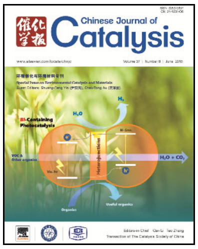
Chinese Journal of Catalysis 37 (2016) 855–862

available at www.sciencedirect.com

ScienceDirect

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



Article (Special Issue on Environmental Catalysis and Materials)

Novel visible-light-responding $InVO_4$-Cu_2O-TiO_2 ternary nanoheterostructure: Preparation and photocatalytic characteristics

Haibo Feng [a,b], Yaping Li [a], Dongming Luo [a], Gongrong Tan [a], Jianbo Jiang [a], Huimin Yuan [a], Sanjun Peng [a], Dong Qian [a,b,*]

[a] *College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, China*

[b] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, Hunan, China*

ARTICLE INFO

Article history:
Received 31 January 2016
Accepted 13 April 2016
Published 5 June 2016

Keywords:
Indium orthovanadate
Cuprous oxide
Titanium dioxide
Nanoheterostructure
Visible light
Photocatalytic degradation
Methyl orange

ABSTRACT

A novel visible-light-responding $InVO_4$-Cu_2O-TiO_2 ternary nanoheterostructure was designed on the basis of the strategy of energy gap engineering and prepared through ordinary wet chemistry methods. The as-prepared nanoheterostructure was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and diffuse reflectance ultraviolet-visible spectroscopy (UV-vis/DRS). The TEM and HRTEM images of 10%$InVO_4$-40%Cu_2O-50%TiO_2 confirm the formation of nanoheterostructures resulting from contact of the nanosized TiO_2, Cu_2O and $InVO_4$ in the size of 5–20 nm in diameter. The $InVO_4$-Cu_2O-TiO_2 nanoheterostructure, when compared with TiO_2, Cu_2O, $InVO_4$, $InVO_4$-TiO_2 and Cu_2O-TiO_2, shows significant enhancement in the photocatalytic performance for the degradation of methyl orange (MO) under visible-light irradiation. With a 9 W energy-saving fluorescent lamp as the visible-light source, the MO degradation rate of 10%$InVO_4$-40%Cu_2O-50%TiO_2 reaches close to 90% during 5 h, and the photocatalytic efficiency is maintained at over 90% after six cycles. This may be mainly ascribed to the matched bandgap configurations of TiO_2, Cu_2O and $InVO_4$, and the formations of two p-n junctions by the p-type semiconductor Cu_2O with the n-type semiconductors TiO_2 and $InVO_4$, all of which favor spatial photogenerated charge carrier separation. The X-ray photoelectron spectroscopy (XPS) characterization for the used 10%$InVO_4$-40%Cu_2O-50%TiO_2 reveals that only a small shakeup satellite peak appears for Cu(II) species, implying bearable photocorrosion of Cu_2O. This work could provide new insight into the design and preparation of novel visible-light-responding semiconductor composites.

1. Introduction

The development of visible-light-responding photocatalysts has become one of the most challenging and urgent topics that needs addressing because of the increasingly grim environmental and energy issues that confront mankind today [1–3]. Since Fujishima et al. [4] reported on water photolysis with titanium dioxide (TiO_2) as the anode in 1972, TiO_2 has been deemed as the most promising photocatalyst due to its outstanding performance, low cost, nontoxicity and stability.

---

* Corresponding author. Tel/Fax: +86-731-88879616; E-mail: qiandong6@vip.sina.com

This work was supported by the National Natural Science Foundation of China (21171174), Provincial Natural Science Foundation of Hunan (09JJ3024), and Provincial Environmental Science and Technology Foundation of Hunan.

DOI: 10.1016/S1872-2067(15)61105-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 6, June 2016

However, the shortcomings of a wide bandgap (3–3.2 eV) and fast photogenerated carriers recombination for TiO_2 hinder its extensive application in photocatalysis [5]. Therefore, improving its visible-light utilization and suppressing the photogenerated carriers recombination are significant foci in the field of photocatalysis.

The sensitization of TiO_2 by narrow bandgap semiconductors has proven to be an effective strategy to enhance its visible-light photocatalytic performance [3,6], resulting in the transfer of the photogenerated carriers from the narrow bandgap semiconductors to TiO_2. In the past, cuprous oxide (Cu_2O), a fascinating p-type semiconductor with a 2.0 eV bandgap, has received significant research interest as a visible-light-responding photocatalyst [7–12]. However, the visible-light photocatalytic activity of bare Cu_2O is commonly comparatively low due to the rapid recombination of photogenerated carriers [13]. In the past few decades, increasing interest has been aroused on the combination of TiO_2 with Cu_2O to form a visible-light-responding heterostructure to be used as photocatalysts and photovoltaic cells because of their favorably matched band structures [14–25].

