

Visible-Light-Driven Nitrogen Fixation Catalyzed by Bi₅O₇Br Nanostructures: Enhanced Performance by Oxygen Vacancies

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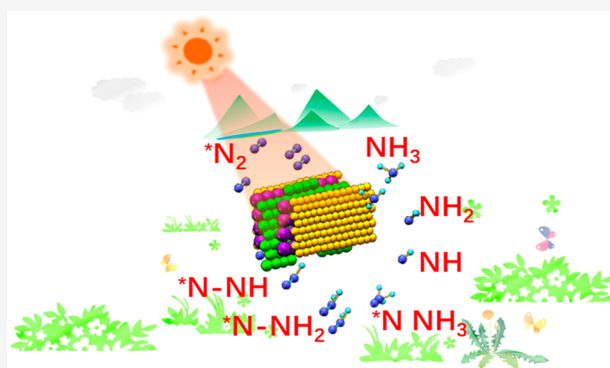


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Supporting Information

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 Bi₅O₇Br 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 Bi₅O₇Br sample prepared at 40 °C (Bi₅O₇Br-40) exhibited the highest electron-transfer rate among the series, producing a large number of O₂^{•-} 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 Bi₅O₇Br 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 (N₂) in the atmosphere.^{1–3} 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.^{4,5} Recently, photocatalytic nitrogen fixation has been attracting extensive interest thanks to its energy and environmental advantages,^{4–7} where artificial photosynthesis is exploited for the direct production of NH₃ from N₂ and H₂O under sunlight with the assistance of an appropriate catalyst.⁸ However, the efficiency of photocatalytic nitrogen fixation is generally low and limited by two major factors: (a) the reduction of one N₂ 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) N₂ adsorption is a necessary step for the catalytic reaction, but most catalysts exhibit only weak N₂ adsorption. Thus, the design and engineering of effective catalysts with high N₂ adsorption and efficient separation of photogenerated electron–hole pairs is key to an improved performance of photocatalytic nitrogen fixation.⁴

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.^{9–13} 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,^{14,15} leading to enhanced carrier mobility and a reduced recombination rate.¹⁶ 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 N₂.¹⁷ Thus, one can envision that the design and engineering of bismuth oxybromide nanostructures may be exploited to markedly advance the photocatalytic fixation of nitrogen.

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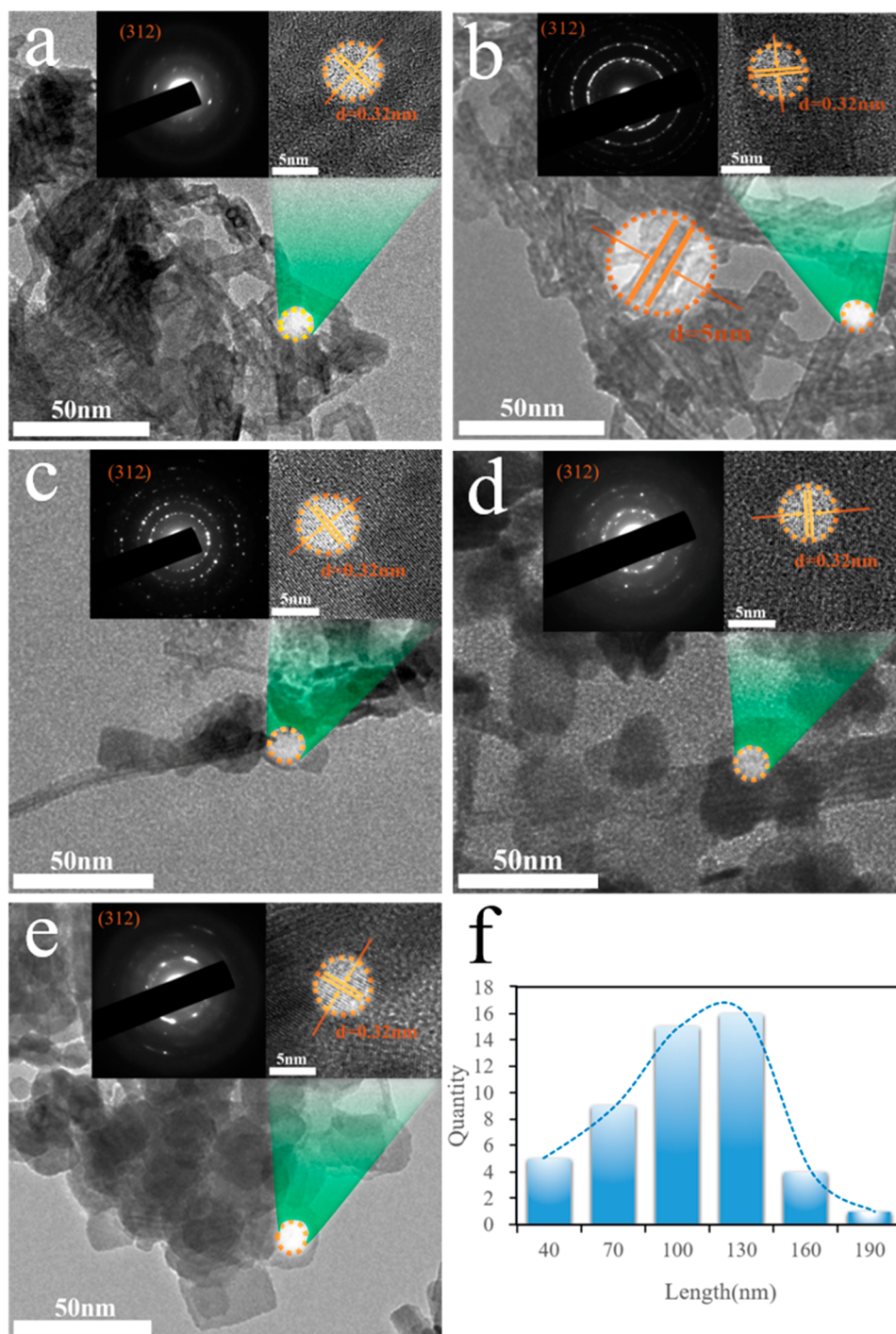


