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Improving visible-light-driven photocatalytic NO oxidation over BiOBr nanoplates through tunable oxygen vacancies

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ABSTRACT

In this work, a series of BiOBr nanoplates with oxygen vacancies (OVs) were synthesized by a solvothermal method using a water/ethylene glycol solution. The number of OVs and facets of BiOBr were tuned by changing the water/ethylene glycol ratio. Although the role of OVs in photocatalysis has been investigated, the underlying mechanisms of charge transfer and reactant activation remain unknown. To unravel the effect of OVs on the reactant activation and photocatalytic NO oxidation process, *in situ* diffuse reflectance infrared Fourier transform spectroscopy, so-called DRIFTS, and theoretical calculations were performed and their results combined. The photocatalytic efficiency of the as-prepared BiOBr was significantly increased by increasing the amount of OVs. The oxygen vacancies had several effects on the photocatalysts, including the introduction of intermediate energy levels that enhanced light absorption, promoted electron transfer, acted as active sites for catalytic reaction and the activation of oxygen molecules, and facilitated the conversion of the intermediate products to the final product, thus increasing the overall visible light photocatalysis efficiency. The present work provides new insights into the understanding of the role of OVs in photocatalysts and the mechanism of photocatalytic NO oxidation.

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1. Introduction

Photocatalytic technology is widely considered a “green” method to address energy shortages and environmental concerns [1–3]. Semiconductor materials are commonly used for photocatalysts and play a crucial role in hydrogen generation [4–6] and environmental protection [7–10]. Unfortunately, the photocatalytic performance of current photocatalysts is limited by a bottleneck, and, thus, it is challenging to develop highly active photocatalysts that utilize solar energy efficiently. The

photocatalytic process is governed by three vital sequential steps: (1) electron excitation, (2) separation and transmission, and (3) depletion [11,12]. By improving these three processes, which are essential and complementary to each other, an efficient photocatalyst can be designed [13–15].

Among the many semiconductors, BiOX (X = Cl, Br, and I) materials have proven to be promising photocatalysts for the photocatalytic degradation of pollutants in water and the air [16–18]. In particular, bismuth oxybromide (BiOBr), where [Bi₂O₂]²⁺ slabs are sandwiched between double Br[−] anion lay-

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ers, has attracted considerable interest for visible light induced photocatalysis owing to its availability and controllable and suitable bandgap [19,20]. Despite its wide range of applications in hydrogen production [21,22], dye degradation [23–25], and heavy metal recovery [26,27], the photocatalytic efficiency remains unsatisfactory. Therefore, different strategies, such as inner architecture modification [28] and surface engineering [29,30], have been employed to enhance the photocatalytic activity of BiOBr [31–33].

To date, the regulation of oxygen vacancies (OVs) is popular among the surface modification techniques because it optimizes photocatalytic properties by influencing light absorption, charge separation and transportation, and surface reactions [34,35], and good results have been obtained in various photocatalytic applications such as pollutant removal, water splitting, and CO₂ reduction [36,37]. Some investigations have demonstrated that OV-induced localized states not only expand the light response range and efficiently capture electrons, resulting in enhanced photoreactivity [38,39], but also affect the photocatalytic mechanism in the catalytic process by altering the physicochemical properties of the surface adsorbates because of the presence of dangling bonds and abundant local electrons on the photocatalyst surface [40]. Although OV-mediated BiOBr catalysts have been applied in various pollutant treatments, both the OV function and photocatalytic mechanism need to be further investigated.

In this study, different numbers of oxygen vacancies were engraved on the BiOBr surface via the modulation of the solvent mixing ratio. The introduction of OVs on BiOBr dramatically boosted the NO removal efficiency via the formation of intermediate energy levels, which enabled the carriers to be efficiently excited, separated, and transferred, thus activating oxygen molecules and providing reactive sites. In this paper, we propose and discuss the mode of formation of OVs, the interactions between OVs and surface-adsorbed oxygen species, and the photocatalytic NO conversion mechanism.

