Oxygen Vacancy Engineering Promoted Photocatalytic Ammonia Synthesis on Ultrathin Two-Dimensional Bismuth Oxybromide Nanosheets

Xiaolan Xue, Renpeng Chen, Hongwei Chen, Yi Hu, Qingqing Ding, Ziteng Liu, Lianbo Ma, Guoyin Zhu, Wenjun Zhang, Qian Yu, Jie Liu, Jing Ma, and Zhong Jin

Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210027, China
Center of Electron Microscopy and State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
Department of Chemistry, Duke University, Durham, North Carolina 27708, United States

ABSTRACT: The catalytic conversion of nitrogen to ammonia is one of the most important processes in nature and chemical industry. However, the traditional Haber-Bosch process of ammonia synthesis consumes substantial energy and emits a large amount of carbon dioxide. Solar-driven nitrogen fixation holds great promise for the reduction of energy consumption and environmental pollution. On the basis of both experimental results and density functional theory calculations, here we report that the oxygen vacancy engineering on ultrathin BiOBr nanosheets can greatly enhance the performance for photocatalytic nitrogen fixation. Through the addition of polymeric surfactant (polyvinylpyrrolidone, PVP) in the synthesis process, V₀-BiOBr nanosheets with desirable oxygen vacancies and dominant exposed {001} facets were successfully prepared, which effectively promote the adsorption of inert nitrogen molecules at ambient condition and facilitate the separation of photoexcited electrons and holes. The oxygen defects narrow the bandgap of V₀-BiOBr photocatalyst and lower the energy requirement of exciton generation. In the case of the specific surface areas are almost equal, the V₀-BiOBr nanosheets display a highly improved photocatalytic ammonia production rate (5.470 μmol·g⁻¹·h⁻¹), which is nearly 10 times higher than that of the BiOBr nanoplates without oxygen vacancies (5.75 μmol·g⁻¹·h⁻¹). The oxygen vacancy engineering on semiconductive nanomaterials provides a promising way for rational design of catalysts to boost the rate of ammonia synthesis under mild conditions.

KEYWORDS: Photocatalytic nitrogen fixation, oxygen vacancies engineering, defect and bandgap modulation, ultrathin bismuth oxybromide nanosheets

Ammonia is one of the most highly produced chemicals in the chemical industry that can serve as a vital precursor for the synthesis of many nitrogenous compounds, especially nitrogen fertilizers. Although nitrogen accounts for 78% of the total volume of the Earth’s atmosphere, the fixation of nitrogen to ammonia under mild conditions remains a grand challenge, owing to the strong and nonpolar N=N triple bond (with bond energy of 945 KJ·mol⁻¹) that makes the nitrogen molecules extremely stable and inert. The traditional Haber-Bosch method for ammonia synthesis is operated at a high temperature of 300–500 °C and a high pressure of 15–25 MPa, undergoing the drawbacks of high energy input and severe environmental impacts. Therefore, it is highly desirable to develop a new strategy to synthesize ammonia with less power consumption and more environmentally friendly process. Notably, the nitrogen-fixing bacteria in nature can carry out the process of nitrogen fixation at room temperature and ambient pressure. Inspired by the natural photosynthesis using sunlight as the driving force, photocatalytic ammonia synthesis has attracted growing research attention. The photocatalytic nitrogen reduction in the TiO₂ system was first reported by Schrauzer. Subsequently, many efforts had been devoted to improve the nitrogen fixation performance of TiO₂-based photocatalysts by the doping of other elements (e.g., Fe) and the assistance of noble metal (such as Os, Ru, Pt). However, the efficiency of photocatalytic dinitrogen reduction is usually low, owing to the easy recombination of photoinduced electrons and holes, the weak adsorption of inert dinitrogen molecules on the
surface of catalysts and the multielectron nature of the reaction. Theoretical analysis and experimental efforts indicate that oxygen vacancies in photocatalysts with abundant localized electrons are conducive to adsorb and activate different target molecules and also can promote electron–hole separation and reduce the energy barrier for interfacial charge transfer. Some recent studies show that the introduction of nitrogen, oxygen, or sulfur vacancies into catalysts can contribute to the photochemical dinitrogen reduction reaction. However, so far the controlled introduction of specific defects in nanostructural materials is still difficult, hence it is very desirable to explore facile and universal strategies for the construction of superior photocatalysts with favorable atomic vacancies and enhanced performance.

