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Ag₃PO₄/Ag₂CO₃ p–n heterojunction composites with enhanced photocatalytic activity under visible light

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ABSTRACT

Formation of a p–n heterojunction rather than p-type or n-type semiconductors can enhance the separation of photogenerated electrons and holes and increase the quantum efficiency of photocatalytic reactions owing to the difference of the electric potential in the inner electric field near the junction, pointing from n toward p. n-Ag₃PO₄/p-Ag₂CO₃ p–n heterojunction composites are prepared through a facile coprecipitation process. The obtained Ag₃PO₄/Ag₂CO₃ p–n heterojunctions exhibit excellent photocatalytic performance in the removal of rhodamine B (RhB) compared with Ag₃PO₄ and Ag₂CO₃. The 40%-Ag₃PO₄/Ag₂CO₃ composite photocatalyst (40 mol% Ag₃PO₄ and 60 mol% Ag₂CO₃) exhibits the best photocatalytic activity under visible light, demonstrating the ability to completely degrade RhB within 15 min. Transient photovoltage characterization and an active species trapping experiment further indicate that the formation of a p–n heterojunction structure can greatly enhance the separation efficiency of photogenerated carriers and produce more free h⁺ active species, which is the predominant contributor for RhB removal.

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1. Introduction

Semiconductor photocatalysis, as a “green” technique for environmental contamination control, has attracted considerable attention since the pioneering work of Fujishima et al. [1]. Although TiO₂, as the earliest used photocatalyst, has been widely studied, its application suffers from the wide band gap that is only responsive to ultraviolet (UV) light, which constitutes only a small fraction of the solar spectrum. Currently, more attention has been devoted to the exploration and fabrication of visible-light-driven photocatalysts such as BiOI [2], Bi₂MO₆ (M = Mo or W) [3,4], MnO₂ [5], CdS [6], g-C₃N₄ [7] and AgX (X = Cl [8], Br [9], I [10]). Among them, Ag-containing na-

nomaterials are considered to be promising candidates (Ag₃VO₄ [11], AgSbO₃ [12], Ag₃PO₄ [13], Ag₂CO₃ [14] and Ag₆Si₂O₇ [15]) because of their narrow band gap and excellent photoconversion efficiency. Notably, the discovery of the Ag₃PO₄ photocatalyst has been almost universally considered as a major breakthrough in the field of visible-light-active photocatalysts with high photooxidative capability for water-splitting and organic dye decomposition. Recently, many studies have been performed to further enhance their photocatalytic activity. However, an insurmountable problem for nearly all the reported Ag-based semiconductor photocatalysts is their poor activity or stability during their photocatalytic process. Therefore, enhancing photocatalytic activity and sta-

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bility for these Ag-based semiconductor photocatalysts is essential.

Formation of a heterojunction (or interface) over two semiconductors has already proven to be an effective way to improve photocatalytic activity or stability, according to previous reports on AgX/Ag₃PO₄ (X = Cl, Br, I) [16], TiO₂/Ag₃PO₄ [17], Ag₂O/Ag₂CO₃ [18], Ag₂CO₃/AgBr [19,20], Ag₃PO₄/BiOBr [21], *g*-C₃N₄/Ag₂CO₃ [22], GO-Ag₂CO₃ [23] and AgI/Ag₂CO₃ [24]. Theoretically, when a p-type semiconductor and n-type semiconductor form a p–n junction, a strong inner electric field will be formed near the junction, pointing from n toward p, owing to the arrangement of the high concentrations of negatively and positively charged ions. The difference of the electric potential in the electric field can enhance the separation of photogenerated electrons and holes, increasing the quantum efficiency of the photocatalytic reactions [25–28]. The p–n junction photocatalysts, p-CuBi₂O₄/n-TiO₂ [29], p-Ag₂O/n-Bi₂O₂CO₃ [30] and p-BiOI/n-TiO₂ [31], have been shown to exhibit a high photocatalytic efficiency compared with other heterojunctions.

Ag₂CO₃ has been confirmed to exhibit a high photocatalytic activity for organic pollutant degradation, because the incorporation of a nonmetallic p-block carbon element into Ag₂O can broaden the band gap, which can enhance the redox ability [20]. Therefore, Ag₂CO₃, as a p-type semiconductor, can form a p–n heterojunction with Ag₃PO₄, which is an n-type semiconductor. To the best of our knowledge, there have been no relevant reports concerning the Ag₃PO₄/Ag₂CO₃ heterojunction.

