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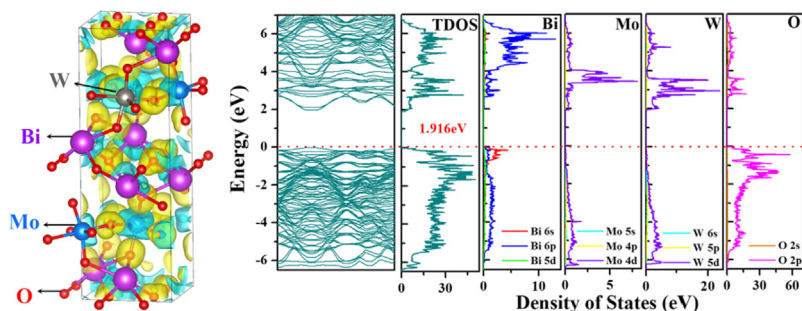
Boosting charge transfer via molybdenum doping and electric-field effect in bismuth tungstate: Density function theory calculation and potential applications

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GRAPHICAL ABSTRACT



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ABSTRACT

Regulating internal electronic structure of photocatalysts via elements doping holds huge potential in tuning efficient charge transfer and boosting high-performance. Herein, molybdenum embedded bismuth tungstate (Bi_2WO_6) is employed to explore the electronic structures and various performances via the assistance of experimental verification and density function theory (DFT) simulation. The band structures and Mo ions doping behaviors of $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ are systematically measured. Doping can induce the distortion of intrinsic electric density and internal electric-field, resulted in efficient charge transfer of $\text{Bi}_2\text{Mo}_{0.4}\text{W}_{0.6}\text{O}_6$. It exhibits much efficient photocatalytic activities under visible-light irradiation, also manifests huge potential as an anode material in lithium-ion batteries (LIBs) which is rarely reported before. This work may provide insights in the development of bismuth-based semiconductors in energy related applications.

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1. Introduction

Owing to the rapid population growth, industrialization and over-exploitation of limited fossil fuels, modern society has confronted with severe energy-related issues and environmental concerns [1–3]. Over the past few decades, tremendous efforts have

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been endeavoured in the development of green technologies for environmental remediation and energy conversion [4,5]. Development and utilization of renewable solar energy is the mainstream method to overcome current problems, in particular, semiconductor photocatalysis is one of the most promising technique [6,7]. By far, TiO₂ has undoubtedly been regarded as the superior photocatalyst for photodegradation of complex organic pollutants. However, it is only active under ultraviolet (UV) irradiation which limits its utilization of solar light and the large scale application [8,9]. Thus, there have been numerous projects aiming at the development of much more efficient visible-light-driven photocatalysts.

Among diverse semiconductor photocatalysts, bismuth compounds, including BiVO₄, Bi₂MoO₆, Bi₂WO₆ and BiOX (X = Cl, Br, I), possess special Aurivillius layered crystal structure and suitable band structure, which arouse considerable attention for ample visible-light harvesting and potential application in photocatalysis [10–17]. As a kind of bismuth-based ternary metal oxides, Bi₂WO₆ is chemical stable and nontoxic with an appropriate band gap energy (*E_g*) of 2.7 eV, whose crystal structure is composed of alternating [Bi₂O₂]²⁺ and [WO₄]²⁻ layers [18–20]. However, suffering from fierce recombination of photoinduced-carriers, the photocatalytic degradation performance of pristine Bi₂WO₆ is still far below expected, which does not meet the demands of practical applications [21]. Up to now, multiple modification approaches have been reported to promote the separation and transfer of carriers, mainly including co-catalyst coupling [22,23], novel structure design with active sites [24,25], elemental doping [26,27] and the construction of composite heterostructures [9,13]. Among these attempts, elemental doping has attracted a surge of attention by its superiority in adjusting the electronic structures and regulating photocatalytic activity. Various elements doped into Bi₂WO₆ have been discussed, such as Bi₂WO_{6-x}F_{2x} [28], bismuth self-doped Bi_{2+x}WO₆ [29], samarium and nitrogen co-doped Bi₂WO₆ [30] and so forth.