Bismuth oxybromide (BiOBr) is a layered ternary oxyhalide semiconductor with the crystalline structure consists of \([\text{Bi}_2\text{O}_2\text{Br}]^{2+}\) slabs intercalated by the double slabs of \(\text{Br}^−\) ions stacked along the \(z\)-direction (Figure 1). Recently, BiOBr nanocrystals has attracted rising attention due to its remarkable photocatalytic performance in visible light range. In this study, we present that oxygen vacancy engineering on ultrathin BiOBr nanosheets can greatly boost the reaction rate of photocatalytic nanoplates without oxygen vacancies, the BiOBr nanosheets. Therefore, compared to the BiOBr nanosheets, the favorable adsorption of \(\text{N}_2\) molecules on the surface of catalysts and the multielectron nature of the reaction. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphological features of the products. Figure 2a shows that the \(V^0\)-BiOBr nanosheets consist of large-scale laminar nanosheets. TEM images further reveal its sheetlike structure and rough surface with a thickness of 4–8 nm (Figure 2b). The high-resolution TEM (HRTEM) image in Figure 2c shows that the lattice fringes of \(V^0\)-BiOBr nanosheets with a lattice spacing of 0.277 nm, corresponding to the (110) planes of tetragonal BiOBr. Additionally, it can be found that there are crystalline boundaries and defects in the HRTEM image of \(V^0\)-BiOBr nanosheets, which is ascribed to the abundant and broadly distributed oxygen vacancies in the \(V^0\)-BiOBr nanosheets. As shown in the inset of Figure 2c, the corresponding fast Fourier transform (FFT) pattern shows a regular pattern, suggesting the single-crystalline characteristic of \(V^0\)-BiOBr nanosheets. The diffraction spots were recorded along the \([001]\) direction. The angle of 45° in FFT pattern is in good agreement with the theoretical value of the angle between (200) and (110) planes. In contrast, the BiOBr nanoplates exhibit a disklike morphology and flat surface, with an average size of ~200 nm and thickness of around 15 nm, as depicted in Figure 2d,e. The HRTEM image of BiOBr nanoplates presents a sharp lattice stripes with a \(d\)-spacing of 0.277 nm (Figure 2f), which is comparable with that of \(V^0\)-BiOBr nanosheets, but with much better crystallinity and uniform contrast, which indicates the ordered single-crystalline structure and fewer defects in BiOBr nanoplates.

The crystallographic structures of the as-synthesized samples were also characterized by XRD analysis. As shown in Figure 3a, the XRD peaks of both \(V^0\)-BiOBr nanosheets and BiOBr nanoplates can be well assigned to the tetragonal BiOBr (JCPDS No. 09-0393). The peak sharpness and relative intensity of \(V^0\)-BiOBr nanosheets are much lower than those of BiOBr nanoplates, mainly owing to the oxygen vacancies in \(V^0\)-BiOBr nanosheets. More specifically, in the case of \(V^0\)-BiOBr nanosheets the intensity ratio of the (110) facet to (001) facet was 2.5, which was smaller than of BiOBr nanoplates (around 3.9). This indicates a preferred (001) orientation in the \(V^0\)-BiOBr nanosheets, which is in accordance with the HRTEM results. The possible reason is that during the nucleation process, the negatively charged \(-\text{C}==\text{O}\) bonds of PVP surfactant molecules tend to bind with the unsaturated and positively charged Bi atoms on the BiOBr surface in order to reduce the surface energy, leading to the...
leading to the formation of facets during the hydrothermal synthetic process, planes of BiOBr, which could significantly suppress the growth of {102} facets. During the hydrothermal synthetic process, planes of BiOBr, which could significantly suppress the growth of {102} facets. High-resolution XPS scans of (c) Bi 4f, (d) Br 3d, and (e) O 1s regions of V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates, respectively. High-resolution XPS scans of (c) Bi 4f, (d) Br 3d, and (e) O 1s regions of V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates, respectively. The XPS spectrum at Bi 4f region (Figure 3c) shows two strong Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ bands of the Bi$^{3+}$ species, respectively. The peaks located at 158.4 and 163.6 eV, which are assigned to Bi atoms close to the oxygen vacancies, and the adsorbed O$_2$ molecules, respectively. Compared to BiOBr nanoplates, the O 1s peak of the oxygen atoms close to the oxygen vacancies in V$_2$O$_3$BiOBr nanosheets is much stronger and down-shifted from 531.8 to 530.6 eV, indicating the presence of more oxygen defects in V$_2$O$_3$BiOBr nanosheets.

