available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Chloridion-induced dual tunable fabrication of oxygen-deficient Bi₂WO₆ atomic layers for deep oxidation of NO

Xianglong Yang [†], Shengyao Wang [†], Ting Chen, Nan Yang, Kai Jiang, Pei Wang, Shu Li, Xing Ding [#], Hao Chen ^{*}

College of Science, Key Laboratory of Environment Correlative Dietology of Ministry of Education, Huazhong Agricultural University, Wuhan 430070, Hubei, China

ARTICLE INFO

Article history:

Received 2 July 2020

Accepted 21 August 2020

Available online 22 November 2020

Keywords:

Oxygen vacancy

Bi₂WO₆ atomic layers

Chloridion

Photocatalysis

NO oxidation

ABSTRACT

Engineering an efficient interface is a trustworthy strategy for designing advanced photocatalytic systems for solar energy conversion. Herein, oxygen-deficient Bi₂WO₆ atomic layers without organic residues were successfully fabricated via a facile solvothermal strategy by the multifunctional regulatory mechanism of introduced chloridion. Both DFT calculations and speciation determination revealed that chloridion displayed a more pronounced effect in the controllable synthesis of oxygen-deficient Bi₂WO₆ atomic layers without organic residues: ultrathinning and defect-engineering. This built-in multi-cooperative interface endowed Bi₂WO₆ with intriguing photoelectrochemical properties, O₂ activation ability, and ultrahigh activity in visible-light powered deep oxidation of NO. A reasonable photocatalytic mechanism was proposed based on *in situ* infrared spectroscopy analysis and theoretical calculations. We believe that this multi-cooperative interface engineering of oxygen-deficient Bi₂WO₆ atomic layers without organic residues could provide new insights into the design of two-dimensional (2D) layered materials with efficient active sites and pave the way for efficient NO photooxidation systems.

© 2021, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Hazardous NO_x emissions from industrial waste gases have become a major source of secondary aerosols, which is the first and foremost factor for the frequent atmospheric haze that threatens the health of human beings [1]. To date, various efficient and environmentally friendly alternative technologies have been exploited to reduce NO_x emissions, including selective catalytic reduction (SCR), selective non-catalytic reduction

(SNCR), and semiconductor-based photocatalysis [2]. Among them, photocatalytic processes for NO_x removal, an advanced oxidation process (AOP), stands out by virtue of its intrinsic greenness and sustainability [3,4]. To improve the efficiency of the abovementioned photocatalytic reaction, current strategies are primarily focused on solar light harvesting and separation of carriers [5,6]. However, the microenvironment of the interface on the catalyst severely restricts the efficiency of NO_x removal based on the principle of gas-solid photocatalytic reac-

^{*} Corresponding author. Tel/Fax: +86-27-87288246; E-mail: hchenhao@mail.hzau.edu.cn[#] Corresponding author. Tel/Fax: +86-27-87288246; E-mail: dingx@mail.hzau.edu.cn[†] These authors contributed equally to this work.

This work was supported by the National Natural Science Foundation of China (51872107, 21607047, 21902055), the Natural Science Foundation of Hubei Province (2016CFB193) and Fundamental Research Funds for the Central Universities (2662020LXP001, 2662016PY088, 2662018QD041, 2015PY120, 2015PY047).

DOI: 10.1016/S1872-2067(20)63708-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 6, June 2021

tion [7]. Consequently, the search for suitable semiconductor photocatalysts for the engineering of interfaces with ultrahigh efficiency is one of the most prospective long-term solutions to cope with the highly desirable NO_x deep oxidation reaction to address air pollution issues.

Various advanced strategies have been delicately designed to promote interface reactions [8–10]. Among them, the realization of two-dimensional materials into a monolayer stands out because of the exposed abundant active sites and shortened carrier transportation distance [11–13]. Conventional atomically thick materials can be controllably fabricated through top-down exfoliation approaches or surfactant-assisted bottom-up strategies owing to the weak van der Waals interaction between layers [14]. For instance, monolayered MoS_2 , WS_2 , BiOBr , and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ were synthesized through ultrasonicated exfoliation [15–18]. Nonetheless, the layers stacked by van der Waals forces still lack sufficient reaction sites to secure ultrahigh catalytic capability, despite the large fraction of exposed surface atoms. Thanks to the pioneering work reported by Zhou et al. [19–21], another layered material, Aurivillius-phase oxides with different layers stacked together by strong chemical bonds have been successfully established as monolayers via surfactant-assisted bottom-up strategies. Distinct from van der Waals layered materials, these kinds of Aurivillius phase oxides are composed of $[\text{Bi}_2\text{O}_2]^{2+}$ layers linking a corner-sharing of octahedra with oxygen atoms bridged, which possesses excellent features of potential oxygen-vacancy (OV) fabrication after laminar construction [22]. It is well known that OVs-engineering is an available strategy to modulate the band structure and electronic properties of oxides [23,24]. Moreover, well-designed OVs could serve as active sites for improved adsorption and activation of substrate molecules [25–27]. Nevertheless, the typical synthetic routes of monolayered Aurivillius phase oxides require severe reaction conditions causing surface organic residues, which may tarnish the catalytic sites of the atomic layers, thus severely limiting the activities of such materials [28–30].

Bearing the aforementioned concepts in mind, engineering multi-cooperative interface via fabrication of oxygen-deficient Bi_2WO_6 atomic layers without organic residues is placed great expectations to introduce more efficient active-sites and avoid the long-chain surfactant residues. Halogen anions were reported to speak loudly in regulating the anisotropic growth of Aurivillius phase oxides and proved to have tight interactions with $[\text{Bi}_2\text{O}_2]^{2+}$ layers [21,29,31]. For instance, Zhou et al. [21] constructed Bi_2WO_6 monolayers with the assistance of CTAB, in which Br^- would bond to the monolayer surfaces to terminate the dangling bonds partly, and hinder the stacking of Bi_2WO_6 through Coulomb repulsion forces. Herein, we propose a simple dual-purpose strategy for fabricating a highly active Bi_2WO_6 atomic layer with a clean and oxygen-depleted surface via the assistance of chloridion. Theoretical calculations were first performed to check the feasibility of this proposal by comparing the influence of different halogens on the surface free energy and OVs formation energy over Bi_2WO_6 . Under the inspiration of theoretical calculations, we successfully constructed defective Bi_2WO_6 atomic layers without organic residues via a

facile solvothermal method with the assistance of chloridion, which displayed ultrahigh performance (64%) in the visible-light powered oxidation of NO_x to innocuous NO_3^- with selectivity exceeding 98%. Systematic characterizations and control measurements were carried out to investigate the specific role of chloridion in the synthesis of Bi_2WO_6 atomic layers, while the origin of the excellent photocatalytic performance was subsequently unveiled by checking the photoelectrochemical properties and O_2 activation ability. Subsequently, a reasonable photocatalytic mechanism for efficient NO_x removal was proposed according to the *in-situ* infrared spectroscopy analysis. This model of fabrication of oxygen-deficient Bi_2WO_6 atomic layers without organic residues might provide new insights into the design and engineering of multi-cooperative interfaces and paves the way for efficient NO_x photooxidation systems.

