Applied Catalysis B: Environmental 221 (2018) 97–107

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Research paper

Hierarchical Z-scheme photocatalyst of g-C_3N_4@Ag/$BiVO_4$ (040) with enhanced visible-light-induced photocatalytic oxidation performance

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ARTICLE INFO

Keywords:
Facets
G-C_3N_4@Ag/$BiVO_4$
Z-Scheme
Photoatalytic oxidation

ABSTRACT

The preferred exposure of (040) crystal facet of $BiVO_4$ is conductive to optimizing its photocatalytic performance. And the great separation of photoinduced electron-hole pairs is also a critical factor for semiconductor photocatalyst. Herein we designed a hierarchical g-C_3N_4@Ag/$BiVO_4$ (040) hybrid photocatalyst, in which Ag was photodeposited on the (040) facets of $BiVO_4$ and subsequently g-C_3N_4 was covered on the surface of Ag/$BiVO_4$ (040). The physical and chemical properties of the synthetic samples were analyzed by several characterization techniques. SEM spectrum clearly reveals the morphology and structure of g-C_3N_4@Ag/$BiVO_4$ (040), suggesting the existence of the hierarchical composite photocatalyst. The visible light absorption wavelength of the composite is increased due to the surface plasmon resonance (SPR) effect of metal Ag nanoparticles, displayed in UV–vis spectrum. The photogenerated electron-hole pairs are also greatly enhanced through the Z-scheme g-C_3N_4@Ag/$BiVO_4$ (040) system with the Ag nanoparticles as the electron mediator. The above synergistic effects of the hybrid photocatalyst result in higher photocatalytic oxidation performance not only for water splitting but also for NO oxidation in gas phase compared with pure $BiVO_4$.

1. Introduction

Semiconductor heterogeneous photocatalysis has been received keen interest in recent years to solve global energy crisis and natural environments deterioration [1,2]. The development of highly active photocatalysts remains a huge undertaking. Previously, we reported the monoclinic $BiVO_4$ with strong photo-oxidation properties, which could efficiently oxidize high concentration NO (~400 ppm) with the help of H_2O_2 under visible light irradiation [3,4]. The strong oxidizing property of $BiVO_4$ is ascribed to its positive valence band value (E_{VB} = 2.7 eV) [5]. The excellent property triggers us to investigate its effects on the oxidation of water to produce O_2 (E_0 (H_2O/O_2) = 1.23 eV) [6] and NO in flue gas to NO_3^- (E_0 (HNO_3/NO) = 0.94 eV) [7] under visible light irradiation, making the material possess versatility.

Theoretical and experimental research have demonstrated that the surface of monoclinic $BiVO_4$ (040) facets can provide more multi-atomic centers BiV_4, which is the origin of the multi-electron transfer and then served as active sites in the photocatalytic reaction [8]. Thus, it's worth constructing the $BiVO_4$ material with a high proportion of (040) facets. However, the photocatalytic performance of the single $BiVO_4$ can be also limited by its low separated rate of photogenerated charge carriers. In order to resolve this problem, many efforts such as doping with nonmetallic [9], combined with graphene [10,11] and constructing heterojunctions [12–14] with two semiconductors have been carried out. Therein, the heterojunction photocatalyst usually displays the higher photoactivity since it is able to facilitate the separation of photogenerated charge carriers to a large extent, and then leaving more electrons and holes participating in the photocatalytic reaction.

Among the numerous heterojunction photocatalysts, the Z-scheme photocatalytic system possesses the potential to achieve larger separation ratio of photo-induced electrons and holes. Generally speaking, the artificial heterogeneous Z-scheme consists of two different semiconductor photocatalysts with suitable band gaps and an electron mediator. In recent years, the noble-metal, such as Au, Pt and Ag were mainly adopted as the electron mediator to transport electrons to improve the photoactivity [15–18]. Zhao et al. constructed an all-solid-state g-C_3N_4/Au/P25 Z-scheme photocatalyst for visible-light-driven H_2