2. Experimental

2.1. Catalyst preparation

To prepare BiOBr with various oxygen vacancies, Bi(NO₃)₃·5H₂O (2 mmol) was added to a distilled water/ethylene glycol mixed solution (60 mL) containing a stoichiometric amount of KBr. The as-mixed solution was magnetically stirred for 30 min before reaction at 160 °C for 24 h in a 100-mL Teflon-lined stainless-steel autoclave. The resultant precipitates were centrifuged and washed twice with distilled water and ethanol. Finally, the product was dried at 40 °C in a vacuum oven. The BiOBr samples were prepared using water/ethylene glycol mixed solvents (60 mL total volume containing 0, 20, 40, and 60 mL ethylene glycol), which were labeled BOB, BOB-1C, BOB-2C, and BOB-3C, respectively.

2.2. Characterization

The crystal phases of the samples were confirmed by X-ray

diffraction (XRD) with Cu K α radiation (Model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with Al K α X ray radiation was conducted on a Thermo ESCALAB 250 spectrometer (USA) to determine the surface properties. The morphology and structure were observed by scanning electron microscopy (SEM, Model JSM-6490, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan). The surface area and porosity of the samples were estimated by measuring the nitrogen adsorption-desorption isotherms on a Micromeritics ASAP 2020 analyzer (USA). Electron spin resonance (ESR) spectra of radicals spin-trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were acquired using a JES FA200 spectrometer. Relevant reactive oxygen species (ROS) were determined in methanolic (DMPO·O₂[−]) and aqueous dispersions (DMPO·OH), respectively. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker ESP 500 spectrometer. The steady-state and time-resolved fluorescence emissions were recorded using a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920) at room temperature. Photoluminescence (PL) spectra were recorded by a HITACHI F-7000 (Japan) Aqualog spectrofluorometer. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained on a scanning UV-vis spectrophotometer (UV-vis DRS, UV-2450, Shimadzu, Japan), equipped with an integrating sphere.

2.3. Evaluation of photocatalytic activity

Visible-light-driven photocatalytic removal of NO was performed in a continuous-flow reactor using a 150-W Xe commercial tungsten halogen lamp fitted with a UV cutoff filter (420 nm) to block UV light. The volume of the rectangular reactor made of polymer glass and covered with Saint-Glass was 4.5 L (30 cm × 15 cm × 10 cm). The initial concentration of NO was diluted to about 600 ppb. Then, 0.20 g of the catalyst was coated onto two glass dishes (12.0 cm in diameter), which were placed in the reactor without irradiation until adsorption-desorption equilibrium was reached. During the reaction process, the concentration of NO was continuously measured using a NO_x analyzer (Thermo Environmental Instruments Inc., model 42c-TL) while analyzing the NO_x (NO_x represents NO + NO₂) concentration. The removal ratio of NO was defined as η (%) = $(1 - C/C_0) \times 100$ %, where C and C_0 are the concentrations of NO in the outlet stream and the feed stream, respectively.

2.4. In situ DRIFTS investigation

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis was performed by using a TENSOR II FT-IR spectrometer (Bruker) equipped with an *in situ* diffuse reflectance cell (Harrick) and a high-temperature reaction chamber (Scheme S1). A Xe lamp (MVL-210, Japan) was used as the irradiation light source. To remove surface impurities, the reaction chamber was charged with the sample and heated to 110 °C in a helium (100 mL/min) atmosphere. After the sample had cooled to room temperature, the real-time IR spectra were

recorded as the analysis background. Then, the gas flow was switched to the reaction mixture (50 mL/min NO, 50 mL/min O₂) to detect NO adsorption without irradiation for 20 min. *In situ* DRIFTS measurements were subsequently taken for 1 h under visible light irradiation.

2.5. Theoretical calculations

All the spin-polarized density functional theory (DFT) calculations with the D2 dispersion correction were performed using the "Vienna *ab initio* simulation package" (VASP 5.4) [41–43] and employed a generalized gradient correlation functional [44]. The projector-augmented wave method was used with a plane-wave basis [45,46]. The cutoff energy was limited to 500 eV, and the Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a $5 \times 5 \times 1$ K points. All atoms were converged to 0.01 eV/Å. Hybrid functionals based on the Heyd-Scuseria-Ernzerhof of (HSE06) method were applied to estimate the exact band structures [47,48]. A $3 \times 3 \times 2$ supercell containing 120 atoms was relaxed with the (001) and (010) facets exposed, respectively. The final optimization of the structural model resulted in the atomic

energy converge to a minimum.

