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The pivotal effects of oxygen vacancy on Bi₂MoO₆: Promoted visible light photocatalytic activity and reaction mechanism

Yanjuan Sun ^{a,b,*}, Hong Wang ^b, Qian Xing ^b, Wen Cui ^b, Jieyuan Li ^c, Sujuan Wu ^a, Lidong Sun ^{a,#}^a State Key Laboratory of Mechanical Transmission, School of Materials Science and Engineering, Chongqing University, Chongqing 400044, China^b Chongqing Key Laboratory of Catalysis and New Environmental Materials, College of Environment and Resources, Chongqing Technology and Business University, Chongqing 400067, China^c College of Architecture and Environment, Sichuan University, Chengdu 610065, Sichuan, China

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ABSTRACT

Bi₂MoO₆, a typical Bi-based photocatalyst, has received increasing interests and been widely applied in various fields. However, the visible light photocatalytic activity of Bi₂MoO₆ is still restricted by some obstacles, such as limited photo-response and low charge separation efficiency. In this work, we developed a facile method to introduce artificial oxygen vacancy into Bi₂MoO₆ microspheres, which could effectively address these problems and realize highly efficient visible light photocatalysis. The experimental and theoretical methods were combined to explore the effects of oxygen vacancy on the electronic structure, photocatalytic activity and the reaction mechanism toward NO removal. The results showed that the addition of NaBH₄ during catalyst preparation induced the formation of oxygen vacancy in Bi₂MoO₆, which plays a significant role in extending the visible light absorption of Bi₂MoO₆. The visible light photocatalytic activity of Bi₂MoO₆ with oxygen vacancy was obviously enhanced with a NO removal ratio of 43.5%, in contrast to that of 25.0% with the pristine Bi₂MoO₆. This can be attributed to the oxygen vacancy that creates a defect energy level in the band gap of Bi₂MoO₆, thus facilitating the charge separation and transfer processes. Hence, more reactive radicals were generated and participated in the photocatalytic NO oxidation reaction. The in situ FT-IR was used to dynamically monitor the photocatalytic NO oxidation process. The reaction intermediates were observed and the adsorption-reaction mechanism was proposed. It was found that the reaction mechanism was unchanged by introducing the oxygen vacancy in Bi₂MoO₆. This work could provide new insights into the understanding of the oxygen vacancy in photocatalysis and gas-phase photocatalytic reaction mechanism.

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1. Introduction

Semiconductor-based photocatalysis has attracted widespread attention, in view of its low-cost, efficient and promising applications in environmental remediation and solar energy

conversion [1–4]. In order to explore extraordinary photocatalysts, four types of photocatalysts have been developed, including metal-containing semiconductors, metal free semiconductors, plasmonic metals and insulators. Among them, the Bi-based photocatalysts, such as Bi₂O₃, BiVO₄, Bi₂WO₆ and

* Corresponding author. Tel/Fax: +86-23-62769785; E-mail: syhsyj@163.com

Corresponding author. E-mail: lidong.sun@cqu.edu.cn

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Bi_2MoO_6 , have been widely investigated because of their unique electronic structure and decent photocatalytic properties [5–10]. However, most of them still face some challenges, such as the limited visible light response and low charge carriers separation [10–12].

Recent reports showed that oxygen vacancy (OV) could extend the photo-response region of photocatalysts and is the most reactive sites for reactants activation over the surface of photocatalysts because of the promoted charge separation and localized electrons in the OV [13,14]. Therefore, it is highly desirable to develop the Bi-based photocatalysts with oxygen vacancy to enhance photocatalytic performance. The Bi_2MoO_6 , a member of Aurivillius family, has attracted considerable attention [15–19], but the limited photocatalytic performance restricts its potential application. In order to enhance the photocatalytic activity, various strategies have been taken, such as doping with heteroatom, formation of heterostructure, and morphology control [15–19]. To the best of our knowledge, the effects of OV on the electronic structure and reaction mechanism of Bi_2MoO_6 is still unclear and therefore needs a systematic investigation.