2. Experimental

2.1. Sample preparation

The chemical reagents were of analytical purity and utilized without further purification. Deionized (DI) water was used throughout this study.

Synthesis of BWO-X ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol at the beginning. Then, 30 mL aqueous solution containing 1 mmol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 0.4 mmol KX ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) was added dropwise to the as-prepared $\text{Bi}(\text{NO}_3)_3$ solution with vigorous stirring. After approximately 1 h, the mixture was transferred into a 100 mL reaction kettle and reacted for 12 h at 160 °C. The as-obtained products were subsequently filtered and washed with DI water and ethanol. The corresponding sample was dried at 60 °C in air and denoted as BWO-X ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) for further use. For comparison, BWO-None was also prepared via the same method without adding KX.

Synthesis of pristine Bi_2WO_6 nanoplates (BWO- H_2O). Typically, 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were completely dissolved in 60 mL of DI water. Then, 1 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added to the solution. After stirring for 1 h, the milk-white mixture was transferred into a 100 mL reaction kettle and heated at 160 °C for 24 h. Finally, the samples were collected via centrifugation, washed with DI water and ethanol, and dried in a vacuum oven.

Treating BWO-Cl and BWO-Br with nitric acid to remove amorphous BiOCl and BiOBr . 100 mg of BWO-Cl or BWO-Br powder were dispersed in 8 mL HNO_3 (1 M) and treated with an ultrasonic wash for an h, and the temperature of the water was maintained within 25–35 °C. After centrifugation, the clear supernatant solution was separated and filtered to remove the catalyst. Then, 50 mg of AgNO_3 were added to the supernatant solution to examine the dissolved Cl^- or Br^- . The corresponding precipitate was washed with DI water for several times until the pH of the supernatant solution was equal to 7.00 and dried in a vacuum oven at 60 °C for 10 h.

Digestion of BWO-Cl and BWO-Br with a mixture solution of HNO_3 and H_2O_2 . 100 mg BWO-Cl or BWO-Br powder were dis-

persed in 10 mL of a mixture solution of HNO_3 and H_2O_2 (4:1) and treated with an ultrasonic bath for 1 h, the temperature of water was maintained within 25–35 °C.

2.2. Photocatalytic performance

The photocatalytic performance of the catalysts was evaluated in terms of NO removal, which was operated in a 4.5 L homemade continuous-flow reactor at ambient temperature. Typically, a dish coating with 100 mg of catalyst was positioned in the middle of the reactor, and a high-power visible LED light source (PLS-LED 100, Beijing Perfectlight) served as the light source. The NO gas was supplied by diluting the 120×10^{-6} NO (Ar balance) to about 6.00×10^{-9} with an air-gas generator. The gas flow rate was controlled at 1 L/min using a gas calibrator. After achieving adsorption-desorption equilibrium, the lamp was turned on. The real-time concentration of NO_x was monitored with a NO_x analyzer (T200, Teledyne API).

2.3. In situ DRIFTS analysis for NO removal

In situ DRIFTS analysis was carried out using the FT-IR spectrometer (IS50, Thermo Fisher) containing the reaction cell and liquid nitrogen-cooled detector. In detail, the micromesh coating with catalysts was first placed in the middle of the cell. Then, Ar (50 mL/min) was utilized to remove the residual gases over the catalysts at 120 °C. After the temperature within the reaction cell dropped to 25 °C, the gas mixture of NO (120×10^{-6} , 10 mL/min) and O_2 (25 mL/min) was introduced

into it for 30 min to guarantee adsorption-desorption equilibrium before visible-light irradiation. The real-time IR signal was collected via a nitrogen-cooled MCT detector.

3. Results and discussion

3.1. DFT calculations

At the onset of this research, DFT calculations were performed to evaluate the potential impacts of different halogens on the formation of defective Bi_2WO_6 atomic layers with exposed (001) facets. Fig. S1 displays the typical crystal structure of orthorhombic Bi_2WO_6 , in which alternating $[\text{Bi}_2\text{O}_2]^{2+}$ layers are linked with a corner-sharing structure of a $[\text{WO}_4]^{2-}$ octahedra. To investigate the thermodynamic stability of atomic Bi_2WO_6 layers with different halogens, the surface free energy (γ) was calculated and is displayed in Fig. 1(a) [21]. Bi_2WO_6 with F[−], Cl[−], or Br[−] exhibited lower γ values (0.048, 0.055, or 0.057 eV/Å²) than the pristine and I[−]-modified Bi_2WO_6 (0.062 and 0.060 eV/Å²), implying the potential ability of F[−], Cl[−], and Br[−] in promoting the formation of atomic Bi_2WO_6 layers. Furthermore, we calculated the energy expenditure in the process of O atom departure, composed of hydrogenation and dehydration, to quantify the relative ease or difficulty in OV formation [32,33]. By comparing the corresponding energy expenditures (Fig. S2 and Table S1), it can be observed that halogen ions, especially Cl[−] and Br[−], can remarkably lower the required energy for OV formation (Figs. 1(a) and 1(b)). More specifically, the departure of O atoms from pristine Bi_2WO_6 is an endother-

Fig. 1. (a) The calculated surface free energy (γ) and formation energy (ΔE) of OVs with the existence of different halogens; (b) The energy expenditure of OVs formation on Bi_2WO_6 {001} facet with the assistance of Cl[−]; (c) Schematic illustration of bottom-up solvothermal strategy to synthesis defective Bi_2WO_6 atomic layers with the assistance of halogens.

mic process (2.49 eV). However, after the introduction of Cl^- or Br^- , the process is converted to be thermodynamically favorable with 1.14 and 0.57 eV of energy emission, respectively, which implies that Cl^- and Br^- anions are well suited for promoting the generation of OVs. Hence, we presume that the introduced Cl^- or Br^- anions may not only suppress the stacking of the Bi_2WO_6 layers but also facilitate the formation of OVs, in short, ultrathinning and defect engineering.

