped Sr$_2$Nb$_2$O$_7$ has been exploited with much narrower band gap for water splitting under the visible light irradiation [36-38]. In this study, we synthesized composite photocatalysts based on the Ag$_3$PO$_4$ and the N-doped Sr$_2$Nb$_2$O$_7$ with adjustable band gaps from a Sr$_2$Nb$_2$O$_7$ precursor by nitridation with NH$_3$ under different temperatures. Iso-propanol (IPA) photodegradation over the heterojunctions under visible-light irradiation was employed for evaluating their photocatalytic properties. The valence-band state of Ag$_3$PO$_4$ and Sr$_2$Nb$_2$O$_{7-x}$N$_x$ were analyzed by X-ray photoelectron spectroscopy (XPS) and the DOS calculation, which helps find the optimal band structure for the best photocatalytic activity.

4.2. Experimental

4.2.1 Photocatalysts preparation. All of the reagents were analytical grade and used without further purification. Nitrogen-doped Sr$_2$Nb$_2$O$_7$ catalysts were obtained by nitriding the Sr$_2$Nb$_2$O$_7$ precursor, which had been by the polymerized complex method as previously report [38]. In a typical synthesis, NbCl$_5$ (High Purity Chemicals, 99.9%) and strontium acetate (Sr(Ac)$_2$•0.5H$_2$O) (Wako Pure Chemical, 99.0%) were dissolved in a stoichiometric ratio in methanol. Citric acid (Wako Pure Chemicals, 98.0%) and ethylene glycol (Wako Pure Chemical, 99.5%) were added, and the solution was kept at 473 K overnight to promote polymerization. After becoming a yellow resin, the mixture was pyrolyzed at 623 K, followed by calcination in air at 923 K and 1073 K
for 2 h each, with intermediate grinding. The obtained white oxide powder was then nitrided under NH$_3$ flow (500 mL·min$^{-1}$) for 3 h at 873K, 923K, 973K, 1023K, 1073K, and 1173 K in a quartz tube reactor. After nitridation, the catalysts were cooled to room temperature under He flow to remove adsorbed NH$_3$ molecules on the surface. The color of the catalysts obtained after nitridation varied from white to dark brown with increasing nitridation temperatures. After-treatment was carried out in atmosphere at 673K for 2 h to reduce the defect. The production of N-doped Sr$_2$Nb$_2$O$_7$ was confirmed by X-ray diffraction analysis. The Ag$_3$PO$_4$ was synthesized by the ion-exchange method as described in our former report [25]. Appropriate amounts of AgNO$_3$ and Na$_2$HPO$_4$ were mixed and milled thoroughly until the initial color changed to yellow. The obtained precipitate was washed with distilled water for several times and dried at room temperature overnight. The Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ heterojunctions were prepared by grinding and mixing individual solids thoroughly in ethanol in an agate mortar. After that, the prepared samples were dried at 60°C and then calcined at 673K for 2h in an oven to construct composite structure, respectively.

4.2.2 Photocatalysts characterization.

The crystal structure of the catalysts obtained was determined a Rigaku Rint-2000 X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda=1.54178$ Å). Scanning electron microscopy images and energy-dispersive X-ray spectroscopy patterns were recorded with a JEOL 6700F field emission scanning electron microscopy. Transmission electron microscope and high-resolution images
were performed with a JEOL 2100F field emission transmission electron microscopy operated at 200 kV. Optical properties were analyzed by UV-visible diffuse reflectance spectroscopy (UV-Vis DRS, Shimadzu, UV-2500) and converted to absorption spectra by the standard Kubelka-Munk method. Elemental analysis of oxynitride samples were carried out by a TCD measurement EMGA-920. The surface area measurements were carried out in a Surface Area Analyzer (BELSORP II). The relative positions of the valence band tops of $\text{Ag}_3\text{PO}_4$ and $\text{Cr-SrTiO}_3$ were investigated by an X-ray photoelectron spectroscopy (PHI Quantera SXM).

### 4.2.3 Theoretical calculations.

The electrical structure was calculated by the DFT with the CASTEP program. Electronic structures of the $\text{Sr}_2\text{Nb}_2\text{O}_7$ and $\text{SrNbO}_2\text{N}$ were investigated via the plane-wave-pseudopotential approach based on the density functional theory (DFT). Geometry optimization model was performed to determine the most stable structures. Then its electronic structure was calculated using a standard Cambridge serial total energy package (CASTEP) code [39,40]. The electron-core interaction was represented via ultrasoft pseudopotentials with a plane-wave basis cutoff energy of 340 eV. The electronic exchange-correlation energy was treated within the frame-work of the local density approximation (LDA). The self-consistent field (SCF) tolerance was all $1\times10^{-6}$ eV/atom.
4.2.4 Photocatalytic reaction.