Figure 1. Representative TEM images of (a) $\text{Bi}_5\text{O}_7\text{Br}-20$, (b) $\text{Bi}_5\text{O}_7\text{Br}-40$, (c) $\text{Bi}_5\text{O}_7\text{Br}-60$, (d) $\text{Bi}_5\text{O}_7\text{Br}-80$, and (e) $\text{Bi}_5\text{O}_7\text{Br}-100$. The left insets are the corresponding SAED patterns, and the right insets are the respective HRETEM images. (f) Length distributions of 50 $\text{Bi}_5\text{O}_7\text{Br}$ nanotubes randomly selected from the $\text{Bi}_5\text{O}_7\text{Br}-40$ sample in panel (b).

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.^{17,18} In fact, a range of strategies have been employed to engineer the BiOBr structure, such as morphological control,^{19,20} exposure of select crystalline facets,²¹ and heterologous hybridization.^{22–27} For instance, Di et al.²⁸ prepared $\text{Bi}_4\text{O}_5\text{Br}_2$ 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.¹⁹ reported a novel low-temperature method for the water-assisted self-assembly of $\text{Bi}_5\text{O}_7\text{Br}$ 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.

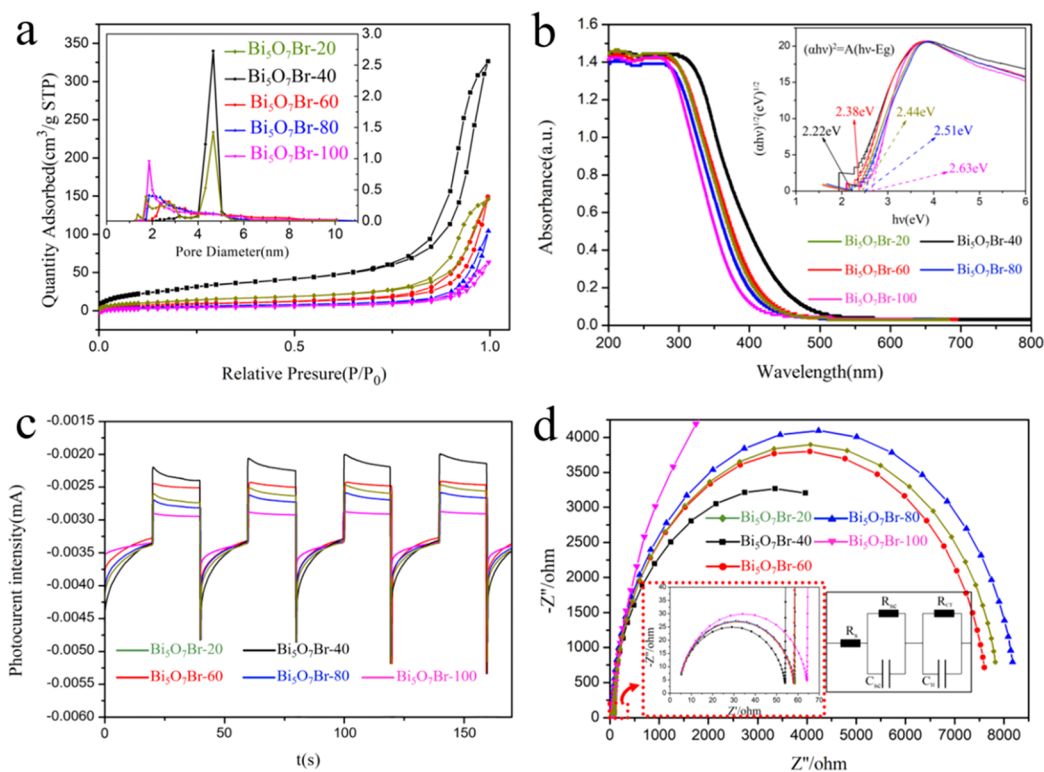


Figure 2. (a) Nitrogen adsorption–desorption isotherms of the series of Bi₅O₇-Br samples. The inset depicts the corresponding pore size distribution curves. (b) UV–vis diffuse reflectance spectra for the various Bi₅O₇-Br samples. The inset shows the $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves. (c) Transient photocurrent response and (d) impedance curves of the various Bi₅O₇-Br samples. In panel (d), the left inset is a close-up image of the boxed area, whereas the right inset is the equivalent circuit used to fit the impedance data, where R_s is the series resistance (including the material resistance and contact resistance of the test system), R_{SC} is the charge-transfer resistance at the Bi₅O₇-Br/electrode interface, and R_{CT} is the charge-transfer resistance at the Bi₅O₇-Br/electrolyte interface. C_{SC} is the capacitance of the Bi₅O₇-Br/electrode interface (i.e., the internal capacitance of the material), and C_H is the capacitance of the Bi₅O₇-Br/electrolyte interface. Symbols are experimental data, and solid curves are the corresponding fits.