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http://dx.doi.org/10.1016/j.apcatb.2017.09.005
Received 2 March 2017; Received in revised form 5 July 2017; Accepted 4 September 2017
Available online 09 September 2017
0926-3373/

evolution, and the Z-scheme sample exhibited higher photocatalytic performance with respect to pure g-C_3N_4. It was attributed to the effective electron transfer and separation rate of photo-induced electron-hole pairs caused by the vectorial electron transfer of P25 → Au → g-C_3N_4 [17]. The Z-scheme $BiVO_4$-Ru/$SrTiO_3$:Rh photocatalyst was synthesized for water splitting under visible light irradiation, which also displayed higher photocatalytic performance than the single component [14]. g-C_3N_4 is also a narrow band gap semiconductor with the CB position at ca. −1.3 eV and the VB position at ca. 1.4 eV vs NHE, which can match well with the $BiVO_4$ with exposed (040) facets to form an Z-scheme photocatalytic system [19,20]. In addition, Ag as relatively cheap noble metal can usually be selected as the "linker" to shuttle the electrons between the two semiconductor components in Z-scheme [18,21]. Up to now, some studies about the g-C_3N_4/Ag/$BiVO_4$ ternary composite [22,23] have been reported, but relative reports about the $BiVO_4$ (040)-based ternary materials were quietly scarce. And in the application filed, the g-C_3N_4/Ag/$BiVO_4$ photocatalysts were usually used in the aqueous phase for decomposition and decolorization of organics, and few ternary composite photocatalyst was used for photocatalytic water oxidation to O_2 and photocatalytic oxidation of NO in gas phase to NO_3^-.

Herein, the g-C_3N_4@Ag/$BiVO_4$ (040) sample was synthesized in this work to construct a hierarchical hybrid photocatalyst, in which the linker metal Ag was photo-deposited on the (040) crystal facet of $BiVO_4$ and the g-C_3N_4 prepared by supramolecular method was wrapped the Ag/$BiVO_4$ (040) by a facile reflux method. The photocatalytic performance of the g-C_3N_4@Ag/$BiVO_4$ (040) composite was focused on photocatalytic oxidation of water to O_2 and NO in gas phase to NO_3^-. The photocatalytic properties of the hierarchical hybrid photocatalyst were also evaluated by the structure, electronic environment and optical properties. The enhanced ability of the photocatalytic oxidation was remarkable, and reasons were discussed. As well, in this paper, the detailed mechanism of the photocatalysis over Z-scheme g-C_3N_4@Ag/$BiVO_4$ (040) sample was also further clarified and discussed.

2. Experimental

2.1. Preparation of g-C_3N_4@Ag/$BiVO_4$ (040) hybrid photocatalyst

2.1.1. Preparation of $BiVO_4$ sample

$BiVO_4$ sample with dominant exposed (040) facets was synthesized by a previously reported method [24]. Typically, 6 mmol Bi$(NO_3)_3$·$5H_2O$ was well dispersed into HNO_3 (2 mol/L, 13.5 mL) aqueous solution under vigorous stirring until a clear solution was formed (A). Meanwhile 6 mmol NH_4VO_3 was dissolved in HNO_3 (2 mol/L, 36.5 mL) aqueous solution with ultrasonic process to form a yellowish orange transparent solution (B). Subsequently, the B solution was added dropwise into the A solution with mechanical agitation. The pH value was adjusted into about 2 by the NH_3·H_2O and subsequently the salmon precipitation was observed. After being stirred for 30 min, the precursor solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 200 °C and autogenous pressure for 24 h. After the autoclave was cooled down to room temperature, the precipitation was collected by centrifugation, washed by deionized water and absolute alcohol for several times, and then dried at 80 °C overnight. The product obtained was denoted $BiVO_4$.

2.1.2. Photo-deposition of Ag on $BiVO_4$ (040) facets

The photoexcited electrons of $BiVO_4$ photocatalyst under light irradiation have been

demonstrated to be driven to (040) facets of $BiVO_4$ [24]. Here, the photo-deposition of the Ag on (040) facets of $BiVO_4$ was achieved with $AgNO_3$ as the precursor, methanol was employed as the hole scavenger. Typically, $BiVO_4$ (0.4 g), $AgNO_3$ (12.6 mg) and 4 mL methanol was successively added to 40 mL deionized water under magnetic stirring. Subsequently, the obtained yellow mixture was irradiated by 350 W Xe light ($\lambda > 420$ nm) for 2 h. The color of the solution turned form vivid yellow to grayish-green, which suggested the generation of Ag species in reaction system. Finally, the obtained 2 wt% Ag/$BiVO_4$ product was centrifuged and dried at 80 °C at vacuum oven for overnight. Then the nominal 1 wt% Ag/$BiVO_4$ and 3 wt% Ag/$BiVO_4$ photocatalysts were also prepared. If there is no special requirement, Ag/$BiVO_4$, as it mentions in the paper, refers to 2 wt% Ag loading on the surface of $BiVO_4$ (040) facets.