3. Results and discussion

3.1. Structural characterization

BiOBr nanoplates were prepared by a typical hydrothermal method [49,50]. As reported, the presence of ethylene glycol favors the formation of oxygen vacancies in the product [51]. To control the oxygen vacancy concentration, one part of water can be replaced by ethylene glycol. Fig. 1(a) depicts the XRD patterns of the as-prepared BiOBr samples. All diffraction peaks of BiOBr can be well indexed to the tetragonal phase of BiOBr (JCPDS 73-2061), indicating that pure BiOBr crystals had been successfully prepared. The OV's of the as-prepared BiOBr sample are clear at low-temperature in the EPR spectrum (Fig. 1(d)). A characteristic OV signal with a *g* factor of about 2.0 was observed for as-prepared BiOBr [52,53]. The rising signal intensity confirms the increase in the OV concentration in BOB-3C compared to that in BOB. Therefore, with increasing ethylene glycol in the reaction solution, the oxygen vacancies increased and the crystallinity of the BiOBr was seriously re-

Fig. 1. (a) XRD patterns of BOB, BOB-1C, BOB-2C, and BOB-3C; (b) XPS survey spectra of BOB and BOB-3C; (c) XPS spectra (Bi 4f) of BOB and BOB-3C; (d) EPR spectra of BOB, BOB-1C, BOB-2C, and BOB-3C.

duced, as shown in Fig. 1(a).

Moreover, Fig. 1(b) shows the detailed elemental composition of the prepared samples, which demonstrate that BOB and BOB-3C contain Bi, O, and Br. The peaks located at approximately 159.1 and 164.4 eV in the Bi 4f XPS spectrum (Fig. 1(c)), corresponding to Bi 4f_{7/2} and Bi 4f_{5/2}, originate from Bi³⁺. These results demonstrate that the concentration of OV on BiOBr can be easily tuned by adjusting the volume of ethylene glycol during the synthesis, enabling us to probe the intrinsic role of the OVs during the photocatalytic oxidation of NO under visible light irradiation.

3.2. Morphological analysis

SEM images of the prepared samples are shown in Fig. 2(a)–2(d), which reveal that all these products have a plate-like structure. With increasing volume of ethylene glycol in the solution, the samples gradually assembled into hierarchical microspheres and the size and thickness of the nanoplates were reduced simultaneously. The TEM images (Fig. 2(e) and 2(f)) show more details of the structure. From the HRTEM image of BOB (Fig. 2(e)), a lattice spacing of 0.277 nm was determined, indicative of the (110) facet, which is perpendicular to the (001) facet. Furthermore, the angles between the (110) and (200) planes are in line with theoretical values of 45° (Fig. 2(e), inset). In the HRTEM image of BOB-3C (Fig. 2(f)), interplanar spacings of 0.282 and 0.202 nm were observed, corresponding to the (102) and (004) planes, and the angle between them is 45.9° (Fig. 2(f), inset). Thus, the BOB nanoplates exhibit (001) exposed facets, whereas the BOB-3C samples display the

(010)-exposed facets. In addition, the (001), (002), (003), and (004) diffraction peaks in the XRD patterns (Fig. 1(a)) became less intense as the volume fraction of ethylene glycol increased, illustrating the increased exposure of the (010) facets [54].

Thus, the addition of ethanol affects particle size and the exposed facets while introducing vacancies. Generally, the crystal growth process occurs by the nucleation and growth of particles from a supersaturated solution [55]. The variation in the single crystallite size is highly correlated with the nucleation rate in the nucleation stage. Based on the Ostwald ripening process, in the growth stage, the total energy of a two-phase system is reduced as the crystallite size increases. In aqueous solution, the formation of BOB is represented by Eq. (1).

