Visible-Light-Driven Nitrogen Fixation Catalyzed by Bi$_2$O$_7$Br Nanostructures: Enhanced Performance by Oxygen Vacancies

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ABSTRACT: Photocatalytic nitrogen fixation represents a green alternative to the conventional Haber–Bosch process in the conversion of nitrogen to ammonia. In this study, a series of Bi$_2$O$_7$Br nanostructures were synthesized via a facile, low-temperature thermal treatment procedure, and their photocatalytic activity toward nitrogen fixation was evaluated and compared. Spectroscopic measurements showed that the tubular Bi$_2$O$_7$Br sample prepared at 40 °C (Bi$_2$O$_7$Br-40) exhibited the highest electron-transfer rate among the series, producing a large number of O$_2^-$ radicals and oxygen vacancies under visible-light photoirradiation and reaching a rate of photocatalytic nitrogen fixation of 12.72 mM·g$^{-1}$·h$^{-1}$ after 30 min of photoirradiation. The reaction dynamics was also monitored by in situ infrared measurements with a synchrotron radiation light source, where the transient difference between signals in the dark and under photoirradiation was analyzed and the reaction pathway of nitrogen fixation was identified. This was further supported by results from density functional theory calculations. The reaction energy of nitrogen fixation was quantitatively estimated and compared by building oxygen-enriched and anoxic models, where the change in the oxygen vacancy concentration was found to play a critical role in determining the nitrogen fixation performance. Results from this study suggest that Bi$_2$O$_7$Br with rich oxygen vacancies can be used as a high-performance photocatalyst for nitrogen fixation.

INTRODUCTION

Nitrogen is one of the most abundant elements on earth, mostly as nitrogen gas (N$_2$) in the atmosphere. Ammonia synthesis is an important reaction in the natural fixation of nitrogen. However, industrial nitrogen fixation, such as the Haber–Bosch process, not only requires high temperature and high pressure but also consumes a large amount of hydrogen. Recently, photocatalytic nitrogen fixation has been attracting extensive interest thanks to its energy and environmental advantages, where artificial photosynthesis is exploited for the direct production of NH$_3$ from N$_2$ and H$_2$O under sunlight with the assistance of an appropriate catalyst. However, the efficiency of photocatalytic nitrogen fixation is generally low and limited by two major factors: (a) the reduction of one N$_2$ molecule requires the transfer of six electrons, but most catalysts cannot produce abundant electrons due to the high recombination rate of photogenerated electrons and holes and (b) N$_2$ adsorption is a necessary step for the catalytic reaction, but most catalysts exhibit only weak N$_2$ adsorption. Thus, the design and engineering of effective catalysts with high N$_2$ adsorption and efficient separation of photogenerated electron–hole pairs is key to an improved performance of photocatalytic nitrogen fixation.

Recent research has shown that BiOX (X = Cl and Br) materials exhibit excellent photocatalytic activity toward nitrogen fixation due to their unique layer structures and appropriate band gaps. Among these, layered bismuth oxybromide (BiOBr) is of particular interest because the inherent internal static electric field can improve the diffusion coefficient (D) of electron–hole pairs, leading to enhanced carrier mobility and a reduced recombination rate. Furthermore, for bismuth oxybromide-based semiconductors, oxygen vacancies (OVs) with abundant localized electrons on the surface have been demonstrated to facilitate the adsorption and activation of N$_2$. Thus, one can envision that the design and engineering of bismuth oxybromide nanostructures may be exploited to markedly advance the photocatalytic fixation of nitrogen.
Notably, because the recombination of photogenerated electron−hole pairs may occur in the interior of the semiconductors before they reach the surface to initiate reactions, various forms of nanostructures, such as nanoparticles, nanotubes, nanowires, and nanosheets, have been prepared to shorten the migration distance. In fact, a range of strategies have been employed to engineer the BiOBr structure, such as morphological control, exposure of select crystalline facets, and heterologous hybridization.