3.2. Fabrication of defective Bi_2WO_6 atomic layers

Under the inspiration of the above theoretical calculations, we subsequently proposed a facile solvothermal strategy to construct defective Bi_2WO_6 atomic layers with the assistance of different halogens. The overall fabrication processes are schematically displayed in Fig. 1(c). Typically, a W source was added to the glycol solution containing a stoichiometric Bi source, forming irregular Bi_2WO_6 seeds. After the introduction of different halogens (KX, X = F, Cl, Br, I), the halogen anions would bond to the $[\text{Bi}_2\text{O}_2]^{2+}$ layers because of the strong electrostatic attraction between them. Thus, the dangling bonds between the $[\text{Bi}_2\text{O}_2]^{2+}$ layers and $[\text{WO}_4]^{2-}$ slabs would be partly terminated, and the Bi_2WO_6 surface would be negatively charged, which would suppress the stacking of the Bi_2WO_6 atomic layers

through Coulomb repulsion forces instead of long-chain surfactant. Moreover, the strong interactions between halogens and Bi atoms in the $[\text{Bi}_2\text{O}_2]^{2+}$ layers could also weaken the neighboring Bi–O bonds, thus lowering the required energy for the departure of O atoms, facilitating the fabrication of oxygen-deficient Bi_2WO_6 atomic layers during the reductive glycol-assisted solvothermal process.

As expected, all the X-ray diffraction (XRD) patterns (Fig. S3(a)) can be indexed to an orthorhombic phase Bi_2WO_6 (JCPDS No. 73-2020), implying that the addition of halogen anions did not affect the crystalline phase of Bi_2WO_6 . For the Raman spectra (Fig. S3(b)), typical stretching modes were also observed for all the samples. Bands around 798 cm^{-1} with two shoulders at 828 and 725 cm^{-1} are indexed to the A_g mode and E_u mode of the WO_6 octahedra, respectively. The band at 307 cm^{-1} could be assigned to translational modes involving simultaneous motions of Bi^{3+} and WO_6^{6-} [34,35]. It is worth noting that BWO-Cl and BWO-Br demonstrate much weaker Raman signals than the other samples, in line with the XRD patterns, demonstrating their poorer crystallinity and smaller crystal size. The morphologies of the samples were examined using TEM and FE-SEM images. Intriguingly, only BWO-Cl and BWO-Br are composed of ultrathin and well-distributed nanosheets (Figs. 2(a), 2(c), and S4), while BWO- H_2O ,

Fig. 2. TEM images of BWO-Cl (a) and BWO-Br (c); AFM images and the corresponding height profile of BWO-Cl (b) and BWO-Br (d); (e) ESR spectra of the samples; (f) The spin concentration and AFM-height of BWO-Cl with different dosages of KCl.

BWO-None, BWO-F, and BWO-I exhibit hierarchical structures assembled from radically grown and thicker sheets (Fig. S5). Moreover, the anisotropic growth of Bi_2WO_6 was clearly found to be restrained stage by stage with the additive dosage increase of Cl^- and Br^- (Figs. S6(c) and 6(f)). A similar phenomenon was also observed with the addition of different chlorine sources, thereby excluding the possible impacts of K^+ cations (Figs. S6(g) and 6(i)). To visually reveal the capacity of Cl^- and Br^- in Bi_2WO_6 ultrathinning, we also recorded the AFM images of representative samples (Fig. S7). BWO- H_2O has an average sheet thickness of 24 nm. For solvothermally synthesized Bi_2WO_6 , the aggregation of the nanosheets was hampered as the dosage of KCl increased from 0 to 0.6 mmol. In line with the aforementioned TEM images, their thickness demonstrates a gradual decrease until the formation of Bi_2WO_6 atomic layers. At the same dosage of KCl and KBr (0.4 mmol), the acquired BWO-Cl and BWO-Br have an average sheet thickness of 1.6 and 2.4 nm (Figs. 2(b) and 2(d)), which agrees well with the 0.82 nm thickness of a monolayer Bi_2WO_6 slab along the [001] direction [21,36]. In addition, avoiding the use of long-chain surfactants endows Bi_2WO_6 layers relatively without organic residues. That is consistent with the aforementioned DFT calculations, the introduced Cl^- and Br^- indeed facilitated the fabrication of Bi_2WO_6 atomic layers.

Notably, although the high electronegativity of fluorine atoms endows BWO-F the lowest γ value, it still displays a hierarchical structure. This might result from the weak interaction between introduced F^- and $[\text{Bi}_2\text{O}_2]^{2+}$ layers, on the basis of the much higher solubility of BiOF relative to BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [37–39], and thus its impacts were ignored. Subsequently, the OV generation on Bi_2WO_6 was indirectly analyzed through EPR tests (Figs. 2(e) and S6) because OVs can stabilize single electrons and endow the material with a paramagnetic signal. As anticipated, typical OV signals at $g = 2.001$ are only observed for BWO-Cl and BWO-Br and gradually strengthened with the increase in the additive dosage of both Cl^- and Br^- , signifying the indispensable ability of Cl^- and Br^- anions in facilitating the formation of OVs [40]. Fig. 2(f) also displays the variations in the spin concentration and AFM-height of representative BWO-Cl with the dosage of KCl, which visually confirmed that Cl^- and Br^- can not only promote the formation of oxygen vacancies but also facilitate the ultrathinning of Bi_2WO_6 layers, complying with the aforementioned DFT calculations. Based on the above discussion, it can be concluded that oxygen-deficient Bi_2WO_6 atomic layers could be successfully fabricated with the assistance of Cl^- or Br^- anions.

