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Highly efficient photocatalytic activities, band alignment of $BiVO_4$/BiOCl {001} prepared by in situ chemical transformation

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ABSTRACT

The proper band alignment of coupled semiconductor plays a key role on enhancing photocatalytic activity due to the valence and conduction difference in the interface to drive the photogenerated charge carrier separation. However, little is known about the exact band alignment of coupled semiconductors due to that most band alignments were schematic by valence of monocomponent, but not consider the interface effect of coupled semiconductors. Herein the novel synthesis strategy via in situ chemical transformation was successfully utilized to prepare $BiVO_4$/BiOCl {001} heterojunctions. The results of transmission electron microscopy (TEM) show that $BiVO_4$/BiOCl photocatalyst was made of BiOCl sheets and $BiVO_4$ nanoparticles. The exact band alignment was experimentally demonstrated in $BiVO_4$/BiOCl through X-ray photoelectron spectroscopy (XPS). The results show that the valence band difference is 0.58 eV which is a driving force valence of band holes from $BiVO_4$ to BiOCl by the valence band offset. While the reductive electrons were driven by conduction band difference (1.27 eV) along the opposite direction compared to the oxidative holes. The large driving force for the charge transport across the interface explains the high photocatalytic activity achieved by the $BiVO_4$/BiOCl.

1. Introduction

Recently, significant interest has been devoted to the application of heterostructured semiconductor (SC) photocatalysts in water cleaning and environmental remediation due to their successful utilization of solar energy [1–8]. Generally, the effective separation of photogenerated electron and hole largely depends on the intrinsic electronic and structural properties of SC [9]. The coupled semiconductor photocatalysts (α-Bi_2O_3/β-Bi_2O_3 [10], BiOI/$ZnTiO_3$ [11], BiO_xCl_y/BiO_mBr_n [12] and Bi_2O_3/$BaTiO_3$ [13]) have enhanced the photocatalytic activities compared to the single phase, which is attributed to a staggered alignment of band edges at the heterointerface [14]. That is to say, it can improve spatial separation of photogenerated electrons and holes in different parts of the heterostructure, thus it is favorable to enhance the photocatalytic performance [15,16]. In recent years, much attractions were focused on $BiVO_4$ for utilization in photocatalytic reactions from highlighted work in 1999 by Kudo et al. [17] due to its appropriate band gap, and favorably positioned band edges [18–22]. As is known, $BiVO_4$ has three different polymorphs, denoted as monoclinic scheelite (ms), tetragonal scheelite (s-t) and tetragonal zircon (z-t), among which, the ms $BiVO_4$ is found to exhibit visible-light-driven photocatalytic activity [23–27]. In the ms $BiVO_4$, the distortion of VO_4 tetrahedron leads to an internal electric field, which is useful for the separation of electron–hole pairs [28,29]. It is known that the VO_4 tetrahedron in $BiVO_4$ does not contact with subsequent one, which leads to undesirable carrier transmission characteristic [30]. As a result, some works ($CuCr_2O_4$/$BiVO_4$ [31], CuO/$BiVO_4$ [32] and Ag_3PO_4/$BiVO_4$ [33]) focused on improvement of carrier migrating of $BiVO_4$ by constructing heterojunction. However, some inherent limitations in conventional synthesis methods, such as uniformity of the synthesized heterostructures [34] and complication of synthesized heterostructure process (synthesis of matrix, and then growth of the second phase on the matrix). Accordingly, it is expected to prepare $BiVO_4$/BiOCl {001} composite heterostructure with a facile technique and the highly efficient electron–hole separation under visible light irradiation. In general, the estimated band alignments were used to explain the enchanced photocatalytic properties of heterojunctions [35–37]. In the case of Wang et al. the alignment of rutile TiO_2 with ZnO showed that the

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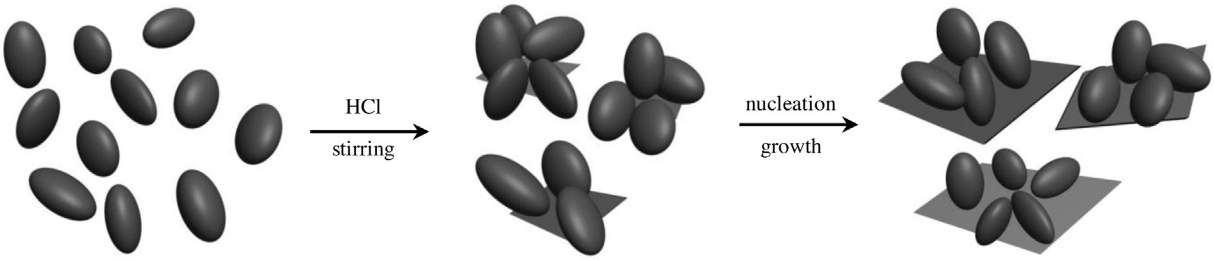

Scheme 1. Fabrication process of heterostructured sheets of $BiVO_4$/BiOCl.

valence band of rutile is 0.14 eV lower by the band offset [38]. Also, one longstanding controversy of the energetic alignment for the band edges of the rutile and anatase polymorphs of TiO_2 was clarified by the band offset [39]. As is known to all, X-ray photoelectron spectroscopy (XPS) could provide a direct means to obtain element core level and VB electronic structure. Within this framework, we tried to experimentally demonstrate the exact band alignment of coupled $BiVO_4$ and BiOCl.