In this work, we prepared Bi_2MoO_6 microspheres with oxygen vacancy by a facile method. The effects of OV on the photocatalytic activity and reaction mechanism were unraveled by the combined experimental and theoretical approaches. The as-prepared catalysts were applied in photocatalytic removal of NO under visible light irradiation. Because of the oxygen vacancy mediated charge separation and formation of defect-level in the band structure, the visible light photocatalytic activity of Bi_2MoO_6 with oxygen vacancy was enhanced with a higher NO removal ratio than the pristine Bi_2MoO_6 (43.5% vs. 25.0%). Besides, the photocatalytic NO oxidation process was dynamically investigated by in situ FT-IR. The reaction intermediates have been observed and the adsorption-reaction mechanism was proposed. This work proposes a new strategy on modification of Bi-based photocatalysts and gains new insights into photocatalytic reaction mechanism for gas pollutant removal.

2. Experimental and calculation

2.1. Synthesis of photocatalysts

All agents were purchased as analytical grade reagent without further purification. In a typical procedure, 1.6866 g of bismuth nitrate pentahydrate and 0.4210 g of sodium molybdate dithydrate were dissolved in 5 mL of ethylene glycol (EG) with magnetic stirring, respectively. Then, the two solutions were mixed together before the addition of 20 mL of ethylene glycol and followed by stirring for 10 min. After all solids were dissolved completely, the aqueous suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was hydrothermally treated under 160 °C for 20 h. Subsequently, the autoclave was cooled to room temperature naturally. The resulting samples were filtered and washed with distilled water and ethanol two times each, and dried at 60 °C for 12 h to obtain pure Bi_2MoO_6 products, which was labeled as BMO.

Afterward, 0.61 g Bi_2MoO_6 was dispersed in 50 mL distilled

water with magnetic stirring. Then, different amounts (0.0029, 0.0057, 0.0285 and 0.0399 g) of sodium borohydride (NaBH_4) were weighted and dissolved in the above suspension containing 0.5 g PVP (polyvinyl pyrrolidone) with stirring for 30 min. After standing for 30 min, the resulting samples were filtered and washed sequentially with distilled water and ethanol, and dried at 40 °C for 12 h to get the Bi_2MoO_6 with oxygen defects. These samples obtained with different amounts of NaBH_4 to Bi_2MoO_6 were labeled as BMO-1, BMO-2, BMO-3 and BMO-4, respectively.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer equipped with intense $\text{Cu K}\alpha$ radiation (Model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with Al $\text{K}\alpha$ X-rays (Thermo ESCALAB 250, United States) was used to investigate the chemical states. The morphological structure was analyzed through a scanning electron microscope (SEM, JEOL model JSM-6490, Japan) and a transmission electron microscope (TEM, JEM-2010, Japan). The electron paramagnetic resonance (EPR) measurements (FLsp920, England) of photocatalyst powders were carried out at –196 °C. Electron spin resonance (ESR) signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were recorded on a JES FA200 spectrometer. ESR measurements were performed prepared by mixing the samples in a 40mM DMPO solution tank (aqueous dispersion for $\text{DMPO}\cdot\text{OH}$ and methanol dispersion for $\text{DMPO}\cdot\text{O}_2^-$) and irradiated with visible light. The UV-vis diffuse reflection spectra (UV-vis DRS) were obtained for the dry-pressed disk samples by using a Scan UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) with 100% BaSO_4 as the standard sample. Photoluminescence (PL, F-7000, HITACHI, Japan) was utilized to investigate the optical properties.

