



Synthesis of hierarchical m-BiVO₄ particles via hydro-solvothermal method and their photocatalytic properties

Yunfeng Ma, Haiqing Jiang*, Xiaochen Zhang, Jiabin Xing, Yunsheng Guan

School of Advanced Materials and Nanotechnology, Xidian University, Xi'an 710071, PR China

Received 2 July 2014; received in revised form 30 July 2014; accepted 31 July 2014

Available online 8 August 2014

Abstract

A facile hydro-solvothermal method based on hydrothermal technique has been developed for the synthesis of monoclinic BiVO₄ powders with hierarchical structures, using Bi(NO₃)₃·5H₂O and NaVO₃ as raw materials, and oleylamine as surfactant. The phase structure and morphology of as-prepared BiVO₄ particles are characterized by X-ray diffraction, field scanning electron microscope and transmission electron microscopy, respectively. The UV–vis absorption spectra and BET special surface areas are also measured. The influences of volume ratio of water/toluene and the pH value of aqueous phase on the morphology of BiVO₄ particles have been investigated to obtain the different shapes. The possible mechanisms for the synthesis technology and shape self-assembly of BiVO₄ are discussed. The results of the photocatalytic activity of as-prepared BiVO₄ show that sphere-like and needle-like BiVO₄ polycrystalline particles exhibit more excellent visible-light photocatalytic and satisfied recycling properties.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Powders: chemical preparation; A. Grain growth; E. Functional applications; BiVO₄; Microstructure

1. Introduction

In recent years, more attentions have been focused on semiconductor photocatalytic degradation and elimination of organic pollutions and production of hydrogen due to the seriously environmental and energy problems [1–4]. As one of the oxide photocatalysts with good chemical and physical properties, TiO₂ has been extensively investigated. However, the applications for photocatalytic are severely limited due to its wide band gap (3.2 eV) which mostly responds to the ultraviolet (UV) light [5,6]. So, it is more important to explore a new visible-light driven photocatalyst with high activity.

As one of new photocatalysts, bismuth vanadate (BiVO₄) has drawn great attention for its excellent performance under visible light illumination [7,8]. Especially, monoclinic BiVO₄ (m-BiVO₄) with band gap of 2.4 eV exists a superior photocatalytic activities over the other phases [9–11]. Moreover, the photocatalytic performance of m-BiVO₄ significantly depends

on the particle shape, size, specific surface area and crystallinity, etc [12–14]. Over the past decades, several different methods and techniques have been applied to synthesize m-BiVO₄ particles, such as co-precipitation [15], aqueous process [16], sonochemical method [17], organic decomposition method [18], solid-state reaction (SSR) [19], and hydrothermal method [20,21]. Among them, the hydrothermal synthesis is widely used for its effective and facile processing to control the morphology and the size of crystals easily. Thus so far, m-BiVO₄ crystallites with different architectures have been widely reported. Yu and Kudo [13] prepared m-BiVO₄ powders with different morphologies by the hydrothermal method through adjusting the pH value of reaction system. Their experimental results demonstrated that the local structure and the crystallinity of m-BiVO₄ played significant roles in the photocatalytic performance for O₂ evolution. Zhang [22] reported to obtain m-BiVO₄ nanosheets via the hydrothermal technique by using sodium dodecyl benzene sulfonate (SDBS) as morphology directing template. The results indicated that m-BiVO₄ nanosheets showed good visible photocatalytic activities determined by the degradation of rhodamine (RB) under sunlight irradiation. Xi [23] reported to get plate-shaped

*Corresponding author. Tel.: +86 13319217520.

E-mail address: hqjiang@mail.xidian.edu.cn (H. Jiang).

m-BiVO₄ with exposed {0 0 1} facets by the hydrothermal technique. The visible-light photoactivic properties for the degradation of organic contaminants were enhanced accordingly as well as for the photocatalytic oxidation of water to O₂. Recently, Jiang [10] reported to obtain m-BiVO₄ crystallites with hyperbranched, polyhedral, porous spherical and octapod-like morphologies by the hydrothermal method with or without the assistance of tri-block copolymer P123. Such porous m-BiVO₄ products showed excellent photocatalytic performance for the removal of phenol and methylene blue. Despite of these exciting developments, most of the m-BiVO₄ particles are limited in the formation of micronparticle, which could decrease their activities. So, it is a big challenge to control the morphology of m-BiVO₄ with desired sizes and shapes by using hydrothermal method.