Electron paramagnetic resonance (EPR) spectra were further employed to identify the oxygen vacancies. As shown in Figure 3f, the EPR spectrum of V$_2$O$_3$BiOBr nanosheets shows a strong peak at 304 mT, confirming the presence of oxygen vacancies, whereas the EPR spectrum of BiOBr nanoplates shows almost no signal. According to the previous reports, oxygen vacancies can delocalize electrons and thus substantially prevent the recombination of photogenerated electrons and holes, beneficial to the photocatalytic processes.

To investigate the effect of oxygen vacancies on the semiconductive and photocatalytic properties, further characterizations were performed on the V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates. UV–vis diffuse reflectance spectra (DRS) show that the absorption edge of V$_2$O$_3$BiOBr nanosheets is red-shifted to 470 nm (Figure 4a), which is 30 nm longer than the absorption edge of BiOBr nanoplates (440 nm). Moreover, compared to BiOBr nanoplates, the V$_2$O$_3$BiOBr nanosheets show a stronger light absorption capability in the visible range between 450–750 nm and also exhibit darker color (as shown in the insets of Figure 4a). The Tauc plots (Figure 4b) reveal the bandgap of V$_2$O$_3$BiOBr nanosheets (2.43 eV) is smaller than that of BiOBr nanoplates (2.69 eV). XPS valence band spectra were employed to further study the band structures of both samples. As shown in Figure 4c, compared to the VB of BiOBr nanoplates (1.50 eV), the valence band maximum (VBM) of V$_2$O$_3$BiOBr nanosheets is shifted to 0.95 eV. According to the combined analysis of band positions based on the Tauc plots and XPS valence band spectra (Figure 4b,c), it can be concluded that the conduction band minimum (CBM) of V$_2$O$_3$BiOBr nanosheets is shifted to $-1.48$ eV, while the CBM of BiOBr nanoplates is $-1.19$ eV. The enhanced light absorption and up-shifted conduction band are beneficial to the photocatalytic performance. The differences in energy band positions between V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates is illustrated in Figure 4d. On the basis of the above analysis, the effect of oxygen vacancies to the photocatalytic nitrogen fixation on V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates can be deduced (Figure 4e). The photoinduced electrons in the V$_2$O$_3$BiOBr nanosheets are first captured by the oxygen vacancies and then participate in the nitrogen reduction reaction, thus facilitating the charge separation and promote the reaction rate. In contrast, the photoinduced electrons generated in the BiOBr nanoplates are directly used to react with N$_2$ and H$_2$O molecules, which may suffer from charge recombination.

Electrochemical impedance spectra (EIS) were used to investigate the charge transport properties and interfacial resistances of the samples (Figure 5a,b). For both V$_2$O$_3$BiOBr nanosheets and BiOBr nanoplates, the arc radii of Nyquist plots under illumination are smaller than those measured.
under dark, owing to the abundant photoinduced electrons and holes on the catalysts generated under illumination. Notably, no matter under dark or under illumination, the arc radii of V\textsubscript{O}-BiOBr nanosheets are smaller than those of BiOBr nanoplates, indicating the oxygen vacancies in V\textsubscript{O}-BiOBr nanosheets can greatly promote charge transport and decrease the interfacial resistance.

