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Full Length Article

Controlled synthesis of Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ heterostructures with enhanced photoelectrochemical activity toward the dye degradation

Junqi Li*, Jian Zhou, Hongjuan Hao, Weijie Li

School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, PR China

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ABSTRACT

Crystal facet dependence is an important approach for optimizing the performance of photocatalyst. In consideration that there is a close correlation between the photoelectric conversion efficiencies and crystal facet, the monoclinic bismuth vanadate (m-$BiVO_4$) with (010) and (110) crystal facets has drawn attention. We designed the Ag nanoparticles modified the (010) facet of the $BiVO_4$ (Ag-$_{010}$BiVO$_4$) and then the Ag-$_{010}$BiVO$_4$ heterogeneous nanostructure was modified by the Fe_2O_3 nanoparticles. In the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$, the (110) facet of the $BiVO_4$ was only modified by the Fe_2O_3 nano-particles to construct the n-n heterojunction structure. Simultaneously, the Z-scheme system was fabricated on the (010) facet of the $BiVO_4$, where was modified by the Ag and Fe_2O_3 nano-particles. We investigated its photoelectrochemical (PEC) and photocatalytic activities by the measurement of the electrochemical performance and degradation of methyl orange (MO). The Ag species in the system is only treated as the solid state electron mediator. As was expected, the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ heterojunction structure exhibited the highest photocurrent density and the smallest impedance. Besides, the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ heterojunction structure exhibited excellent redox ability and the MO could be degraded 92% after 150 min. It is worth noting that the outstanding performance should be attributed to the synergistic effect of n-n and Z-scheme system in the different facets, which facilitated the separation of holes and electrons in the opposite direction.

1. Introduction

With the research of controllable crystal facets [1], lots of investigations have been conducted on the dependence of reactivity, in particular PEC, on the exposed crystal facets of materials [2,3]. Recently, the $BiVO_4$ with exposed specific (010) and (110) facets were synthesized and affirmed that the valence band edge and conduction band edge of the (110) facet were slightly higher than its (010) facet [4–12]. The photogenerated electrons and holes can be separated on (010) facet ($_{010}$BiVO$_4$) and (110) facet ($_{110}$BiVO$_4$), respectively, with reduction and oxidation reactions occurring separately on each facet. (Eq. (1)) [9,13].

$$BiVO_4 + hv \rightarrow e^-({}_{010}BiVO_4) + h^+({}_{110}BiVO_4) \quad (1)$$

Thus, the exposed specific facet of the $BiVO_4$ exhibits the considerable advantages with enhanced photoelectrochemical activity toward the dye degradation. However, in this single-component photocatalyst, the photo-generated electrons can recombine with the holes due to the electrons in the conduction band (CB) easily return to the valence band (VB).

Given the above facts, the specific facets of $BiVO_4$ with different energy band levels are supposed to play key roles in affecting the performance of the heterojunctions materials [5]. Over the past years, the metal-doped coupled-semiconductor [9,13], Z-scheme [14,15] and n-n heterojunction [16] were investigated and designed, which greatly overcome the drawbacks of single-component photocatalyst [17–22]. Yan et al. [16] constructed the n-n junction Ag_3PO_4/Fe_2O_3 heterogeneous nanostructures which tremendously enhanced the separation efficiency of the photon-generated carrier. Fe_2O_3, an n-type photocatalyst with narrow band gap and wide absorption range, can form the n-n heterogeneous nanostructures with the Monoclinic $BiVO_4$. Because the flat band potential (which corresponds to the position of the Fermi level [23]) of Fe_2O_3 is more negative than that of $BiVO_4$, the electrons keep on flowing from the Fe_2O_3 to $BiVO_4$ until the Fermi levels become coincident [24]. As a result, the electron and hole

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* Corresponding author.
E-mail address: sfmlab@163.com (J. Li).

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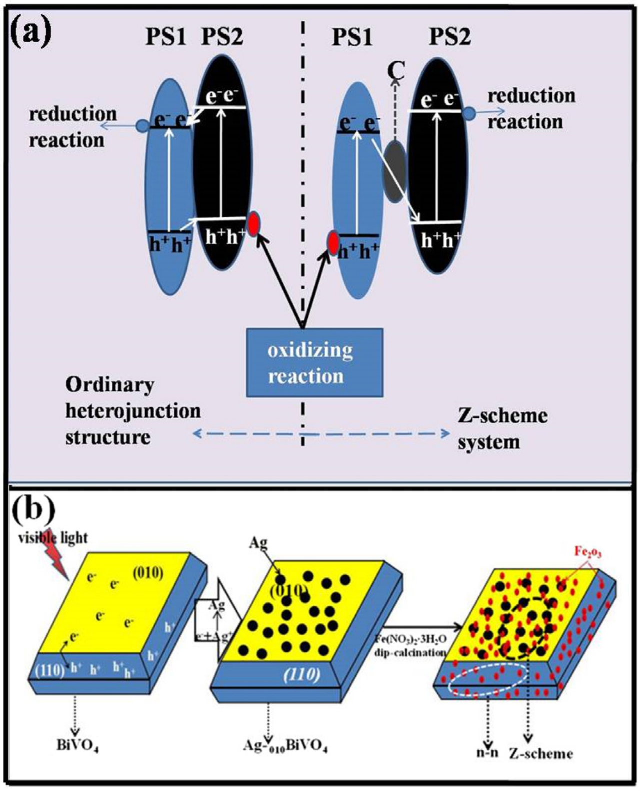

