Synergistic effects of crystal structure and oxygen vacancy on Bi$_2$O$_3$ polymorphs: intermediates activation, photocatalytic reaction efficiency, and conversion pathway

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Abstract

This work unraveled the synergistic effects of crystal structure and oxygen vacancy on the photocatalytic activity of Bi$_2$O$_3$ polymorphs at an atomic level for the first time. The artificial oxygen vacancy is introduced into $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ via a facile method to engineer the band structures and transportation of carriers and redox reaction for highly enhanced photocatalysis. After the optimization, the photocatalytic NO removal ratio on defective $\beta$-Bi$_2$O$_3$ was increased from 25.2% to 52.0% under visible light irradiation. On defective $\alpha$-Bi$_2$O$_3$, the NO removal ratio is just increased from 7.3% to 20.1%. The difference in the activity enhancement is associated with the different structure of crystal phase and oxygen vacancy. The density functional theory (DFT) calculation and experimental results confirm that the oxygen vacancy in $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ could promote the activation of reactants and intermediate as active centers. The crystal structure and oxygen vacancy could synergistically regulate the electrons transfer pathway. On defective $\beta$-Bi$_2$O$_3$ with tunnel structure, the reactants activation and charge transfer were more efficient than that on $\alpha$-Bi$_2$O$_3$ with zigzag-type configuration because the defect structures on the surface of $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ were different. Moreover, the in situ FT-IR revealed the mechanisms of photocatalytic NO oxidation. The photocatalytic NO conversion pathway on $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ can be tuned by the different surface defect structures. This work could provide a novel strategy to regulate the photocatalytic activity and conversion pathway via the synergistic effects of crystal structure and oxygen vacancy.

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1. Introduction

In the past decade, photocatalysis as a green technology has received increased attention since its diverse applications in environmental remediation and solar energy conversion [1–4]. Generally, the photocatalytic efficiency involves three aspects: (1) the light absorption ability of photocatalyst [5]; (2) the separation and transportation efficiency of charge carriers [6,7]; (3) the redox reaction associating with photo-induced reactive radicals [8–10]. Therefore, comprehensive catalyst design in terms of visible-light utilization, charge carrier separation, and redox capacity of reactive radicals is essential and urgent for achieving highly efficient photocatalytic efficiency [11–13].

Primarily, the photo-absorption efficiency is the prerequisite of photocatalysis and is known to be strongly related to the physicochemical properties of photocatalyst, particularly reflecting in crystal structure which determines the band structure [14]. For semiconductor-based photocatalysts, crystalline structure is crucial in a complex photochemical conversion process including optical properties, and charge separation. For example, Kudo et al. [15] demonstrated that the photocatalytic performance of monoclinic BiVO$_4$ was much higher than that of tetragonal structure of BiVO$_4$, which can be ascribed to the different crystal structures and band
gaps. Linsebigler et al. [13] reported that anatase TiO2 exhibited much higher photocatalytic activities than that of rutile TiO2, resulting from the differences among optical properties, band gap, and the recombination rate of charge carriers of the polymorph [16]. Also, crystal structure has been demonstrated to have crucial effect on many kinds of photocatalysis (such as Ga2O3 [11], WO3 [17], Bi2O3 [18], BiPO4 [19], etc.).

Meanwhile, photocatalytic efficiency is greatly dependent upon the efficient separation, transportation, and transformation of charge carriers for the subsequent redox reaction. Recently, vacancy-engineering as one of the most studied and effective methods has been proposed to manipulate the properties including electrical transport, surface structure and band structures. Li et al. [20] reported that MSnO3 (M = Ca, Sr and Ba) with oxygen defect induced efficient separation efficiency of photo-generated carriers, contributing to outstandingly photocatalytic performance. The oxygen defects containing TiO2 was beneficial for accelerating the activation of O2 to form superoxide radical species (•O2−) for the oxidation of pollutants [21,22]. The introduction of defects could induce the localization of charge carriers, which can not only facilitate the adsorption and activation of reactants but also accelerate the separation of photo-generated carriers [20,23,24]. However, few studies have been devoted to explore the synergistic effects of crystal structure and vacancy-engineering on the regulation of band structures and transportation of carriers, aiming to realize efficient visible-light utilization, charge carrier separation and redox reaction for photocatalysis.