During the crystal growth phase, BiOBr crystals grow by dissolving small nuclei to reduce the total surface free energy of the system. Despite the high surface energy of the (110) facet, H⁺ ions are captured on the terminal oxygen atoms on the (001) surface in solution, causing the crystal to grow along the exposed (001) facet [56], and the nanoplates stack to reduce the surface energy of the system. In the presence of the ethylene glycol solution, H⁺ ions are first consumed by the esterification reaction, which facilitates the growth of the lower energy (010) facet [57]. The nanoplates self-assemble into hierarchical microspheres by hiding the (001) facets to decrease the total interfacial energy. Moreover, ethylene glycol is more viscous than water [58], slowing the expansion of the nuclei and resulting in the formation of smaller nanoplates and the exposure of more defects.

The Brunauer-Emmett-Teller (BET) surface areas and porous structures of the as-prepared photocatalysts were investigated by N₂ adsorption-desorption experiments. As shown in Fig. S1, the as-prepared samples show a type-IV adsorption isotherm with an H₂ hysteresis loop. The larger specific surface areas of the as-prepared BiOBr samples (Table S1) with increasing volume of ethylene glycol can be attributed to the smaller crystallite size and hierarchical structure of BiOBr, which improves NO adsorption on the surface of the photocatalysts and improves the photocatalytic activity.

3.3. Photocatalytic activity evaluation and optical properties

3.3.1. Photocatalytic evaluation and reactive oxygen species

The removal of NO was carried out under visible light ($\lambda > 400$ nm) illumination. Fig. 3(a) shows the photocatalytic performance in the presence of samples fabricated with various water/ethylene glycol ratios. The samples were kept in the dark until adsorption equilibrium was reached. Over 30 min of visible light photocatalytic oxidation, BOB-3C exhibited the highest visible light photocatalytic activity of the as-prepared samples. The NO removal ratios of BOB and BOB-3C are about 3.8% and 38.7%, respectively. The photocatalytic activity of the BiOBr nanoplates increased with increasing addition of ethylene glycol (Table S1). The corresponding reaction rate constants were determined with a first-order model (Table S1) and calculated to be 8.7 min^{−1} for BOB-3C, which is much higher than that of BOB (0.6 min^{−1}). Because of the reaction products

Fig. 2. (a) SEM images of BOB, (b) BOB-1C, (c) BOB-2C, and (d) BOB-3C. (e) HRTEM images of BOB and (f) BOB-3C. The corresponding fast Fourier transforms (FFT) patterns (inset).

Fig. 3. (a) Photocatalytic activity evaluation of BOB, BOB-1C, BOB-2C, and BOB-3C; DMPO spin-trapping ESR spectra in a methanol dispersion for $\text{DMPO} \cdot \text{O}_2^-$ (b) and an aqueous dispersion for $\text{DMPO} \cdot \text{OH}$ (c).

covering the catalyst surface, the contact of the pollutant with the catalyst was hindered. As a result, there was a slight decrease in catalyst activity over time. However, the surface contaminants could be removed by simple flushing, and the catalyst could be recycled.

Thus, we can surmise that the adjusted mixed solvent ratio efficiently enhances the photocatalytic performance by synergistically introducing vacancies and controlling the exposed facets.

The ROS are considered to be involved in the photocatalytic reaction, where superoxide radicals ($\cdot\text{O}_2^-$) play a crucial role in the oxidation of NO. Accordingly, the effect of the OV on $\cdot\text{O}_2^-$ deserves attention. The adsorption and activation of oxygen by the OVs were confirmed by DFT calculations. The E_{ads} of O_2 on defect-free and defective BiOBr are -0.08 and -0.13 eV, respectively, and the O–O bond lengths are 1.22 to 1.25 Å, respectively (Fig. 4(a)). This result implies that the OVs can accelerate the adsorption of O_2 molecules on the surface of the photocatalyst by reducing the oxygen adsorption energy and promoting its activation by weakening the O–O bonds. The charge difference distribution of BiOBr (Fig. 4(b)) has been analyzed to provide detailed information. On the surface of the defective BiOBr, electrons are transferred from the OVs to O_2 molecules, forming $\cdot\text{O}_2^-$ [59]; this phenomenon is not observed in the defect-free BiOBr. In addition, NO adsorption on defect-free and defective BiOBr was compared. The E_{ads} of O_2 decreases from -0.27 to -0.88 eV from defect-free to defective, respectively, and, similarly, the N–O bond length is elongated from 1.17 to 1.27 Å (Fig. 4(c)). This proves that OVs can reduce the adsorption energy of NO and promote its adsorption and oxidation.