3.3. Indispensable role of Cl^-

In light of the indispensable role of Cl^- or Br^- in the fabrication of defective Bi_2WO_6 atomic layers, we resorted to high-resolution (HR) TEM and XPS to investigate the speciation of Cl^- and Br^- anions. In the HRTEM images, orthogonal lattice fringes were measured to be 0.272 and 0.273 nm (Fig. S8), assigned to the (020) and (200) planes of Bi_2WO_6 , implying the {001} exposed facets of the nanosheets [21]. This was further confirmed by the atomic-resolution HAADF-STEM images of

the representative BWO-Cl, in which a legible interplanar lattice ascribed to the (200) and (020) planes can be easily observed from the top view of the nanosheets (Fig. 3(a)), demonstrating the exposed clean surfaces. In addition, the side view (Fig. 3(b)) clearly reflects the ultrathin nanosheets with a thickness of ca. 1.6 nm, which is consistent with the previous AFM results and exactly coincides with that of the monolayer Bi_2WO_6 sheet along the [001] direction (corresponding to 1 of the unit cell size in the c -axis direction). Moreover, lattice spacings of 0.193 and 0.274 nm were also observed, assigned to the (220) and (006) planes of Bi_2WO_6 , respectively. Notably, the simulated patterns of Bi and W ions on the (1 $\bar{1}$ 0) and (001) planes of Bi_2WO_6 agreed well with the lattice (inset of Fig. 3), consistent with our established atomistic models, demonstrating the successful fabrication of atomic Bi_2WO_6 layers. To confirm the existence and distribution of chloridion, EDX mapping images were acquired, which displayed the distribution of Bi, W, O, and Cl elements, respectively (Fig. 3(c)). As can be seen, the Cl element is homogeneously dispersed in the overall area of the selected area of BWO-Cl.

XPS was further utilized to investigate the chemical states of the as-synthesized samples. No significant difference was observed in the Bi 4f and W 4f XPS spectra (Figs. S9(a)–9(c)) [41], which could be ascribed to the limited concentration of introduced oxygen vacancies. As for O 1s spectra, the peak located at 529.9 eV corresponding to Bi–O bond in BWO-Cl and BWO-Br was much weaker than that in BWO- H_2O or BWO-None, indicating the partial departure of O atoms bonded with Bi atoms under the reductive solvothermal circumstance (Fig. 3(d)) [42,43]. An additional peak at 531.8 eV was observed in the O 1s spectra of BWO-None, BWO-Cl, and BWO-Br, which can be indexed to the O–H bond of surface hydroxyl or H_2O on the basis of the FT-IR spectra (Fig. S9(d)) [44]. Most importantly, Cl 2p peaks (199.5 and 198.0 eV) and Br 3d peaks (69.3 and 68.3 eV) were observed for BWO-Cl and BWO-Br, close to the binding energies of Cl 2p in BiOCl and Br 3d in BiOBr , respectively (Fig. 3(e)) [29,45,46]. This implies that the introduced Cl^- and Br^- anions might directly bond with the surficial Bi atoms or exist in the form of amorphous BiOX reported by Li's group [29].

For further confirmation, we treated the BWO-Cl and BWO-Br with 1 M HNO_3 or digestion reagents (HNO_3 and H_2O_2), respectively, and employed ion chromatography to determine the dissolution quantity of Cl^- and Br^- anions (Table 1). Notably, the amorphous BiOX ($\text{X} = \text{Cl}, \text{Br}$) is soluble in HNO_3 , while Bi_2WO_6 is not. Both amorphous BiOX and Bi_2WO_6 are soluble in digestion reagents (HNO_3 and H_2O_2). Therefore, the detected Cl^- and Br^- in the HNO_3 solution must be derived from the amorphous BiOX ($\text{X} = \text{Cl}, \text{Br}$), while the Cl^- and Br^- in the digestion reagents (HNO_3 and H_2O_2) demonstrate their total amounts. Surprisingly, the amount of Cl^- and Br^- anions dissolved in the digestive solution was much higher than that dissolved from amorphous BiOX , implying that only part of the introduced Cl^- and Br^- anions substitute WO_4^{2-} to form amorphous BiOCl and BiOBr regions, while most of them are bonded with Bi atoms and suppress the stacking of the Bi_2WO_6 layers, and favor the departure of adjacent O atoms.

Fig. 3. Atomic-resolution HAADF-STEM images of the BWO-Cl nanosheets, the top-view (a) and the side-view (b); (c) EDS mapping of the representative BWO-Cl nanosheets; XPS spectra O 1s of BWO-H₂O, BWO-None, BWO-Cl, and BWO-Br (d), Cl 2p of BWO-Cl and Br 3d of BWO-Br (e).

Based on the above results and discussion, a plausible mechanism was proposed for the fabrication of defective Bi₂WO₆ atomic layers without organic residues. As a typical Aurivillius oxide, Bi₂WO₆ is composed of [Bi₂O₂]²⁺ layers linked with a corner-sharing structure of [WO₄]²⁻ octahedra. BiOX (X = Cl, Br), also featuring a layered structure, is stacked by the repetitive unit of (X-Bi-O-Bi-X) via van der Waals interactions [47]. During our synthetic process, only Cl⁻ or Br⁻ anions would bond to the [Bi₂O₂]²⁺ layers because of the strong electrostatic attraction between them. As a consequence, the stacking of the Bi₂WO₆ layers along the [001] direction would be suppressed, thus leading to ultrathin structures without the introduction of a long-chain surfactant. Meanwhile, the strong interactions between Cl⁻ (or Br⁻) and Bi atoms in the [Bi₂O₂]²⁺ layers would also weaken the adjacent Bi–O bonds, lower the required energy for the departure of O atoms, thereby facilitating the formation of oxygen vacancies. As a result, Bi₂WO₆ atomic layers with relatively clean and oxygen-depleted surfaces were successfully fabricated with the assistance of Cl⁻ or Br⁻ anions. Nevertheless, excessive Cl⁻ or Br⁻ anions would compete with and partially substitute WO₄²⁻, destroying the regular crystal structure and yielding amorphous BiOCl or BiOBr regions (Fig. S8).

3.4. Photoelectrochemical properties

Thereafter, systematic characterizations were carried out to unveil the impacts of ultrathinning and defect-engineering on the photoelectrochemical properties of Bi₂WO₆. The UV-Vis absorption spectra in Fig. 4(a) reveal that BWO-Cl and BWO-Br possessed much stronger light-harvesting capacity in the Vis-NIR region, compared with BWO-H₂O and BWO-None. The faint blue-shift of the light absorption edges after the introduction of Cl⁻ and Br⁻ can be ascribed to the existence of oxygen vacancies and quantum size effects of the ultrathin structure [14]. To understand the variation of photoabsorption in the Vis-NIR region theoretically, theoretical calculations were performed to determine the band structures and density of states of BWO and BWO-OVs (Fig. S10). Intriguingly, an extra inter-

Table 1

The determination of Cl⁻, Br⁻, and Bi³⁺ in the samples after washing and digestion.