Inspired by the previous reports mentioned above, a series of novel Ag₃PO₄/Ag₂CO₃ p–n heterojunction composite photocatalysts were prepared through a simple coprecipitation process and then characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy and transient photovoltage (TPV) measurements. The photocatalytic activities of the samples were determined by measuring the degradation of rhodamine B (RhB) in an aqueous solution under UV-vis light irradiation. Additionally, the active species during photocatalytic reactivity were also investigated by the addition of free radical scavengers such as isopropanol (IPA), 1,4-benzoquinone (BQ) and sodium oxalate [32].

2. Experimental

2.1. Photocatalyst synthesis

All chemicals (Sinopharm Chemical Reagent Co., Shanghai, China) were of analytical grade purity and used without further purification. Briefly, 252 mg NaHCO₃ and 312 mg NaH₂PO₄·2H₂O were dissolved in 80 mL deionized water under stirring. Then, 40 mL AgNO₃ aqueous solutions (approximately 0.3 mol/L) was added dropwise to the solution under stirring. The precipitate was collected by centrifugation, washed three times with deionized water after stirring for 12 h and dried in air at 70 °C for 12 h to yield the 40%-Ag₃PO₄/Ag₂CO₃ composite photocatalyst (40 mol% Ag₃PO₄ and 60 mol% Ag₂CO₃). For comparison, other samples, such as Ag₃PO₄, Ag₂CO₃, and

Ag₃PO₄/Ag₂CO₃ with different Ag₃PO₄ concentrations (10%, 20%, 30%, 50%, 60%) were prepared in a similar procedure, but with different weight additives.

2.2. Catalyst characterization

The crystal structure of the composite photocatalysts was characterized using a Bruker D8 Advance X-ray powder diffractometer under nickel-filtered Cu-K_α radiation operating at 40 kV and 40 mA. TEM images were recorded using a Tecnai G2 F20 transmission electron microscope at an accelerating voltage of 200 kV. UV-vis diffuse reflectance spectra (DRS) were measured using a Cary 5000 spectrophotometer (Agilent, Santa Clara, USA). The transient surface photovoltage data were recorded by a 500 MHz digital oscilloscope (TDS 3054C, Tektronix, Beaverton, OR, USA) in the procedure reported by Fan et al. [33]. We placed the powder sample on the ITO electrode and another ITO electrode was used to press it to obtain a film composed of the powder sample. A laser pulse ($\lambda = 355$ nm with a pulse width of 4 ns) using the third-harmonic from a Nd:YAG laser (Quantel Brilliant Eazy: BRILEZ/IR-10) was employed as the light source.

2.3. Photocatalytic activity measurements

The photocatalytic performances of the prepared samples were evaluated by the degradation of RhB in a XPA-7 photochemical reactor (Xujiang electromechanical plant, Nanjing, China). A 500 W, high-pressure Xenon lamp with a 420-nm cutoff filter was used as the visible-light source. Photocatalyst (20 mg) was added to 50 mL of an aqueous solution of RhB with an original concentration of $c_0 = 20$ mg/L. The suspension was magnetically stirred for 30 min in the dark to obtain an adsorption-desorption equilibrium among the photocatalyst, organic substances and water prior to irradiation. During the whole process, the suspension was vigorously stirred in the photoreactor. Identical amounts (3 mL) of the suspension were removed and centrifuged at given intervals during illumination. The absorbance of the solution was measured using a UV-vis spectrophotometer (Agilent Cary 5000).

To detect the active species during photocatalytic reactivity, hydroxyl radicals ($\bullet$ OH), superoxide radicals ($O_2^{\bullet-}$) and holes (h^+) were investigated by adding 1.0 mmol/L IPA (a quencher of $\bullet$ OH), BQ (a quencher of $O_2^{\bullet-}$) and sodium oxalate (a quencher of h^+) into the water phase as a diagnostic tool. This method was similar to the former photocatalytic activity test.