In the photocatalytic measurement, a 300 W Xe arc lamp (7 A imported current, focused through a 45 × 45 mm shutter window) equipped with a set of glass filters (L42 + HA30, 420 nm < λ < 800 nm, HOYA.CO.,JAPAN) and a water filter was used as the light source. Under such condition, the illumination intensity was about 30.5 mW cm\(^{-2}\). The 0.2 g of sample was evenly spread over a dish with an area of 8.5 cm\(^2\) in a 500 mL of a borosilicate glass vessel. Then the inside atmosphere of the vessel was exchanged by artificial air [V (N\(_2\)) : V(O\(_2\)) = 4 : 1] for 10 min to remove gaseous impurities. After the sample was sealed in the vessel, gaseous isopropyl of Isopropyl alcohol (IPA) was injected into the vessel (the initial concentration of IPA was about 1250 ppm ~ 1500 ppm). Before irradiation, the sample was kept in the dark to ensure an adsorption-desorption equilibrium of IPA on the sample. The final products of the photocatalytic oxidation of IPA were CO\(_2\) and H\(_2\)O. To evaluate the photocatalytic activity, the IPA and CO\(_2\) were measured by using a gas chromatography (GC-2014, Shimadzu Corp., Japan) equipped with a methanizer and a flame ionization detector (FID).

4.3 Results and Discussion

4.3.1 Physical properties and band structures of the Sr\(_2\)Nb\(_2\)O\(_7\)\(_x\)N\(_x\)

Fig. 4.1 shows X-ray diffraction (XRD) patterns of Sr\(_2\)Nb\(_2\)O\(_7\)\(_x\)N\(_x\). The N-doped Sr\(_2\)Nb\(_2\)O\(_7\) samples named as SNON-873, SNON-923, SNON-973, SNON-1023, SNON-1073, and SNON-1173 for the samples were nitrided under 873K, 923K,
973K, 1023K, 1073K, and 1173K, respectively. The XRD pattern for Sr$_2$Nb$_2$O$_7$, prepared as the parent oxide, is consistent with that of layered perovskite type Sr$_2$Nb$_2$O$_7$ [41,42]. Meanwhile, the XRD pattern of oxynitride (nitrided at 1173K) is in agreement with the reported cubic structure of SrNbO$_2$N. The intensity of diffraction peaks of the orthorhombic phase decreased with nitridation temperature and later completely disappeared at 1173 K. On the contrary, the diffraction peaks of cubic phase (oxynitrides) were observed even at 973 K, and their intensity increased with nitridation temperature. The results reveal the possibility of co-existence of the Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N phases. The effect of each phase on band-gap will be discussed latter. The XRD pattern of sample nitrided at 1173 K is without any impurity phase and is consistent with that of the cubic phase of SrNbO$_2$N. Thus we conclude that nitrogen doping of the pure layered oxide catalyst transforms the orthorhombic Sr$_2$Nb$_2$O$_7$ structure to the cubic oxynitride SrNbO$_2$N.

![Figure 4.1. The XRD patterns of Sr$_2$Nb$_2$O$_{7-x}$N$_x$ (x=0~2.07).](image)

Elemental analysis of oxynitride samples indicates that nitrogen was doped in the samples with different content. As shown in Table 1, elemental analysis of oxynitride
samples indicates that they pick up nitrogen corresponding to stoichiometry of $\text{Sr}_2\text{Nb}_2\text{O}_7_x\text{N}_x$ ($x=0 \sim 2.07$), with higher $x$ values at higher nitriding temperatures.