To reveal the mechanism for the enhancement of photocatalytic efficiency further, the ROS were observed by DMPO spin-trapping ESR measurements. For BOB-3C, a stronger $\text{DMPO} \cdot \text{O}_2^-$ signal intensity than that of BOB was observed (Fig. 3(b)). This result is in accordance with the theoretical calculations (Fig. 4), which indicate that more molecular oxygen is activated by the OVs in BOB-3C, generating more $\cdot\text{O}_2^-$ for photocatalysis. Because of the lack of $\cdot\text{OH}$ species, no $\cdot\text{OH}$ signals were detected for BOB. In contrast, $\cdot\text{OH}$ species are observable under visible light excitation in BOB-3C (Fig. 3(c)). The valence band (VB) and conduction band (CB) of BiOBr were evaluated using Eqs. (2) and (3) [60].

$$E_{\text{VB}} = X - E^{\text{e}} + 0.5 E_{\text{g}} \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (3)$$

here, E_{g} represents the band gap of the semiconductor, X is the electronegativity of the semiconductor calculated from the electronegativity of the constituent atoms, and E^{e} is the energy of free electrons on the hydrogen scale (ca. 4.5 eV). The E_{VB} and E_{CB} of BiOBr were calculated to be 3.18 and 0.73 eV, respectively. The holes left in the VB of BiOBr (3.18 eV) induce the production of $\cdot\text{OH}$ [59,61] because it is more positive than the $\text{OH}/\cdot\text{OH}$ redox potential (1.99 eV). It seems that the CB potential of BiOBr (0.73 eV) is less negative than the redox potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV). Notably, the CB is wide, so electrons can be photoexcited to higher levels of the conduction band. As a result, superoxide radicals can still be generated. This result is also shown by the ESR measurements (Fig. 3(b)). Under visible light irradiation, BOB-3C produces $\cdot\text{O}_2^-$ radicals through the reaction of O_2 with electrons. Therefore, the O_2 -activated cata-

Fig. 4. (a) Optimized O_2 adsorption on BiOBr (left) and BiOBr containing oxygen vacancies (BiOBr-OV) (right); (b) Charge density difference of BiOBr (left) and BiOBr-OV (right); (c) Optimized NO adsorption on BiOBr (left) and BiOBr containing oxygen vacancies (BiOBr-OV) (right). Electron accumulation is shown in blue and depletion in yellow. The isosurfaces are set to $0.005 \text{ eV } \text{\AA}^{-3}$.

lyst surface promoted the production of $\bullet\text{O}_2^-$ radicals. From the calculations (Fig. 4(a) and 4(b)), O_2 activation is promoted by the oxygen vacancies. Thus, $\bullet\text{O}_2^-$ radicals are generated on the defective BiOBr.

3.3.2. Light absorption, electron excitation, and migration

The optical properties of the as-prepared samples were also investigated. Fig. 5(a) shows the UV-vis DRS spectra of BiOBr nanoplates. It is obvious that all these samples exhibit a high absorption in the range of 200–450 nm. However, the samples with more OV's show optical absorption in the range 450–800 nm. The band gap energy of BiOBr was calculated using

$$\alpha h\nu = A(h\nu - E_g)^{n/2},$$

where α , h , ν , A , E_g , and n are the absorption coefficient, Planck's constant, light frequency, proportionality constant, band gap

energy, and transition coefficient, respectively. The bandgap energies of these samples were estimated to range from 2.45 to 2.7 eV (Fig. 5(a), inset). To clarify the reasons for the enhanced absorption of light, the hybrid DFT method was utilized to calculate the total density of states (TDOS) by theoretical simulation. As shown in Fig. 5(d), the defective intermediate level was detected in the middle of the band gap because of the introduction of OVs, which formed a platform for electron transition and extended the range of light absorption. This result is consistent with the UV-vis DRS result (Fig. 5(a)). Furthermore, this defective level lowers the photon energy required for electron transition, facilitating electron excitation, separation, and transformation. PL (Fig. 5(b)) quenching was observed in the prepared BiOBr nanoplates as the amount of OVs increased, probably because electrons can be transmitted through the intermediate