Indium orthovanadate ($InVO_4$), an n-type semiconductor with a bandgap of 2.0 eV, has also enjoyed considerable attention as a visible-light-responding photocatalyst for hydrogen evolution by water splitting [26–28] and organic pollutants degradation [29,30]. Similarly, $InVO_4$ commonly exhibits negligible photocatalytic activity because of its poor adsorption capability and facile photogenerated carrier recombination [31]. Therefore, much research effort has been directed towards the development of TiO_2-$InVO_4$ composite photocatalyst [31–39].

Based on the strategy of energy gap engineering, compositing p-type Cu_2O and n-type $InVO_4$ semiconductors with n-type semiconductor TiO_2 to construct a novel ternary heterostructure can be expected to display improved visible-light photocatalytic performance because of coupling of their different energy levels and the unique properties of the formed heterostructures. Herein, we demonstrate a facile wet chemistry route to fabricate a novel $InVO_4$-Cu_2O-TiO_2 ternary nanoheterostructure that shows enhanced photocatalytic performance compared with the $InVO_4$-TiO_2 and Cu_2O-TiO_2 binary nanoheterostructures used for the degradation of methyl orange (MO) under visible-light irradiation. Furthermore, for the purpose of practical application, an ordinary 9 W energy-saving fluorescent lamp was used as the visible-light resource. To the best of our knowledge, no works have been documented on the fabrication of $InVO_4$-Cu_2O-TiO_2 ternary nanoheterostructure for organic pollutant photodegradation.

2. Experimental

All chemical reagents used in the experiments were of analytical purity and employed without further purification.

2.1. *Synthesis of $InVO_4$ nanoparticles*

$InVO_4$ nanoparticles were prepared by a facile hydrothermal method similar to that reported by Ge et al [32]. In a typical experiment, 0.001 mol $InCl_3$ was dissolved in 10 mL deionized water, and 20 mL of 0.05 mol/L NH_4VO_3 solution was then added dropwise under magnetic stirring. The pH value of the resulting mixture was adjusted to about 7 with 2 mol/L NaOH solution. After that, the mixture was kept stirring for 30 min and sonicating for 10 min before being transferred into a 60 mL Teflon-lined stainless steel autoclave. Hydrothermal reaction then proceeded at 120 °C for 8 h. Finally, the produced white slurry was centrifuged, washed with deionized water 3 times and dried at 60 °C for 12 h to give white $InVO_4$ nanoparticles.

2.2. *Synthesis of 16.67%$InVO_4$-83.33%TiO_2 nanoheterostructure*

An $InVO_4$-TiO_2 nanoheterostructure was synthesized by a sol-gel method. Typically, 0.0667 g of the as-prepared $InVO_4$ was dispersed in a mixture solvent of 5 mL deionized water and 5 mL ethanol, and 10 mL of 0.1% cetyltrimethylammonium bromide (CTAB) solution was then added and followed by sonicating for 10 min. A solution composed of 1.42 mL tetrabutyl titanate and 18.58 mL anhydrous alcohol was also added under magnetic stirring, and the resulting suspension was kept stirring for 30 min. Finally, the produced white slurry was centrifuged, washed with deionized water 3 times, dried at 60 °C for 12 h and calcined at 450 °C for 3 h to give the 16.67%$InVO_4$-83.33%TiO_2 nanoheterostructure. In addition, TiO_2, 5%$InVO_4$-95%TiO_2 and 10%$InVO_4$-90%TiO_2 were prepared via a similar route by changing the starting material ratios.

2.3. *Synthesis of 50%Cu_2O-50%TiO_2 nanoheterostructure*

A Cu_2O-TiO_2 composite was synthesized *via* an easy precipitation route similar to that reported by Huang et al. [15]. 0.4159 g $Cu(Ac)_2{\cdot}H_2O$ was dissolved in 50 mL anhydrous ethanol to obtain a deep green solution, and 0.15 g of the as-prepared TiO_2 was dispersed in the solution assisted by sonication for 10 min. 50 mL glucose solution (0.13 mol/L) as reducing agent and 60 mL NaOH solution (0.3 mol/L) in the mixed solvent of 35 mL anhydrous ethanol and 25 mL deionized water were added dropwise to the suspension in sequence under magnetic stirring, and then the resulting suspension was heated to 80 °C and kept stirring for 30 min. After the suspension was cooled to room temperature, the precipitates were collected by centrifugation, washed with anhydrous ethanol 2 times and deionized water 2 times, and then dried at 60 °C for 12 h in vacuum. Cu_2O, 30%Cu_2O-70%TiO_2 and 70%Cu_2O-30%TiO_2 were also prepared by a similar route through altering the starting material ratios.

2.4. *Synthesis of 10%$InVO_4$-40%Cu_2O-50%TiO_2 nanoheterostructure*

The as-prepared $InVO_4$-TiO_2 nanoheterostructure was coupled with Cu_2O by a simple precipitation route. In a typical experiment, 0.3328 g $Cu(Ac)_2{\cdot}H_2O$ was dissolved in 50 mL anhydrous ethanol, and 0.18 g of the as-prepared 16.67%$InVO_4$-83.33%TiO_2 nanoheterostructure was dispersed in the solution