Samples		Cl (mg·g ⁻¹)	Br (mg·g ⁻¹)	Bi (mg·g ⁻¹)
Washing with 1M HNO ₃	BWO-H ₂ O	0.00	0.00	14.56
	BWO-None	0.00	0.00	14.96
	BWO-Cl	1.31	0.00	67.20
	BWO-Br	0.00	3.66	90.00
Digestion with HNO ₃ and H ₂ O ₂	BWO-H ₂ O	0.00	0.00	530.00
	BWO-None	0.00	0.00	516.00
	BWO-Cl	12.12	0.00	352.00
	BWO-Br	0.00	19.96	384.00

Fig. 4. (a) Diffuse reflectance ultraviolet-visible spectra, (the inset is the plots of $(ah\nu)^{1/2}$ versus photon energy $(h\nu)$); (b) schematic band diagrams of the samples; (c) Photocurrent response spectra; (d) Photocatalytic NO removal over the BWO-H₂O, BWO-None, BWO-Cl, and BWO-Br; (e) Cyclic NO removal tests and (f) corresponding NO₂ concentration.

mediate band was observed within the band gap of BWO-OVs, indicating the development of defect levels, which explains the extended photoresponse region of BWO-Cl and BWO-Br [42]. Further, their band positions were pinpointed on the basis of the Mott-Schottky curve and valence-band XPS spectra (Fig. S11). The respective data are shown in Fig. 4(b) and summarized in Table S2, suggesting the feasibility of $\cdot O_2^-$ generation over them. Fig. 4(c) displays the photocurrent response spectra, in which BWO-Cl and BWO-Br featured higher photocurrents than BWO-H₂O and BWO-None, demonstrating the fast interfacial charge transfer in the ultrathin and defective Bi₂WO₆ layers. Similarly, BWO-Cl and BWO-Br also demonstrated smaller radii in the electrochemical impedance spectra (Fig. S12(a)), corresponding to their superior conductivity. However, BWO-Cl and BWO-Br exhibited a slightly higher fluorescence than BWO-None (Fig. S12(b)), which could be ascribed to the excessive photoinduced e^-/h^+ pairs. From the perspective of electron dynamics, such a dramatic increase in both charge separation and transfer efficiency ensured more charge carriers from BWO-Cl and BWO-Br to participate in the catalytic reaction, which might remarkably ameliorate the photocatalytic ability of Bi₂WO₆.

3.5. Deep oxidation of NO

For confirmation, we constructed a real-time monitoring apparatus (Fig. S13) to compare the performances of as-obtained catalysts with the anthropogenically derived NO as the model pollutant, which has received extensive attention because of its range of environmental problems [48]. The kinetic curves of NO removal with different catalysts are displayed in Fig. 4(d). As anticipated, the defective BWO-Cl and BWO-Br exhibited superior photocatalytic performances with

ultimate NO removal rates of 64% and 58%, respectively, compared with BWO-H₂O (35%), BWO-None (49%), and other state-of-art catalysts, such as defective TiO₂, self-doped Bi₂MoO₆, and defective BiOCl (Table S3). Notably, the NO removal efficiency over BWO-H₂O decreased gradually after 30 min, which should be attributed to the synergetic effects of NO₃⁻ accumulation and a lack of active-sites. As the oxidation of NO proceeds, the produced NO₃⁻ accumulates and covers the limited active-sites on the BWO-H₂O surface, thus lowering the NO removal activity. In addition, the noxious intermediate product NO₂ released over BWO-Cl and BWO-Br (8×10^{-9} – 12×10^{-9}) shown in Fig. S14(a), was also much lower than that over BWO-H₂O ($> 20 \times 10^{-9}$) and BWO-None ($> 35 \times 10^{-9}$), indicating that most of the NO was directly oxidized to NO₃⁻ (Fig. S14(b)) with a selectivity exceeding 98%. For a better comparison, we also assessed the catalytic performance of Bi₂WO₆ samples with varying dosages of halogens and HNO₃-treated BWO-Cl (Fig. S15). The NO removal efficiency demonstrated a typical peak-shape trend as the dosages increasing from 0.1 to 0.6 mmol and hit the breakthrough by adding 0.4 mmol KCl or KBr. Even after 4 consecutive photocatalytic cycles (1 h for each cycle), the catalysts BWO-Cl and BWO-Br presented no significant decrease in performance (activity and selectivity) (Figs. 4(e) and 4(f)). Notably, after removing the amorphous BiOX by HNO₃ washing, the catalyst retained its original catalytic performance, thereby demonstrating that the trifling amorphous BiOX on the Bi₂WO₆ surface had no effect on its photocatalytic performance.

As previous reports suggested that reactive oxygen species (ROS) are notably relevant for NO removal, trapping measurements were conducted to investigate the reaction mechanism [14,49]. K₂Cr₂O₇, triethanolamine (TEOA), tert-butyl alcohol (TBA), p-benzoquinone (PBQ), and β -carotene were utilized as

the scavengers for e^- , h^+ , $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and $^1\text{O}_2$, respectively (Figs. S16(a) and 16(b)). It can be observed that 88%, 81%, and 40% removal of NO was hampered by trapping e^- , $\bullet\text{O}_2^-$, and $^1\text{O}_2$, respectively. Considering the significant roles of photoinduced electrons in the generation of ROS, $\bullet\text{O}_2^-$ and $^1\text{O}_2$ are inferred to be the main active species for removing NO. Their contributions to the NO removal system were further verified by electron spin resonance (ESR) spectra (Figs. S16(c)–16(e)), where BWO-Cl and BWO-Br generated more $\bullet\text{O}_2^-$ and $^1\text{O}_2$ than the defect-free BWO- H_2O and BWO-None under visible-light irradiation. Since all the ROS originate from the absorption and conversion of O_2 , we subsequently checked the physisorption and chemisorption of O_2 over the Bi_2WO_6 samples. Fig. S17(a) revealed the calculated adsorption energies of O_2 over pristine and defective Bi_2WO_6 . Obviously, the defect-free Bi_2WO_6 {001} surface was fairly inert for O_2 adsorption. In contrast, O_2 in the bridging mode interacted strongly with the clean and oxygen-depleted surfaces, since there are no surface organic residues impeding the O_2 adsorption. On the one hand, O_2 of the lower $2\pi^*$ orbital energy can accept the localized electrons around OV. This result was further verified by the BET and TPD results (Figs. S17(b) and S17(c)). Taking the extremely low concentration of NO into account, aerobic catalytic NO removal should follow the Eley-Rideal mechanism [49], through which NO would attack the $\bullet\text{O}_2^-$ located at OV previously.