Fig. 5. UV-vis DRS spectra (a) and PL spectra (b) of the BiOBr samples; (c) Nanosecond-level time-resolved fluorescence spectra surveyed at room temperature for BOB and BOB-3C; (d) Density of states (DOS) of BiOBr with (001) facets exposed (labeled as (001) BiOBr), with (001) facets exposed and the introduction of oxygen vacancies (labeled as (001) BiOBr-OV), with (010) facets exposed (labeled as (010) BiOBr), and with (001) facets exposed and the introduction of oxygen vacancies (labeled as (010) BiOBr-OV). The Fermi level is set to 0 eV.

level (Fig. 5(d)). The charge-carrier separation in the BOB and BOB-3C samples was investigated by surface photovoltage (SPV) measurements. BOB exhibited a negligible SPV response, but the peak intensity was enhanced after OVVs were introduced to the BiOBr surface (Fig. S3). Thus, electron-hole recombination is undoubtedly inhibited by the increase in the number of vacancies. In addition, the introduction of OVVs also causes the CB and VB edges to shift to lower energy, which results in the holes having a greater oxidizing ability.

Fig. 5(c) shows the nanosecond-level time-resolved fluorescence decay spectra whose curve is fitted by a biexponential decay function to illustrate the charge motion dynamics. Compared with BOB, the charge carrier lifetime in BOB-3C is longer, indicating that the introduced OVVs effectively boost charge transfer and carrier separation.

3.4. *In situ* DRIFTS investigation and photocatalytic NO oxidation mechanism

To unravel the NO surface adsorption and oxidation changes arising from the important effects of the OVVs, we conducted a dynamic monitoring study using *in situ* DRIFT measurements. Fig. 6 shows the time evolution of the IR spectra during the NO + O₂ adsorption process over BOB. Tables S2–S5 list the assignment of the observed bands. Peaks were observed at 1142 and 1071 cm⁻¹ for NO, 785 cm⁻¹ for NO₂, and 804–917 and 1180 cm⁻¹ for nitrites (Fig. 6(a)). NO and NO₂ (Eq. (4)) can be physically adsorbed on the surface of the sample. In the adsorption process, NO first attacks surface free OH groups and

the surface active oxygen groups, such as coordinated unsaturated oxygen, promoting the oxidation of NO to monodentate nitrite on the photocatalyst surface (steps (i) and (ii) in Fig. 7(a)) [62–64].

Concerning NO adsorption on BOB-3C (Fig. 6(b)), the physical absorption of NO (1142 and 1071 cm⁻¹) and NO₂ (783 cm⁻¹) are similar to those of BOB, whereas the chemical adsorption of NO is different. In particular, adsorption bands corresponding to bidentate nitrogen oxides (940, 947, and 1022 cm⁻¹) appear in the NO adsorption process over BOB-3C. Nitrate was not detected over BOB (Fig. 6(a)), whereas the stretching vibrations of monodentate nitrates (947 cm⁻¹) and bridging nitrates (1169 and 1125 cm⁻¹) were observed over BOB-3C (Fig. 6(b)). This observation suggests that OVVs can promote the transformation of monodentate nitrite to bidentate nitrogen oxides and, even further, to nitrates. A band corresponding to O₂⁻ (1097 cm⁻¹) was detected, presumably because of the surface-bound O₂⁻, which was formed by the adsorption of O₂ molecules on oxygen vacancies. For BOB-3C, NO is first adsorbed on the BOB-3C surface through a similar pathway (step (i) in Fig. 7(b)). Upon the induction of the OVVs, monodentate nitrites are quickly converted to bidentate nitrites (step (ii) in Fig. 7(b)). The OVVs activate O₂ to surface •O₂⁻ because of the abundant localized electrons (steps (i) and (iii) in Fig. 7(c)). Then, surface •O₂⁻ can further oxidize nitrites to nitrates (steps (ii) and (iv) in Fig. 7(c)).

