



Research Paper

Enhanced visible-light photocatalytic activity of Bi₂MoO₆ nanoplates with heterogeneous Bi₂MoO_{6-x}@Bi₂MoO₆ core-shell structure



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ABSTRACT

A series of Bi₂MoO₆ (BMO) nanoplates with a heterogeneous Bi₂MoO_{6-x}@Bi₂MoO₆ core/shell structure were successfully obtained by reduction with CaH₂ at 140 °C and subsequent reoxidation in air under low temperatures (≤ 250 °C). It is found that the oxygen vacancies mainly exist in the core, while the shell is formed by surface disorder layer with few oxygen vacancies, which is almost stoichiometric. The controllable growth of the surface disorder layer can be realized by the reduction and/or reoxidation temperatures. The reoxidized BMO with the surface disorder layer exhibits about five times higher visible-light photocatalytic activity toward phenol degradation and an order of magnitude higher activity toward methylene blue (MB) degradation than those of the unmodified sample. The visible-light absorption is mainly dominated by the oxygen vacancies through the modulation of the band gap structure, which promote the solar light utilization and photogenerated charge carriers. Density functional theory calculation shows that BMO is a direct band gap semiconductor. It is suggested that the surface disorder layer could suppress the direct recombination of photogenerated carriers and improve surface reactivity, and results in the enhancement of the photocatalytic activity. In addition, the existence of the stoichiometric surface disorder can promote the catalyst stability. It is demonstrated that the reduction- reoxidation method applied here is simple, easily control, and beneficial for the design and realization of heterogeneous core-shell nanostructured photocatalysts to improve visible and infrared optical absorption by engineering the surface disorder and the oxygen vacancies inside core of Bi₂MoO₆ nanoplates and the related nanostructured photocatalysts.

1. Introduction

The waste water problem from industries and human societies has become increasingly in recent years [1,2]. As an efficient method for the decomposition or mineralization of organic contaminants, semiconductor photocatalysis technology has attracted much attention due to its low cost, environmental harmlessness, efficient degradation rate, and stability in reaction [3,4]. For practical applications of photocatalysis technology, a perfect photocatalyst is expected, which should have a proper band gap to provide energetic electrons, efficient photogenerated charge separation and migration, and also a large inhibition of the photocorrosion process [5,6]. Moreover, a smaller enough band gap to allow for efficient absorption overlap with the solar spectrum is also necessary for the photocatalyst to effectively utilize the solar energy [7,8]. Up to now, TiO₂ semiconductor is the most investigated and applied photocatalyst. However, the relatively wide

band gap (~ 3.2 eV for anatase phase or 3.0 eV for rutile phase) limits its photocatalytic applications, because only ultraviolet light fraction in solar light can be absorbed by TiO₂ (lower than 3–5%). Thus, TiO₂ is not an ideal photocatalyst to efficiently utilize sunlight in naturally environmental purification or remediation [9,10]. The exploration of facile, mild, and effective routes for the rational synthesis of visible-light responsive catalysts with superior photocatalytic activity is highly desired.

It is well known that the photocatalytic activity of photocatalysts is strongly dependent on morphology and structure. Therefore, for a practical application in photocatalysis, the fabrication of desired morphologies and textures is important as well as control in crystallinity, surface area, and composition. Nowadays, many efforts have been devoting to developing high efficient visible light harvesting photocatalysts. Oxygen vacancy, the most general defect in oxide semiconductors, provide a new approach to control the charges

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separation process, and engineer the electronic structure of semiconductors [11]. Introducing oxygen vacancies into the lattice of TiO_2 photocatalysts can modify the electronic properties and enhance the photocatalytic activity of TiO_2 [12,13]. Several studies have reported that the oxygen vacancies have been achieved by doping with metal ions or non-metal or rare earth elements [14,15]. Besides, different from impurity incorporation, self-doping that produces Ti^{3+} species in TiO_2 has also been demonstrated [13]. Through doping, the solar absorption characteristics of TiO_2 have been improved to some extent. However, theoretical and experimental investigations have demonstrated that doping dose not inevitably translate into a higher photocatalytic activity since the impurity or defect states can trap electrons and facilitate non-radiative recombination, which will reduce the photocatalytic performance [16,17]. For example, nitrogen-doped TiO_2 exhibits the greatest optical response to solar radiation [18], but its absorption in the visible and infrared remains insufficient.

On the other hand, to improved visible-light photocatalytic activity, tailoring the surface structure at the nanoscale under varied synthesis conditions has long been employed for endowing them distinctive properties and gaining insights into the surface structure related properties [19]. Chen et al. [20] reported that the black TiO_2 with surface disorder obtained by high-pressure hydrogenation treatment shows remarkably enhanced solar absorption and superior solar-driven photocatalytic activity, which has triggered tremendous interest over the world, since it presented a new approach to enhancing photocatalytic performance. Surface disorder can be observed by high resolution transmission electron microscopy (HRTEM) as an amorphous shell [20,21], although the atomic level structure has not yet been fully investigated. Surface disorder can affect the photocatalytic activities in different ways. In some cases, the disordered lattice can induce mid-gap states below Fermi level, resulting in large blue shift of VB maximum [22], which is beneficial for visible-light absorption. In addition, surface disorder can decrease spatial overlap of photoexcited holes and electrons, resulting in an enhancement of charge separation [23]. In the recent years, the introduction of surface disorder has been extended to BiOCl [24], ZnO [25] and BiFeO_3 [26], which has obviously improved the visible-light photocatalytic activity. However, the function of the surface disorder layer in the photocatalytic activity is still unclear.