To compare the nitrogen adsorption capability of V\textsubscript{O}-BiOBr nanosheets and BiOBr nanoplates, volumetric N\textsubscript{2} adsorption measurements were performed under room temperature (Figure 5c). The result reveals that the V\textsubscript{O}-BiOBr nanosheets are able to absorb N\textsubscript{2} molecules, while the BiOBr nanoplates can hardly absorb N\textsubscript{2} at mild conditions. DFT calculations also reveal the energetically unfavorable adsorption of N\textsubscript{2} molecule on BiOBr slab model without the oxygen vacancies, as detailed below. These result suggest that the introduction of oxygen vacancies is very conductive to the adsorption of inert N\textsubscript{2} molecules, which bene\textsubscript{fi}ts to the reaction rate and conversion efficiency of nitrogen photofixation.

The photocatalytic nitrogen fixation activities of V\textsubscript{O}-BiOBr nanosheets and BiOBr nanoplates were evaluated and compared. The concentration of generated ammonia was measured by Nessler’s reagent colorimetric method and carefully calibrated (Figure S2). There is no ammonia detected in the absence of photocatalyst or light illumination, suggesting the photocatalyst and light illumination are essential to the nitrogen fixation. Under the visible-light illumination of 300 W Xe lamp with a 420 nm cutoff filter, the V\textsubscript{O}-BiOBr nanosheets display a much higher photocatalytic activity for ammonia production than that of BiOBr nanoplates (Figure 5d). The V\textsubscript{O}-BiOBr nanosheets show an average rate of photocatalytic ammonia generation of 49.04 μmol·g\textsuperscript{-1}·h\textsuperscript{-1} within 2 h, while the average rate of photocatalytic ammonia generation of BiOBr nanoplates is only 2.83 μmol·g\textsuperscript{-1}·h\textsuperscript{-1}. Under the full-range light illumination without cutoff filter, the photocatalytic rate of V\textsubscript{O}-BiOBr nanosheets and BiOBr nanoplates increased to 54.7 and 5.75 μmol·g\textsuperscript{-1}·h\textsuperscript{-1}, respectively.

To confirm the N source and the proton source of the produced NH\textsubscript{3} are originated from N\textsubscript{2} and H\textsubscript{2}O, the controlled experiments of photochemical N\textsubscript{2} fixation on V\textsubscript{O}-BiOBr nanosheets under different conditions and atmospheres with the full spectrum irradiation of 300 W Xe lamp (50 mg photocatalyst + 100 mL solvent). (i) The time histograms of ammonia concentrations obtained with different samples and test conditions.
almost no impact on photocatalytic performance of nitrogen fixation.

Besides, room-temperature EPR spectroscopy was performed to evaluate the relative concentrations of oxygen vacancies on Vo-BiOBr nanosheets before and after the UV-visible light irradiation, respectively. As shown in Figure S3, the signal intensity of the EPR spectra shows almost no change before and after the UV-visible light irradiation, indicating that the Xe lamp irradiation without cutoff filter cannot produce more oxygen vacancies on Vo-BiOBr nanosheets. In view of the identical chemical compositions and the comparable specific surface areas between V_o-BiOBr nanosheets and BiOBr nanoplates, it can be concluded that the oxygen vacancies generated during the synthesis process of V_o-BiOBr nanosheets are responsible for the significantly improved photocatalytic activity for nitrogen fixation.

As shown in Figure 5f, after working for 12 h under illumination (repeated 6 testing cycles for 2 h periods), the V_o-BiOBr nanosheets still maintain the ability of photocatalytic N_2 fixation, delivering a total ammonia production amount of 30.9 mmol and an average ammonia generation rate of 5.15 mmol g^-1 h^-1, indicating the good stability during the photocatalytic process. In addition, SEM and XRD characterizations (Figures S4 and S5) show that the morphology and crystalline structure of V_o-BiOBr nanosheets and BiOBr nanoplates remain almost unchanged after long-term testing, further confirming the well-preserved structural integrity of the BiOBr photocatalysts.