2.3. Visible light photocatalytic NO removal

The photocatalytic activity was investigated by determining the removal ratio of NO at ppb levels (500 ppb) in a continuous-flow reactor (rectangular reactor, 30 cm × 15 cm × 10 cm). The concentration of NO was continuously detected by a NO_x analyzer (Thermo Environmental Instruments Inc., Model 42c-TL), which can monitor the concentrations of NO, NO_2 , and NO_x (NO_x represents $\text{NO} + \text{NO}_2$). The as-prepared sample (0.2 g) was dispersed and coated onto two glass dishes (12.0 cm in diameter) for photocatalytic activity tests. A 150 W commercial tungsten halogen lamp was vertically placed outside and above the reactor and the lamp was turned on when adsorption-desorption equilibrium was achieved. The removal ratio (η) of NO was calculated as $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 are the concentrations of NO in the outlet steam and feeding stream, respectively.

2.4. In situ FT-IR investigation on photocatalytic NO oxidation

In situ infrared test equipment was composed of a Tensor II

FT-IR spectrometer (Bruker, Germany) and in-situ reflection reaction as shown in Fig. S1 (in the Supporting Information). The photocatalyst was placed in the reaction chamber. The reaction chamber was equipped with three gas ports and two coolant ports. High-purity He, high-purity O₂ and 100 ppm of NO (in He) mixture was fed into the reaction system and a three-way ball valve was used to switch the target gas (NO) and purge gas (He). The total gas flow rate was 100 mL min⁻¹ and the concentration of NO was 50 ppm by the dilution of O₂. The chamber is enclosed with a dome with three windows, two for IR light entrance and detection, and one for illuminating of the photocatalyst. The observation window was UV quartz and ZnSe for the other two windows. A high pressure mercury lamp (MVL-210, Optpe, Japan) was used for UV light source.

2.5. DFT calculations

Density functional theory (DFT) calculations were performed using VASP software (Code 5.4), applying the generalized gradient correlation function [20]. A plane wave basis was set with the projector-augmented wave method [21]. Gaussian width was set to 0.2 eV and the energy was cut-off at 500 eV. A $3 \times 3 \times 1$ K points were sampled in the Brillouin zone. All electronic structures were conducted until the geometry structures were relaxed below 0.03 eV/Å.

3. Results and discussion

3.1. Structure of photocatalysts

Fig. 1a shows the XRD patterns of Bi₂MoO₆ (BMO) and Bi₂MoO₆ with oxygen defect (BMO-X, X = 1, 2, 3 or 4). It is observed that the diffraction peaks of BMO and BMO-X are in line with the orthorhombic Bi₂MoO₆ (JCPDS Card No. 21-0102). The peak intensity of BMO-X slightly decreases with the addition of sodium borohydride, which weakens the crystallinity of the samples. A peak shift toward large diffraction angle is also visible because of the oxygen vacancies that could modify the binding environment. The morphology of BMO and BMO-X was characterized by SEM. Fig. S2a and S2b reflect that the BMO consists of microspheres assembled with lots of capsule-like nanorods. The morphology is altered when sodium borohydride is introduced into the reaction system. Some nanoparticles are produced and located at interspace of the capsule-like nanorods in BMO-2 (Fig. S2c and S2d). For BMO-4 with more addition of sodium borohydride, the capsule-like nanorod architectures disappear and the whole microspheres are mainly assembled with smaller nanoparticles (Fig. S2e and S2f). The morphology transformation of samples can be ascribed to the addition of the reductive sodium borohydride that could inhibit the anisotropic growth of crystal.

The detailed elemental composition and oxidation state of the as-prepared samples were characterized by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1b, it is obvious that Bi 4f consists of two characteristic peaks at 158.9 and 164.4 eV, respectively, which correspond to Bi 4f_{7/2} and Bi 4f_{5/2}.

Fig. 1. XRD patterns of the as-prepared samples (a); XPS spectra of Bi 4f (b), Mo 3d (c) and O 1s (d) of BMO and BMO-4.