For instance, Di et al. prepared Bi$_4$O$_5$Br$_2$ ultrathin nanosheets via an ionic-liquid-assisted solvothermal method under pH control, which effectively increased the electron-transfer rate and greatly improved the photocatalytic degradation of ciprofloxacin. Wang et al. reported a novel low-temperature method for the water-assisted self-assembly of Bi$_5$O$_7$Br nanotubes (average cross-sectional diameter 5 nm), which diminished the electron-migration distance and increased the electron-transfer rate, resulting in a significant increase in the rate of nitrogen fixation. However, optimization of the material structure and hence the fixation performance remain lacking.

**Figure 1.** Representative TEM images of (a) Bi$_5$O$_7$Br-20, (b) Bi$_5$O$_7$Br-40, (c) Bi$_5$O$_7$Br-60, (d) Bi$_5$O$_7$Br-80, and (e) Bi$_5$O$_7$Br-100. The left insets are the corresponding SAED patterns, and the right insets are the respective HRETM images. (f) Length distributions of 50 Bi$_5$O$_7$Br nanotubes randomly selected from the Bi$_5$O$_7$Br-40 sample in panel (b).
In this study, a series of Bi\textsubscript{5}O\textsubscript{7}Br nanostructures were prepared by a facile thermal procedure in a water bath at controlled temperatures (20 to 100 °C) and exhibited apparent photocatalytic activity toward nitrogen fixation under visible light photoirradiation (>400 nm). Among the series, the sample prepared at 40 °C stood out as the best catalyst, which coincided with the smallest band gap, largest OV content, highest photocurrents, best diode-like characteristics, and lowest charge-transfer resistance. The dynamics of nitrogen fixation was also monitored by in situ infrared spectroscopy using a synchrotron radiation source. It was found that the adsorption of nitrogen was indeed facilitated by the OVs, which played a key role in the determination of the photocatalytic activity, in good agreement with results from density functional theory (DFT) calculations. Taken together, these results highlight the significance of structural engineering in the development of high-efficiency photocatalysts toward nitrogen fixation.

**EXPERIMENTAL SECTION**

**Material Preparation.** All chemicals were of analytical purity, purchased from Aladdin and used without further purification. Deionized water was used in all experiments.

**Preparation of Bi\textsubscript{5}O\textsubscript{7}Br Nanostructures.** Bi\textsubscript{5}O\textsubscript{7}Br nanostructures were synthesized by a water-induced self-assembly method. In brief, 50 mL of an ammonia solution and 3 mmol of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O were added to five beakers, which were then heated to five different temperatures: 20, 40, 60, 80, and 100 °C. After 10 min of heating, an equal amount of KBr was added to the beakers under magnetic mixing, followed by the dropwise addition of 5 mL of deionized water until a translucent solution was obtained. The resulting mixtures were heated for 10 days before being separated by centrifugation at 10 000 rpm, rinsed with cyclohexane and absolute ethanol several times, and finally dried at 60 °C for 12 h. The obtained products were denoted as Bi\textsubscript{5}O\textsubscript{7}Br-T, with T being the heating temperature.

**Characterization.** The material morphologies were analyzed by high-resolution transmission electron microscopy measurements (HRTEM, JEOL 2010 F). X-ray diffraction (XRD) patterns were acquired with a Bruker D8 Advance X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo Kratos Axis Supra instrument. All binding energies were referenced to the C 1s peak at 284.6 eV. Raman spectra were recorded at room temperature using a micro Raman spectrometer (Renishaw RM-1000) in backscattering geometry with a 532 nm laser as the excitation source. Electron spin resonance (ESR) spectra were collected with a Bruker ER200-SRC-10/12 spectrometer. Because of the chemical reactivity of superoxide radicals (O\textsubscript{2}⁺) in water, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used to trap O\textsubscript{2}⁺ in methanol, whereas hydroxyl radicals did not react with water so the ESR signals were acquired in water. The OV signals were detected directly with solid Bi\textsubscript{5}O\textsubscript{7}Br powders. Brunauer–Emmett–Teller (BET) surface areas were analyzed with a nitrogen adsorption apparatus (BET, Mike ASAP2020). Optical absorbance and UV–vis diffuse reflectance spectra (DRS) were measured with a Thermo UV-2600 UV–vis spectrophotometer. Electrochemical impedance spectra (EIS) were acquired with a CHI 760e electrochemical workstation. Photoluminescence spectroscopy measurements were conducted with an Edinburgh Instruments FLS980 Spectrometer.