3. Results and discussion

3.1. Textural property analysis

Figure 1 shows the XRD patterns of the Ag₃PO₄/Ag₂CO₃ samples. The peaks at 18.5° (020), 20.6° (110), 32.6° ($\bar{1}$ 01), 33.7° ($\bar{1}$ 30), 37.1° (040) and 39.6° (031) are indexed to that of monoclinic Ag₂CO₃ (JCPDS 26-339). The peaks at 21.0° (110), 29.8° (200), 33.4° (210), 36.7° (211), 47.9° (310), 52.8° (222), 55.1° (320) and 57.4° (321) are indexed to that of cubic Ag₃PO₄

Fig. 1. XRD patterns of the samples. (1) Ag_2CO_3 ; (2) Ag_3PO_4 ; (3) 10%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$; (4) 20%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$; (5) 30%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$; (6) 40% (50%, 60%) - $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$.

(JCPDS 70-702). No impurities were detected in Ag_3PO_4 and Ag_2CO_3 . From Fig. 1, the diffraction peaks of both Ag_3PO_4 and Ag_2CO_3 can be observed in the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite samples when the Ag_3PO_4 concentration is below 40%. Along with the increase of the concentration of Ag_3PO_4 , the intensities of the diffraction peaks of Ag_2CO_3 decrease and these of Ag_3PO_4 increase. When the concentration of Ag_3PO_4 was increased to 40%, there were no longer any diffraction peaks of Ag_2CO_3 and only that of Ag_3PO_4 was present, even with a further increase of the concentration of Ag_3PO_4 .

3.2. TEM and EDS test

Figure 2 shows the TEM images and the corresponding EDS spectra of the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalyst. Smaller Ag_3PO_4 particles were observed to be dispersed on the surface of larger Ag_2CO_3 particles. At these places, which are shown by arrows in Fig. 2(a) and (b), the interfaces were clearly connected by different materials, which are shown by the different light, shade and gray scale. The close proximity of the two semiconductors proved that a heterojunction was formed between Ag_3PO_4 and Ag_2CO_3 in the composites. To further dis-

Fig. 2. TEM images (a, b) and the corresponding EDS spectra (c, d) of 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalyst.

tinguish the components of the composites, we employed EDS to confirm the compositions at selected areas. Only elemental P, not elemental C, was present at region D according to the quantification results of EDS. Elemental C, O, Ag and P, and the Cu signals resulting from the copper grid were present at region C. The atomic compositions of elemental C and P were 10.434% and 8.757%, respectively. These results indicate that Ag_2CO_3 and Ag_3PO_4 were present at region C, and Ag_2CO_3 was the dominant component. However, Ag_2PO_3 was the dominant component at region D. A core-shell $\text{Ag}_2\text{CO}_3@\text{Ag}_3\text{PO}_4$ structure was presumed in which the Ag_3PO_4 was coated on the Ag_2CO_3 surface.

3.3. Optical property analysis

Figure 3(a) shows UV-vis diffuse reflectance spectra of the as-prepared photocatalysts, which reflects the ability to harvest solar energy. The spectra displays that pure Ag_2CO_3 and Ag_3PO_4 have absorption edges at approximately 474 nm and 520 nm, respectively. When the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ heterostructure was formed, a mixed absorption character, owing to the spectral superposition of Ag_2CO_3 and Ag_3PO_4 , was observed. In particu-

Fig. 3. UV-vis diffuse reflectance spectra of photocatalysts (a) and the band gap energies (E_g) of photocatalysts (b).

lar, when the content of Ag_3PO_4 was 30% and 40%, the absorption intensity of the heterostructure catalyst was remarkably enhanced in the visible region, compared with that observed for pure Ag_3PO_4 .

The band gap energies (E_g) of Ag_2CO_3 and Ag_3PO_4 were estimated using Eq. (1) [34]:

$$\left(\frac{Ah\nu}{K}\right)^2 = h\nu - E_g \quad (1)$$

where A , ν , E_g and K are the absorbance, light frequency, band gap energy and a constant, respectively. Therefore, the E_g of Ag_2CO_3 and Ag_3PO_4 were calculated to be 2.62 and 2.40 eV from the plots of $(Ah\nu)^2$ versus $h\nu$, as shown in Fig. 3(b). The E_g of the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite was 2.55 eV, which was between that of Ag_2CO_3 and Ag_3PO_4 .

In addition, the valence band (VB) and conduction band (CB) edge potentials of Ag_2CO_3 and Ag_3PO_4 were also determined to study the energy band matching, using the following empirical formulas [34]:

$$E_{\text{VB}} = X - E_e + 0.5 E_g \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (3)$$

where E_{VB} is the VB edge potential, E_{CB} is the CB edge potential, X is the electronegativity of the semiconductor, E_e is the energy of free electrons on the hydrogen scale (about 4.5 eV) and E_g is the band gap energy of the semiconductor. Herein, the E_{VB} were estimated to be 2.83 and 2.86 eV for Ag_2CO_3 and Ag_3PO_4 , respectively. Correspondingly, the E_{CB} of Ag_2CO_3 and Ag_3PO_4 were further calculated to be 0.21 and 0.43 eV, respectively. Therefore, the energy bands of Ag_2CO_3 and Ag_3PO_4 are well matched as an interactive structure.