To visually reveal the conversion pathways and reaction mechanism of photocatalytic NO oxidation over the samples, *in situ* DRIFTS tests were performed in a unique reaction cell (Fig. S18) to dynamically check the reaction intermediates and products on the catalyst surface. Fig. S19(a)–S19(d) depicted

the IR spectra of the NO (120×10^{-6} , 10 mL/min) and O_2 (25 mL/min) interaction with the samples prior to irradiation, where all the bands showed positive growth and remarkable differences could be observed between BWO- H_2O and other samples. The respective attributions of the bands are listed in Table S4. Bands located at 1623, 1528, and 1288 cm^{-1} were assigned to the monodentate nitrite, bridged nitrate, and monodentate nitrate on the surface of BWO- H_2O [41,50,51]. In the case of the other samples, adsorption peaks centered at 1623, 1456, and 832 cm^{-1} were observed, which can be assigned to monodentate nitrite, linear nitrite, and monodentate nitrite, respectively [41,51,52]. The differences in NO absorption modes might originate from the introduced OV, which support the O_2 in bridging mode interacting strongly with the surface. The DRIFTS spectra of the NO oxidation process over the samples were also recorded under visible-light irradiation (Figs. 5(a), 5(b), S19(e), and S19(f)). The band at 1623 cm^{-1} displayed obvious negative growth as the light was on, suggesting the effective conversion of absorbed NO. At the same time, new bands at 1534, 1498, 1278, 997, and 865 cm^{-1} were noticed to rise along with the irradiation time. Among these, bands at 1534 and 1278 cm^{-1} over BWO- H_2O were assigned to the bridging nitrate and monodentate nitrate, respectively. The new bands at 1498 and 997 cm^{-1} were ascribed to the different vibration modes of bidentate nitrate [41,51,53], and the band at 865 cm^{-1} could be assigned to the O–O stretching mode of surface peroxo species [49]. Notably, BWO-Cl and BWO-Br displayed a more remarkable increase in the signals of monodentate nitrate, and the band at 865 cm^{-1} was only detected in their spectra, corresponding to their superior photocatalytic per-

Fig. 5. *In situ* DRIFTS spectra of NO and O_2 interaction with BWO- H_2O (a) and BWO-Cl (b) under visible-light irradiation; (c) Calculated reaction pathways for NO photoconversion over BWO and BWO-OVs, “*” represents adsorption on the substrate. d) Illustration of the solar-driven deep oxidation of NO.

formance in selective NO oxidation with the assistance of active $\bullet\text{O}_2^-$. To determine the fantastic NO removal reactivity of oxygen-deficient Bi_2WO_6 {001} facets in thermodynamics, corresponding DFT calculations were conducted. Fig. 5(c) illustrates the calculated stepwise Gibbs free energy for NO conversion. Notably, all the processes of NO oxidation are exothermic, except for the desorption of HNO_3 . The conversion of NO to HNO_3 on oxygen-deficient Bi_2WO_6 is more thermodynamically favorable than that on pristine Bi_2WO_6 , according to the corresponding energy expenditure, which well explains the much improved photocatalytic activity of deficient Bi_2WO_6 atomic layers. Integrating the above results, the major procedures of NO removal are shown in Fig. 5(d) and summarized in the following steps: (1) the deficient Bi_2WO_6 atomic layers facilitate the absorption and activation of O_2 , (2) the absorbed O_2 is converted into reactive $\bullet\text{O}_2^-$ and $^1\text{O}_2$ under light irradiation; and (3) in the presence of ROS, NO is completely oxidized to NO_3^- , which would subsequently be hydrogenated to HNO_3 and departure from the surface of the catalysts.

4. Conclusions

In summary, oxygen-deficient Bi_2WO_6 atomic layers without organic residues were successfully obtained via a facile solvothermal method with the assistance of Cl^- or Br^- . Various characterizations and DFT calculations indicated that the introduced Cl^- and Br^- anions play an indispensable role in the controllable synthesis of Bi_2WO_6 , suppressing the stacking of the Bi_2WO_6 layers and facilitating the formation of OV. As a result, the built-in multi-cooperative interface endowed BWO-Cl and BWO-Br atomic layers with fantastic photoelectrochemical properties and O_2 activation ability, and hence demonstrated ultrahigh performance in visible-light powered NO oxidation. According to *in situ* infrared spectroscopy analysis, a reasonable photocatalytic mechanism for efficient NO removal was also proposed. We believe that this multi-cooperative interface engineering via fabrication of oxygen-deficient Bi_2WO_6 atomic layers could provide new insights into the design and preparation of defective atomically-thick 2D materials and pave the way to construct efficient NO photooxidation systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Electronic supporting information

Supporting information is available in the online version of this article.