**Table 1** The physical properties of $\text{Sr}_2\text{Nb}_2\text{O}_7_x\text{N}_x$ nitrided at different temperature.

<table>
<thead>
<tr>
<th>Samples with different nitridation temperatures</th>
<th>Doped nitrogen (wt %)</th>
<th>Band gap (eV)</th>
<th>$\text{Ag}_3\text{PO}_4$/N-doped $\text{Sr}_2\text{Nb}_2\text{O}_7$ (mass ratio=1:1)</th>
<th>Surface area ($\text{m}^2\text{g}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}_2\text{Nb}_2\text{O}_7$</td>
<td>0.00</td>
<td>3.96</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>SNON-873</td>
<td>0.01</td>
<td>3.42</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-873</td>
<td>3.06</td>
</tr>
<tr>
<td>SNON-923</td>
<td>0.04</td>
<td>3.06</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-923</td>
<td>1.89</td>
</tr>
<tr>
<td>SNON-973</td>
<td>1.51</td>
<td>2.23</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-973</td>
<td>2.81</td>
</tr>
<tr>
<td>SNON-1023</td>
<td>2.42</td>
<td>2.15</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-1023</td>
<td>3.01</td>
</tr>
<tr>
<td>SNON-1073</td>
<td>3.64</td>
<td>1.91</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-1073</td>
<td>2.27</td>
</tr>
<tr>
<td>SNON-1173</td>
<td>6.18</td>
<td>1.87</td>
<td>$\text{Ag}_3\text{PO}_4$/SNON-1113</td>
<td>2.13</td>
</tr>
</tbody>
</table>

Fig. 4.2 shows UV-Vis diffuse reflectance (DR) spectra of the pure oxide and N-doped samples prepared at different nitridation temperatures. The absorption spectrum of $\text{Sr}_2\text{Nb}_2\text{O}_7$ indicates that it can absorb solar energy with a wavelength shorter than ~300 nm. The increase in nitridation temperature shifted the photon absorption of the photocatalysts into the visible range. The pure oxide showed the absorption only in the UV region (~300 nm), whereas nitrided samples showed increased and extended absorption in the range of 350 ~ 600 nm. There was a slight red-shift of the main absorption peak, but the visible light absorption appeared mostly as a shoulder to the main peak. All nitride samples absorbed light in the visible region, although the level of background absorption was high, probably owing to the production of reduced Nb species (e.g., $\text{Nb}^{3+}$ and $\text{Nb}^{4+}$) during nitridation [36]. In
accordance, the colour of the sample is changed from white to deep red belong with the nitridation temperature increasing.

Figure 4.2 UV-vis diffuse reflectance spectrum (a) and the calculated band gaps (b) of Sr$_2$Nb$_2$O$_{7-x}$N$_x$ (x=0~2.07).
Furthermore, the band gaps of the as-prepared samples were obtained based on the calculation of band-structure. For a crystalline semiconductor, the optical absorption near the band edge can be described by the equation [17]:

\[(\alpha \nu)^n = A(\nu - E_g)\]

Where \(\alpha\), \(\nu\), \(A\), \(h\), and \(E_g\) represent the absorption coefficient, light frequency, proportionality constant, plank constant and band gap, respectively. In the equation, \(n\) depends on the transition characteristic of the photocatalyst. For an indirect semiconductor, \(n\) equals 0.5, while \(n\) is 2 for a direct semiconductor. The the \((\alpha \nu)\) versus the band energy is shown in Fig. 4.2 (b). In order to compare the enhanced absorption of \(\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x\), the relative ratios of light absorption is utilized in this work. After the integral transformation of absorption spectra (400 nm < \(\lambda\) < 800 nm), we can obtain the relative ratios of samples as shown in Fig. 4.2 (c). We can clearly find out that the light absorptions of nitrogen doped samples are enhanced. Compared with the \(\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x\) (x=0.003, 873K), the light absorption of other samples nitrided at higher temperatures are increased with 1.85, 11.30, 14.59, 26.75, and 40.81 times, respectively.

![The schematic band structures of \(\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x\) (x=0-2.07).](image)

**Figure 4.3** The schematic band structures of \(\text{Sr}_2\text{Nb}_2\text{O}_{7-x}\text{N}_x\) (x=0-2.07).
Chapter 4

For a directely observation, the experimental band-gaps are listed in Table 1 and shown in Fig. 4.3. We can find that the band gaps of the N-doped samples were narrowed along with the nitridation temperature increasing. Since the band gap of SrNbO$_2$N is settled, the reason for the band-gap narrowing of Sr$_2$Nb$_2$O$_{7-x}$N$_x$ is attributed to the contribution of orthorhombic phase.

The optical absorption property of a photocatalyst is largely dependent on the band structure, thus the theoretical calculation of the band structure helps understanding its photophysical and photocatalytic properties [23]. The Sr$_2$Nb$_2$O$_7$ and the SrNbO$_2$N were chosen as the examples. The corresponding crystal structures of pure Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N are illustrated in Fig. 4.4. The oxide Sr$_2$Nb$_2$O$_7$ is a (110) layered perovskite of the Carpy and Galy type with a space group of Cmc21, and an orthorhombic unit cell with lattice parameters of a =3.930 Å , b = 26.726 Å, c= 5.683 Å[39], while oxynitride SrNbO$_2$N is a non-layered cubic structure with a space group of Pm$^3$ m, a =b = c = 4.044 Å.