As shown in Fig. 6(c) and 6(d), the final products of photocatalytic NO oxidation (nitrites and nitrates) over both of samples were notably increased because the adsorbed NO₂⁻ was

Fig. 6. *In situ* DRIFTS spectra (a, b) of NO adsorption and visible light reaction (c, d) processes over BOB (a, c) and BOB-3C (b, d).

Fig. 7. The conversion pathways for the adsorption and photocatalytic oxidation of NO over BOB and BOB-3C.

oxidized by $\cdot\text{O}_2^-$ (Eq. (8)) and $\cdot\text{OH}$ (Eq. (9)) under visible light irradiation. To observe the generated surface-bound O_2^- , we investigated the peak at 1097 cm^{-1} (Fig. 6(d)) corresponding to NO oxidation under visible light irradiation over BOB-3C. The surface-bound O_2^- was found to be rapidly consumed by visible light, while NO_3^- ($1299, 1276, 1047, 997$, and 948 cm^{-1}) gradually accumulates. Notably, the increase in nitrates and decrease in surface-bound O_2^- and NO (retrore peak at 1071 cm^{-1}) occurred simultaneously. This confirms that the adsorption of oxygen by OV in the photocatalytic removal of NO plays a crucial role. The peaks of final products over BOB-3C (Fig. 6(d)) are much more intense than that over BOB (Fig. 6(c)), implying a faster NO oxidation rate by increasing the amount of OV. Obviously, the OV on BOB-3C accelerates the photocatalytic oxidation of NO. Because of the unique surface properties, NO is immobilized on the surface of the sample, allowing for a readier reaction with the surface-generated ROS. The OV improves the electron transfer efficiency by boosting the migration of electrons to reactants. In addition, the OV provides perfect sites for enhanced O_2 adsorption and activation [27]. As the active sites of the photocatalytic reaction, the OV activates oxygen molecules to promote NO adsorption and oxidation, inducing the oxidation of the intermediate products into the final product.

Based on the above experimental and characterization results, the mechanism of enhanced photocatalytic NO oxidation is discussed. From the *in situ* DRIFTS analysis results, the NO conversion path over the sample surface is changed by the introduction of OV. For this reason, the specific surface area is not a decisive factor in the photocatalytic process, even though the larger specific surface area favors the adsorption of NO on the photocatalyst surface; this results in easier contact between the reactive oxygen species produced on the photocatalyst surface and the reactants. To understand the effect of the facets on the photocatalytic performance of BiOBr, we prepared BiOBr nanoplates with exposed (010) facets (labeled BiOBr-H) by a typical hydrothermal method [65,66]. The NO removal ratio of BiOBr-H was only 16.0% under visible light, which is much lower than that of BOB-3C and even lower than that of BOB-2C (Fig. S2). Therefore, increasing the number of OV is key to improving the photocatalytic NO oxidation efficiency.

When the as-prepared sample is irradiated with visible light, the electrons are excited from the VB to the CB in BiOBr (Fig. 8). The OV introduces an intermediate defective level, providing a new route for electronic transitions, which enables the excited electrons to transfer easily to the CB via a lower energy pathway. The recombination of photogenerated charges is further inhibited by the OV because it provides a platform for the transfer of electrons to the reactants. The presence of OV is

Fig. 8. Proposed mechanism of photocatalysis in BOB-3C for NO removal.

conductive to the adsorption and activation of O_2 , thereby increasing the production capacity of reactive oxygen species and significantly improving the photocatalytic activity.

4. Conclusions

BiOBr nanoplates with different OV concentrations were synthesized by a simple solvothermal method using water/ethylene glycol mixed solutions with different mixing ratios. The photocatalytic NO oxidation efficiency over the BiOBr nanoplates increases with increasing number of OVs. With a combined theoretical and experimental approach, we have investigated the role of OVs during the photocatalysis process. First, the OVs provides an intermediate energy level, forming a platform for electronic transition to extend the range of light absorption. Secondly, as adsorption sites and electron traps, OVs accelerate the migration of electrons to reactants to improve electron-transfer efficiency and, thus, effectively quench charge recombination. Additionally, the introduction of OVs provides abundant electrons for the activation of O_2 molecules, dramatically promoting the production of ROS for the photocatalytic removal of NO and, simultaneously, contributing to the

reformation of the conversion pathway for photocatalytic NO oxidation. This investigation provides a deep insight into the significance of the introduced OVs for molecular oxygen activation and pollutant removal under visible light, thus providing a strategy to control and explore OVs for high-performance photocatalysts.

