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Fabrication of In_2O_3-Ag-Ag_3PO_4 composites with Z-scheme configuration for photocatalytic ethylene degradation under visible light irradiation

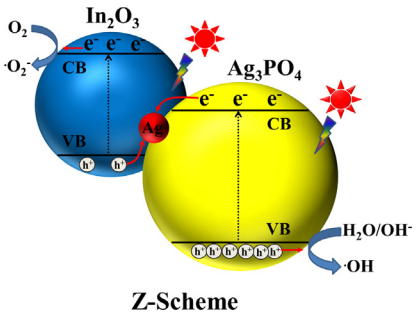
Xuxing Chen [a,b], Rong Li [b], Xiaoyang Pan [b], Xintang Huang [a,*], Zhiguo Yi [b,c,*]

[a] Institute of Nanoscience and Nanotechnology, Department of Physics, Central China Normal University, Wuhan 430079, China
[b] CAS Key Laboratory of Design and Assembly of Functional Nanostructures & Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 350002, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- In_2O_3-Ag-Ag_3PO_4 composites with Z-scheme configuration are fabricated.
- The photocatalysts show efficient activities toward ethylene degradation under visible light irradiation.
- The stability of Ag_3PO_4 was obviously improved.
- The reaction process of ethylene photodegradation was investigated by in-situ IR.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic degradation of ethylene under visible light remains a challenge at the frontiers of chemistry. In this study, In_2O_3-Ag-Ag_3PO_4 composite semiconductors with Z-scheme configuration were fabricated for the first time by in-situ synthesis of Ag_3PO_4 on In_2O_3 and subsequent photoreduction of Ag_3PO_4 to generate nano silver. Their performances on photocatalytic degradation of ethylene under visible light illumination were investigated. Results demonstrated that both the activity of ethylene photocatalytic degradation and Ag_3PO_4 photostabilization are considerably improved by making such a Z-scheme composite. According to the material design perspective and the application in the field of environmental pollutant remediation, the present research will provide potential value for further study on the removal of HC (Hydrocarbons) from the atmosphere and the stability concern of Ag_3PO_4 and other materials with photocorrosion.

1. Introduction

Nowadays, given the increasing social concern on human health and environmental pollution, removing volatile organic compounds (VOCs) from air has attracted widespread attention because these atmospheric VOCs could lead to photochemical smog and cause adverse health effects. As a gaseous VOC, ethylene (C_2H_4) gas in the atmosphere can induce disease susceptibility and physiological disorders even in a trace amount [1,2]. Consequently, removing the trace amounts of C_2H_4 from the air is imperative [3–7].

Since 1972, Fujishima and Honda reported the pioneering work on photocatalytic decomposition of water into H_2 and O_2 by TiO_2 electrodes [8]. Semiconductor photocatalysis has received

* Corresponding authors at: CAS Key Laboratory of Design and Assembly of Functional Nanostructures & Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou 350002, China (Z. Yi).
E-mail addresses: xthuang@phy.ccnu.edu.cn (X. Huang), zhiguo@fjirsm.ac.cn (Z. Yi).

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remarkable attention as an effective and most promising strategy in the field of solar energy conversion and environmental pollution remediation [9–25]. As the most promising strategy for the decomposition of atmospheric C_2H_4, heterogeneous photocatalytic oxidation has also attracted considerable attention in the past few decades [26–30]. However, most of the effective photocatalysts are wide-bandgap semiconductor, and they only work under UV light illumination because visible-light responsive semiconductor photocatalysts cannot reduce O_2 to form O_2^- and oxidate OH^- to form ·OH simultaneously [31–33]. As we previously reported, an appropriate semiconductor photocatalyst for photocatalytic oxidation of C_2H_4 should satisfy the following criteria: First, the conduction band (CB) minimum should be more negative than the reduction potential of O_2 ($O_2 + e^- \rightarrow O_2^-$, −0.33 V vs. NHE) [34]. Second, the valence band (VB) maximum should be more positive than the oxidation potential of OH^- ($OH^- + h^+ \rightarrow \cdot OH$, +2.59 V vs. NHE), [35–37] and finally, the bandgap should be larger than 2.92 eV. Therefore, an appropriate semiconductor photocatalyst can only absorb ultraviolet (UV) light, and exploring semiconductor photocatalysts for highly efficient oxidation of ethylene under visible light illumination remains a challenging task.

Inspired by natural photosynthesis of plants, scientists have designed some artificial photosynthesis systems for photocatalytic water splitting, in which two semiconductors that can perform photocatalytic oxidation or reduction of water were employed to compose a Z-scheme configuration, along with an electron mediator [38–40]. Based on the knowledge aforementioned, it could be possible to design an efficient photocatalyst for removing ethylene under visible light irradiation by fabricating a Z-scheme configuration with two narrow bandgap semiconductors. As well known, under visible light illumination, silver orthophosphate (Ag_3PO_4) is a considerably efficient semiconductor for water oxidation and organic degradation in water solution [41]; nevertheless, the CB minimum of Ag_3PO_4 (about +0.50 V vs. NHE) is lower than the reduction potential of O_2 ($O_2 + e^- \rightarrow O_2^-$, −0.33 V vs. NHE). Thus, when Ag_3PO_4 is used to photooxidize C_2H_4, the photo-excited electrons will be accumulated on the CB of Ag_3PO_4. Consequently, Ag_3PO_4 will decompose to form Ag nanoparticles and then gradually deactivate. However, if employ Ag_3PO_4 (the energy level of the VB edge of Ag_3PO_4 is about + 2.85 V vs. NHE) as a photocatalyst for the oxidation of OH^- to generate ·OH and introduce another semiconductor for the reduction of O_2 to generate O_2^- to fabricate a Z-scheme system. In this system, the in-situ formed Ag nanoparticles can serve as electron mediator bridging the transfer of photogenerated electrons from the CB of Ag_3PO_4 to the VB of the introduced semiconductor. Consequently, enhanced C_2H_4 photooxidation performance and improved stability of Ag_3PO_4 could thus be anticipated.