Bi2O3 is a single metal oxide semiconductor with appropriate band gap and has four polymorphs (monoclinic α-, tetragonal β-, body-centered γ-, and face-centered δ-), which endows Bi2O3 with different photocatalytic performance under visible light irradiation. Different from traditional metal oxides (such as TiO2, ZnO and Fe2O3) which are so stable that it is hard to introduce vacancies, the surface Bi–O bond of Bi2O3 with low energy can be easily attacked to construct oxygen defects [25–28]. Therefore, we introduce oxygen vacancy into α-Bi2O3 and β-Bi2O3 via a facile method to explore the synergistic effects of crystal structure and oxygen vacancy on photocatalysis. Correspondingly, the photocatalytic NO removal ratio of defective α-Bi2O3 increase from 7.3% to 20.0%, and importantly the NO removal ratio on defective β-Bi2O3 increases from 25.2% to 52.0% under visible light irradiation, which can be ascribed to the different photo-adsorption properties, separation efficiencies of charge carriers and redox capacity. Concretely, the difference in crystal structures induces different optical properties, and the introduction of oxygen defects could facilitate the activation of reactants and simultaneously accelerate the separation of photo-generated carriers. According to the density functional theory (DFT) calculation simulation, the delocalized charge carriers have been converged, contributing to efficient separation of carriers and the adsorption and activation of O2 and H2O for the generation of •O2 and •OH participating in further photocatalytic NO oxidation. Besides, reaction process and promotion mechanism of photocatalysis have been elaborated by in situ FTIR spectra and the theoretical simulation. This work could provide a novel perspective to optimize the photocatalytic performance via the synergistic effects of crystal structure and oxygen vacancy.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and used without further treatment. Bismuth nitrate pentahydrate, cetyltrimethylammonium bromide (CTAB), NaBH4, oxalic acid were purchased from Chengdu KeLong Chemical Co., LTD. (Chengdu, China). Nitric acid and sodium hydroxide were obtained from Chongqing Chuang-Dong Chemical (group) Co., LTD (Chongqing, China). 2.0 g of Bi(NO3)3·5H2O was first dissolved in dilute HNO3 (1 mol/L, 20 mL) to prevent the hydrolyzation of Bi3+. And then, 0.1 g of CTAB was added to the above solution as surfactant and stirred continuously. Two copies of the above solution were prepared and labeled as A and B, respectively. Then, with constant stirring at 60 °C for 30 min, NaOH (200 mL, 0.21 mol/L) aqueous solution was slowly dropped into the A solution and the oxalic acid (0.4 g) were added into the above B solution, respectively. Finally, the mixture from A solution was filtered, washed, dried at 80 °C for 8 h, and then calcined in air at 350 °C for 2 h. After cooled to room temperature, the obtained products were labeled as α-Bi2O3. Similarly, the obtained B solution was washed by ethanol and deionized water and dried at 80 °C for 8 h. Then, the crucible with a cover was calcined in air at 270 °C for 2 h and the prepared samples were named as β-Bi2O3.

The α-Bi2O3 (1.0 mmol) was added into deionized water (100 mL) containing 1.0 g PVP. Subsequently, 20 mL NaBH4 with different molar ratio (30, 50, 70 and 90 μmol/L) used as deoxidizer was slowly dropped into the above solution under constant stirring for 1 h. The obtained product was gathered, rinsed thoroughly with ethanol and deionized water for several times, and dried in air at 60 °C which was labeled as α-Bi2O3-30, 50, 70 and 90, respectively. Similarly, the precursor was adjusted to β-Bi2O3 without changing the conditions, and their resulting samples were treated as β-Bi2O3-X (X = 30, 50, 70, and 90), respectively.

2.2. Characterization

The as-obtained catalysts were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectrometry spectrum (UV–vis DRS), photoluminescence spectra (PL), electron spin resonance (ESR) and Electron paramagnetic resonance (EPR) measurements. Detailed descriptions on different characterizations were given in Supplementary Materials (online).