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Graphical Abstract

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Improving visible-light-driven photocatalytic NO oxidation over BiOBr nanoplates through tunable oxygen vacancies

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Oxygen vacancies have several roles in photocatalysis, including the introduction of intermediate energy levels to enhance light absorption and promote electron transfer. The vacancies act as active sites for the catalytic reaction and activation of oxygen molecules, facilitating the conversion of intermediate products to the final product and, thus, increasing the overall efficiency of visible light photocatalysis.

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通过可控的氧空位增强 BiOBr 纳米片可见光催化 NO 氧化性能

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摘要: BiOBr 具有独特的层状纳米结构和合适的可调节的能带结构, 因而广泛应用于光催化领域中。但其可见光催化效率仍需要进一步提高。最近, 氧空位调控技术广泛应用于光催化剂改性中。本文研采用溶剂热法 (采用水/乙二醇溶液) 合成了一系列具有氧空位的 BiOBr 纳米片。通过改变水/乙二醇的比例调节 BiOBr 氧空位的量和晶面, 以增强其可见光催化活性。虽然有关氧空位在光催化中的作用已有研究, 但氧空位对电荷转移和反应物活化影响的机理仍不清楚。因此, 本文采用 X 射线衍射、扫描电镜、透射电镜、荧光光谱 (PL)、紫外-可见漫反射光谱 (UV-Vis DRS)、电子自旋共振 (ESR)、电子

顺磁共振 (EPR) 和比表面积-孔结构 (BET-BJH) 分析等手段考察了含有氧空位的 BiOBr 纳米片的物理化学性质, 通过原位红外光谱研究了样品可见光催化氧化 NO 的转化路径及反应机理. 同时结合密度泛函理论 (DFT) 计算进一步揭示氧空位对电子激发、电子-空穴分离和转移、以及光催化氧化反应过程的影响.

表征结果表明, 采用水/乙二醇混合溶液的方法制得了 BiOBr 样品 (BOB, BOB-1C, BOB-2C, 和 BOB-3C), 其表面氧空位随着混合溶液中乙二醇溶液的增加而增加. 另外, BiOBr 样品均呈纳米片层状, 且随着乙二醇溶液的增加, BiOBr 纳米片逐渐组装成紧密结合的球状结构. BET-BJH 测试结果显示, BOB-3C 的比表面积 ($15.34 \text{ m}^2/\text{g}$) 显著高于 BOB ($1.1 \text{ m}^2/\text{g}$). UV-Vis DRS 结果表明, BOB-3C 具有比 BOB 更良好的可见光吸收能力. 可见光催化去除 NO 的测试结果表明, BOB-3C 的光催化活性 (38.9%) 明显高于 BOB (4.1%). ESR 研究发现, BOB-3C 能产生比 BOB 更多的活性氧化物种 ($\bullet\text{O}^-$ 自由基和 $\bullet\text{OH}$ 自由基). 由此可见, 因表面氧空位浓度的变化, 而使 BOB 和 BOB-3C 表现出不同的理化特性. 同时 DFT 计算也印证了光催化过程中氧空位对氧气吸附活化、NO 吸附氧化和能带结构的影响. 可见光催化氧化 NO 的原位红外光谱表明, BOB-3C 与 BOB 相比, 光催化氧化 NO 的转化路径发生了变化, 表明氧空位对 NO 氧化起到了促进作用.

氧空位在光催化中表现出多功能性, 包括引入中间能级以增强光吸收, 促进电子转移, 充当催化反应和氧分子活化的活性位点, 促进反应产物转化为最终产物, 从而增强样品可见光光催化效率. 为揭示氧空位在光催化剂中的作用和光催化 NO 氧化机理提供了新的思路.

关键词: BiOBr 纳米片; 氧空位; 原位红外; 转化路径; NO 氧化

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