3.4. Photocatalytic activity and durability

The photocatalytic activities of the photocatalysts were evaluated by measuring the degradation of RhB in aqueous solution. Fig. 4 showed that the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalyst exhibits the highest degradation rate among all photocatalysts: RhB was degraded completely under Xe lamp irradiation for 15 min. When the pure Ag_3PO_4 and Ag_2CO_3 were used as the photocatalysts, the degradation rates of the RhB were only 40% and 10%, respectively. Including additional

Fig. 4. Dynamic curve of RhB degradation over different photocatalysts under visible light. Reaction conditions: 500 W Xe lamp, 420 nm cutoff filter, RhB solution 20 mg/L, catalyst 50 mg.

Ag_3PO_4 coupled into Ag_2CO_3 was good for enhancing the degradation rate when the composition of Ag_3PO_4 was below 40%. However, when the Ag_3PO_4 composition exceeded 40%, the degradation rate started to decrease.

We also investigated the photocatalytic durability of the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ photocatalyst through five cycles for the photocatalytic decomposition of RhB solution, and the corresponding results were shown in Fig. 5(a). Fig. 5(b) showed that the photocatalytic degradation ability for the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ photocatalyst continuously decreased as the number of cycling tests increased, which is proposed to arise from the decomposition of Ag_3PO_4 and Ag_2CO_3 to metallic silver (Ag^0), as has been reported in many studies [35,36]. The decrease in photocatalytic efficiency is negligible after the third cycle, which can be attributed to the formed Ag^0 acting as a good trap for the electrons and thus enabling activity stability in the usage process [34].

3.5. Photocatalytic mechanism of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ photocatalyst

Figure 6 shows the trapping experiments of the active spe-

Fig. 5. (a) Cycling runs in photocatalytic degradation of RhB in the presence of 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$; (b) XRD patterns of used 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ after five cycles.

Fig. 6. Trapping experiments of the active species during the photocatalytic reaction.

cies during the photocatalytic reaction under visible-light irradiation. IPA is a well-known $\bullet\text{OH}$ scavenger, which can react quickly with all the $\bullet\text{OH}$ produced in the catalyst/RhB system. The results showed that adding IPA as an $\bullet\text{OH}$ scavenger did not change the decolorization rate of the RhB over Ag₃PO₄, Ag₂CO₃, and Ag₃PO₄/Ag₂CO₃ catalysts. This implies that the $\bullet\text{OH}$ radicals do not play a dominant role in RhB degradation.

However, the addition of sodium oxalate caused a noticeable decrease in the photocatalytic activity for the three photocatalysts. Sodium oxalate is an h^+ scavenger and quickly reacts with h^+ at the interface of the catalysts, reducing the number of active species available for RhB decolorization. Furthermore, the addition of BQ (a quencher of $\text{O}_2^{\bullet-}$) led to an obvious decrease in the photocatalytic activity for the Ag₃PO₄ and Ag₃PO₄/Ag₂CO₃ catalysts. Combining the results obtained by the additions of IPA, BQ and sodium oxalate as scavengers, it can be concluded that h^+ and $\text{O}_2^{\bullet-}$ are the principal active species for RhB degradation. Specifically, h^+ is the predominant contributor for all the photocatalysts. The influence of sodium oxalate on the photocatalysts has been evaluated according to the equation: $I = (D_1/D_0) \times 100\%$, where D_0 is the degradation ratio of RhB without any additives and D_1 is the degradation ratio of RhB with the addition of sodium oxalate. The value of I for the 40%-Ag₃PO₄/Ag₂CO₃ composite catalyst was 15.6%, which is much lower than that of Ag₃PO₄ (44.8%) and Ag₂CO₃ (57.1%). All results suggest that the 40%-Ag₃PO₄/Ag₂CO₃ composite photocatalyst is able to produce more free h^+ active species than Ag₃PO₄ and Ag₂CO₃.