Fig. 2. The typical TEM and HRTEM images of BMO (a, b) and of BMO-4 (c, d).

of Bi^{3+} . And no any other peaks of low oxidation state of Bi species are observed. Fig. 1c shows the XPS signals located at 232.6 and 235.4 eV that can be attributed to $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ orbitals, respectively, corresponding to Mo^{6+} in the samples [22]. Moreover, the O 1s peaks can be fitted into two peaks at 529.90 and 539.84 eV (Fig. 1d), which can be attributed to the Bi–O and Mo–O, respectively [23–26]. It is worth to note that the peak intensity of Bi–O is slightly decreased for BMO-4 compared to that of BMO, which may result from the lack of O atom in partial Bi–O to form the oxygen vacancies [23].

Fig. 2 displays the TEM images of BMO and BMO-4. The observed morphology of BMO and BMO-4 is consistent with SEM images (Fig. S2). The lattice fringe can be clearly observed for the two samples with spacing of 0.308 nm, corresponding to the spacing of (131) plane of the orthorhombic phase of Bi_2Mo_6 (Fig. 2b and 2d). The lattice spacing of 0.284 nm can be ascribed to the presence of Bi metal on the catalyst. Fig. S3 shows the EDX elemental mapping of the BMO-4 sample, demonstrat-

ing that the Bi, Mo and O elements co-exist and well disperse in BMO-4.

3.2. The pivotal effects of oxygen vacancies

To investigate the nature of oxygen vacancies in the catalysts, low-temperature solid-state electron paramagnetic resonance (EPR) was also employed on BMO and BMO-4, as shown in Fig. 3b. The ESR signal at $g = 2.0002$ can be attributed to the oxygen vacancies [27,28]. A weak EPR signal is detected in BMO, indicating that there is little oxygen vacancies in BMO. In contrast, the signal of BMO-4 at $g = 2.0002$ becomes significantly strong, indicating that a mass of oxygen vacancies are produced with the addition of NaBH_4 . Under visible light irradiation, these signals of BMO and BMO-4 are intensified, indicating that the electrons can be mobilized. The signal of BMO-4 is stronger than that of BMO, which implies that the presence of oxygen defects could increase the sensitivity of visible light response. Usually, this is because the oxygen vacancies produced in semiconductors can form a defect level in the band gap [26,27]. To confirm the presence of and intermediate level, DFT calculations have been conducted. As the calculated density of states represented (Fig. 3b), middle level is formed within the bandgap of OV-BMO due to the formation of oxygen vacancies. Thus, the boosted charge transfer arises from a foothold on the middle springboard in the BMO-4.

The UV-vis DRS was utilized to investigate the optical absorption property of the as-synthesized photocatalysts in the range of 200–800 nm. As shown in Fig. 4a, BMO reflects photo-absorption edge at about 480 nm because of the intrinsic band gap transition [30]. Following the production of oxygen vacancies, the absorbance of BMO-X in the visible region is significantly enhanced. Generally, the stronger absorption ability is more favorable for the photocatalytic reaction, because the more photogenerated carriers can be produced to participate the photocatalysis. As shown in Fig. 4b, the band gap is slightly decreased from 2.40 eV of BMO to 2.07 eV of BMO-4.

The PL emission is an effective method to investigate the separation efficiency of photoexcited electron-hole pairs [31]. Fig. 5a shows the comparison of the PL spectra of the

Fig. 3. The EPR spectra (a) and the calculated density of states (b) of BMO and BMO-4.

Fig. 4. UV-vis DRS (a) and bandgap (b) of BMO and BMO-X.

Fig. 5. The PL spectra of BMO and BMO-4 (a) and calculated charge density difference of OV-BMO (b). The purple, red and grey spheres depict Bi, O and Mo atoms, respectively. Charge accumulations were in blue and depletion in yellow.

as-synthesized BMO and BMO-4. Generally, a weak PL intensity is generally indicative of a high separation efficiency of electron-hole pairs [32–34]. Obviously, the Bi_2MoO_6 with oxygen vacancies (BMO-4) show significantly diminished PL intensity. This result may be caused by the presence of oxygen vacancies that modify the electronic structure of pristine Bi_2MoO_6 . Furthermore, the calculated charge density difference of OV-BMO (Fig. 5b) shows that the surface electrons can be localized around the OV site of BMO, which is in favor of the charge separation and reactant activation. This result indicates that the enhanced charge separation in BMO-4 is attributed to the modified electronic structure by the oxygen defects. Moreover, the electron localization could provide extra active sites for reactant activation (such as O_2 and NO), which significantly boost radical production and pollutant conversion in BMO-4.