2.1.3. Preparation of g-C_3N_4@Ag/$BiVO_4$ (040) sample

The floccular g-C_3N_4 was synthesized as follows: 0.8 mmol cyanuric acid, 0.4 mmol melamine and 0.4 mmol 2,4-diamino-6-methyl-1,3,5-triazine were mixed in 100 mL deionized water, and vigorously stirred for 12 h to make sure a reiterative dynamic dissolution to allow the formation of crystalline supramolecular complex. Then the milky suspension was centrifuged and washed with deionized water several times. The resulting powders were dried at 60 °C overnight under vacuum conditions and calcined at 550 °C for 4 h at a heating rate of 2 K min^{-1} under N_2 atmosphere.

The g-C_3N_4@Ag/$BiVO_4$ (040) sample was prepared by a reflux method. An appropriate amount of floccular g-C_3N_4 and Ag/$BiVO_4$ (040) sample were added to 50 mL deionized water, and then the mixture was obtained by a reflux reaction at 90 °C for 3 h. The obtained g-C_3N_4@Ag/$BiVO_4$ (040) photocatalyst was washed with water, and finally dried in an oven at 80 °C overnight. The obtained photocatalysts with different mass ratios of g-C_3N_4 were named as 50% g-C_3N_4@Ag/$BiVO_4$, 100% g-C_3N_4@Ag/$BiVO_4$ and 150% g-C_3N_4@Ag/$BiVO_4$. And unless otherwise noted, g-C_3N_4@Ag/$BiVO_4$, as it appears in the paper, represents the 100% g-C_3N_4@Ag/$BiVO_4$ sample. The photocatalyst g-C_3N_4@$BiVO_4$ was also prepared via the same process, but replacing Ag/$BiVO_4$ with $BiVO_4$.

2.2. Characterizations

The structural and chemical information for prepared samples were measured by X-ray diffraction (XRD, Cu Kα, Purkinjie XD-3), Fourier transform infrared (FT-IR) spectroscopy (Nicolet IS10, USA), Field-emission scanning electron microscope (SEM, FEI Quanta 250F), Brunauer-Emmett-Teller (BET, Quantachrome, autosorb IQ), X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA), UV–vis diffuse reflectance spectrum (DRS, Shimadzu UV-2600), Photoluminescence spectrum (PL, He-Cd laser, Labram-HR800), Electron paramagnetic resonance (EPR, Bruker EMX-10/12-type spectrometer).

The Mott-Schottky measurements were performed on a CHI 760D electrochemical workstation (shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, a Pt wire as counter electrode, and a standard Ag/AgCl in saturated KCl as reference electrode. An aqueous solution of 0.5 mol/L Na_2SO_4 (pH 6.8) was used as electrolyte and purged with N_2 prior to each experiment. The working electrode was prepared by dip-coating: 10 mg photocatalyst was added into 1 mL ethyl alcohol and 50 μL Nafion solution to form slurry, and then dip-coated onto a 1 cm × 1 cm FTO glass electrode. Subsequently, the films were dried at 80 °C overnight and calcined at 180 °C for 2 h at N_2 atmosphere. The variations of photoinduced current density with time (*i–t* curve) and electrochemical impedance spectroscopies (EIS) were measured with a 350 W Xe light (with 420 nm filter) as the light source and 0.5 mol/L Na_2SO_4 as the electrolyte.

2.3. The photocatalytic oxidation reaction

2.3.1. The photocatalytic water oxidation

The photocatalytic O_2 evolution tests (Labsolar-III AI, Perfect Light, China) were carried out in $NaIO_3$ aqueous solution under visible light from 350 W Xe light equipped with a 420 nm cut filter. In each experiment, 90 mg photocatalyst was dispersed in 90 mL $NaIO_3$ aqueous solution (0.2 M) in a 200 mL reactor with a top widow made of Pyrex at