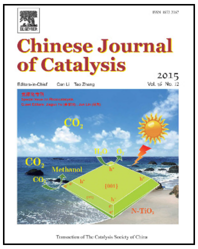
Chinese Journal of Catalysis 36 (2015) 2186–2193

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Article (Special Issue on Photocatalysis)

Ag_3PO_4/Ag_2CO_3 p–n heterojunction composites with enhanced photocatalytic activity under visible light

Wenjun Fa [a], Ping Wang [b], Bing Yue [b], Fengling Yang [c], Dapeng Li [a], Zhi Zheng [a,*]

[a] *Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, Xuchang University, Xuchang 461000, Henan, China*

[b] *The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China*

[c] *The College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan 467000, Henan, China*

ARTICLE INFO

Article history:
Received 13 September 2015
Accepted 1 November 2015
Published 20 December 2015

Keywords:
Silver phosphate
Silver carbonate
Composite catalyst
p–n heterojunction
Visible light
Transient photovoltage

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-Ag_3PO_4/p-Ag_2CO_3 p–n heterojunction composites are prepared through a facile coprecipitation process. The obtained Ag_3PO_4/Ag_2CO_3 p–n heterojunctions exhibit excellent photocatalytic performance in the removal of rhodamine B (RhB) compared with Ag_3PO_4 and Ag_2CO_3. The 40%-Ag_3PO_4/Ag_2CO_3 composite photocatalyst (40 mol% Ag_3PO_4 and 60 mol% Ag_2CO_3) 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.

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 TiO_2, 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], Bi_2MO_6 (M = Mo or W) [3,4], MnO_2 [5], CdS [6], g-C_3N_4 [7] and AgX (X = Cl [8], Br [9], I [10]). Among them, Ag-containing nanomaterials are considered to be promising candidates (Ag_3VO_4 [11], $AgSbO_3$ [12], Ag_3PO_4 [13], Ag_2CO_3 [14] and $Ag_6Si_2O_7$ [15]) because of their narrow band gap and excellent photoconversion efficiency. Notably, the discovery of the Ag_3PO_4 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-

---

* Corresponding author. Tel/Fax: +86-374-2968988; E-mail: zzheng@xcu.edu.cn

This work was supported by the National Natural Science Foundation of China (21007053, 51302241), the Education Department of Henan Province (2012GGJS-174), and Xuchang University Science Research Foundation (2015011).

DOI: 10.1016/S1872-2067(15)61004-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 12, December 2015

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/Ag_3PO_4 (X = Cl, Br, I) [16], TiO_2/Ag_3PO_4 [17], Ag_2O/Ag_2CO_3 [18], $Ag_2CO_3/AgBr$ [19,20], $Ag_3PO_4/BiOBr$ [21], *g*-C_3N_4/Ag_2CO_3 [22], GO-Ag_2CO_3 [23] and AgI/Ag_2CO_3 [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-$CuBi_2O_4$/n-TiO_2 [29], p-Ag_2O/n-$Bi_2O_2CO_3$ [30] and p-BiOI/n-TiO_2 [31], have been shown to exhibit a high photocatalytic efficiency compared with other heterojunctions.

Ag_2CO_3 has been confirmed to exhibit a high photocatalytic activity for organic pollutant degradation, because the incorporation of a nonmetallic p-block carbon element into Ag_2O can broaden the band gap, which can enhance the redox ability [20]. Therefore, Ag_2CO_3, as a p-type semiconductor, can form a p–n heterojunction with Ag_3PO_4, which is an n-type semiconductor. To the best of our knowledge, there have been no relevant reports concerning the Ag_3PO_4/Ag_2CO_3 heterojunction.

Inspired by the previous reports mentioned above, a series of novel Ag_3PO_4/Ag_2CO_3 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 $NaHCO_3$ and 312 mg $NaH_2PO_4\cdot 2H_2O$ were dissolved in 80 mL deionized water under stirring. Then, 40 mL $AgNO_3$ 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%-Ag_3PO_4/Ag_2CO_3 composite photocatalyst (40 mol% Ag_3PO_4 and 60 mol% Ag_2CO_3). For comparison, other samples, such as Ag_3PO_4, Ag_2CO_3, and Ag_3PO_4/Ag_2CO_3 with different Ag_3PO_4 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 (λ = 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 (•OH), superoxide radicals ($O_2^{\bullet-}$) and holes (h^+) were investigated by adding 1.0 mmol/L IPA (a quencher of •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 Ag_3PO_4/Ag_2CO_3 samples. The peaks at 18.5° (020), 20.6° (110), 32.6° (–101), 33.7° (–130), 37.1° (040) and 39.6° (031) are indexed to that of monoclinic Ag_2CO_3 (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 Ag_3PO_4