2.3. Evaluation of visible-light photocatalytic activity

The photocatalytic activity was investigated by determining the removal ratio of NO at ppb levels (500 ppb, part per billion) in a continuous-flow reactor (rectangular reactor, 30 cm × 15 cm × 10 cm) (Scheme S1 online). The concentration of NO was continuously detected by a NO analyzer (Thermo Environmental Instruments Inc., Model 42c-TL), which can monitor the concentrations of NO, NO₂, and NO (NOX, NO represents NO + NO₂). The as-prepared samples (0.20 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 (the light intensity is 0.16 W/cm²) 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 \( \eta = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \), where \( C_t \) and \( C_0 \) are the concentrations of NO in the outlet steam and the feeding stream, respectively.

2.4. In situ DRIFTS investigation

In the FTIR measurements were implemented using a Tensor II FTIR spectrometer (Bruker) with an in situ diffuse reflectance cell (Harrick) and display as shown in Scheme S2 (online). Detailed description of the experiment condition for in situ DRIFTS device was gained in Supplementary materials (online).
2.5. Theoretical calculations

DFT calculations were conducted using the “Vienna ab initio simulation package” (VASP5.4) [29,30], utilizing a generalized gradient correlation function. A plan-wave basis set with a cut-off energy at 450 eV and the projector-augmented wave method framework was exercised [31]. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a Monkhorst-pack grid. All atoms were converged to 0.01 eV/Å. Hybrid function based on the Heyd-Scuseria-Ernzerhof (HSE06) method was implemented to value the exact band structure [32,33]. Detailed information on theoretical calculations was given in Supplementary Materials (online).

3. Results and discussion

3.1. Phase structures and chemical composition

The powder XRD patterns of as-prepared samples are shown in Fig. 1. The XRD patterns demonstrate that Bi and O elements coexist in the as-prepared samples. According to the high-resolution XPS spectra of O 1s (Fig. 1c), the peaks at 529.38 and 530.80 eV are characteristic of lattice oxygen in oxide semiconductors and oxygen species (OH⁻ or CO₃²⁻) chemisorbed at defect sites [34], respectively. The characteristic binding energy of Bi 4f₇/₂ and Bi 4f₅/₂ are located at 158.50 and 163.80 eV, respectively, which indicates the existence of Bi³⁺ in these samples (Fig. 1d) [35].

The morphology and structure of the as-prepared are presented in Figs. 2 and S1 (online). As shown in Fig. 2b, α-Bi₂O₃-50 with rod-like architectures is composed of more interlaced nanorods with a size around 2–3 μm, which is similar to that of pure α-Bi₂O₃ (Fig. 2a). According to Fig. 2c and d, β-Bi₂O₃-50 inherits the randomly stacked sheet-like structures of pristine β-Bi₂O₃. The TEM images further confirms the nanorods and nanosheets architecture of α-Bi₂O₃-50 and β-Bi₂O₃-50 samples (Fig. 2e and g), respectively, which are similar to the pristine α-Bi₂O₃ and β-Bi₂O₃ (Fig. S1a and b online). This result reveals that morphological structure of α-Bi₂O₃-50 and β-Bi₂O₃-50 has not been changed after the introduction of defects.

Furthermore, HRTEM image (Fig. 2f) indicates that α-Bi₂O₃-50 nanorods with lattices fringes of approximately 0.26 nm, which are in agreement to the (2 0 0) facets of α-Bi₂O₃ (Fig. S1c online). The inset in the Fig. 2f represents the selected-area electron diffraction (SAED) pattern of α-Bi₂O₃ samples. The set of diffraction spots is indexed monoclinic α-Bi₂O₃, and the angle (48.2°) between the (2 0 0) and (1 2 0) planes is in well accordance with their respective theoretical values. Therefore, α-Bi₂O₃-50 sample is composed to expose (2 0 0) facet. In contrast, As shown in Fig. 2h, the HRTEM image of β-Bi₂O₃-50 indicated that the lattice