![Simulated Crystal Structures](image)

**Figure 4.4** The simulated crystal structures of pure Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N.

Based on the crystal structure, the band-structure was calculated by DFT. As
shown in the Fig. 4.5 (a,c), the electronic calculation indicates that Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N are both indirect band gap semiconductor. Moreover, the energy-band calculation indicates that the computed band-gap of the SrNbO$_2$N (Eg = 1.1 eV) is much narrower than that of the Sr$_2$Nb$_2$O$_7$ (Eg = 2.8 eV).

![Figure 4.5](image)

**Figure 4.5** DFT calculation of Sr$_2$Nb$_2$O$_7$ (a,b) and SrNbO$_2$N(c,d): energy band dispersion (a,c) and density of states(b,d).

In order to confirm the reason of band narrowing, the total and projected partial densities of states (DOS) of the Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N are investigated, where the top of the valence band was set to 0 eV. As shown in Fig. 4.5 (b,d), the states at top of valence band for Sr$_2$Nb$_2$O$_7$ was contributed by O 2p orbitals. Moreover, the states at conduction band minimum are the contribution of Nb 4d, which is in accordance with previous report. For the SrNbO$_2$N, the major contribution in the top of valence band comes from O 2p hybridized with N 2p orbitals. It is clear from DOS studies that the
band-gap gets narrowed due to mixing N 2p with O 2p orbitals from nitrogen doping. The N 2p orbitals have higher potential energies than O 2p orbitals [38], their hybridization lifts up the top of the valence band from the position of the Sr$_2$Nb$_2$O$_7$, which also makes the material to shift the optical absorption into the visible light region (as illustrated in Fig.4.3).

Moreover, the conduction band bottoms of Sr$_2$Nb$_2$O$_7$ and SrNbO$_2$N are significantly different. As shown in the Fig. 4.5 (a,c), the energy level of conduction band bottom in Sr$_2$Nb$_2$O$_7$ is higher than that in SrNbO$_2$N. The reason may be due to the variant octahedral ligand field of Sr$_2$Nb$_2$O$_7$ which changes Nb-O bond lengths and O-Nb-O bond angles (as listed in Table 2) of the basic cubic crystal structure of the SrNbO$_2$N. The tilts of Nb-O bonds and the shifts of bond lengths contribute to lower the energy of the conduction band bottom when crystal structure changes from the orthorhombic of Sr$_2$Nb$_2$O$_7$ to the cubic of SrNbO$_2$N (as illustrated in Fig.4.5).

<table>
<thead>
<tr>
<th>Material</th>
<th>Nb-O Bond length / Å</th>
<th>O-Nb-O bond angle / degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrNbO$_2$N</td>
<td>2.029</td>
<td>90.00</td>
</tr>
<tr>
<td>(a-o) 1.95</td>
<td>(a-o-c) 89.63</td>
<td>(a-o-d) 85.85</td>
</tr>
<tr>
<td>(b-o) 1.94</td>
<td>(a-o-e) 89.63</td>
<td>(a-o-f) 97.16</td>
</tr>
<tr>
<td>Sr$_2$Nb$_2$O$_7$</td>
<td>(c-o) 1.985</td>
<td>(b-o-c) 88.33</td>
</tr>
<tr>
<td>(d-o) 2.25</td>
<td>(b-o-e) 88.33</td>
<td>(b-o-f) 98.75</td>
</tr>
<tr>
<td>(e-o) 1.985</td>
<td>(c-o-d) 82.13</td>
<td>(d-o-e) 82.13</td>
</tr>
<tr>
<td>(f-o) 1.85</td>
<td>(e-o-f) 97.83</td>
<td>(f-o-c) 97.83</td>
</tr>
</tbody>
</table>

Moreover, the calculated band-gaps of the samples are significantly less than the experimental results. For instance, the calculated band gap of Sr$_2$Nb$_2$O$_7$ is about 2.8 eV (see Fig.4.5a) which is narrower than the experimental band gap 3.96 eV. This is
understandable since the band gap calculated by DFT is generally smaller than the experimental result, which is considered as a feature of the DFT calculation [43].

4.3.2 Characterizations and photoactivities of the Ag₃PO₄/Sr₂Nb₂O₇₋ₓNx composite photocatalysts under visible light irradiation

The Ag₃PO₄/Sr₂Nb₂O₇₋ₓNx (x=0~2.07) composite photocatalysts were synthesized via solid surface reaction. The N-doped Sr₂Nb₂O₇ samples named as SNON-873, SNON-923, SNON-973, SNON-1023, SNON-1073, and SNON-1173 for the samples were nitrided under 873K, 923K, 973K, 1023K, 1073K, and 1173K, respectively.