3.3. Active species trapping and photocatalytic performance

The $\bullet\text{OH}$ radicals and $\bullet\text{O}_2^-$ radicals are the most important oxidation species in the photocatalytic reactions. The $\bullet\text{OH}$ radicals come from the oxidation of H_2O by photogenerated holes and the $\bullet\text{O}_2^-$ radicals are produced via the O_2 reduction with

the photogenerated electrons [35,36]. These active species are detected by DMPO-ESR spin-trapping as shown in Fig. 6. Under the irradiation of visible light, as shown in Fig. 6a, four characteristic peaks of DMPO- $\bullet\text{OH}$ adducts with an intensity ratio of 1:2:2:1 are distinctively detected and the peak intensity of DMPO- $\bullet\text{O}_2^-$ adducts with an intensity ratio of 1:1:1:1 are also detected in Fig. 6b [32,37]. Further observations indicate that the signals of $\bullet\text{OH}$ radicals and $\bullet\text{O}_2^-$ radicals for BMO-4 are both much stronger than that of BMO. This result also suggests that BMO-4 could generate more radicals to participate in the photocatalysis, which can be ascribed to the oxygen vacancies in BMO-4 that could boost charge separation and electron localization and promote the production of radicals.

NO is stable and cannot be directly photo-decomposed under light illumination without the aid of photocatalysts [38]. In order to demonstrate the potential capability for air purification, the as-synthesized photocatalysts were applied in removal of the ppb-level NO in gas phase [39,40]. For comparison, the photocatalytic activities of all samples were tested under identical experimental conditions. Fig. 7 shows that the photocatalytic activity of BMO is limited with a NO removal ratio of 25.0% after reaching equilibrium in 30 min. However, the pho-

Fig. 6. DMPO-ESR spin-trapping spectra of BMO and BMO-4 for detection of hydroxyl radicals ($\cdot\text{OH}$) (a) and superoxide radicals ($\cdot\text{O}_2^-$) (b).

photocatalytic NO removal ratio of BMO-2, BMO-3, and BMO-4 is increased to 43.5%, 38.4%, and 37.0%, respectively. Remarkably, the superior photocatalytic NO removal ratio of BMO-2 (43.5%) even outperforms that of other types of decent visible-light photocatalysts, such as BiOBr (21.3%), BiOI (14.9%), C-doped TiO_2 (21.8%), N-doped TiO_2 (36.5%), and g- C_3N_4 (32.7%) under the same test conditions [41,42]. BMO-4 reaches extremely high performance of 54.0% in 6 min because of the more oxygen vacancies produced by adding sodium borohydride [43]. The oxygen vacancies exert the following positive effects on enhancing the photocatalytic activity. First, the band structure of BMO has been modified for allowing efficient visible light utilization. Second, the charge separation efficiency is highly increased to enable efficient production of reactive radicals. Third, the electron localization around oxygen vacancy is favorable for the charge transfer and reactants activation.

3.4. In situ FT-IR investigation on the reaction mechanism

Fig. 8 shows the in-situ FT-IR spectra for NO adsorption in the dark and photocatalytic conversion processes under visible light irradiation over the surface of BMO and BMO-4. During the adsorption process (Fig. 8a and 8b), the bands at 1062 and 1070 cm^{-1} can be assigned to NO adsorbed on BMO and BMO-4

Fig. 7. Photocatalytic activities of the samples for NO purification in air under visible light illumination.