Fig. 1. The XRD patterns (a) and XPS spectra (b-d) of α-Bi₂O₃, β-Bi₂O₃, α-Bi₂O₃-50 and β-Bi₂O₃-50.
fringe of 0.38 nm corresponds to the (2 2 0) facets of β-Bi$_2$O$_3$ (Fig. S1d online). The corresponding SAED pattern (the insets in Fig. 2h) reveals (2 2 0) and (4 0 0) facets with an interfacial angle of 45°. The angels between typical planes are in line with their respective theoretical values [36]. Thus, the surface of the β-Bi$_2$O$_3$-50 sample could be regarded as (2 2 0) facets. As shown in Fig. S2a and b (online), it is illustrated that the layers of bismuth and oxygen atoms of α-Bi$_2$O$_3$ are alternately arranged in a zigzag manner [12,37,38], while large tunnels penetrate the crystal structure of β-Bi$_2$O$_3$ along the Z-direction [12,39]. According to the above result, it is concluded that α-Bi$_2$O$_3$-50 and β-Bi$_2$O$_3$-50 are inclined to expose (2 0 0) and (2 2 0) facets respectively during the synthesis process. The differences in the selectively exposed facet well determine the different atomic arrangements of crystal structure. And the synthetic process for generation of α-Bi$_2$O$_3$-X and β-Bi$_2$O$_3$-X is presented in Fig. S3 (online).

3.2. Optical properties, band structures, and the transfer pathway of charge

The UV–vis DRS were employed to illustrate the optical properties and band structure of the as-prepared samples. As shown in Fig. 3a and b, the absorption edge of α-Bi$_2$O$_3$ sample is around 470 nm and however β-Bi$_2$O$_3$ displays light absorption edge at 550 nm, indicating that crystal phase could significantly influence the band structure. The crystal structure endows uniquely arrange-
ment order and coordination number of surface atoms, thus contributing to diverse properties. Compared with the pristine \( \alpha - \text{Bi}_2\text{O}_3 \) and \( \beta - \text{Bi}_2\text{O}_3 \), the light absorption range of \( \alpha - \text{Bi}_2\text{O}_3 - \text{X} \) and \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) have been expanded into full spectra up to 800 nm along with red shifts, which can be ascribed to the introduction of defects. Moreover, the band gaps of \( \alpha - \text{Bi}_2\text{O}_3 \), \( \beta - \text{Bi}_2\text{O}_3 \), \( \alpha - \text{Bi}_2\text{O}_3 - 50 \), and \( \beta - \text{Bi}_2\text{O}_3 - 50 \) (Fig. S4 online) are determined to 2.6, 2.1, 1.9, and 1.6 eV, by deduced from the intercepts of the tangents to the plots of \( (x\text{hv})^2 \) vs. photon energy [40].

To further study the existence and the nature of defects, low-temperature solid state electron paramagnetic resonance (EPR) spectra of as-prepared samples are employed. As shown in Fig. 3c and d, all samples show a paramagnetic resonance at \( g = 2.002 \) both in dark and under visible light irradiation, confirming the generated of oxygen defects on the surface [41–43]. In dark, the weak EPR signals of \( \alpha - \text{Bi}_2\text{O}_3 \) and \( \beta - \text{Bi}_2\text{O}_3 \) can be attributed to the inevitable intrinsic defects of oxide materials. The increased intensity of EPR signals are derived from the introduction of numerous defects via the reduction treatment of \( \alpha - \text{Bi}_2\text{O}_3 - 50 \) and \( \beta - \text{Bi}_2\text{O}_3 - 50 \) samples. Observably, under visible light irradiation, EPR signals of \( \alpha - \text{Bi}_2\text{O}_3 - 50 \) and \( \beta - \text{Bi}_2\text{O}_3 - 50 \) are further enhanced, indicating that the oxygen defects are sensitive to light and could enormously boost the charge separation and accelerate the charge transportation.

In addition, the density of states (DOS) (Fig. 3e) and projected density of states (PDOS) are simulated via DFT calculation to further demonstrate the influence of oxygen defects on the band structure. In comparison with the pure \( \alpha - \text{Bi}_2\text{O}_3 \) and \( \beta - \text{Bi}_2\text{O}_3 \), middle energy levels have been observed in the band gap structure of \( \alpha - \text{Bi}_2\text{O}_3 - 50 \) and \( \beta - \text{Bi}_2\text{O}_3 - 50 \) samples. Subsequently, according to the projected density of states (PDOS), the introduction of defect level mainly can be ascribed to the 1s orbital states of O atom inducing oxygen vacancy. Besides, the valence band (VB) edges are slightly shifted to lower energy levels on defect-controlled samples, which suggest that \( \alpha - \text{Bi}_2\text{O}_3 - 50 \) and \( \beta - \text{Bi}_2\text{O}_3 - 50 \) are endowed with much higher oxidation ability. Therefore, combining with experimental characterization and theoretical calculation, oxygen defects can be introduced by a facile method, which could simultaneously enhance the absorption in visible light region and facilitate the mobility of charge carriers.