References

- [1] Y. Chen, G. Shen, Y. Lang, R. Chen, L. Jia, J. Yue, M. Shen, C. Du, B. Shan, *J. Catal.*, **2020**, 384, 96–105.
- [2] J. Liu, Z. Zhao, C. Xu, J. Liu, *Chin. J. Catal.*, **2019**, 40, 1438–1487.
- [3] J. Liao, L. Chen, M. Sun, B. Lei, X. Zeng, Y. Sun, F. Dong, *Chin. J. Catal.*, **2018**, 39, 779–789.
- [4] G. Jiang, X. Li, M. Lan, T. Shen, X. Lv, F. Dong, S. Zeng, *Appl. Catal. B*, **2017**, 205, 532–540.
- [5] T. Huang, Y. Li, X. Wu, K. Lv, Q. Li, M. Li, D. Du, H. Ye, *Chin. J. Catal.*, **2018**, 39, 718–727.
- [6] J. Low, J. Yu, M. Jaroniec, S. Wageh, A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [7] X. Chang, T. Wang, J. Gong, *Energy Environ. Sci.*, **2016**, 9, 2177–2196.
- [8] S. Bai, N. Zhang, C. Gao, Y. Xiong, *Nano Energy*, **2018**, 53, 296–336.
- [9] H. Shang, M. Li, H. Li, S. Huang, C. Mao, Z. Ai, L. Zhang, *Environ. Sci. Technol.*, **2019**, 53, 6444–6453.
- [10] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, **2011**, 293, 269–271.
- [11] Y. Sun, S. Gao, F. Lei, C. Xiao, Y. Xie, *Acc. Chem. Res.*, **2015**, 48, 3–12.
- [12] Y. Sun, S. Gao, F. Lei, Y. Xie, *Chem. Soc. Rev.*, **2015**, 44, 623–636.
- [13] M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, H. Zhang, *Nat. Chem.*, **2013**, 5, 263–275.
- [14] S. Wang, X. Ding, X. Zhang, H. Pang, X. Hai, G. Zhan, W. Zhou, H. Song, L. Zhang, H. Chen, J. Ye, *Adv. Funct. Mater.*, **2017**, 27, 1703923.
- [15] X. Fan, P. Xu, D. Zhou, Y. Sun, Y.C. Li, M. A. Nguyen, M. Terrones, T. E. Mallouk, *Nano Lett.*, **2015**, 15, 5956–5960.
- [16] Z. Zeng, Z. Yin, X. Huang, H. Li, Q. He, G. Lu, F. Boey, H. Zhang, *Angew. Chem. Int. Ed.*, **2011**, 50, 11093–11097.
- [17] J. Wu, X. Li, W. Shi, P. Ling, Y. Sun, X. Jiao, S. Gao, L. Liang, J. Xu, W. Yan, C. Wang, Y. Xie, *Angew. Chem. Int. Ed.*, **2018**, 57, 8719–8723.
- [18] J. Li, G. Zhan, Y. Yu, L. Zhang, *Nat. Commun.*, **2016**, 7, 11480.
- [19] J. Liu, L. Wang, W. Song, M. Zhao, J. Liu, H. Wang, Z. Zhao, C. Xu, Z. Duan, *ACS Sustainable Chem. Eng.*, **2019**, 7, 2811–2820.
- [20] L. Liang, F. Lei, S. Gao, Y. Sun, X. Jiao, J. Wu, S. Qamar, Y. Xie, *Angew. Chem. Int. Ed.*, **2015**, 54, 13971–13974.
- [21] Y. Zhou, Y. Zhang, M. Lin, J. Long, Z. Zhang, H. Lin, J. C. Wu, X. Wang, *Nat. Commun.*, **2015**, 6, 8340.
- [22] N. Zhang, R. Ciriminna, M. Pagliaro, Y. J. Xu, *Chem. Soc. Rev.*, **2014**, 43, 5276–5287.
- [23] X. Chen, L. Liu, P. Y. Yu, S. S. Mao, *Science*, **2011**, 331, 746–750.
- [24] J. Yan, G. Wu, N. Guan, L. Li, Z. Li, X. Cao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 10978–10988.
- [25] K. Zhao, L. Zhang, J. Wang, Q. Li, W. He, J. J. Yin, *J. Am. Chem. Soc.*, **2015**, 135, 15750–15753.
- [26] H. Li, J. Shang, Z. Ai, L. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 6393–6399.
- [27] H. Li, J. Li, Z. Ai, F. Jia, L. Zhang, *Angew. Chem. Int. Ed.*, **2018**, 57, 122–138.
- [28] J. Hou, S. Cao, Y. Wu, F. Liang, Y. Sun, Z. Lin, L. Sun, *Nano Energy*, **2017**, 32, 359–366.
- [29] X. Cao, Z. Chen, R. Lin, W. C. Cheong, S. Liu, J. Zhang, Q. Peng, C. Chen, T. Han, X. Tong, Y. Wang, R. Shen, W. Zhu, D. Wang, Y. Li, *Nat. Catal.*, **2018**, 1, 704–710.
- [30] C. Dong, C. Lian, S. Hu, Z. Deng, J. Gong, M. Li, H. Liu, M. Xing, J. Zhang, *Nat. Commun.*, **2018**, 9, 1252.
- [31] S. Wang, X. Ding, N. Yang, G. Zhan, X. Zhang, G. Dong, L. Zhang, H. Chen, *Appl. Catal. B*, **2020**, 265, 118585.
- [32] B. J. Morgan, G. W. Watson, *J. Phys. Chem. C*, **2009**, 113, 7322–7328.
- [33] T. Jing, Y. Dai, W. Wei, X. Ma, B. Huang, *Phys. Chem. Chem. Phys.*, **2014**, 16, 18596–18604.
- [34] R. Shi, G. Huang, J. Lin, Y. Zhu, *J. Phys. Chem. C*, **2009**, 113, 19633–19638.

Graphical Abstract

Chin. J. Catal., 2021, 42: 1013–1023 doi: 10.1016/S1872-2067(20)63708-1

Chloridion-induced dual tunable fabrication of oxygen-deficient Bi_2WO_6 atomic layers for deep oxidation of NO

Xianglong Yang, Shengyao Wang, Ting Chen, Nan Yang, Kai Jiang, Pei Wang, Shu Li, Xing Ding*, Hao Chen*
Huazhong Agricultural University

Chloridion plays an indispensable role in the fabrication of oxygen-deficient Bi_2WO_6 atomic layers: ultrathinning and defect-engineering. The as-prepared BWO-Cl displayed intriguing photoelectrochemical properties and O_2 activation ability, thereby exerting ultrahigh activity in the visible-light powered deep oxidation of NO.