In the present study, In_2O_3 was introduced on the basis of the following considerations: I) a narrow bandgap (2.8 eV) helps for visible light absorption; II) a highly negative CB minimum (−0.62 V vs. NHE) is beneficial for O_2 reduction, and the appropriate VB edge (+2.18 V vs. NHE) contributes to the photo-generated electrons transfer from the CB bottom of Ag_3PO_4 to the VB edge of In_2O_3; and III) facile synthetic route and cheap raw materials favor photocatalyst fabrication and practical application [42–44]. Moreover, the VB maximum of In_2O_3 is higher than the oxidation potential of OH^- ($OH^- + h^+ \rightarrow \cdot OH$, +2.59 V vs. NHE). Hence, fabricating such a Z-scheme composite will also be beneficial for In_2O_3 to photooxidize C_2H_4. On basis of the aforementioned considerations, we fabricated for the first time a series of In_2O_3-Ag-Ag_3PO_4 Z-scheme photocatalysts through a facile route. We also examined their performance on C_2H_4 photodegradation under visible light illumination.

2. Experimental

2.1. Materials

All raw materials, namely, $In(NO_3)_3{\cdot}4.5H_2O$, oxalate dihydrate ($H_2C_2O_4{\cdot}2H_2O$), $AgNO_3$ and NaH_2PO_4, were commercially available from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of pure In_2O_3

In_2O_3 powders were prepared by a modified method based on the literature. In a typical procedure, First, 0.01 mol $In(NO_3)_3{\cdot}4.5H_2O$ and 0.02 mol oxalate dihydrate were respectively dissolved in 100 mL of deionized water at ambient temperature. Second, the oxalic acid solution was added dropwise to the In $(NO_3)_3{\cdot}4.5H_2O$ solution, and the white indium oxalate precipitates formed immediately. Finally, the obtained precipitates were filtered from the mixture solution and calcined at 350 °C under air atmosphere for 2 h. The TGA curve of indium oxalate sample is shown in Supporting Information (Fig. S1).

2.2.2. Synthesis of pure Ag_3PO_4

Ag_3PO_4 powders were prepared by the precipitation method based on our previous report [41]. In a typical procedure, 0.003 mol $AgNO_3$ and 0.002 mol NaH_2PO_4 were dissolved in 20 mL of deionized water at ambient temperature, respectively. Subsequently, the NaH_2PO_4 solution was promptly poured into the $AgNO_3$ solution, and the color of the solution was rapidly changed to yellow. The obtained yellow Ag_3PO_4 precipitates were washed and filtered with deionized water for three times, and then dried at room temperature for 24 h.

2.2.3. Synthesis of In_2O_3-Ag-Ag_3PO_4 photocatalysts

The In_2O_3-Ag_3PO_4 photocatalysts with different mass ratios were synthesized by an in-situ precipitation method. In a typical procedure, first, 1.000 g of In_2O_3 particles were dispersed in 100 mL of distilled water, and then sonicated for 10 min. Second, appropriate amounts of NaH_2PO_4 were immediately added into the In_2O_3 dispersed water, and magnetically stirred for 15 min. Afterward, appropriate amounts of $AgNO_3$ solution was added by dropwise to the dispersed In_2O_3 solution. Finally, when the solution was stirred overnight, the resultant photocatalysts were filtered and sufficiently washed with deionized water for three times, then dried at room temperature. To form In_2O_3-Ag-Ag_3PO_4 composites with Z-scheme configuration, the In_2O_3-Ag_3PO_4 composite photocatalysts were irradiated for 5 min under Xe lamp. The resultant photocatalysts with nominal mass ratio of 95%, 90%, 70% and 50% In_2O_3 were denoted as 95-IO-Ag-5-AP, 90-IO-Ag-10-AP, 70-IO-Ag-30-AP and 50-IO-Ag-50-AP, respectively.

2.3. Characterization

Powder X-ray diffraction (PXRD) analyzed using a Rigaku Miniflex II X-ray diffractometer equipped with Cu Kα radiation (0.154178 nm, 40 kV, and 10 mA). The scan rate was 5° min^{-1}, and the scan range (2) was 20°–80°. The morphology of all samples was characterized by scanning electron microscopy (SEM, JSM-6700F), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) (JEM-2010 and FEI, Tecnai G^2 F20 FEG TEM). The UV–visible diffusive reflection spectra (DRS) of all samples were collected by the UV–Vis-NIR spectrophotometer