Photoluminescence (PL) is used to further investigate the separation efficiency of charge carriers. As shown in Fig. 3f and g, the PL intensity of \( \beta - \text{Bi}_2\text{O}_3 \) is much lower than that of \( \alpha - \text{Bi}_2\text{O}_3 \) under identical conditions, indicating the high separation efficiency of photo-generated electrons-holes. The dramatic differences are highly related to the specific crystal structures. The zigzag-type configuration of \( \alpha - \text{Bi}_2\text{O}_3 \) sample (Fig. S2a online) intends to induce the recombination of the carriers and thus leads to high PL intensity, while the tunnels structure in \( \beta - \text{Bi}_2\text{O}_3 \) sample (Fig. S2b online) can provide the channels for the charge carriers transfer and separation [12]. In addition, the PL intensity of \( \alpha - \text{Bi}_2\text{O}_3 - \text{X} \) and \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) samples has been greatly diminished, indicating that the introduction of oxygen vacancy could further promote the separation and transformation of charge carriers. The quenching of PL peaks can be attributed to the fact that the formation of vacancies functioned as trapping sites to induce the delocalized photo-generated carriers to be converged and then accelerate the separation efficiency. Furthermore, an increased photocurrent signal directly implies a higher efficiency of charge separation. Rapidly enhanced photocurrent on defective \( \alpha - \text{Bi}_2\text{O}_3 - \text{X} \) and \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) can be detected (Fig. S5 online), which is well consistent with the PL results. Therefore, the construction of oxygen defects in a proper crystal structure exerts synergistic effects on the regulation of light absorption capacity, band structure and the migration of charge carriers and thus the optimized photocatalytic efficiency can be achieved.

3.3. Photocatalytic performance, active species, and molecular activation

The photocatalytic performance of as-prepared samples was investigated by photocatalytic NO removal under visible irradiation. As shown in Fig. 4a, \( \alpha - \text{Bi}_2\text{O}_3 \) sample exhibits poor visible light photocatalytic activities (about 8.0%) due to the large band gap and rapid recombination of photo-generated electrons-holes. Along with the construction of oxygen defects, the photocatalytic activities of \( \alpha - \text{Bi}_2\text{O}_3 - \text{X} \) samples have been increased and \( \alpha - \text{Bi}_2\text{O}_3 - 50 \) sample with proper defects concentration exhibits the highest activity (about 20.0%). Notably, the photocatalytic NO removal ratio of pristine \( \beta - \text{Bi}_2\text{O}_3 \) (25.2%) is much higher than that of \( \alpha - \text{Bi}_2\text{O}_3 \) and all defect-controlled \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) samples (Fig. 4b), which can be attributed to from the excellent optical properties and separation efficiency of carriers arising from the unique crystal structure. In addition, the photocatalytic activities of all defect-controlled \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) samples have been promoted and the highest photocatalytic NO removal ratio is achieved around 52.0%. Interestingly, the photocatalytic activities of as-prepared samples obeyed the sequence: \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \times \beta - \text{Bi}_2\text{O}_3 > \alpha - \text{Bi}_2\text{O}_3 - \text{X} > \alpha - \text{Bi}_2\text{O}_3 \), which is well consistent with BET surface areas (Table S1 online). Beside, as displayed in Fig. S6 (online), the photocatalytic NO removal ratio of \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) (52.0%) sample is far exceeding that of commercial P25 (about 20.2%) under visible light irradiation, indicating that the optimized \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) has great potential in photocatalytic degradation pollution. Most importantly, the \( \beta - \text{Bi}_2\text{O}_3 - \text{X} \) sample maintains relatively durable photocatalytic activity (Fig. S7 online), with no obvious deactivation or the catalyst poisoning after five repetitive. And the recycled catalyst can be regenerated by water washing to remove the nitrate on the catalyst surface. Therefore, specific crystal structure with appropriate vacancy-engineering could realize the synergistic effect on photo-electric property to realize the highly efficient photocatalysis.