![Figure 4.6](image)

**Figure 4.6** (a) The XRD patterns of as-prepared samples, TEM images (b,c), and UV-vis diffuse reflectance spectrum (d) of Ag₃PO₄/SNON-1023.

Fig. 4.6 (a) shows the XRD pattern of the single photocatalysts and composite photocatalysts. The indexed diffraction peaks can be ascribed as Ag₃PO₄, Sr₂Nb₂O₇,
and SrNbO$_2$N, respectively. Peaks related to other titanates were not observed in the synthesized samples, indicating that the single photocatalysts didn’t react with each other. As shown in Fig. 4.6 (b), the TEM image of the SNON-1023 reveals that it belongs to layered material which is accordance with previous report [38]. Moreover, Fig. 4.6 (c) shows that two materials are well connected, which is advantageous for the inter-particle photocarrier transfer between Ag$_3$PO$_4$ and SNON-1023. Fig.4.6 (d) shows the UV-Vis absorption spectra of Ag$_3$PO$_4$, SNON-1023, and Ag$_3$PO$_4$/SNON-1023 composite. The absorption spectrum of Ag$_3$PO$_4$ indicates that it can absorb solar energy with a wavelength shorter than ~530 nm. Moreover, the two absorption edges reveal an indirect band gap of 2.36 eV and a direct transition of 2.43 eV, which are generally in agreement with our previous work [22]. Meanwhile, the light absorption of SNON-1023 is obviously weaker than that of Ag$_3$PO$_4$ below 500 nm, but stronger in the region above 500 nm. The reason may be due to the narrowed band structure and oxygen vacancy introduced by N-doping. As a result, the heterojunction exhibits stronger absorption over 500 nm than that of Ag$_3$PO$_4$.

Figure 4.7. The evolution rate of acetone (a) and CO$_2$ (b) over as-prepared composite photocatalysts.

Gaseous Isopropyl alcohol (IPA) was chosen as a model pollutant for the
evaluation of photocatalytic activities of the Ag₃PO₄/N-doped Sr₂Nb₂O₇ composite photocatalysts. The photocatalytic conversions of IPA to CO₂ over different photocatalysts were carried out under visible light irradiation (420 nm<\lambda<800 nm). As shown in Fig.4.7, all of the individual photocatalysts exhibit lower activities with comparison of composite photocatalysts. The evolution rates of acetone and CO₂ of the Sr₂Nb₂O₇ are about 5.2 ppmh⁻¹ and 0.49 ppmh⁻¹, respectively. The understandable reason is that the wide band structure makes it cannot response the visible light irradiation. For the Sr₂Nb₂O₇₋ₓNₓ nitride at different temperatures, the evolution rates of acetone and CO₂ are also very low. The reason may be due to the narrowed band structure. Although the N-doped samples can absorb more visible light, the recombination of generated electrons/holes may be very easily due to their narrowed band structures. The reason for the low activity of Ag₃PO₄ can be explained as we previously reported [17], which is attributed to the redox potentials of electrons and holes. After constructing the composite photocatalysts, all of the composite photocatalysts exhibited higher photoactivity than the individual material. In comparison, the Ag₃PO₄/SNON-1023 composite photocatalyst exhibited best activity with the evolution rates of acetone and CO₂ are about 173.3 ppmh⁻¹ and 10.32 ppmh⁻¹, which is significantly higher than that of other composite photocatalysts. When nitridation temperature < 1023K, the evolution rates of acetone and CO₂ increase; however, when the nitridation temperature > 1023K, the evolution rates of acetone and CO₂ decreases.

To investigate the activity in more details, the degradation of IPA over time for
Ag₃PO₄/SNON-1023 and pure photocatalysts were analyzed (Fig. 4.8a). In the presence of Ag₃PO₄/SNON-1023 sample, 96% of the IPA is degraded within 6.5 h of irradiation. In contrast, the IPA decomposition ratios are 4.8 % and 36.3 % over pure Ag₃PO₄ and SNON-1023 after 10 h of irradiation respectively. Moreover, as shown in Fig. 4.8b, the amount of CO₂ evolution over Ag₃PO₄/SNON-1023 is much higher than that of pure Cr-SrTiO₃ and Ag₃PO₄ respectively. There is 284.1 ppm of CO₂ obtained by Ag₃PO₄/SNON-1023 in comparison with 7.7 ppm and 66.8 ppm achieved by Ag₃PO₄ and SNON-1023, respectively. The evolution of acetone was also investigated. As shown in Fig.4.8c, the Ag₃PO₄/SNON-1023 exhibits the highest activity in acetone evolution (about 173.3 ppmh⁻¹) in the first 6.5 h irradiation. After that, the evolution curve got highest peak which means all of the IPA was degraded into acetone and CO₂. In comparison, the Ag₃PO₄ and the SNON-1023 exhibited much lower activity with the rate about 4.8 ppmh⁻¹ and 17.8 ppmh⁻¹, respectively.

