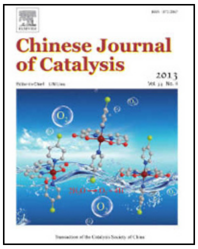
Chinese Journal of Catalysis 34 (2013) 1617–1626

available at www.sciencedirect.com

ScienceDirect

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



Article

Effect of sulfur doping on the photocatalytic performance of $BiVO_4$ under visible light illumination

Zhenxuan Zhao [a], Hongxing Dai [a,*], Jiguang Deng [a], Yuxi Liu [a], Chak Tong Au [b,#]

[a] *Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China*

[b] *Department of Chemistry and Center for Surface Analysis and Research, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong, China*

A R T I C L E I N F O

Article history:
Received 11 March 2013
Accepted 5 June 2013
Published 20 August 2013

Keywords:
Sulfur doping
Bismuth vanadate
Visible-light-driven photocatalyst
Olive-like morphology
Methlyene blue degradation
Formaldehyde degradation

A B S T R A C T

Porous monoclinic bismuth vanadate ($BiVO_{4-\delta}$) and sulfur-doped bismuth vanadates ($BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$) were synthesized by a dodecylamine-assisted alcohol-hydrothermal route in the absence and presence of thiourea or Na_2S. The physicochemical properties of the materials were characterized and their photocatalytic performance for the degradation of methylene blue and formaldehyde under visible light was evaluated. The samples have a single phase monoclinic scheetlite crystal structure with a porous olive-like morphology, surface areas of 8.4–12.5 m^2/g, and bandgap energies of 2.40–2.48 eV. Surface Bi^{5+}, Bi^{3+}, V^{5+}, and V^{4+} species were present on the S-doped $BiVO_{4-\delta}$ samples. Sulfur doping influenced the surface Bi^{5+}/Bi^{3+}, V^{5+}/V^{4+}, and O_{ads}/O_{latt} molar ratios, and the amount of sulfur doped had an important effect on the photocatalytic performance. Under visible light, $BiVO_{4-\delta}S_{0.08}$ performed the best in the photodegradation of methylene blue and formaldehyde. A higher surface oxygen species concentration and a lower bandgap energy were responsible for the excellent visible light photocatalytic performance of $BiVO_{4-\delta}S_{0.08}$.

1. Introduction

Photocatalytic technology is one of the most effective pollution control method. Various kinds of effective and low cost photocatalysts for the degradation of organic pollutants have been investigated. TiO_2 has a large bandgap energy (≥ 3.2 eV) and it is only active under UV light, which is only 4% of the solar energy. In recent years, considerable attention has been paid to the synthesis of visible light-responsive photocatalysts. A number of heteroatoms (N, C, S, or F) and metals (La, Fe, or Cr) were used to dope TiO_2 to make its bandgap energy narrower (to 2.5–3.0 eV). Meanwhile, Ti-free mixed oxide photocatalysts, such as Bi_3NbO_7 [1] and $Bi_2W_2O_9$ [2], with bandgap energies of 2.0–3.8 eV were reported to have high photocatalytic activity for the degradation of organic materials under visible light illumination. $BiVO_4$ is an effective photocatalyst for the splitting of water [3] and the oxidative degradation of rhodamine B (RhB) [4], methyl orange [5], methylene blue (MB) [6], copper acetylacetonate [7,8], 4-alkylphenols [9], and phenol [5].

It is well known that the catalytic performance of a photocatalyst is related to its surface area, crystal structure, oxygen deficiency, pore structure, crystallite size, and particle morphology. Monoclinic scheetlite $BiVO_4$ exhibits a higher photo-

---

* Corresponding author. Tel: +86-10-6739-6118; Fax: +86-10-6739-1983; E-mail: hxdai@bjut.edu.cn

Corresponding author. Tel: +852-3411-7067; Fax: +852-3411-7348; E-mail: pctau@hkbu.edu.hk

The work was supported by the National Natural Science Foundation of China (21077007), the Discipline and Postgraduate Education Foundation (005000541212014), the Funding Project for Academic Human Resources Development in Institutions of Higher Learning under the Jurisdiction of Beijing Municipality (PHR201107104), and Hong Kong Baptist University Foundation (FRG2/09-10/023).

DOI: 10.1016/S1872-2067(12)60632-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 8, August 2013

catalytic activity than its tetragonal zircon and tetragonal scheelite counterparts [10,11], which is because it has a lower bandgap energy (2.4 eV) than they do (2.9–3.1 eV). Hierarchical $BiVO_4/Bi_2O_2CO_3$ nanocomposites have shown good photocatalytic performance in the degradation of RhB due to their unique two-dimensional sheet-like morphology, large surface area, and high crystallinity [12]. The doping of a small amount of a heteroatom X (X = F, N, S) into the lattice of a parent metal oxide can result in the narrowing of the band gap by the hybridization of the X 2*p* and O 2*p* orbitals, thus enhancing the absorption of visible light [13]. Furthermore, the generation of oxygen vacancies from X doping can also enhance photocatalytic activity. For example, the formation of oxygen vacancies in TiO_2 induced by F- and N-doping is the main factor for the enhancement in visible light-responsive catalytic activity [14]. The doping of F^- into the $SrTiO_3$ lattice narrows its band gap and generates Ti^{3+} and oxygen vacancies, hence promoting electron mobility [15].