**Photocatalysis.** Photocatalytic N\textsubscript{2} fixation experiments were conducted at ambient temperature using a 300 W Xe lamp with a
400 nm cutoff filter located approximately 10 cm from the sample. First, 0.025 g of the Bi$_5$O$_7$Br samples prepared above was dispersed in 100 mL of deionized water in a cell equipped with water circulation. Second, the mixture was continuously stirred in the dark and bubbled with high-purity N$_2$ at a flow rate of 50 mL min$^{-1}$ for 30 min before being exposed to visible light irradiation ($\lambda > 400$ nm). An aliquot (3 mL) of the reaction solution was removed every 3 min. The concentration of NH$_4$$^+$ was quantified by using Nessler’s reagent as a chromogenic agent that can be detected at 420 nm with a Thermo UV-2600 UV–vis spectrometer.27

**DFT Calculations.** First-principles calculations in the framework of DFT, including structural and electronic performances, were carried out on the basis of the Cambridge Sequential Total Energy Package (CASTEP).27 The exchange-correlation functional under the generalized gradient approximation (GGA) and the revised Perdew–Burke–Ernzerhof functional were adopted to describe the electron–electron interactions.29 An energy cutoff of 400 eV and a k-point sampling set of 1 $\times$ 2 $\times$ 1 were chosen for the calculations,30 with a force tolerance of 3 eV Å$^{-1}$, an energy tolerance of 1.0 $\times$ 10$^{-5}$ eV per atom, and a maximum displacement of 1.0 $\times$ 10$^{-5}$ Å.

A pristine Bi$_5$O$_7$Br (1) surface, which contains 104 atoms (including 40 Bi, 8 Br, and 56 O atoms), was used in the calculations, in comparison to Bi$_5$O$_7$Br with 1 oxygen vacancy (Bi$_5$O$_7$Br–O, which contained 40 Bi, 8 Br, and 55 O atoms) and Bi$_5$O$_7$Br with one additional oxygen (Bi$_5$O$_7$Br$\cdot$O, which consisted of 40 Bi, 8 Br, and 57 O atoms). The oxygen defects were located near the adsorption site. The core electrons were treated with ultrasoft pseudopotentials.31 The vacuum space along the z direction was set to 15 Å to avoid interactions between the two slab models. The bottom atomic layers were fixed, and the rest of the atomic layers and absorbed molecules were relaxed during all calculations. The sample structures were first examined by TEM measurements. From Figure 2a inset, the band gap can be estimated to be 2.44 eV for Bi$_5$O$_7$Br–20, 2.22 eV for Bi$_5$O$_7$Br–40, 2.38 eV for Bi$_5$O$_7$Br–60, 2.51 eV for Bi$_5$O$_7$Br–80, and 2.63 eV for Bi$_5$O$_7$Br–100. That is, the Bi$_5$O$_7$Br–40 sample exhibited the smallest band gap in the series.

Photoelectrochemistry and electrochemical impedance measurements were then carried out to examine the dynamics of photogenerated electrons in the Bi$_5$O$_7$Br samples. Under the irradiation of a 300 W Xe lamp that provided simulated solar light radiation (100 mW cm$^{-2}$), photocurrent curves were acquired by linear sweep voltammetry (LSV) scans under chopped illumination with a fixed time interval. From Figure 2c, one can see that the Bi$_5$O$_7$Br–40 sample exhibited the highest photocurrent among the series.12,38,39 with an instantaneous photocurrent response of about 1.5 μA, in comparison to 0.9–1.1 μA for other samples. It should be noted that a higher photogenerated current suggests a more efficient separation of photogenerated electron–hole pairs. This indicates that Bi$_5$O$_7$Br–40 stood out as the best photocatalyst among the series of samples. Consistent results were obtained in electrochemical impedance spectroscopy studies under AM 1.5 G illumination. The results are shown in Figure 2d and are fitted with the equivalent circuit in the right inset, with the fitting results summarized in Table 1. It can be