[44]. At the same time, the absorption peaks of bridged nitrates (1640 cm^{-1}) and NO_2^- (1286 , 989 and 1392 cm^{-1}) are dramatically increased for BMO-4, while those for BMO are relatively flat [45]. This result is attributed to the fact that the adsorbed O_2 could be activated by abundant free electrons localized by oxygen defects in BMO-4 to form superoxide radical ($\cdot\text{O}_2^-$) [46]. Hence, the NO could be partially oxidized to the final products (NO_3^- or NO_2^-) in the dark.

After visible light irradiation (Fig. 8c and 8d), the absorption peaks of nitrites (at 940 cm^{-1}), monodentate nitrates (at 1275 , 1276 and 1509 cm^{-1}) and bidentate nitrates (at 997 , 1015 , 1435 , 1392 , 1512 and 1711 cm^{-1}) can be detected in BMO and BMO-4 [37,41,47]. The appearance of those final products demonstrates that the photocatalytic NO oxidation is triggered by the reactive radicals. The IR bands of final products are significantly enhanced in BMO-4 in comparison with those which have no obvious change in BMO. In addition, the bridged nitrates (1640 cm^{-1}) disappear and are converted to more stable bidentate nitrates apart from the distinctly increased diverse forms of final products in BMO-4. Those observations can be ascribed to the fact that the oxygen vacancies could promote charge separation and mass production of radicals to enhance the photocatalytic oxidation [48,49]. This is consistent with the photocatalytic activity test that BMO-4 possesses much higher photocatalytic performance than that of BMO (Fig. 7). The corresponded photocatalytic reaction processes and reaction mechanism are proposed as follows (Eqs. 1–7 and Fig. 8).

Based on the extensive discussions, the pivotal effects of oxygen vacancies in Bi_2MoO_6 on the photocatalytic activity and reaction mechanism are illustrated in Fig. 9. The oxygen vacancies exert favorable effects in the aspects of extending the photo-response, enhancing the charge separation, formation of the localized electrons and thus boost the radical production

Fig. 8. In situ IR spectra of NO adsorption (a, b) and visible light reaction processes (c, d) over BMO and BMO-4.

Fig. 9. The diagram of photocatalytic reaction for NO removal over BMO and BMO-OVs.

[50–53].

4. Conclusions

A visible-light-driven photocatalyst Bi_2MoO_6 (BMO) with oxygen vacancies has been rationally designed and fabricated via a gentle and simple method. The Bi_2MoO_6 with oxygen vacancies (BMO-X) showed highly enhanced visible light photocatalytic performance for NO purification compared with that of the pristine Bi_2MoO_6 . This is primarily attributed to the oxygen vacancies that could provide an intermediate level in the band gap. This could promote the charge transfer and separation processes, and localize the abundant electrons to activate the adsorbed O_2 and generate reactive radicals. The adsorption

and reaction mechanism of photocatalytic oxidation NO was systematically studied by in situ FT-IR. The relevant reaction mechanism of photocatalytic NO oxidation was proposed. With the existence of oxygen vacancies in BMO-4, the production rate of the final products is promoted. This work opens a new avenue for the modification of Bi-based semiconductors and a new approach to unravel the mechanism of gas phase photocatalytic reaction.

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Graphical Abstract

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The pivotal effects of oxygen vacancy on Bi₂MoO₆: Promoted visible light photocatalytic activity and reaction mechanism

Yanjuan Sun*, Hong Wang, Qian Xing, Wen Cui, Jieyuan Li, Sujuan Wu, Lidong Sun*

Chongqing University; Chongqing Technology and Business University; Sichuan University

Oxygen vacancies promote the production rate of the final products in Bi₂MoO₆, because they provide an intermediate level to promote the charge transfer and separation, and localize the abundant electrons to activate the adsorbed O₂ and generate reactive radicals.