To further investigate the reactive species in photocatalytic NO oxidation process, the DMPO spin-trapping ESR spectra of as-prepared samples are implemented in methanol dispersion for DMPO- radical (Fig. 4c) and in aqueous dispersion for DMPO-OH radicals (Fig. 4d). In dark, no signals are observed. However, in comparison with \( \alpha - \text{Bi}_2\text{O}_3 \), \( \beta - \text{Bi}_2\text{O}_3 \) and \( \alpha - \text{Bi}_2\text{O}_3 - 50 \), much stronger DMPO spin-trapping signals of reactive oxygen species (\( \cdot \text{O}_2 \) and \( \cdot \text{OH} \)) have been detected over \( \beta - \text{Bi}_2\text{O}_3 - 50 \) under visible light irradiation. Besides, the intensity of active species (\( \cdot \text{O}_2 \) and \( \cdot \text{OH} \)) are enhanced in the order of \( \beta - \text{Bi}_2\text{O}_3 - 50 > \beta - \text{Bi}_2\text{O}_3 > \alpha - \text{Bi}_2\text{O}_3 - 50 > \alpha - \text{Bi}_2\text{O}_3 \), which is well consistent with the photocatalytic performance. Therefore, the adsorption and activation of gas molecular (\( \text{O}_2 \) and \( \text{H}_2\text{O} \)) have been promoted by the construction of oxygen vacancy to induce the formation of \( \cdot \text{O}_2 \) and \( \cdot \text{OH} \) radicals for the photocatalytic NO oxidation.

The adsorption and activation of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) molecules on the active sites were subsequently studied by DFT calculation. As depicted by the charge difference distribution of as-prepared samples (Fig. 5), \( \text{O}_2 \) molecule prefer to obtain electron from electron-efficient areas and thus be activated for the formation of \( \cdot \text{O}_2 \) radicals. And inversely, the \( \text{H}_2\text{O} \) molecule tends to donate electrons to electron-deficient areas and thus be activated for the formation of \( \cdot \text{OH} \) radicals. Besides, according to the calculation of Bader charge [44], the total charge of \( \text{O}_2 \) for \( \beta - \text{Bi}_2\text{O}_3 \) (\( q = -0.22 \) e) is more negative than that for \( \alpha - \text{Bi}_2\text{O}_3 \) (\( q = -0.0064 \) e), which indicates that the tunnel structure in \( \beta - \text{Bi}_2\text{O}_3 \) is beneficial to facilitate the adsorption and activation of \( \text{O}_2 \) molecule than the zigzag-type configura-
tion of \( \alpha \)-Bi\(_2\)O\(_3\) (Fig. 5a and c). Similarly, as shown in Fig. 5b and d, the excellent tunnels structure of \( \beta \)-Bi\(_2\)O\(_3\) also promote the activation of H\(_2\)O molecule and the total charge of H\(_2\)O molecule is +0.0135 e on \( \beta \)-Bi\(_2\)O\(_3\). Observably, after the introduction of oxygen defects, much higher total charge of O\(_2\) molecule \((\Delta q = 1.26 \text{ e})\) and H\(_2\)O molecule \((\Delta q = +0.0196 \text{ e})\) have been achieved. Correspondingly, the adsorption and activation of reactants have been significantly promoted to induce the generation of reactive oxygen radicals, which is well in correspondence with the ESR result. Therefore, the construction of oxygen vacancy in the unique tunnel structure further make the delocalized charge carriers to be converged and thus accelerate the spatial separation of charge carriers to realize a highly efficient photocatalytic NO removal.