| Sample          | $R_S$ (Ω) | $R_{SC}$ (Ω) | $R_{CT}$ (Ω) |
|-----------------|-----------|--------------|--------------|
| Bi$_5$O$_7$Br–20| 4.3       | 54.6         | 7846         |
| Bi$_5$O$_7$Br–40| 4.0       | 54.2         | 6537         |
| Bi$_5$O$_7$Br–60| 4.3       | 54.3         | 7611         |
| Bi$_5$O$_7$Br–80| 4.3       | 54.9         | 8194         |
| Bi$_5$O$_7$Br–100| 4.7     | 59.5         | 15140        |

**RESULTS AND DISCUSSION**

The sample structures were first examined by TEM measurements. It can be seen from Figure 1 that the samples prepared at temperatures of (a) 20, (b) 40, and (c) 60 °C all exhibited rather well-defined nanotubular structures with a cross-sectional diameter of ca. 5 nm and a length of ca. 100 nm (mostly between 80 and 150 nm, Figure 1f). Yet at higher temperatures, a plate-like morphology became increasingly apparent, as manifested in the (d) Bi$_5$O$_7$Br–80 and (e) Bi$_5$O$_7$Br–100 samples, with a side length of 20–30 nm. This structural evolution suggests that water-assisted self-assembly decreases whereas the fraction of the smaller pores increases. This is consistent with the morphological variation of the samples, which show a tubular structure for samples prepared at low temperatures but a flaky structure at high temperatures (Figure 1).33

The formation of Bi$_5$O$_7$Br was further confirmed by XRD measurements. From Figure S1, a series of diffraction peaks can be identified at 2θ = 24.46, 30.18, 32.64, 46.76, 51.18, and 56.62°, which can be readily indexed to the (312), (004), (600), (604), (314), and (912) facets of the tetragonal phase of Bi$_5$O$_7$Br (JCPDS card no. 038-0493).34–37 No other diffraction peaks can be observed, indicating that the samples were a pure crystalline phase. Consistent results were obtained in Raman spectroscopic measurements (Figure S2), where all Bi$_5$O$_7$Br samples showed two major vibrational bands at ca. 85 and 125 cm$^{-1}$ due to the A$_1g$ and E$_g$ modes of Bi–Br stretching vibrations, respectively.38

First, 0.025 g of the Bi$_5$O$_7$Br samples prepared above was dispersed in 100 mL of deionized water in a cell equipped with water circulation. Second, the mixture was continuously stirred in the dark and bubbled with high-purity N$_2$ at a flow rate of 50 mL min$^{-1}$ for 30 min before being exposed to visible light irradiation ($\lambda > 400$ nm). An aliquot (3 mL) of the reaction solution was removed every 3 min. The concentration of NH$_4$$^+$ was quantified by using Nessler’s reagent as a chromogenic agent that can be detected at 420 nm with a Thermo UV-2600 UV–vis spectrometer.27,28
seen that Bi$_5$O$_7$Br-40 exhibited the lowest charge-transfer resistance ($R_{CT}$, 6537 $\Omega$) among the series. This correlates well with the highest photocurrents observed in Figure 2c.\textsuperscript{40} In addition, one can see that Bi$_5$O$_7$Br-40 also exhibited the lowest internal resistance ($R_s$, 4.0 $\Omega$) and interfacial resistance ($R_{SC}$, 54.2 $\Omega$).