Many researchers also focus on bismuth molybdate (Bi₂MoO₆), another bismuth-containing ternary metal oxide that possesses much smaller *E_g* of 2.5 eV whereas less photocatalytic activity, which is isostructural with Bi₂WO₆ [26,28]. Actually, pioneers have successfully synthesized stable Bi₂Mo_xW_{1-x}O₆ solid solution after the introduction of Mo⁶⁺ into pristine Bi₂WO₆, for the expectation to integrate the virtue of both Bi₂WO₆ and Bi₂MoO₆. Yu's group [31] firstly declared that the obtained Bi₂Mo_{0.25}W_{0.75}O₆ nanosheets exhibited superior photodegradation properties, and it could decompose more than 95% of MB within 200 min under visible-light irradiation. Hu's group [32] further reported that three-dimensional porous Bi₂Mo_{0.21}W_{0.79}O₆ microstructures displayed efficient photocatalytic O₂ evolution under visible-light irradiation. However, current reports largely regard the improved photocatalytic properties are ascribed to the intrinsic Aurivillius layered structure, novel designed morphologies and well-adjusted band gap energy [33,34]. It is still not clear yet how the electronic structures regulate after Mo ions embedded into Bi₂WO₆ crystals, especially for the specific doping behaviors [32,35]. Thus, it is worthy to in depth investigate the interconnections between the electronic structures and various performances over Mo⁶⁺ confined in Bi₂WO₆. Motivated by the aforementioned consideration, Bi₂Mo_xW_{1-x}O₆ nanosheets are systematically probed by the assistance of various methods. Experimental investigation and theoretical simulation of the specific doping behaviors of Mo⁶⁺ are conducted, especially for the band gaps and electronic structures. The enhanced electric-field effect and separation of charge carriers are further verified. Bi₂Mo_xW_{1-x}O₆ are further applied in the photocatalytic degradation of Rh-B and tetracycline hydrochloride (TC-HCl) under visible-light irradiation, as well as an anode material in LIBs. This work may provide insight in the development of semiconductors with multiple applications toward environmental remediation and energy conversion.

2. Experimental section

2.1. Preparation of Bi₂Mo_xW_{1-x}O₆

All chemicals mentioned in this work were analytical grade without further purification. The Bi₂Mo_xW_{1-x}O₆ (x = 0.2, 0.4 and 0.6) nanostructures were synthesized following the modified solvothermal method [32], and the molar ratio of Bi:(W + Mo) was set as 2:1. In a typical preparation of Bi₂Mo_{0.4}W_{0.6}O₆, bismuth nitrate pentahydrate (2.0 mmol) was dissolved into ethylene glycol (25 ml), and sodium tungstate dihydrate (0.4 mmol) with ammonium molybdate tetrahydrate (0.09 mmol) were added into another container with ethylene glycol (25 ml). After ultrasonic dissolving, the homogeneous solution that contained W⁶⁺ and Mo⁶⁺ was added into bismuth source container slowly. Then, being stirred vigorously under room temperature for several minutes, the pH value of the suspension was adjusted to about 7 by adding sodium hydroxide solution dropwise. Later, the above suspension was transferred into Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. Afterward, pure Bi₂WO₆ and Bi₂MoO₆ were also synthesized under the same condition without the corresponding addition of ammonium molybdate tetrahydrate and tungstate dihydrate, respectively.

2.2. Characterization

The crystalline phases of the obtained samples were recorded by XRD (D/max 2550, Rigaku) using Cu K α irradiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 10–80°. The micro-structures were confirmed by field emission transmission electron microscope and high resolution transmission electron microscope (TEM/HRTEM, Titan G2 60-300, FEI Co. Ltd.), as well as lattice fringe calibration. The optical properties of products were measured by the UV-visible diffuse reflectance spectrophotometer (UV-vis DRS, Evolution 220, Thermo Fisher Scientific), using BaSO₄ powders as reference materials. The photoluminescence spectra (PL) were obtained at the excitation wavelength of 240 nm on a fluorescence spectrophotometer (F-4600, Japan's Hitachi LTD).

2.3. Photocatalytic activities assessments

Photocatalytic activities were measured by the degradation of Rh-B and TC-HCl on a reactor that equipped by a 500 W Xe lamp with a 420 nm UV cut-off filter. Typically, samples (10 mg) were dissolved in Rh-B solution (20 mg·L⁻¹, 15 ml) or TC-HCl (30 mg·L⁻¹, 15 ml), then put them in darkness with constant stirring for 2 h to obtain adsorption-desorption equilibrium. During each interval, about 3 ml suspension was extracted to centrifuge. Afterwards, the concentration of each supernatant was tested by UV-vis spectrophotometer. Detection of active species was conducted under similar process comparing to photocatalytic degradation, except the addition of different scavengers.

2.4. Photoelectrochemical tests

The photoelectrochemical measurements were carried out in a three-electrode cell on CHI660E electrochemical workstation, consisting of a working electrode, a Ag/AgCl reference electrode and a platinum sheet as counter electrode, meanwhile sodium sulfate (0.5 M) solution was used as the electrolyte. The working electrode was prepared as follows: samples (20 mg) were dissolved in ethylene glycol (20 ml) with Nafion solution (50 μ l) and ultrasonically dispersed to form a homogeneous suspension, then it was placed to magnetically stir for another 24 h. Afterward, the suspension (100 μ l) was drop-coated onto the indium tin oxide (ITO) glasses

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