Applied Surface Science 399 (2017) 10–19

Contents lists available at ScienceDirect

Applied Surface Science

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

Full length article

Enhanced photocatalytic performance of $BiVO_4$ in aqueous $AgNO_3$ solution under visible light irradiation

Chien-Kai Huang[a], Tsunghsueh Wu[b], Chang-Wei Huang[a], Chi-Yung Lai[c], Mei-Yao Wu[d,*], Yang-Wei Lin[a,*]

[a] Department of Chemistry, National Changhua University of Education, Changhua City, Taiwan
[b] Department of Chemistry, University of Wisconsin-Platteville, Platteville, USA
[c] Department of Biology, National Changhua University of Education, Changhua, Taiwan
[d] Research Centre for Traditional Chinese Medicine, Department of Medical Research, China Medical University Hospital, Taichung City, Taiwan

ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form 5 December 2016
Accepted 5 December 2016
Available online 7 December 2016

Keywords:
$BiVO_4$
$AgNO_3$ solution
Photoreduction
Visible-light-induced degradation
Disinfection
Ag^+ sensing

ABSTRACT

Monoclinic-phase bismuth vanadate ($BiVO_4$) with a 2.468 eV band gap exhibited enhanced synergic photodegradation activity toward methylene blue (MB) when combined with silver ions (Ag^+) in an aqueous solution under visible light irradiation. The mass ratio of $AgNO_3$ to $BiVO_4$ and the calcination temperature were discovered to considerably affect the degradation activity of $BiVO_4/Ag^+$. Superior photocatalytic performance was obtained when $BiVO_4$ was mixed with 0.01%(w/v) $AgNO_3$ solution, and complete degradation of MB was achieved after 25 min visible light irradiation, outperforming $BiVO_4$ or $AgNO_3$ solution alone. The enhanced photodegradation was investigated using systematic luminescence measurements, electrochemical impedance spectroscopy, and scavenger addition, after which a photocatalytic mechanism for MB degradation under visible light irradiation was identified that involved oxygen radicals and holes. This study also discovered the two dominating processes involved in enhancing the electron–hole separation efficiency and reducing their recombination rate, namely photoreduction of Ag^+ and the formation of a $BiVO_4/Ag$ heterojunction. The synergic effect between $BiVO_4$ and Ag^+ was discovered to be unique. $BiVO_4/Ag^+$ was successfully used to degrade two other dyes and disinfect *Escherichia Coli*. A unique fluorescent technique using $BiVO_4$ and a R6G solution to detect Ag^+ ions in water was discovered.

1. Introduction

Using semiconductor-based photocatalysts to degrade pollutants under visible light irradiation is a promising technique for treating wastewater containing organic dyestuffs [1,2]. Among all investigated photocatalytic semiconductors, bismuth vanadate ($BiVO_4$) is the most promising visible-light-responsive photocatalyst with a narrow band gap of 2.4 eV [3]. Previous studies have successfully synthesized and utilized $BiVO_4$, reporting that it is suitable for the photodegradation of organic pollutants and photocatalytic O_2 evolution under visible light irradiation [4–8]. Liu et al. demonstrated solvothermal synthesis of nanostructured $BiVO_4$ with a highly exposed (010) facet, which achieved 97% methylene blue (MB) degradation under sunlight irradiation within 4 h [4,5]. Zhu et al. discovered a template-free hydrothermal synthesis route for production of a visible-light-responsive $BiVO_4$ photocatalyst that degraded 98% MB within 150 min [9]. Wang et al. reported that a $BiVO_4$ photocatalyst synthesized using solution combustion degraded 99.2% rhodamine B (RhB) under visible light irradiation within 4 h [10]. Evidently, utilizing $BiVO_4$ alone to treat polluted water is not efficient because it requires a long time to degrade dyes. This is due to its low photocatalytic activity caused by inefficient separation of electron–hole pairs. Thus, an innovative strategy to enhance the photocatalytic efficiency of $BiVO_4$ is greatly needed for improving visible-light-activated wastewater treatment techniques [11,12].

Previous reports have revealed that combining $BiVO_4$ with Ag enhances the separation efficiency of photogenerated electron–hole pairs [13–16]. Hu et al. demonstrated a facile and novel dual-ion-exchange method together with visible-light-induced reduction for the synthesis of mesoporous $BiVO_4/Ag/AgCl$ heterostructures that exhibited high photocatalytic activity for methyl orange degradation under visible light illumination (95.4% degradation within 60 min) [17]. The preparation of these heterostructures involved a complicated and time-consuming

---

* Corresponding authors.
E-mail addresses: meiyaowu0919@gmail.com (M.-Y. Wu), linywjerry@cc.ncue.edu.tw (Y.-W. Lin).

http://dx.doi.org/10.1016/j.apsusc.2016.12.038

four-step process of solvothermal treatment (140 °C for 8 h), ion-exchange (25 °C for 4 h), calcination (400 °C for 2 h), and visible light reduction (25 °C for 2 h). Another synthesis strategy involved two hydrothermal processes and yielded Ag nanoparticles decorated with hollow $BiVO_4$ microspheres [18]. These $BiVO_4$/Ag composite microspheres photodegraded 99% of rhodamine 6G (R6G) under visible light irradiation within 60 min. Yin et al. reported a single-step solvothermal method for preparing hollow Ag/$BiVO_4$ composites with large surface areas and high photocatalytic activity that degraded more than 98% of MB in 100 min [19]. Finally, Xu et al. reported a series of metallic silver and graphene (GR) codoped $BiVO_4$ ternary systems (Ag/GR/$BiVO_4$) synthesized using a single-step solvothermal method [12]. Their prepared photocatalysts exhibited significantly high photocatalytic activity and achieved complete degradation of RhB under visible light irradiation within 120 min. However, these photocatalysts still required more than 1 h to degrade dyestuffs. Table 1 summarizes these different Ag/$BiVO_4$-based photocatalysts, including their synthesis method, catalytic performance, and target dye molecule.