The elemental composition and valence state of the Bi$_5$O$_7$Br samples were then studied and compared by XPS measurements. Figure 3a shows the full survey spectra of the Bi$_5$O$_7$Br samples, where elements of Bi (157.25−166.34 eV), Br (66.03−70.58 eV), O (528.46−535.29 eV), and C (284.81 eV) can be readily identified. On the basis of the integrated peak areas, the atomic ratio of Bi/Br was estimated to be ca. 4.83, close to the stoichiometric ratio of Bi$_5$O$_7$Br. Results from XPS measurements can also be used to determine the energy of the valence band (VB).\textsuperscript{39} From Figure 3b, the VB of the Bi$_5$O$_7$Br-40 sample can be calculated to be $-0.56$ eV versus NHE. This means that the conduction band (CB) lies at ca. $+1.66$ eV, considering a band gap of ca. 2.2 eV that was obtained from UV−vis measurements (Figure 2b). The corresponding high-resolution scans of the Br 3d electrons can be found in Figure 3c, where deconvolution yields two main peaks at 67.6 and 69.2 eV due to the 3d$_{5/2}$ and 3d$_{3/2}$ electrons of Br$^-$. The high-resolution scans of the Bi 4f electrons are shown in Figure 3d, which entail two main peaks at 158.7 and 163.9 eV, consistent with the 4f$_{7/2}$ and 4f$_{5/2}$ electrons of Bi$^{3+}$. In the O 1s scans (Figure 3e), there are three O species that can be ascribed to the lattice oxygen in the sample interior (529.5 eV), OVs (530.5 eV), and absorbed oxygen on the sample surface (532.2 eV).\textsuperscript{36,37} On the basis of the integrated peak areas, the OV concentration was found to vary among the series of samples: Bi$_5$O$_7$Br-40 (14.6%) > Bi$_5$O$_7$Br-60 (14.2%) > Bi$_5$O$_7$Br-100 (11.9%) > Bi$_5$O$_7$Br-80 (10.6%) > Bi$_5$O$_7$Br-20 (9.5%). That is, Bi$_5$O$_7$Br-40 exhibits the highest OV content in the series.

ESR measurements were then carried out to detect the formation of radical species and OVs. It can be seen that the quantities of O$_2^-$ ($g = 2.453$, Figure 4a) and OV ($g = 2.001$, Figure 4b) produced by Bi$_5$O$_7$Br-40 upon photoirradiation were significantly higher than those in the dark. Consistent behaviors can be seen with other samples in the series, where Bi$_5$O$_7$Br-40 produced the largest quantities of O$_2^-$ radicals and OVs (Figures S3 and S4), suggesting the most efficient separation of the photogenerated electron−hole pairs.\textsuperscript{38,39} Note that the production of a large number of OVs was conducive to N$_2$ adsorption and fixation (vide infra).\textsuperscript{13,27,40,41} By contrast, no obvious hydroxyl radical signal was detected with the Bi$_5$O$_7$Br-40 and Bi$_5$O$_7$Br-100 samples in the dark or under photoirradiation (Figure S5).\textsuperscript{42}

Figure 3. (a) XPS survey spectra of the series of Bi$_5$O$_7$Br samples. (b) Valence-band (VB) analysis of the Bi$_5$O$_7$Br-40 sample. The inset is a diagram of the electronic energy levels. High-resolution scans of the (c) Br 3d, (d) Bi 4f, and (e) O 1s electrons of the Bi$_5$O$_7$Br samples. Dotted curves are experimental data, and shaded peaks are deconvolution fits.
Consistent behaviors were observed in photoluminescence measurements. From Figure S6, all Bi$_5$O$_7$Br samples can be seen to exhibit a prominent emission peak at ca. 473 nm, and the Bi$_5$O$_7$Br-40 sample displayed the lowest peak intensity among the series. Because electron–hole recombination is responsible for the photoluminescence emission, a low...
can see that after 500 cycles, the Bi$_5$O$_7$Br-40 sample showed which was 9.8 times those of other Bi$_5$O$_7$Br samples and 122.5 times those of relevant BiOBr catalysts reported in the literature (Table S1).44

Remarkably, the Bi$_5$O$_7$Br samples prepared above indeed exhibited apparent photocatalytic activity toward nitrogen fixation under visible light illumination. The quantity of NH$_4^+$ generated was quantified by using Nessler’s reagent as a chromogenic probe (Figure S7). From Figure 4c, one can see that Bi$_5$O$_7$Br-40 produced the largest quantity of NH$_4^+$ after 30 min of photoirradiation at 3.18 mM, and the rate of nitrogen fixation was estimated to be 12.72 mM g$^{-1}$ h$^{-1}$, which was 9.8 times those of other Bi$_5$O$_7$Br samples and 122.5 times those of relevant BiOBr catalysts reported in the literature (Table S1).44