Herein we use a novel in situ chemical transformation to prepare $BiVO_4$/BiOCl heterojunction. And its photocatalytic performance was evaluated by photodegradation of Rhodamine B (RhB). To the best of our knowledge, exact band alignment of corresponding components in $BiVO_4$/BiOCl has not been experimentally reported. In this paper, synthesized $BiVO_4$, BiOCl and $BiVO_4$/BiOCl were investigated by XPS based on their Bi 4f core levels, valence band structures and energy gaps. It is demonstrated that the $BiVO_4$ exhibits higher valence and conduction band levels than those of BiOCl in the $BiVO_4$/BiOCl. In addition, this work may provide new insights into the fabrication of nanocomposite photocatalysts via in situ chemical transformation technique.

2. Experimental details

All the chemicals were analytical grade and used without further purification. The typical preparation of $BiVO_4$, BiOCl and $BiVO_4$/BiOCl photocatalysts was as follows: 10.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved into 20 ml HNO_3 (1 mol L^{-1}). Bi was in excess of 5 at% compensating for losses in the annealing. 20 mmol $C_6H_8O_7$ were added to this $Bi(NO_3)_3$ solution, then 80 ml deionized water added. After that, pH value of solution increased to 7 by adding aqueous ammonia (25% mass concentration), and this was labeled as solution A. 10 mmol NH_4VO_3 and $C_6H_8O_7$ were dissolved in 100 ml deionized water. Solution B was thereby obtained. Subsequently, solution A was slowly transferred into the solution B, and then pH was adjusted to 7. After 6 h in water bath, the precursor powder was obtained by various subsequent process such as drying, ashing (heat treatment at 120 °C), grinding. Crystallization was achieved by calcination of the amorphous gel at 425 °C for 3 h in air atmosphere. The solids obtained are the ms bismuth vanadate. Bi_2O_3 was utilized as raw material to prepare BiOCl by precipitation transformation technique. Bi_2O_3 was dispersed ultrasonically in 20 ml deionized water for 15 min. 0.01 M HCl solution was gradually dropped into above dispersed solution until all the Bi_2O_3 was transformed into BiOCl. After the mixture was stirred for 12 h, the corresponding precipitation was filtered to obtain bare BiOCl. As for the preparation of $BiVO_4$/BiOCl, we use $BiVO_4$ and HCl as substrate and transforming reagent, respectively. When $BiVO_4$ particles and HCl solution were mixed, the HCl could resolve the outside of $BiVO_4$ particle to form the second phase BiOCl nanosheets. The concentrations of the Bi ($BiVO_4$) and Cl (0.01 M HCl) source were varied to prepare composites with different $BiVO_4$/BiOCl ratios (the stoichiometric ratios with 1:0.25 and 1:0.5 were labelled as CM1 and CM2 respectively) (see Scheme 1). After they were stirred for 12 h, filtering, the corresponding $BiVO_4$/BiOCl composites were prepared. Finally, the as-prepared $BiVO_4$/BiOCl and BiOCl powders were dried at 80 °C for 12 h.

The crystal structures of various photocatalysts were determined by X-ray diffraction (XRD; Model D/MAX-3B, Tokyo, Japan) excited by Cu Kα radiation, a sampling interval of 0.02°, and a scan speed of 4° min^{-1}. The XRD phases present in the samples were identified with the help of JCPDS data files. The Rietveld refinement analyses were performed using Match 2 coupled with Fullprof software based on the XRD data of two samples namely CM1 and CM2. Their morphology and crystalline structure were determined by transmission electron microscopy (TEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) performed by means of a G^2 F20 (FEI Tecnai) with operating voltage of 200 kV. All UV–vis diffuse reflectance spectra studies were recorded on a Shimadzu UV-2401PC UV/vis scanning spectrophotometer equipped with a diffuse reflectance accessory. XPS measurements were performed on a Thermo Escalab 250 with a monochromatic Al Kα ($h\nu = 1486.6$ eV) as the X-ray radiation source, which has been calibrated on work function and Fermi energy level (E_F). The XPS analysis was done at room temperature and pressures were typically in the order of less than 10^{-7} Pa. The accuracy of the XPS binding energies (BE) is 0.1 eV. Charging of samples was corrected by referencing the C 1s peak (284.6 eV) arising from adventitious carbon. The specific surface area measurements were obtained by using a multi-function adsorption instrument (MFA-140 of Beijing Builder Company). Before measurement, the samples were degassed under vacuum at 110 °C for 2 h.

RhB was employed as a probe dye to evaluate the photocatalytic activities of the samples. Typically, the 100 ml RhB solution (20 $mg \cdot L^{-1}$) was mixed with 0.1 g photocatalyst, dark stirring 30 min magnetically before irradiation to reach adsorption–desorption equilibrium between photocatalyst and dye molecules. The photocatalytic activity of each sample was tested using a 500 W xenon lamp. Appropriate amount of solution was centrifuged to remove photocatalysts to test the intensity changes of the absorption peak. The dye concentration was determined by the UV757CRT UV–vis spectrophotometer. At a given time interval, the above steps were repeated to test the absorbance in order to determine the degradation rate of RhB. The photocatalytic experiments were all conducted at room temperature.

3. Results and discussion

At the initial stage, $BiVO_4$ was partly dissolved in the solution by the H^+ (Eq. (1)). Then, the BiO^+ was generated via the progressive hydrolysis of Bi^{3+} (Eq. (2)). In this process, BiOCl nuclei generates due to small solubility product constant (1.8×10^{31}) as displayed in Eq. (3) [40]. Thus, another function of HCl is to provide Cl ions to react with BiO^+. Finally, with the gradual growth