Many groups have reported the synthesis and photocatalytic applications of S-doped photocatalysts. For example, S-doped TiO_2 exhibited a much higher activity than the N-doped and undoped counterparts [16]. Long et al. [17] found that the S 3*p* orbital is located above the top of the valence band (VB) and it is mixed with the O 2*p* state, thus decreasing the bandgap energy. During their investigation of a S-doped ZnO photocatalyst, Shen et al. [18] observed that the intensity of the UV emission peak decreased with increased S concentration. Li et al. [14] reported that S-doped $In(OH)_3$ was responsive to visible light for the degradation of acetone and dyes. However, there have no reports on the synthesis and photocatalytic applications of S-doped $BiVO_4$ in the literature.

Previously, our group reported the synthesis and physicochemical property characterization of porous and morphological diverse monoclinic $BiVO_4$ samples, such as a porous octapod-like monoclinic $BiVO_4$ for the removal of phenol and MB [19], a porous spherical $BiVO_4$ for the degradation of methyl orange [20], polyhedral, rod-like, leaf-like, and spherical $BiVO_4$ for the degradation of MB [21], three-dimensionally ordered macroporous $BiVO_4$ for the degradation of phenol [22], and flower-, sheet-, and rod-like and spherical $BiVO_4$ for the degradation of methyl orange [23]. In this paper, we report the synthesis and photocatalytic activity of S-doped $BiVO_4$ with a porous olive-like morphology for the degradation of MB and formaldehyde under visible light illumination.

2. Experimental

2.1. Catalyst preparation

Porous olive-like $BiVO_4$ was prepared by the dodecylamine (DA)-assisted alcohol-hydrothermal method [5] using $Bi(NO_3)_3·5H_2O$ and NH_4VO_3 as metal source, DA as surfactant, and ethanol and ethylene glycol (EG) as solvent. Concentrated nitric acid (5 ml) and DA (30 mmol) were added to 25 ml of ethanol and EG (volumetric ratio = 1:1) mixed solution. $Bi(NO_3)_3·5H_2O$ (10 mmol) and NH_4VO_3 (10 mmol) were dissolved in the mixed solution. The pH value was adjusted to 1.5 using NaOH aqueous solution containing absolute ethanol and EG (volumetric ratio = 1:1). The mixture (80 ml) was transferred into a Teflon-lined stainless steel autoclave for alcohol-hydrothermal treatment at 100 °C for 12 h. After washing with deionized water and ethanol and drying at 80 °C overnight, the solid was calcined in air using a ramp of 1 °C/min from room temperature (RT) to 450 °C and kept at this temperature for 4 h, thus obtaining the $BiVO_4$ sample.

The S-doped $BiVO_4$ photocatalysts were synthesized using three methods. One was the DA-assisted alcohol-hydrothermal method. The procedure was the same as for $BiVO_{4-\delta}$ preparation, except that the pH value was adjusted to 1.5 using Na_2S solution containing absolute ethanol and EG (ethanol/EG volumetric ratio = 1:1). The second method was to use uncalcined olive-like $BiVO_4$ soaked in a thiourea aqueous solution ($BiVO_4$/thiourea molar ratio = 1:2) under stirring and then dried at RT. The material obtained was calcined using a ramp of 1 °C/min in a muffle furnace at 300 °C for 2 h and 450 °C for 3 h. The third method was the same as that of the second one, except that the $BiVO_4$/thiourea molar ratio was 1:4. Inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis indicated that the S content was 1.17, 0.49, and 0.78 wt% for the S-doped $BiVO_4$ samples with Na_2S and thiourea ($BiVO_4$/thiourea molar ratios of 1:2 and 1:4) as sulfur source, respectively, i.e., the samples were $BiVO_{4-\delta}S_{0.12}$, $BiVO_{4-\delta}S_{0.05}$, and $BiVO_{4-\delta}S_{0.08}$, respectively.

All chemicals (AR) were purchased from Beijing Chemicals Company and used without further purification.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the $BiVO_4$ and S-doped $BiVO_4$ catalysts were recorded on a Bruker/AXS D8 Advance X-ray diffractometer operated at 40 kV and 35 mA with a Cu K_α X-ray irradiation source (λ = 0.15406 nm). The surface areas were determined by N_2 adsorption at –196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before measurement, the catalyst was degassed at 250 °C for 3 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) was conducted on a Gemini Zeiss Supra 55 apparatus operated at 10 kV. Transmission electron microscope (TEM) images of typical samples were obtained using a JEOL JEM-2010 instrument. X-ray photoelectron spectroscopy (XPS) was used to determine the Bi 4*f*, V 2*p*, O 1*s*, and S 1*s* binding energies (BEs) of surface bismuth, vanadium, oxygen, and sulfur species, respectively, with Mg K_α ($h\nu$ = 1253.6 eV) as the excitation source. Before the XPS measurement, the catalyst was pretreated in an O_2 flow of 20 ml/min at 450 °C for 1 h. After cooling to room temperature, the catalyst was transferred to a holder in a Glove Bag (Instruments for Research and Industry, USA) that was filled with He, and then the holder was transferred into the spectrometer chamber under He. Before being analyzed in the analysis chamber, the pretreated catalyst was outgassed in the preparation chamber for 0.5 h. The C 1*s* signal at BE = 284.6 eV was taken as a reference for BE calibration. The chemical composition of the samples was analyzed using X-ray fluorescence