To unravel the roles of the various radicals generated in the photocatalytic process, benzoquinone (BQ), isopropanol (IPA), and ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) were used as the respective scavengers for OVs, ·OH, and O$_2$·. From Figure 4d, it can be seen that after 30 min of visible light irradiation the addition of BQ and EDTA-2Na significantly inhibited nitrogen fixation, while only a slight decrease was observed with IPA.45,46 This suggests that O$_2$· and OVs were the two primary radicals involved in nitrogen fixation under visible light irradiation, with a minor contribution from ·OH. This is consistent with the lack of ·OH$^-$ production, as manifested in ESR measurements (Figure S5).

The stability of the Bi$_5$O$_7$Br samples was then tested by cycling voltammetric measurements.47,48 From Figure S8, one can see that after 500 cycles, the Bi$_5$O$_7$Br-40 sample showed the highest stability among the series, with virtually no change in the voltammetric curves, whereas a marked diminishment of the voltammetric currents can be seen with other samples.49

Consistent results were obtained in microscopic and spectroscopic measurements. From the SEM and TEM images in Figure S9, one can see that the Bi$_5$O$_7$Br-40 sample exhibited no obvious change in the morphology before and after the stability test, and the XPS profiles (Figure S10) remained virtually invariant.

In order to unravel the photocatalytic mechanism of nitrogen fixation by the Bi$_5$O$_7$Br catalysts, in situ infrared spectroscopic measurements were carried out using a synchrotron radiation source. Figure 5a shows the IR spectra of N$_2$ adsorption on Bi$_5$O$_7$Br-40 in the dark for up to 40 min, where a series of vibrational bands can be identified: peak i (3555 cm$^{-1}$) due to the N–H stretch, peak ii (3360 cm$^{-1}$) due to adsorbed N$_2$, and peak vi (1557 cm$^{-1}$) due to adsorbed CO$_2$, peak v (1624 cm$^{-1}$) due to adsorbed N$_2$, and peak vi (1557 cm$^{-1}$) due to adsorbed NH$_3$. The intensity of these vibrational bands grew with adsorption time. Upon visible light photoirradiation (Figure 5b), one can see a significant and fast change in the IR signals. Specifically, peaks i, iii, and iv were markedly weakened, while peaks ii, v, and vi were obviously enhanced, suggesting an enhanced adsorption of N$_2$ and the conversion of N–H to NH$_3$.50,51

Figure 5c shows the in situ IR spectra during photocatalytic nitrogen fixation for up to 35 min. It can be seen that with increasing photoirradiation time the IR signals became intensified accordingly. In comparison with data collected in the dark (Figure 5a), peaks i and iii were significantly strengthened, but peak v (adsorbed N$_2$) was obviously weakened, suggesting the effective cleavage of the N≡N bond and the subsequent formation of NH$_3$. In fact, the N–H bending vibrations (peaks iv and vii) increased in intensity after prolonged photoirradiation.52–54

Figure 6 shows the structural models of anoxic Bi$_5$O$_7$Br–O, pristine Bi$_5$O$_7$Br, and oxygen-enriched Bi$_5$O$_7$Br (Bi$_5$O$_7$Br+O). The black circle represents the site of an oxygen vacancy, and the yellow triangle refers to the site of the additional oxygen. (b) Reaction energy diagram of nitrogen fixation catalyzed by Bi$_5$O$_7$Br–O, Bi$_5$O$_7$Br, and Bi$_5$O$_7$Br+O. (c) Schematic pathway of nitrogen fixation. (d) Nitrogen adsorption energy (eV) on the surfaces of Bi$_5$O$_7$Br–O, Bi$_5$O$_7$Br, and Bi$_5$O$_7$Br+O.
the IR spectra acquired after 35 min of visible light illumination before the light was turned off. In comparison with the results in Figure 5b, one can see that upon the switching off of the light source, peaks i and ii remained virtually unchanged, and peaks iii, iv, and vi increased significantly, indicating an increasing concentration of N–H bonds and a large number of N₂ molecules adsorbed on the catalyst surface.55,56 Taken together, these results suggest that the ready adsorption of nitrogen onto Bi₅O₇Br-40 was likely responsible for the excellent nitrogen fixation performance. This can be ascribed to the high concentration of OVs in the sample (Figure 3), as manifested below in DFT calculations.