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氧空位对Bi₂MoO₆的关键作用：促进可见光光催化活性和反应机理

孙艳娟^{a,b,*}, 王 红^b, 邢 倩^b, 崔 雯^b, 李解元^c, 吴素娟^a, 孙立东^{a,#}

^a重庆大学材料科学与工程学院, 机械传动国家重点实验室, 重庆400044

^b重庆工商大学环境与资源学院, 催化与新环境材料重庆市重点实验室, 重庆400067

^c四川大学建筑与环境学院, 四川成都610065

摘要: Bi₂MoO₆(BMO)作为一种典型的Bi基光催化剂, 近年来受到越来越多的关注并被广泛应用. 然而, Bi₂MoO₆的可见光光催化活性仍然存在一些限制, 如有限的光响应范围和低电荷分离效率. 为了提高光催化活性, 研究者采取了各种策略, 包括元素掺杂、形成异质结构和形貌控制等. 早期研究表明, 氧空位可以拓展光催化剂的光吸收区域, 并且氧空位是光催化剂表面反应物活化最活跃的位点, 可以促进电荷分离和使电子局域化. 因此, 制备具有氧空位的Bi基光催化剂可能是提高其光催化性能的有效途径. 然而, 氧空位对Bi₂MoO₆电子结构和光催化反应机理的影响尚不清楚.

本文通过在制备过程中加入NaBH₄诱导氧空位形成, 合成出了具有氧空位的可见光驱动的Bi₂MoO₆微球(BMO-X). 利用UV-vis DRS光谱研究了合成后的光催化剂的光学吸收性能, 发现在产生氧空位后, BMO-4在可见区域的吸收显著增强, 带隙从BMO的2.40 eV降低到BMO-4的2.07 eV. 通常, 较强的光吸收能力对光催化反应更有利, 因为可以产生更多的光生载流子参与光催化作用. 将所制备的催化剂用于光催化净化NO, 结果表明具有氧空位的Bi₂MoO₆(BMO-4)的可见光催化NO净化效率为43.5%, 远高于本体Bi₂MoO₆(BMO)的可见光光催化活性(25.0%). 结合实验表征和理论计算结果, 探讨了氧空位对Bi₂MoO₆电子结构和光催化净化NO反应机理的影响. 采用低温固态电子顺磁共振(EPR)检测了催化剂中的氧空位, 在BMO中仅检测到弱的EPR信号, 表明BMO中几乎没有氧空位, 而BMO-4上的EPR信号非常强, 表明NaBH₄的引入诱导产生了大量的氧空位. DFT计算确认BMO-4的带隙内有中间能级形成. XPS测试结果表明, 与BMO相比, BMO-4的Bi–O峰值强度略有下降, 可能是由于部分Bi–O中缺少O原子以形成氧空位所致. PL结果表明, 具有氧空位的Bi₂MoO₆(BMO-4)显示出显著降低的光激发电子-空穴对分离效率, 可能是由于氧空位改变了Bi₂MoO₆的电子结构. 此外, 理论计算结果发现具有氧空位的Bi₂MoO₆的表面电子可以位于氧空位周围, 这有利于电荷分离和反应物活化. 同时, 该结果表明BMO-4中增强的电荷分离归因于氧缺陷对改进的电子结构的影响. 此外, 电子局域化可以为反应物活化提供额外的活性位点(O₂, NO等), 这可以促进BMO-4中自由基的产生和污染物转化. 利用原位红外光谱动态监测光催化NO氧化过程. 与本体Bi₂MoO₆相比, 引入氧空位后的Bi₂MoO₆光催化净化NO的反应机理未改变. 但是, BMO-4上终产物的特征峰强度显著增大. 此外, BMO-4上明显增加的多种形式的最终产物, 桥接硝酸盐消失并转化为更稳定的双齿硝酸盐. 这些结果可归因于氧空位可以促进电荷分离和自由基的大量产生, 从而增强光催化氧化性能. 本工作为理解光催化氧空位和气相光催化反应机理提供了新的见解.

关键词: 氧空位; 光催化; 反应机理; 原位红外光谱; 一氧化氮净化

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*通讯联系人. 电话/传真: (023)62769785; 电子信箱: syhsyj@163.com

#通讯联系人. 电子信箱: lidong.sun@cqu.edu.cn

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