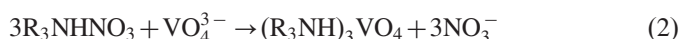
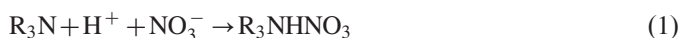
In our manuscript, a facile and modified hydro-solvothermal technique is applied to fabricate m-BiVO₄ polycrystalline particles, from the direct reaction of Bi[CH₃(CH₂)₆COO]₃ and (R₃NH)₃VO₄ complexes in water/toluene medium in the presence of oleylamine (OM) as a surfactant. Through this approach, the advantages of hydro- and solvo-thermal [24,25] methods and the crucial effects of pH value [4,23,26] (referring to the pH value of aqueous phase in all the manuscript) on morphology fabrication can be fully controlled. Meanwhile, the uniform m-BiVO₄ particles with different shapes are selectively synthesized, such as sphere, ellipse, needle, dog-bone, coarse rod, cuboid and cluster. The influences of volume ratio of water/toluene (*W/T*) and pH value on the controllable morphology and photocatalytic activity of m-BiVO₄ are studied as well. The possible evolution mechanisms for the different shaped particles under different factors are also proposed.

2. Experimental

2.1. Experimental principle

In this paper, the low cost and aqueous soluble inorganic precursors were used to synthesize BiVO₄ particles. During the synthetic process of pre-synthesized Bi[CH₃(CH₂)₆COO]₃ and (R₃NH)₃VO₄ complex precursors, tri-*n*-octylamine (TOA) and octylic acid (OA) as phase transfer catalysts were selected to transfer different aqueous inorganic precursors to non-polar organic toluene phase [25]. After mixing two different complex solutions and adding a moderate amount of volume of OM and water, the final mixed solution was transferred into titanium kettle and autoclaved to synthesize BiVO₄ powders. The schematic diagram of the synthesis technology is clearly shown in Scheme 1.

Hereinafter, the proposed reaction mechanism of pre-synthesized VO₄(TOA)₃ complexes is shown in Eqs. (1) and (2).

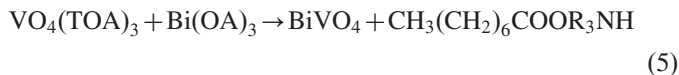


In Eqs. (1) and (2), R represents octyl group.

Eqs. (3) and (4) represent the proposed mechanism of pre-synthesized Bi(OA)₃.



The synthesis chemical reaction of BiVO₄ is shown as following:



2.2. Experimental raw materials

All starting materials were used as received without further purification. Bismuth nitrate (Bi(NO₃)₃·5H₂O, AR), sodium metavanadate (NaVO₃, AR), nitric acid (65%, HNO₃, AR), tri-*n*-octylamine ((CH₃(CH₂)₇)₃N, AR) and Oleylamine (C₁₈H₃₅NH₂, AR) were purchased from Shanghai Jingchun Reagent. Octylic acid (C₇H₁₅COOH, AR) was purchased from shanghai Guoyao Reagent. Toluene (C₇H₈, AR), cyclohexane (C₆H₁₂, AR), sodium hydroxide (NaOH, AR) and ethanol (C₂H₅OH, AR) were purchased from Tianjin Hongxing Reagent. Water used in our experiments was of high purity deionized water.

2.3. Synthesis of BiVO₄ particles

2.3.1. Preparation of Bi(OA)₃ complex

First, 1.77 mmol Bi(NO₃)₃·5H₂O was dissolved in 30 ml 1 mol/l HNO₃ solution. With 1.3 g NaOH added into the solution, a white colloid suspension was formed after stirring. Then, 30 ml toluene with amounts of octylic acid was added into above-mentioned solution. A phase transfer process took place after intensely stirring for 30 min. A white colloid Bi(OA)₃ complex suspended in upper toluene was obtained after separating from aqueous phase through separating funnel. Named as solution 1.

2.3.2. Preparation of VO₄(TOA)₃ complex

First, a brown aqueous solution was obtained after 1.77 mmol NaVO₃ was dissolved into 30 ml HNO₃ solution (pH=0.5). Then, 30 ml toluene with amounts of tri-*n*-octylamine was added into the above-mentioned solution. After intensely stirring for 30 min, the color of toluene phase in upper layer changed from colorless to deep brown. The deep brown of VO₄(TOA)₃ complex toluene solution was obtained after separating from aqueous phase through separating funnel. Named as solution 2.

2.3.3. Synthesis of BiVO₄ particles

Solution 1 and solution 2 were mixed to obtain solution 3. Appropriate volumes of solution 3, water and OM were mixed and transferred into 100 ml titanium kettle. The final solution was sealed and autoclaved at different temperatures for 20 h. The obtained products were centrifugal separated and washed twice by cyclohexane and ethanol, respectively. After dried under vacuum conditions at 80 °C for 10 h, vivid yellow

Download English Version:

<https://daneshyari.com/en/article/1460527>

Download Persian Version:

<https://daneshyari.com/article/1460527>

[Daneshyari.com](https://daneshyari.com)