Scheme 1. (a) Schematic illustration of the redox ability about ordinary heterojunction structure and Z-scheme, (b) Schematic illustration of the formation of Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ sample.

accumulate in the BiVO$_4$ and the Fe_2O_3 region, respectively [25]. Similar to the n-n heterojunction-type photocatalytic system, the Z-scheme photocatalytic system also features the spatial isolation of photo-generated electrons and holes, which reduces the bulk electron-hole recombination [14]. The exposed facet of BiVO$_4$ is getting more and more attention to construct the Z-scheme photocatalytic system with strong redox ability and has a noticeable light absorption capability in the visible-light region. Zhou et al. [14,9] reported an All-solid-state Z-scheme system which exhibited higher photocatalytic efficiency and strong redox ability. In the Z-scheme, the conductor (Au, Ag, Pt) forms the Ohmic contact with low contact resistance and can acted as an electron transfer mediator [14]. It was reported that the photo-generated electrons in the CB of the photocatalyst1 (PS1) could transfer from the conductor (C) to recombination with the holes left in the VB of the photocatalyst2 (PS2) (Scheme 1a). Afterwards, the electrons and holes (n-n, p-n heterojunction) would leave in the CB of the PS2 and VB of the PS1. As a result, the Z-scheme can realize the effective separation of and low recombination of the photo-generated electrons and holes. It's worth noting that the Z-scheme can enhance the redox ability compared with the conventional heterojunction structure (Scheme 1a).

In this study, an n-n-Z system was constructed to overcome the aforementioned weaknesses and achieved the wide absorption range, high charge-separation efficiency and strong redox ability. It was worth pointing out that the Z-scheme system was constructed in the $_{010}$BiVO$_4$ and n-n heterogeneous nanostructures was formed in the $_{110}$BiVO$_4$. The PEC and photocatalytic activity of the prepared Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ heterogeneous composite was studied under visible light irradiation. Detailed mechanism about the PEC of this Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ heterostructure was further proposed. Such distinctive n-n-Z-scheme system has got over the weakness of the aforementioned and realized the high charge-separation efficiency and strong redox ability.

2. Experimental

2.1. The design of the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ n-n-Z system based on the BiVO$_4$

Scheme 1(b) exhibited the schematic illustration for the conception of the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ n-n-Z system. The mainly exposed crystal facets of BiVO$_4$ are made up of two kinds facets, which denotes as (010) and (110) in the light of Li's report [9,12]. The photogenerated electrons and holes can separate on the (010) and (110) facet, respectively, due to their different energy levels in the CB and the VB of these facets [26,27]. On account of this finding, the reduction reaction ($e^- + Ag^+ = Ag$) could take place and the Ag nano particles were selectively deposited on the (010) facet and successfully formed the Ag-$_{010}$BiVO$_4$ sample. The VB = +2.48 eV and CB = +0.28 eV of Fe_2O_3 [28] were more negative than the BiVO$_4$ (VB = +2.75∼ + 2.78 eV and CB = +0.31∼ + 0.32 eV) [29–31], respectively. Thus, the BiVO$_4$ can form the n-n heterojunction structure with Fe_2O_3 nano-particles. The surface of the Ag-$_{010}$BiVO$_4$ was modified by the Fe_2O_3 nano-particles through the impregnation calcination. As a result, the Ag and Fe_2O_3 nano-particles exist in the (010) facet of the BiVO$_4$, on which the Z-scheme system was constructed. Besides, only Fe_2O_3 nano-particles exist in the (110) facet of BiVO$_4$, where the n-n heterojunction structure was formed. Both the n-n heterojunction and Z-scheme system may be increase the transfer channel of the photo-induced electrons and holes. Besides, the Z-scheme in the Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ system can enhance the redox ability.

2.2. Preparation of BiVO$_4$ sample

BiVO$_4$ nanocrystals with dominant exposed specific (010) and (110) fact was prepared according to the previous literature [27]. In detail, 5 mmol $NaVO_3 \cdot 2H_2O$ was added to 20 mL of 2 M NaOH solution under magnetic stirring, and 5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 20 mL of 2 M nitric acid solution, respectively. The two mixtures were stirred for 30 min and subsequently mixed together. Successively, 2 mL glacial acetic acid was dropped to the mixed solution and stirred for 1 h. The mixed solution was transferred into the 100 mL Teflon-lined stainless-steel autoclave maintaining at 180 °C for 24 h. A yellow powder was filtered and washed by water and ethanol for several times, and then dried at 60 °C overnight in a vacuum oven.

2.3. Synthesis of Ag-$_{010}$BiVO$_4$ sample

A photo-deposition procedure in which Ag nanoparticles were used to decorate the BiVO$_4$ on their (010) crystal facet was proposed. The BiVO$_4$ powder was added to ethanol followed by the addition of $Ag(NO_3)_3$ (4 mM). The obtained mixture was vigorously stirred for 3 h with irradiation using 500 W Xe lamp. The Ag-BiVO$_4$ were collected through centrifugation and washed several times with distilled water in order to remove any remaining impurities and finally dried at 60 °C for 12 h in vacuum.

2.4. Synthesis of Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ sample

The n-n-Z-scheme Fe_2O_3 modified Ag-$_{010}$BiVO$_4$ composite was synthesized using impregnation-calcination technique: First of all, 0.5 g Ag-BiVO$_4$ was dispersed in 300 mL distilled water, 0.05 g $Fe(NO_3)_2 \cdot 3H_2O$ was added to the above suspension. The mixed suspension was evaporated (about 8 h) in a water bath at 80 °C. Then the mixture was calcined at 150 °C for 3 h to obtain the Fe_2O_3