



Photocatalytic properties of the g-C₃N₄/ {010} facets BiVO₄ interface Z-Scheme photocatalysts induced by BiVO₄ surface heterojunction

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ABSTRACT

The g-C₃N₄/ {010} facets BiVO₄ interface Z-scheme photocatalysts is fabricated by ultrasonic dispersion method. The density functional theory (DFT) shows that the differences of the energy levels in the conduction bands and the valence bands between the {010} and {110} facets of BiVO₄ is about 0.37 and 0.31 V (vs. NHE, pH = 7), respectively. Therefore, the co-exposed {010} and {110} facets of BiVO₄ can form surface heterojunction, which promotes the {010} facets of BiVO₄ with negative charge. The zeta potential indicates that layered g-C₃N₄ with positive charge. The Raman, FT-IR and XPS analysis demonstrates that the layered g-C₃N₄ is anchored on the {010} facets of BiVO₄ through strong interface electrostatic interaction, which leads to form a built-in electric field at the contact interface. Under the built-in electric field driving, photogenerated electrons in the CB of {010} facets of BiVO₄ rapidly recombines with the holes in the VB of g-C₃N₄ to form the interface Z-scheme heterostructure. That is, BiVO₄ surface heterojunction ultimately induces the formation of interface Z-scheme heterostructure. The interface Z-scheme heterostructure not only facilitates the space separation of the photo-generated carriers, but also accumulates electrons in the more negative potentiated CB of g-C₃N₄ and holes in the more positive VB of {110} facets of BiVO₄. Consequently, by means of the I-t, LSV and EIS measurements, the g-C₃N₄/ {010} facets of BiVO₄ interface Z-scheme photocatalysts presents extraordinary photoelectrochemical performance. More importantly, the degradation rate of g-C₃N₄/ {010} facets of BiVO₄ interface Z-scheme photocatalysts can reach the highest 88.3% within 30 min under visible light irradiation, and the mineralization ability (96.03%) is about 2.24 and 3.32 times as high as that of BiVO₄ (42.83%) and g-C₃N₄ (28.89%), respectively.

1. Introduction

With increasing environmental pollution and energy crises, semiconductor-based heterogeneous photocatalysis has attracted worldwide attention due to its application in solar energy conversion and environmental remediation [1–3]. However, the rapid recombination and weak redox ability of photogenerated carriers result in low photocatalytic efficiency and limit its practical applications. Therefore, the key to improving the photocatalytic performance is to overcome the aforementioned problems [4].

Recent investigations on crystal facet engineering of semiconductors have proved that the exposed highly active crystalline facets of semiconductors can promote the photocatalytic activity. Li et al. demonstrated that effective charge separation could be achieved on different

crystal facets of BiVO₄, and the photoinduced electrons and holes could migrate to {010} and {110} facets, respectively [5]. Yu et al. also reported that the {110} and {001} facets of anatase TiO₂ could form “surface heterojunctions” due to the different band structures and edge positions, which facilitated the effective separation of photogenerated carriers, and the enhanced photocatalytic activity [6]. However, for the single-component photocatalyst, the photo-excitation and separation process of the photo-induced electron-hole pairs on the same semiconductor, and carriers are apt to be bulk phase recombination. Compared with the single photocatalysts, the heterojunction photocatalysts usually display a higher photocatalytic activity because of the space separation of photogenerated electrons and holes [4].

The semiconductor heterostructures primarily include metal dopants, P-N heterojunctions and Z-scheme heterojunctions [7,8]. Among

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them, Z-scheme heterostructures not only facilitate the effective spatial separation of photo-induced electron-hole pairs, but also enhance the redox ability of photocatalysts due to the increase in redox potential [4]. Therefore, the Z-scheme heterojunction photocatalyst has a good development potential.

The monoclinic BiVO_4 is a visible-light active photocatalyst with a narrow band gap of 2.40 eV. However, the photocatalytic ability of pure BiVO_4 is still not impressive because of the poor carrier transport properties and excessive recombination [9]. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has a good chemical stability and a large specific surface area due to its two-dimensional layered conjugate structure [10]. The $\text{g-C}_3\text{N}_4$ with a band gap of 2.7 eV and the photogenerated electrons in the CB of $\text{g-C}_3\text{N}_4$ possess strong reduction ability. Adversely, the holes with the low oxidant ability in the VB of $\text{g-C}_3\text{N}_4$ are not enough to oxidize OH^- to hydroxyl radicals reported by Wang et al [11]. Therefore, the photocatalytic performance of $\text{g-C}_3\text{N}_4$ is limited.

In order to improve the photocatalytic performance of BiVO_4 semiconductor-based photocatalyst, BiVO_4 hybridized $\text{g-C}_3\text{N}_4$ has attracted extensive attention due to the matching band edge position [12–14]. However, the Z-scheme heterostructure composed of the layered $\text{g-C}_3\text{N}_4$ and {010} facets of BiVO_4 induced by BiVO_4 surface heterojunction have not yet been discussed. Herein, the monoclinic BiVO_4 with the co-exposed {010} and {110} facets were synthesized, which could form the surface heterojunction, and proposed that the layered $\text{g-C}_3\text{N}_4$ and {010} facets of BiVO_4 formed a direct interface Z-scheme structure, resulting in the enhanced photocatalytic activity of the BiVO_4 .

2. Experimental

2.1. Preparation of the co-exposed {010} and {110} facets of BiVO_4

First of all, 6 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was completely dissolved into 30 mL of 1 M HNO_3 aqueous solution, and stirred for 30 min at room temperature to form a solution. Second, 6 mmol NH_4VO_3 was added into the solution with vigorous stirring for 2 h to get a precursor. Then it was added to Teflon-lined autoclaves with the packing ratio of 80%, maintaining at 70 °C for 15 h, and then naturally cooled until room temperature. The precipitates were filtered and washed with deionized water and ethanol, respectively for three times. Finally, the samples were dried at 80 °C for 12 h.