- [35] L. Zhang, Y. Man, Y. Zhu, *ACS Catal.*, **2011**, 1, 841–848.
 [36] Y. Zhou, Z. P. Tian, Z. Y. Zhao, Q. Liu, J. H. Kou, X. Y. Chen, J. Gao, S. C. Yan, Z. G. Zou, *ACS Appl. Mater. Interfaces*, **2011**, 3, 3594–3601.
 [37] W. Su, J. Wang, Y. Huang, W. Wang, L. Wu, X. Wang, P. Liu, *Scripta Mater.*, **2010**, 62, 345–348.
 [38] K. Ren, J. Liu, J. Liang, K. Zhang, X. Zheng, H. Luo, Y. Huang, P. Liu, X. Yu, *Dalton Trans.*, **2013**, 42, 9706–9712.
 [39] M. S. Kandanapitiye, M. Gao, J. Molter, C. A. Flask, S. D. Huang, *Inorg. Chem.*, **2014**, 53, 10189–10194.
 [40] X. Y. Kong, Y. Y. Choo, S. P. Chai, A. K. Soh, A. R. Mohamed, *Chem. Commun.*, **2016**, 52, 14242–14245.
 [41] L. Wang, K. Xu, W. Cui, D. Lv, L. Wang, L. Ren, X. Xu, F. Dong, S. Dou, W. Hao, Y. Du, *Adv. Funct. Mater.*, **2019**, 29, 1808084.
 [42] X. Yang, S. Wang, N. Yang, W. Zhou, P. Wang, K. Jiang, S. Li, H. Song, X. Ding, H. Chen, J. Ye, *Appl. Catal. B*, **2019**, 259, 118088.
 [43] X. Xu, X. Ding, X. Yang, P. Wang, S. Li, Z. Lu, H. Chen, *J. Hazard. Mater.*, **2019**, 364, 691–699.
 [44] Z. Wei, Y. Liu, J. Wang, R. Zong, W. Yao, J. Wang, Y. Zhu, *Nanoscale*, **2015**, 7, 13943–13950.
 [45] F. Dong, Y. Sun, M. Fu, Z. Wu, S. C. Lee, *J. Hazard. Mater.*, **2012**, 219, 26–34.
 [46] L. Sun, L. Xiang, X. Zhao, C. Jia, J. Yang, Z. Jin, X. Cheng, W. Fan, *ACS Catal.*, **2015**, 5, 3540–3551.
 [47] L. Ye, Y. Su, X. Jin, H. Xie, C. Zhang, *Environ. Sci. Nano*, **2014**, 1, 90–112.
 [48] X. Ding, W. Ho, J. Shang, L. Zhang, *Appl. Catal. B*, **2016**, 182, 316–325.
 [49] H. Li, H. Shang, X. Cao, Z. Yang, Z. Ai, L. Zhang, *Environ. Sci. Technol.*, **2018**, 52, 8659–8665.
 [50] W. Wang, G. McCool, N. Kapur, G. Yuan, B. Shan, M. Nguyen, U. M. Graham, B. H. Davis, G. Jacobs, K. Cho, X. Hao, *Science*, **2012**, 337, 832–835.
 [51] W. C. Huo, X. A. Dong, J. Y. Li, M. Liu, X. Y. Liu, Y. X. Zhang, F. Dong, *Chem. Eng. J.*, **2019**, 361, 129–138.
 [52] G. Jiang, X. Li, M. Lan, T. Shen, X. Lv, F. Dong, S. Zhang, *Appl. Catal. B*, **2017**, 205, 532–540.
 [53] Y. Zhou, Z. Zhao, F. Wang, K. Cao, D. E. Doronkin, F. Dong, J. D. Grunwaldt, *J. Hazard. Mater.*, **2016**, 307, 163–172.

Cl⁻诱导的含氧空位原子层厚 Bi_2WO_6 的可控合成及其深度氧化NO性能

杨祥龙[†], 汪圣尧[†], 陈婷, 杨楠, 江开, 汪佩, 李淑, 丁星[#], 陈浩^{*}

华中农业大学理学院, 环境食品教育部重点实验室, 湖北武汉430070

摘要: 开发具有高量子效率的半导体光催化材料是极具前景的解决能源短缺和环境污染问题的策略。在已报道的诸多光催化材料中, 超薄二维(2D)材料表现突出, 凭借其高效的载流子分离传输性能备受研究者的青睐。然而, 苛刻的合成条件、缺乏表面活性位点等问题制约了其应用。因此, 温和可控地合成具有大量活性位点的原子层厚2D材料具有重要的意义。作为典型的Aurivillius氧化物, Bi_2WO_6 具有独特的层状晶体结构和合适的能带位置; 另一方面, 其表面Bi–O键的能量较低, 氧原子在缺氧条件下经热处理容易逸出, 进而产生氧空位。已知氧空位引入是调节半导体能带组成和电子结构的有效手段, 不仅能改善其光电性能, 而且能提供反应活性位点; 因此, Bi_2WO_6 是设计合成具有大量活性位点(氧空位)的原子层厚2D材料的理想平台。基于此, 本文拟开发温和可控的合成策略, 制备表面相对干净的含氧空位原子层厚 Bi_2WO_6 材料, 并将其用

于大气污染物NO的氧化去除。

本文首先通过理论计算预测了卤素离子在调控 Bi_2WO_6 晶体生长和表面氧空位引入方面的作用,发现卤素离子尤其是 Cl^- 不仅能减小原子层厚 Bi_2WO_6 的表面能(γ),使其稳定存在;而且能降低 $\text{Bi}_2\text{WO}_6(001)$ 晶面上氧空位生成能(ΔE)。受此启发,我们设计了 Cl^- 辅助的溶剂热法,成功制备了含表面氧空位的原子层厚 Bi_2WO_6 材料;并利用高分辨透射电镜技术、X射线光电子能谱等考察了 Cl^- 的存在形式,及其调控 Bi_2WO_6 晶体生长和表面氧空位形成的机理: Cl^- 因为静电作用吸附在 $[\text{Bi}_2\text{O}_2]^{2+}$ 层上,一方面抑制 Bi_2WO_6 原子层堆积;另一方面, Cl^- 与 $[\text{Bi}_2\text{O}_2]^{2+}$ 层上Bi原子成键,削弱相邻的Bi–O键,利于O原子逸出形成表面氧空位。在此基础上,将设计合成的含氧空位的原子层厚 Bi_2WO_6 材料用于空气污染物NO的光催化去除。结果表明, Cl^- 辅助合成的BWO-Cl可见光催化去除NO的效率高达64%;且其氧化NO至 NO_3^- 的选择性为98%。为了进一步分析BWO-Cl在NO氧化反应中的高活性和高选择性的原因,进行了理论计算与光电化学测试、活性物种分析、原位漫反射红外光谱(in-situ DRIFTS)等表征。结果表明,反应的高活性源于材料原子层厚2D结构及其表面丰富的氧空位对光电性质的改善;高选择性则归因于氧空位增强了 Bi_2WO_6 吸附活化 O_2 为 $\cdot\text{O}_2^-$ 的能力,促使NO沿着热力学有利的路径氧化至 NO_3^- 。该工作初步展示了卤素离子在调控 Bi_2WO_6 晶体生长及表面氧空位引入方面的重要作用,对设计合成高活性的原子层厚2D材料具有指导意义;与此同时,材料在NO氧化方面展现出的高活性与高选择性也为构建高效的NO去除体系提供了新思路。

关键词: 氧空位; 原子层厚 Bi_2WO_6 ; 氯离子; 光催化; NO氧化

收稿日期: 2020-07-02. 接受日期: 2020-08-21. 上网日期: 2020-11-22.

*通讯联系人. 电话/传真: (027)87288246; 电子信箱: hchenhao@mail.hzau.edu.cn

#通讯联系人. 电话/传真: (027)87288246; 电子信箱: dingx@mail.hzau.edu.cn

† 共同第一作者.

基金来源: 国家自然科学基金(51872107, 21607047, 21902055); 湖北省自然科学基金(2016CFB193); 中央高校基本科研业务费专项基金(2662020LXP001, 2662016PY088, 2662018QD041, 2015PY120, 2015PY047).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).