The dynamic information of photoinduced charge carriers in the system can be obtained by TPV, which contributes to a further understanding of the photocatalytic ability of the composite photocatalysts. Fig. 7 shows the TPV spectra of the pure Ag₃PO₄, Ag₂CO₃ and 40%-Ag₃PO₄/Ag₂CO₃ composite photocatalysts. According to previous reports by Wang's group [33,37], a positive TPV response implies that photoinduced electrons transfer towards the bulk and photoinduced holes transfer to the surface and accumulate there. While a negative TPV response implies that photoinduced holes transfer towards the bulk and photoinduced electrons transfer to the surface and accumulate there.

Figure 7 shows some interesting features. (1) TPV signals of Ag₃PO₄ and 40%-Ag₃PO₄/Ag₂CO₃, as n-type semiconductor and p-n heterojunction, respectively, are positive, indicating the accumulation of positive charge near the surface. However, TPV signals of Ag₂CO₃, as a p-type semiconductor, are negative, suggesting negative charge accumulation near the surface. (2) It is typical for the surface photovoltage in semiconductors, where charge carriers are separated, to drift in the electric field of the surface space-charge region when the time is longer than 1×10^{-7} s. (3) Furthermore, an obvious retardation is observed in the TPV of 40%-Ag₃PO₄/Ag₂CO₃ in comparison with that of bare Ag₃PO₄ at times longer than 1×10^{-7} s. Hence, it is possible that the presence of the interface between Ag₃PO₄ and Ag₂CO₃ can reduce the transfer rate and inhibit the recombination of photoinduced charge carriers. (4) The time of the maximums (t_{max}) of the TPV can provide information about the recombination time of the photoinduced charge carriers. The value of t_{max} for the 40%-Ag₃PO₄/Ag₂CO₃ composite catalyst (1×10^{-7} – 1×10^{-3} s) is higher than that of the Ag₃PO₄ catalyst (5.74×10^{-8} – 1×10^{-4} s), which indicates that the recombination rate of charge carriers in the 40%-Ag₃PO₄/Ag₂CO₃ composite catalyst is lower than that in the Ag₃PO₄ catalyst.

On the basis of the above data, it is believed that a p-n het-

Fig. 7. TPV of the samples. The wavelength and intensity of the laser pulse are 355 nm and 200 μJ , respectively.

Fig. 8. Proposed photocatalytic mechanism for $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ photocatalyst.

erojunction is successfully formed in the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite catalyst. This results in the effective separation of photoinduced electron-hole pairs and the low recombination rate of charge carriers, which correspond to its highest photocatalytic activity.

Based on the above calculations and experimental results, a rough schematic energy band model of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalyst can be proposed, as depicted in Fig. 8. The CB position of Ag_2CO_3 is more negative than that of Ag_3PO_4 and the VB position of Ag_3PO_4 is more positive than that of Ag_2CO_3 . Thus, under visible-light irradiation, the excited electrons in the CB of Ag_2CO_3 can rapidly transfer to the CB of Ag_3PO_4 . At the same time, photoinduced holes in the VB of Ag_3PO_4 can transfer to the VB of Ag_2CO_3 . However, the formation of the p-n heterojunction greatly increases the separation of photoexcited electrons and holes, suppressing electron-hole recombination, which results in the enhanced photocatalytic performance of the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite.

4. Conclusions

A series of novel $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalysts were synthesized through a simple coprecipitation process and the 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite photocatalyst showed impressive photocatalytic behavior compared with both Ag_3PO_4 and Ag_2CO_3 in the degradation of RhB under visible-light irradiation. The enhanced photocatalytic activity of 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ composite arose from the fact that a p-n heterojunction was successfully formed between n-type Ag_3PO_4 and p-type Ag_2CO_3 , which led to the effective separation of photoinduced electron-hole pairs and the low recombination rate of charge carriers. Therefore, more free h^+ active species could be produced to oxidize the organic pollutant.

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Graphical Abstract

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Ag₃PO₄/Ag₂CO₃ p–n heterojunction composites with enhanced photocatalytic activity under visible light

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n-Ag₃PO₄/p-Ag₂CO₃ p–n heterojunction composites are prepared via a facile coprecipitation process. 40%-Ag₃PO₄/Ag₂CO₃ catalyst exhibited highest photocatalytic activity under visible light. Transient photovoltage proved the effective separation of photoinduced electron-hole pairs in Ag₃PO₄/Ag₂CO₃ catalysts.