Herein, we report another strategy to degrade dyestuffs under visible light irradiation within one hour. Monoclinic-phase $BiVO_4$ was prepared in a single step under hydrothermal conditions (180 °C, 24 h). The photocatalytic performance of $BiVO_4$ and its synergy with an optimal concentration of Ag^+ ions was evaluated based on the degradation kinetics of MB. To the best of our knowledge, no study related to the silver ion–enhanced photocatalytic performance of $BiVO_4$ (denoted hereafter as $BiVO_4/Ag^+$) has been published. We also propose a possible photocatalysis mechanism based on experimental observations that clarify how MB is degraded. Finally, we report a novel way to detect Ag^+ ions in water through the use of $BiVO_4$ and R6G.

2. Material and methods

2.1. Chemicals

All chemicals used were analytical reagent grade. All solutions were prepared using ultrapure water, which was obtained from a Milli-Q water system manufactured by Millipore (Illinois, USA). High-performance liquid chromatography–grade methanol, ethanol, and *tert*-butanol (t- BuOH) were purchased from Merck Millipore (Massachusetts, USA). $AgNO_3$, $Bi(NO_3)_3{\cdot}5H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, NaCl, $CaCl_2{\cdot}2H_2O$, $Sr(NO_3)_2$, $BaCl_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $FeCl_3$, $FeCl_2$, $HgCl_2$, $Cu(NO_3)_2{\cdot}2{\cdot}5H_2O$, $HAuCl_4{\cdot}3H_2O$, $PtCl_4$, KCl, NH_4VO_3, 1,2-diaminoethane, NaOH, ethylenediamine tetraacetic acid (EDTA), tri-ethanol amine (TEOA), *p*-benzoquinone, and HNO_3 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dyestuffs (MB, RhB, and R6G) were purchased from Invitrogen (Eugene, OR, USA).

2.2. Preparation

$BiVO_4$ was prepared using a hydrothermal method described previously [9] with a slight modification. First, $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 at a molar ratio of 1:1 were mixed in a beaker. Ultrapure water (39.6 mL), 1 M HNO_3 (10 mL), and 1,2-diaminoethane (0.4 mL) were added to the beaker, and the mixture was stirred with a magnetic stirring bar at 25 °C for 10 min. The resulting yellow precipitate was transferred to a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 24 h. After three centrifugation-and-washing cycles alternated with ultrapure water and ethanol washing, the solution was oven dried at 50 °C for 5 h. A yellow $BiVO_4$ solid was thus obtained.

2.3. Photodegradation activity

The MB photodegradation activity of $BiVO_4$ and $BiVO_4/Ag^+$ under visible light illumination ($\lambda > 420$ nm, 70 W/cm^2) was evaluated using a Xe lamp. In the experiments, a fixed amount of photocatalyst (0.0500 g) was added to an aqueous MB solution (50 mL, 10 ppm) at 25 °C that did or did not contain 0.01%(w/v) $AgNO_3$. To ensure an adsorption–desorption equilibrium, the mixture was stirred in the dark for 30 min prior to the commencement of visible light illumination. The mixture was stirred with a magnetic stirring bar during the illumination, and at fixed time intervals an aliquot of the solution (1.000 mL) was sampled from which a trace amount of the photocatalyst was removed by centrifugation.

Table 1
Comparison of photocatalytic properties and practical applications of different Ag/$BiVO_4$-based photocatalysts.

Photocatalyst	Synthesis method	Photocatalytic activity ($\lambda > 420$ nm)	Target	Ref.
Ag-$BiVO_4$	Wet impregnation method	86% degradation (0.2 g photocatalyst/15 mgL^{-1} MB) within 8 h (100 W)	MB	[14]
$BiVO_4$/Ag/AgCl	Hydrothermal process/dual ion exchange reaction	95.4% degradation (5 mg photocatalyst/10 mgL–^{1} MO) within 60 min (500 W)	MO, phenol	[17]
$BiVO_4$/Ag	Hydrothermal process	99% degradation (50 mg photocatalyst/2 × 10^{-5} M R6G) within 60 min (500 W)	R6G	[18]
Ag/$BiVO_4$	Solvothermal process	98% degradation (50 mg photocatalyst/2 × 10^{-5} M MB) within 100 min (350 W)	MB	[19]
Ag/GR/$BiVO_4$	Solvothermal method	>99% degradation (150 mg photocatalyst/10 mgL^{-1} RhB) within 120 min (300 W)	RhB	[12]
$BiVO_4$@C/Ag	Hydrothermal process/*in situ* reduction method	95% degradation (50 mg photocatalyst/10 mgL^{-1} RB) within 6 h (150 W)	RhB	[23]
Ag doped $BiVO_4$	Metal decomposition/photoreduction method	94% elimination efficiency of phenol within 4 h (150 W/1.0 V)[a]	Phenol	[34]
Ag/$BiVO_4$	Hydrothermal process	75% degradation (0.2 g photocatalyst/10 mgL^{-1} MO) within 240 min (500 W)	MO	[35]
$BiVO_4/Ag^+$	Hydrothermal process	99% degradation (50 mg photocatalyst/10 ppm MB) within 30 min (150 W)	MB, RhB, R6G	This study
Used $BiVO_4/Ag^+$	Hydrothermal process	90% disinfection (5 mg photocatalyst/10^{8} cfumL^{-1} cells) within 60 min (150 W)	*E. Coli*	This study

[a] Photoelectrocatalytic process.