To understand the origins of enhanced photocatalytic N_2 fixation performance on V_o-BiOBr nanosheets, it is important to gain a fundamental insight into the role of oxygen vacancies in reaction mechanism through theoretical simulations. DFT calculations were carried out to investigate the possible reaction pathways of N_2 fixation on the V_o-BiOBr (001) surface with a slab model, as shown in Figure S6. For the N_2 fixation on the exposed V_o-BiOBr (001) surface, DFT calculations confirm that the reaction pathway favors the hydrogenation of distal N_1 atom (N^*≡N^*), as indicated by the reaction steps 1–4 (Figure 6a). As confirmed by above studies, the rich oxygen vacancies on V_o-BiOBr are responsible for the N_2 adsorption and enhanced catalytic activity. Briefly, N_2 molecules are first absorbed onto the oxygen vacancies on the V_o-BiOBr (001) surface and activated at the reaction step 1, with the length of N≡N bond increases from 1.11 to 1.24 Å (Figure 6b). The following step 2 is the key step of the hydrogenation of distal N_1 atom to yield N≡NH*, which is exergonic with an energy change of 1.0 eV (Figure 6c). The subsequent intermediate hydrogenation product at the step 3 is N≡NH*, associated with the reduction of N≡N bond to N≡N bond. At the step 4, N≡NH* is further hydrogenated to generate an intermediate of N≡NH^* with a single N≡N bond length of 1.47 Å (Figure 6b), then an energy input of 1.07 eV is required to cleave the N≡N bond (Figure 6c).

This leads to the release of the first NH_2 molecule after the N≡N bond splitting. The subsequently formed three intermediates are NH*, NH*_*, and NH^*_*, which were found to be also exergonic with the energy outputs of 3.34, 3.58, and 3.15 eV, respectively. Finally, the amine intermediate NH^*_* requires another energy input of 1.03 eV to release the second NH_2 molecule. In contrast, for the N_2 fixation on the BiOBr (001) surface without oxygen vacancies, DFT calculation indicates that N_2 molecule is difficult to adsorb and activate on the BiOBr (001) surface, as evidenced by the increase of O–N^3 distance from 3.23 Å (step 1) to 3.63 Å (step 4) (Figure S7), which is consistent with the above experimental results. These calculation results indicate that the oxygen vacancies on V_o-BiOBr (001) surface are crucial to the N_2 fixation, which is conducive to the N_2 adsorption and formation of intermediates for ammonia production.

In summary, here we demonstrate that the introduction of oxygen vacancies in BiOBr photocatalyst by the surfactant-assisted synthesis has great effect on the photocatalytic activity for nitrogen fixation. On the basis of detailed characterizations and tests, it is confirmed that the oxygen defects can enhance the light absorption, narrow the bandgap, and change the positions of conduction band and valence band. Moreover, the oxygen vacancies can effectively inhibit the recombination of photogenerated electrons and holes. DFT calculations indicate that the oxygen vacancies can facilitate the adsorption and activation of inert N_2 molecules. As a result, the photocatalytic activity of V_o-BiOBr nanosheets is much superior to that of BiOBr nanoplates without vacancies. This work points out a feasible way to design high-performance photocatalysts for solar-driven ammonia synthesis via the vacancy and defect engineering.
(001) surface, the calculated energy change and the variation of O−N distance, and schematic structure of N₂ molecule on the BiOBr (001) surface without oxygen vacancies. (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: zhongjin@nju.edu.cn. Phone: +86-18115605182.

ORCID

Jie Liu: 0000-0003-0451-6111
Jing Ma: 0000-0001-5848-9775
Zhong Jin: 0000-0001-8860-8579

Author Contributions

X.X., R.C., and H.C. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Key R&D Program of China (2017YFA0208200, 2016YFB0700600, 2015CB659300), Projects of NSFC (21872069, 51761135104, 21573108), National Science Foundation of Jiangsu Province (BK20180008, BK20150583, BK20160643), High-Level Entrepreneurial and Innovative Talents Program of Jiangsu Province, and the Fundamental Research Funds for the Central Universities of China (020151830146). We are also grateful to the High-Performance Computing Center of Nanjing University and Nanxin Pharm Co., Ltd., Nanjing, for the help of the quantum Chemical calculations in this paper.

■ REFERENCES

(2) Knobloch, D. J.; Lobkovsky, E.; Chirik, P. Nat. Chem. 2010, 2, 30–35.