3.4. In situ DRIFTS investigation and photocatalysis reaction mechanism

The in situ DRIFTS were further employed to reveal the intermediates and products during the adsorption-reaction processes, and directly elaborate the reaction pathway and mechanism. The spectra of the NO adsorption process on as-prepare samples are shown in Fig. 6. The absorption bands of N\(_2\)O\(_3\) (962 cm\(^{-1}\)) \([45]\), NO\(^{-}\) (1162 and 1190 cm\(^{-1}\)) \([46,47]\) are observed, which is due to the chemical adsorption of NO on \( \alpha \)-Bi\(_2\)O\(_3\). Also, the characteristic peak at 844, 1058 and 1230 cm\(^{-1}\) which assigned to final products (NO\(_2^{-}\) and NO\(_3^{-}\)) are detected, which can be attributed to the slow oxidation of O\(_2\) with NO \([45,48]\). As for \( \beta \)-Bi\(_2\)O\(_3\), the assignment of adsorption peaks like monodentate NO\(_3^{-}\) (925 cm\(^{-1}\)), N\(_2\)O\(_3\) (962 cm\(^{-1}\)), N\(_2\)O\(_2\)
Bi2O3-50 sample and the intensities gradually are strengthened. The observed peaks of final products including bidentate NO3 (1500–1550, 1635 cm\(^{-1}\)) and NO2 (1060 and 1080 cm\(^{-1}\)) are markedly observed on β-Bi2O3-50 (Fig. 7d). The boosted generation of final products is perfectly matched with the enhanced production of active species and photocatalytic performance on β-Bi2O3-50 sample. Therefore, the synergistic effects of the specific crystal structure and oxygen vacancies could greatly promote the adsorption and activation of reactants for the completely photocatalytic NO oxidation.

According to in situ DRIFT spectra, the reaction pathway of samples is proposed and correspondingly followed the route of NO → N\(_2\)O\(_2\) → NO\(_2\)/NO\(_3\) → NO\(_2\). Subsequently, DFT calculations were utilized on the basis of reaction pathway to elaborately reveal the enhancement of the adsorption/activation of reactants on α-Bi2O3-50 and β-Bi2O3-50 by analyzing the adsorption energies (Table S4 online). As shown in Fig. 8, the adsorption energy major intermediates on β-Bi2O3-50 is much higher than that of α-Bi2O3-50, indicating that the adsorption and activation of reactants on β-Bi2O3-50 is greatly promoted and also well matching the boosted intensity of IR band (Fig. 7).

In conclusion, the acceleration of NO molecules and the facilitated transformation of intermediates have been realized under the synergistic effects of crystal structure and oxygen vacancy, contributing to the optimization of photocatalytic performance [54–57].
4. Conclusions

In conclusion, we develop defect-controlled $\alpha$-Bi$_2$O$_3$ and $\beta$-Bi$_2$O$_3$ via a facile method to explore the synergistic effects of crystal structure and oxygen vacancy on photocatalysis and thus realize the highly efficient photocatalytic NO removal. The introduction of oxygen defects further accelerates the separation of photo-generated carriers and also facilitates the activation of reactants. Subsequently, the boosted generation of final products has been demonstrated on $\beta$-Bi$_2$O$_3$-50 by in situ FTIR and DFT calculations, which is well match with the formation of active species and the photocatalytic performance. In combination with the in situ FTIR and DFT calculations results, the photocatalytic reaction process and promotion mechanism of $\alpha$-Bi$_2$O$_3$-50 and $\beta$-Bi$_2$O$_3$-50 were proposed. The $\beta$-Bi$_2$O$_3$-50 facilitated the transformation of N$_2$O$_2$ into NO$_2$/NO$_2^-$ during adsorption activation, while the N$_2$O$_2$ → NO$_2$/NO$_2^-$ process is inhibited on $\alpha$-Bi$_2$O$_3$-50. The activation of major intermediates on $\beta$-Bi$_2$O$_3$-50 is more efficient than that on $\alpha$-Bi$_2$O$_3$-50, and then the intermediate products can be transformed into the final target products more smoothly. This work could not only provide new insights into the photocatalysis mechanism involved with the combined effects of defects, crystal structure, but also provide a new strategy to develop the structure-tunable photocatalysts.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions
Fan Dong, Yanjun Sun and Ben Lei designed the study. Fan Dong, Yanjun Sun and Jianping Sheng provided the support on experimental feasibility. Ben Lei, Wen Cui, Hong Wang, Peng Chen performed characterization and analysis under the supervision of Fan Dong. Ben Lei and Jieyuan Li performed the VASP calculation. Ben Lei wrote the paper. Fan Dong revised the paper. All authors contributed to the interpretation of the results and improvement of the paper.

Appendix A. Supplementary materials

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References
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