2.2. Preparation of $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ hybrid photocatalysts

Pure $\text{g-C}_3\text{N}_4$ was synthesized by calcining urea directly at 550 °C for 3 h in a semi-closed crucible with a lid in air atmosphere using a heating rate of 5 °C min^{-1} . After being naturally cooled to room temperature, the pale-yellow $\text{g-C}_3\text{N}_4$ was obtained.

The $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ composites were obtained according to the following procedure: First, a certain amount of $\text{g-C}_3\text{N}_4$ powder was added into deionized water to be magnetically stirred for 30 min at room temperature with the pH value is 5.03. Then, it was ultrasonically stirred for 1 h to completely disperse to form a suspension and the pH value is 5.01. After that, the BiVO_4 power was added into the $\text{g-C}_3\text{N}_4$ suspension and stirred for 30 min under natural light. Then, the product was filtered and washed with deionized water and ethanol, respectively and dried at 70 °C to obtain $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ coupled photocatalysts. The mass ratios of the resulting samples were as follows: $\text{g-C}_3\text{N}_4:\text{BiVO}_4 = 2:8, 4:6, 6:4, 8:2$. The coupled photocatalysts with these different mass ratios were denoted here as B8G2, B6G4, B4G6, B2G8, respectively.

The crystalline structures of the samples were characterized by a powder X-ray diffraction (XRD; D/max-2200PC) with Cu K radiation in the range of 10–70°. The voltage and the applied current were 40 kV and 80 mA, respectively. The Raman scattering spectra (Renishaw invia) measurements were detected by excitations with 532 nm.

Infrared spectra were recorded on a Fourier transform infrared (FT-IR; VECTOR-22) spectrometer at room temperature by the standard KBr disk method. The surface analysis was performed by an X-ray photoelectron spectroscopy (XPS) (Model XSAM800, Shimadzu-Kratos Co., Ltd., Japan). The morphologies were observed on a field emission scanning electron microscopy (FE-SEM, S4800, Hitachi). The microstructures were examined by a transmission electron microscope and high-resolution transmission electron micrographs (TEM, TecnaiG2F20 S-TWIN, FEI). Thermogravimetric analysis of the samples was determined on a thermal analyzer in air with a heating rate of 5 °C/min from room temperature to 550 °C (TG, STA409PC, Germany). The zeta potential of the as-prepared samples was examined by a nano particle size and zeta potential analyzer (NAMO-ZS, Malvern, U.K.). The UV–vis absorption spectra were obtained by a diffuse reflectance spectroscopy (DRS, Agilent Cary 5000) in the range of 200–800 nm, using BaSO_4 as the reference.

2.3. Computational details

All of the density functional calculations were investigated using the plane-wave pseudopotential method, implemented with the Cambridge Sequential Total Energy Package (CASTEP) code. The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used to depict the exchange-correlation effects. The plane-wave cutoff energy was 400 eV for all the calculations. The k-point meshes were set as $6 \times 6 \times 3$ of the bulk BiVO_4 , $3 \times 6 \times 1$ of the {010} surface and $4 \times 4 \times 1$ of the {110} surface. Interaction between the valence electrons and the ion core was substituted by an ultrasoft pseudopotential. The self-consistent convergence accuracy was set at 1×10^{-5} eV per atom, the convergence criterion of the force between atoms was 0.03 eV/Å, and the maximum displacement was 0.001 Å. The optimized lattice parameters of BiVO_4 were found to be $a = 5.14$ Å, $b = 5.15$ Å and $c = 11.64$ Å, in good agreement with experimental values ($a = 5.19$ Å, $b = 5.09$ Å and $c = 11.70$ Å). The {010} and {110} surface slabs were built with a bottom 5, 10 layers fixed and the top 5 and 10 layers relaxed, respectively. A vacuum layer of 12 Å was selected on each surface to eliminate the interactions between the surface atoms.

2.4. Evaluation of photocatalytic activity

The photocatalytic performance of all the prepared catalysts was evaluated by the degradation of Rhodamine B under visible light irradiation of a 500 W Xenon lamp, which was conducted in an XPA-7 photochemical reactor. The photocatalytic degradation products of RhB were examined by high performance liquid chromatography (HPLC, waters e2695) equipped with a UV–vis detector using a C18 inverted-phase column (250×4.6 mm, 5 μm) at 550 nm. The mobile phase was a mixture of methanol and water (V:V = 6:4) with a flow rate of 0.8 mL min^{-1} .

During the degradation experiment, a total of 0.05 g photocatalyst was added into 50 mL RhB solution (5×10^{-6} mol/L) each time, and then the solution was stirred in darkness for 30 min before the illumination to achieve an adsorption-desorption equilibrium between the photocatalyst and RhB molecules. For a certain period of time, 5 mL of suspension was withdrawn regularly and centrifuged to remove the photocatalyst. Then the concentration of RhB supernatants was analyzed by a UV–vis spectrophotometer (SP-756p). Different contents of benzoquinone (BQ) (1 mmol/L), ethylene diamine tetraacetic acid-disodium salt (EDTA-2Na) (1 mmol/L), and tert-butyl alcohol (TBA) (0.3 mL) were introduced into the solution of RhB prior to catching $\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$, respectively.

2.5. Photoelectrochemical analysis

All the photoelectrochemical measurements were executed on an electrochemical work station (CHI660E), using a standard three-

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