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Photocatalytic Activity of Hierarchically Nanoporous $BiVO_4/TiO_2$ Hollow Microspheres

Yang Zhou [a], Guohua Jiang [a,b,*], Rijing Wang [a,b], Xiaohong Wang [a,b]
Ruanbing Hu [a,b], Xiaoguang Xi [a,b]

[a] *Department of Materials Engineering, College of Materials and Textile, Zhejiang Sci-Tech University Hangzhou 310018, China*

[b] *Key Laboratory of Advanced Textile Materials and Manufacturing Technology (ATMT), Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China*

Abstract

The hollow microspheres containing monoclinic scheelite $BiVO_4$ and anatase TiO_2 nanocrystals were easily prepared through a simple one-step template-free method. $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 were used as $BiVO_4$ precursor and $(NH_4)_2TiF_6$ as TiO_2 precursor to produce the target products in the presence of glucose under the high temperature pyrolysis. The products were characterized with SEM, XRD, TEM and UV-vis DRS. The as-prepared hollow microspheres showed high photocatalytic activity, which was demonstrated by degradation of acetic acid solution under visible-light irradiation (λ >420 nm).

Keywords: Semiconductors; Photocatalytic Property; Hierarchically Structure; Hollow Microspheres

1 Introduction

TiO_2 is a very important multifunctional material because of its peculiar and fascinating physicochemical properties, and its wide variety of potential uses in diverse fields such as solar energy conversion, environmental purification, water treatment and antibacterial materials [1-4]. However, the large band gap of pure TiO_2 (E_g=3.0 eV for rutile, E_g=3.2 eV for anatase) limits its application as the electron–hole pairs can only be formed by UV light at wavelength shorter than 387 nm [5, 6]. Thus, only a small portion of the solar spectrum can be utilized for photo-oxidation reaction under the presence of TiO_2. The development of a general method for endowing TiO_2 with visible-light response and concomitantly increasing their UV-light activity should dramatically expand their viability [7-9]. To this end, doping of various transition metals and anions has been extensively studied [9-12]. Amongst different studies of oxides with activity under visible-light irradiation, $BiVO_4$ has received special attention [13]. $BiVO_4$ crystallizes in three different polymorphs, i.e. tetragonal zircon, monoclinic distorted scheelite and tetragonal scheelite. Due to

*Corresponding author.
Email address: polymer_jiang@hotmail.com (Guohua Jiang).

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its relatively narrow band gap (~2.4 eV), the monoclinic form exhibits the higher photocatalytic activity for chemical reactions induced with visible-light irradiation [14, 15].

On the other hand, there has been considerable interest in the synthesis of micrometer and nanometer sized hollow spheres because of their widespread potential applications in catalysis, drug delivery, chromatography separation, chemical reactors, controlled release of various substances, and protection of environmentally sensitive biological molecules [16, 17]. Several micrometer and nanometer sized hollow spheres of transition metal oxides have been prepared due to researchers' unremitting effort using soft templating methods [18, 19] and mesoporous silica as hard template [20, 21]. However, such methods have disadvantages. Soft templating methods usually lead to the formation of mesoporous structure with amorphous walls, while the hard templating methods usually involve multistep processes and sometimes lead to the damage of pore structures during the removal of hard templates [22-24].

Monodisperse nanocrystals display novel properties which stimulated intensive research on the synthesis of monodisperse nanocrystals for their fundamental and technological importance [25, 26]. However, there are still problems with obtaining the mesoporous structure with monodisperse microspheres for the enhancement of the structural stability and photocatalytic property of $BiVO_4$ and TiO_2. With this in mind, we proposed one-step hydrothermal and pyrolysis treatment for the preparation of hierarchically nanoporous $BiVO_4/TiO_2$ hollow microspheres. One of the advantages of this method is that the nanoporous $BiVO_4/TiO_2$ hollow microspheres can be prepared without assistance of templates synthesized beforehand. High photocatalytic activity on the degradation of acetic acid is investigated for typical samples of $BiVO_4/TiO_2$ hollow microspheres under visible light.

2 Experimental

2.1 Materials

All chemicals were analytically graded and used as the starting materials without further purification. Glucose, $Bi(NO_3)_3{\cdot}5H_2O$, NH_4VO_3 and $(NH_4)_2TiF_6$ were purchased from East of China Chemical Regent Co.

2.2 Preparation of $BiVO_4/TiO_2$ Hollow Composite Microshperes

In a typical synthesis of colloidal carbon spheres, 4 g of glucose and 0.84 g of $(NH_4)_2TiF_6$ were dissolved in 35 mL of distilled water to form a clear solution. 0.5 g of $Bi(NO_3)_3{\cdot}5H_2O$ and 0.7 g of NH_4VO_3 were dissolved in dilute HNO_3 and NaOH aqueous solution respectively. After stirring for 0.5 h, the three solutions were mixed. The mixture was then sealed in a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 ℃ for 24 h. The products were washed by distilled water and ethanol three times each and dried in air at 60 ℃ for 8 h. The final products were obtained through a heat treatment at 400 ℃ in air for 4 h with a heating rate of 2 ℃ min^{-1}.

2.3 Characterization

The samples were characterized by powder X-ray Diffraction (XRD) performed on a Rigaku-Dmax