As a member of Aurivillius family, Bi_2MoO_6 (BMO) with the layered bismuth oxide family are of special interest due to their dielectric, ion-conductive, luminescent and catalytic properties [27,28]. Recent results revealed that Bi_2MoO_6 may be a potential candidate as an excellent photocatalyst and solar-energy-conversion material for water splitting and degradation of organic compounds under visible-light irradiation [29,30]. However, when illuminated under visible light irradiation, the relatively high recombination rate of photogenerated electrons/holes pairs for pure Bi_2MoO_6 hinders its widely application. Approaches such as doping [31,32] and heterojunction formation [33] have been adopted to suppress the recombination of photogenerated electrons/holes pairs. Moreover, as a highly anisotropic semiconductor oxide with a layered crystal structure, the photocatalytic performance of BMO is very sensitive to the exposed surface [30,34]. In the present study, Bi_2MoO_6 nanoplates with a heterogeneous $\text{Bi}_2\text{MoO}_{6-x}/\text{Bi}_2\text{MoO}_6$ core-shell structure were controllably synthesized by a simple reduction-reoxidation method using CaH_2 as reductant. Unlike the situation in the black hydrogenated TiO_2 nanocrystals [20] with a crystalline core and highly disordered/doped surface layer, it is found that the oxygen vacancies of BMO are “healed” through subsequent low-temperature ($\leq 250^\circ\text{C}$) reoxidation in the core, while surface disorder layer with few oxygen vacancies is grown, which led to an enhanced photo-generated charge transfer and separation, and visible-light photocatalytic activity. The reoxidized BMO exhibits about five times higher visible-light photocatalytic activity toward phenol degradation and one order of magnitude higher activity toward methylene blue (MB) degradation than those of the unmodified BMO. It is demonstrated that the reduction-reoxidation method applied here is simple, easily

control, and beneficial for the design and realization of heterogeneous core-shell nanostructured photocatalysts to improve visible and infrared optical absorption by engineering the surface disorder and the oxygen vacancies inside core of Bi_2MoO_6 nanoplates.

2. Experimental

2.1. Sample preparation

Bi_2MoO_6 nanoplates were synthesized by co-precipitation method. Materials and reagents, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, HNO_3 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, CaH_2 were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. China. 29.1042 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 5.2965 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 150 mL of 5 M HNO_3 solution and 150 mL of 5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution, respectively. Then the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solution was slowly added into the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution with continuously stirring. The pH value was adjusted to about nine using concentrated ammonia. After stirring for 30 min at room temperature, the suspension was dried at 120°C overnight and washed by deionized water to remove NH_4NO_3 . And then, the well-crystallized Bi_2MoO_6 (denoted as BMO-AP) was obtained by heating the resulting powder at 300°C for 5 h.

Reduced Bi_2MoO_6 , denoted as BMO-Rd, was synthesized by reducing BMO-AP with CaH_2 as a reductant. 1 g of BMO-AP was mixed with 1 g of CaH_2 and ground. During the grinding procedure, moderate amount of petroleum ether was added in order to avoid deliquescence of CaH_2 in moist air. After sufficient grinding, the mixture was sealed in an evacuated 20 mL capacity glass tube and heated at 140°C for more than 12 h until it totally turned into black, which is to ensure that oxygen vacancies were homogeneously introduced throughout the entire nanoplate. It is found that the sample did not change its color obviously at 100°C but partly decomposed to metallic Bi at 180°C , indicating that the synthesis of BMO-Rd is sensitive to reducing temperature. Besides, the reduction is also sensitive to the ratio of BMO-AP to CaH_2 , and the loading degree of the glass tube. After reduction, excess CaH_2 and the by-products were washed out with 0.1 M NH_4Cl methanol solution (typically 4×100 mL). And the residue was further washed with pure methanol and dried under vacuum.

To obtain the reoxidized samples, BMO-Rd was divided into several parts, and two of them were annealed at 150°C and 250°C in air for 5 h, respectively, with a heating rate of $1^\circ\text{C}/\text{min}$. After annealing, the color of the sample turned into pale yellow (at 150°C) or yellow (at 250°C). The reoxidized samples are denoted as BMO-Ro150 and BMO-Ro250 respectively, according to the annealing temperatures.

2.2. Material characterization

Crystallographic phases and purity of the samples were identified using an X-ray diffractometer (XRD, Rigaku TTR III) with $\text{Cu K}\alpha$ ($\lambda = 1.54187 \text{ \AA}$) radiation. The morphology and microstructure were determined by transmission electron microscopy (TEM, JEOL JEM-2100F) with an accelerating voltage of 200 kV. Photoluminescence spectra of powder samples were conducted on a Raman spectrometer (HORIBA LABRAM HR) excited by a 325 nm He-Cd laser. The UV–vis-NIR diffuse reflectance spectra were obtained using a UV–vis-NIR spectrophotometer (Shimadzu SOLID3700) equipped with an integrating sphere. Magnetic measurements were carried out on a superconducting quantum interference device (SQUID) from Quantum Design. Fourier transform infrared spectra (FTIR) were recorded on a FTIR-7600 spectrometer from Lambda Scientific Pty Ltd, using the KBr pellet method. Surface oxidation states and valence band (VB) were investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250Xi). The Brunauer-Emmett-Teller (BET) specific surface areas of the prepared samples were analyzed by nitrogen adsorption/desorption isotherms at liquid nitrogen temperature with an Autosorb-iQ analyzer, Quantachrome Instruments.

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