In order to examine the influence of OVs on the nitrogen fixation performance, DFT calculations were performed with three structural models: pristine Bi₅O₇Br, anoxic Bi₅O₇Br–O, and oxygen-enriched Bi₅O₇Br+O (Figure 6a). From the reaction energy diagram of the nitrogen fixation pathway of \( \text{N}_2 \rightarrow \text{NNH} \rightarrow \text{NNH}_2 \rightarrow \text{NH}_3 \rightarrow \text{N} + \text{H}_3 \rightarrow \text{N} \rightarrow \text{NH} \rightarrow \text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{NH} \) (Figure 6c), one can see that N₂ adsorption on Bi₅O₇Br–O was indeed favored by the most negative adsorption free energy (≈−0.017 eV) for the initial N₂ activation (\( \text{N}^* \)), in comparison to −0.008 eV for pristine Bi₅O₇Br and −0.001 eV for pristine Bi₅O₇Br+O (Figure 6d).

Furthermore, on the three catalysts, one can see that the \( \text{N} \rightarrow \text{N} \rightarrow \text{NH} \) step exhibits the greatest energy barrier (Figure 6b), suggesting that this is the rate-determining step in the reaction pathway (Figure 6c), and this energy barrier varies among the samples, decreasing from 3.213 eV for Bi₅O₇Br+O to 3.019 eV for Bi₅O₇Br and to 2.963 eV for Bi₅O₇Br–O. In addition, the adsorption free energy of the \( \text{NH}_2 \) product increases from −1.698 eV for Bi₅O₇Br+O to −1.717 eV for Bi₅O₇Br and −1.969 eV for Bi₅O₇Br–O. Taken together, these results suggest that the oxygen-deficient Bi₅O₇Br–O represents the optimal catalyst for nitrogen adsorption and activation and hence ammonia synthesis. Note that whereas hydrazine (\( \text{H}_2\text{NNH}_2 \)) is a common intermediate in the electrochemical reduction of nitrogen for ammonia synthesis, no such species was detected experimentally in the present study.

In summary, these results show that photocatalytic N₂ fixation by Bi₅O₇Br, \( \text{N}_2 + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 2\text{NH}_3 \), most likely involves four major steps (Figure 7): (i) under visible light irradiation, part of the O atoms escape in the form of O₂ from the Bi₅O₇Br surface, creating sufficient surface OVs; (ii) N₂ is chemisorbed and activated on the OVs; (iii) the photoexcited electrons are injected into the activated N₂ and reduce it to NH₃ which is dissolved in water in the form of NH₄⁺; and (iv) after reaction, the photoinduced OVs are refilled by capturing O from water, leading to a good recovery to the original stable OV-free composition.57,58

**CONCLUSIONS**

In this study, a series of Bi₅O₇Br catalysts were prepared by a facile thermal precipitation process at different temperatures and exhibited excellent photocatalytic activity toward nitrogen fixation to ammonia. Among these, the sample prepared at 40 °C showed the best performance, which exhibited nanotubular morphology, a large specific surface area (>100 m²g⁻¹), a suitable absorption edge, maximum photocurrent, a high concentration of O₂⁻, and abundant OVs under photoradiation. In situ infrared spectroscopic measurements showed that the unique Bi₅O₇Br-40 morphological and electronic characteristics facilitated the adsorption and activation of N₂ and the subsequent formation of NH₃, consistent with results from DFT calculations. Results from this study indicate that Bi₅O₇Br nanostructures may be exploited as effective photocatalysts toward the fixation of nitrogen to ammonia under visible light irradiation, a unique technology toward a sustainable future.39–62

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c05097.

**Additional experimental data (PDF)**

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Notes
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