Ag₃PO₄/Ag₂CO₃ p–n异质结复合光催化剂的制备及增强的可见光催化性能法文君^a, 王平^b, 岳冰^b, 杨凤岭^c, 李大鹏^a, 郑直^{a,*}^a许昌学院表面微纳材料研究所, 河南省微纳能量储存与转换材料重点实验室, 河南许昌461000^b郑州大学化学与分子工程学院, 河南郑州450001^c平顶山学院化学化工学院, 河南平顶山467000

摘要: 半导体光催化氧化技术作为一种“绿色技术”, 被广泛应用于环境污染物治理和太阳能转化领域. 高效、稳定、可回收利用的催化剂的开发是光催化技术发展的一个重要方向. Ag系半导体光催化剂因在可见光分解水制氢及降解有机污染物等方面表现出优异的催化性能而广受关注. 然而, 该催化剂失活快制约了其应用. 因此, 提高Ag系半导体材料的光催化稳定性成为近年来研究的一个热点.

研究发现, 在半导体的表面或者界面形成p–n异质结是提高催化剂光催化性能和稳定性的有效途径. 理论上讲, 当p型半导体和n型半导体形成p–n结以后, 在两种半导体接触边缘的附近处存在着正、负空间电荷分列两边的偶极层, 产生了从n型半导体指向p型半导体的内建电场. 内建电场的存在使得p型半导体与n型半导体之间产生了电位差, 即内建电势差. 这种电势差能够有效促进电子和空穴的分离, 达到光生电子和空穴对分离、转移和传递的目的, 从而抑制电子和空穴的复合, 提高光催化效率. Ag₂CO₃是p型半导体, 其导带为0.21 eV, 价带为2.83 eV; Ag₃PO₄是n型半导体, 其导带为0.43 eV, 价带为2.86 eV. 两者能带结构匹配, 能形成p–n异质结.

因此, 本文采用简单的共沉淀法, 制备了不同比例的Ag₃PO₄/Ag₂CO₃复合光催化剂, 并通过X射线衍射、透射电镜、X射线光电子能谱、紫外-可见漫反射光谱以及瞬态光电压谱等对其进行了表征. 透射电镜照片显示, 粒径较小的Ag₃PO₄颗粒均匀的分布在粒径较大的Ag₂CO₃周围. P元素和C元素的摩尔比接近于投料比. Ag₃PO₄/Ag₂CO₃复合催化剂的吸收光谱体现出两种催化剂的混合特征, 在可见光区的吸收强度增加. 瞬态光电压表征不仅证实了Ag₂CO₃是p型半导体, Ag₃PO₄是n型半导体, 更说明了40%-Ag₃PO₄/Ag₂CO₃复合光催化剂的载流子寿命较长. 罗丹明B(RhB)的降解实验证实40%-Ag₃PO₄/Ag₂CO₃(Ag₃PO₄与Ag₂CO₃的

摩尔比为40%:60%)复合催化剂的光催化效率最高, 500 W氙灯(附加420 nm截止波长的滤光片)照射15 min后, RhB就能被完全降解, 而纯的 Ag_3PO_4 和 Ag_2CO_3 对RhB的降解率只有40%和10%。循环实验发现, 前两次循环中由于单质银的生成导致催化剂活性下降, 但从第三次循环开始其催化活性趋于稳定。此外, 还通过添加草酸钠(空穴的清除剂)、异丙醇(羟基自由基的清除剂)和对苯醌(超氧自由基的淬灭剂)等来判断光催化过程中起主要作用的活性自由基。实验证实空穴是 $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ 光催化剂在降解RhB过程中产生的主要活性自由基物种。 $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ 光催化剂相对于单纯的 Ag_3PO_4 和 Ag_2CO_3 有更高的空穴产生能力。当可见光照到复合催化剂表面时, Ag_2CO_3 导带上的激发电子能够快速转移到 Ag_3PO_4 的导带上, 同时 Ag_3PO_4 价带上的光生空穴能够快速转移到 Ag_2CO_3 的价带上。 p-n 结的形成提高了光生电子和空穴的分离效率, 抑制了电子和空穴的再结合, 因此, 复合光催化剂光催化降解效率提高。

综上所述, $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ 之间能形成有效 p-n 结, 40%- $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ 复合光催化剂表现出最佳的光催化性能。

关键词: 磷酸银; 碳酸银; 复合催化剂; p-n 异质结; 可见光; 瞬态光电压表征

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