Moreover, the overall reaction of the deep photocatalytic oxidation of IPA to CO₂ is shown as below:

\[
\text{CH}_3\text{CHOHCH}_3 + 5\text{H}_2\text{O} + 18\text{h}^+ \rightarrow 3\text{CO}_2 + 18\text{H}^+ 
\]

Therefore, the AQE of the photocatalyst in IPA photodecomposition could be calculated by the equation:

\[
\text{AQE} = \frac{[N(\text{CO}_2) \times 6 + N(\text{acetone})]}{N(\text{photons})} \times 100 \%
\]

In which, \([N(\text{CO}_2)]\) and \(N(\text{acetone})\) signify the mole number of generated CO₂ and generated acetone in unit time; \([N(\text{photons})]\) signify the number of incident photons in unite time;
In this work, the AQE of the Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ (x=0.82) were calculated as 0.13%.

![Figure 4.8](image)

**Figure 4.8** Photocatalytic degradation of IPA under visible light irradiation (400nm<λ<800nm), the changes of concentration of IPA (a), the evolution rate of CO$_2$ (b), and acetone evolution rate (c) with irradiation time (h).
(b) and acetone (c) over the Ag₃PO₄, SNON-1023 and Ag₃PO₄/SNON-1023 composite photocatalyst.

**4.3.3 The mechanism for the enhanced activity**

Since photocatalytic activity is largely dependent on the band structure, the investigations of conduction band (CB) and the valence band (VB) are necessary for understanding the enhanced photocatalytic activity [37–40]. As we previously reported, a good matching of the CB and VB levels of the composite photocatalysts can realize the vectorial transfer of photogenerated charge carriers from one to the other, which can contribute to improving the photocatalytic efficiency [41]. Therefore, we also compared the relative position of the VB tops of the Ag₃PO₄ and SNON-1023 via their VB x-ray photoelectron spectroscopy (XPS) spectra.

![Figure 4.9 The VB-XPS spectra of Ag₃PO₄ and SNON-1023.](image)

As shown in Fig. 4.9 the VB top of Ag₃PO₄ is 1.02 V higher than that of SNON-1023. As we previously reported [25, 26], the band gap of Ag₃PO₄ is 2.45 eV, and its CB and VB positions are +0.45 eV and +2.90 eV (vs. NHE), respectively. Considering the band gap of SNON-1023 is about 2.15 eV (see Table 2), the
potentials of VB and CB are thus +1.88 eV and -0.27 eV, respectively.

As illuminated in Fig.4.10, the potential difference between corresponding band levels can drive the charge carriers from one material to its neighbor to form a spatial separation between electrons and holes. And then, the electrons and holes were aggregated which is advantageous for the multi-electron reactions.

![Figure 4.10](image)

**Figure 4.10** The Schematic band structure of Ag$_3$PO$_4$/SNON-1023 composite photocatalyst.

On the other hand, the photocatalytic activities of other composite photocatalysts are much lower than that of Ag$_3$PO$_4$/SNON-1023 composite photocatalyst. The reason may be due to the redox potential of generated holes. Although the band structure of the composites would promote the separation of electrons/holes pairs, the redox ability of holes would be lowered after transferring due to the position of the valence band of the Sr$_2$Nb$_2$O$_{7-x}$N$_x$. All in all, when the band gap of Sr$_2$Nb$_2$O$_{7-x}$N$_x$ is wider than 2.15 eV, the position of the valence band is more positive than that of SNON-1023 which lowered the efficiency of holes transferring; when the band gap of
Sr$_2$Nb$_2$O$_{7-x}$N$_x$ is narrower than 2.15 eV, the position of the valence band is so high that the redox potential of transferred holes is lowered and the recombination of electron/hole pairs is enhanced. Therefore, the optimal band gap is of the N-doped Sr$_2$Nb$_2$O$_7$ is around 2.15 eV which can make the balance between the separation of electron/hole pairs and the redox potential of holes. Moreover, the surface areas of the samples were also measured by nitrogen adsorption method. As shown in Table 2, there is no obviously difference between each sample which excludes the effects of the surface area on the photoactivity.

### 4.4 Conclusions

A new heterojunction based on Ag$_3$PO$_4$ and Sr$_2$Nb$_2$O$_{7-x}$N$_x$ was designed to attain the efficient elimination of gaseous IPA under visible light irradiation. The study of the electric structure indicates that the valence band of the Sr$_2$Nb$_2$O$_7$ was lifted up due to mixing N 2p with O 2p orbitals from nitrogen doping which result in narrower band gap. Moreover, the band gap could be continually adjusted by the nitridation with NH$_3$ under different temperatures. The photocatalytic characterizations indicated that all of these composite photocatalysts exhibited higher efficiency than the individual samples under visible light-irradiation; in particular, the Ag$_3$PO$_4$/Ag$_3$PO$_4$/Sr$_2$Nb$_2$O$_{7-x}$N$_x$ ($x=0.82$) composite photocatalyst showed the highest catalytic performance (CO$_2$ evolution rate, 10.3 ppmh$^{-1}$). The results reveal that the relative potentials of the valance band and the conduction band between the Ag$_3$PO$_4$ and the Sr$_2$Nb$_2$O$_{7-x}$N$_x$ has significant effects on the photoactivity, and the optimal band gap of
the Sr$_2$Nb$_2$O$_{7-x}$N$_x$ is about 2.15 eV and the potentials of VB and CB are thus +1.88 eV and -0.27 eV, respectively. The present work is evidences that fabricating heterojunctions with proper hand structure to establish a new chemical reaction process is an effective strategy to enhance photocatalytic efficiency or attain new photocatalytic application. The results and discussions herein supply useful informations for further developing the other heterojunction photocatalysts.

Reference


Soc. 2011, 133, 12334–12337.


Chapter 5 General conclusions and future prospects

5.1 General conclusions

In conclusion, a series of new composite photocatalysts based on Ag₃PO₄ were successfully synthesized with enhanced photocatalytic activities in purification of air pollutants and water pollutants. Constructing composite photocatalysts has been proved to be a useful strategy to improve the photocatalytic activity of Ag₃PO₄ under visible light irradiation. The application of these synthetic routes for fabricating Ag₃PO₄-based composite photocatalysts will advance the development of photocatalytic materials. The detailed conclusion for each part is summarized as follows:

(1) For photocatalytic purification of water pollutant, a new composite photocatalyst Ag₃PO₄/In(OH)₃ was successfully synthesized via an in-situ precipitation method in the silver-ammine solution. The surface-electric properties of the Ag₃PO₄/In(OH)₃ composite photocatalysts could be continually adjusted by the In(OH)₃ and the variation tendency of surface-electric properties was in accordance with that of photocatalytic activities, which indicates that surface-electric property is closely related to the enhanced photoactivity. The results of photocatalytic degradation prove that the composite photocatalyst Ag₃PO₄/In(OH)₃ is more efficient than the individual materials. More particularly, the best activity was obtained at molar ratio 1.65:1.0 (Ag₃PO₄ to In(OH)₃) with the rate constant $k_{app}=1.75 \text{ min}^{-1}$, which is significantly higher than that of the individual Ag₃PO₄ ($k_{app}=0.35 \text{ min}^{-1}$).
(2) For photocatalytic purification of air pollutants, a new heterojunction based on Ag₃PO₄ and Cr-SrTiO₃ was designed to attain the efficient elimination of gaseous IPA under visible light irradiation. The study of energy-band potentials via valence-band XPS demonstrated that the potentials of the conduction band (-0.45 eV) and the valence band (+2.05 eV) of the Cr-SrTiO₃ are more negative than that of Ag₃PO₄ (+0.45 eV and +2.90 eV, respectively), which is advantageous for the separation and transfer of electrons/holes pairs between these two photocatalysts. The photocatalytic characterizations indicated that the calcination temperature and mass ratio of the Ag₃PO₄/Cr-SrTiO₃ dominate the photocatalytic activity of the heterojunctions. All of these heterojunctions could degrade IPA under visible light-irradiation; in particular, the Ag₃PO₄/ Cr-SrTiO₃ (mass ratio, 1:4, 500°C) sample showed the highest catalytic performance (CO₂ evolution rate, 13.2 ppmh⁻¹), which was about 33 times higher than that of pure Ag₃PO₄.

(3) Followed by above work, a series of new heterojunctions based on Ag₃PO₄ and Sr₂Nb₂O₇₋ₓNₓ with adjustable band structures was successfully synthesized to attain the efficient elimination of gaseous IPA under visible light irradiation. The study of the electronic structure indicates that the valance band of the Sr₂Nb₂O₇ was lifted up due to mixing N 2p with O 2p orbitals from nitrogen doping which result in narrower band gap. Moreover, the band gap could be continually adjusted by the nitridation with NH₃ under different temperatures. The photocatalytic characterizations indicated that all of these composite photocatalysts exhibited higher efficiency than the individual samples under visible light-irradiation; in
particular, the Ag\textsubscript{3}PO\textsubscript{4}/Sr\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7-\textdelta}N\textsubscript{x} (x=0.82) composite photocatalyst showed the highest catalytic performance (CO\textsubscript{2} evolution rate, 10.32 ppm h\textsuperscript{-1}). The results reveal that the relative potentials of the valance band and the conduction band between the Ag\textsubscript{3}PO\textsubscript{4} and the Sr\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7-\textdelta}N\textsubscript{x} have significant effects on the photoactivity, and the optimal band gap of the Sr\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7-\textdelta}N\textsubscript{x} is about 2.15 eV and the potentials of VB and CB are +1.88 eV and -0.27 eV, respectively.

5.2 Future prospects

In this work, new composite photocatalysts have been designed and developed, including Ag\textsubscript{3}PO\textsubscript{4}/ In(OH)\textsubscript{3}, Ag\textsubscript{3}PO\textsubscript{4}/ Cr-SrTiO\textsubscript{3}, and Ag\textsubscript{3}PO\textsubscript{4}/ N-doped Sr\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7}. All composites exhibit higher photocatalytic activities than that of individual material. In the future, challenges and opportunities will co-exist in the development of novel composite photocatalysts:

(1) Recently, semiconductor photocatalyst has become a hot spot in material research. However, it’s very difficult to explore totally new semiconductors with high photocatalytic efficiency under light irradiation. In this regard, constructing composite photocatalyst based on visible-light sensitive semiconductors or UV-light sensitive semiconductors provides a facile and very important way to obtain efficient photocatalyst system. There is no doubt that it will greatly enlarge the numbers of efficient photocatalysts.

(2) In general, the recombination of photo-generated electron-hole pairs, the redox potential of generated electron, and the surface status of photocatalysts are
considered as factors that limit their photocatalytic performances in practical applications. In this regard, constructing composite photocatalysts can improve the separation of electron-hole pairs, adjust the surface properties and optimize the redox potentials to obtain higher photocatalytic activity. Therefore, composite photocatalyst has promising potential in practical applications in future.

(3) Besides the advantages and opportunities of composite photocatalysts, there are also some challenges in constructing composite photocatalyst. In general, the transfer of electrons and holes between the semiconductors is determined by the relative potentials and interfacial connection. Therefore, the great challenges are the suitable electronic structures of semiconductors and the interfacial connection between semiconductors.

(4) Since the potential of the conduction band of Ag₃PO₄ is quite positive, Ag₃PO₄ can easily be reduced to Ag⁰ during in the photocatalytic reactions. Composite structure can partly inhibit the reduction but cannot prohibit it completely. Therefore, promoting the stability of Ag₃PO₄ during in the photocatalytic reactions is still a great challenge in the future research.
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**Academic Achievements**

1. Papers


4) Han Zhou, Jianjun Guo, Peng Li, Tongxiang Fan, Di Zhang and Jinhua Ye: Leaf-architectured 3D Hierarchical artificial photosynthetic system of pervoskite titanates towards CO₂ photoreduction into hydrocarbon. Scientific Reports, (2013), DOI: 10.1038/srep01667.

2. Presentations

1) Jianjun Guo, Shuxin Ouyang, Tetsuya Kako and Jinhua Ye: Synthesis and characterization of a new heterojunction Ag₃PO₄/Cr-SrTiO₃ for photodegradation of gaseous organic pollutants under visible light irradiation.
2) Jianjun Guo, Shuxin Ouyang, Tetsuya Kako and Jinhua Ye: A new heterojunction Ag$_3$PO$_4$/Cr-SrTiO$_3$ towards efficient elimination of gaseous organic pollutants under visible light irradiation. 第 19 回シンポジウム「光触媒反応の最近の展開」（2012 年 12 月，東京大学・日本）

3) Jianjun Guo, Shuxin Ouyang, Tetsuya Kako and Jinhua Ye: Sol-gel hydrothermal synthesis of a self-assembled In(OH)$_3$ photocatalyst for photoreduction of CO$_2$. 第 18 回シンポジウム「光触媒反応の最近の展開」（2011 年 12 月，東京大学・日本）