In this study, a series of Bi₅O₇-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 diffusion of photo-generated electron–hole pairs, 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 Bi₅O₇-Br Nanostructures. Bi₅O₇-Br nanostructures were synthesized by a water-induced self-assembly method. In brief, 50 mL of an ammonia solution and 3 mmol of Bi(NO₃)₃·5H₂O 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.²⁷ The obtained products were denoted as Bi₅O₇-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 K α radiation ($\lambda = 1.5418$ 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 (O₂^{•-}) in water, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) was used to trap O₂^{•-} 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 Bi₅O₇-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) and transient photocurrents were acquired with a CHI 760e electrochemical workstation. Photoluminescence spectroscopy measurements were conducted with an Edinburgh Instruments FLS980 Spectrometer.

Photocatalysis. Photocatalytic N₂ 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 Bi₅O₇Br 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 N₂ 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 NH₄⁺ 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.^{1,27}

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).²⁸ 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 × 2 × 1 were chosen for the calculations,³⁰ with a force tolerance of 3 × 10⁻² eV Å⁻¹, an energy tolerance of 1.0 × 10⁻⁵ eV per atom, and a maximum displacement of 1.0 × 10⁻³ Å.

A pristine Bi₅O₇Br (1) surface, which contains 104 atoms (including 40 Bi, 8 Br, and 56 O atoms), was used in the calculations, in comparison to Bi₅O₇Br with 1 oxygen vacancy (Bi₅O₇Br–O, which contained 40 Bi, 8 Br, and 55 O atoms) and Bi₅O₇Br with one additional oxygen (Bi₅O₇Br+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 adsorbed molecules were relaxed during all calculations. The Gibbs free energy for all N₂ reduction reactions was defined as follows

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (1)$$

where ΔE , ΔZPE , *T*, and ΔS are the adsorption energy, zero-point energy difference, reaction temperature, and entropy difference between the adsorbed state and the gas phase, respectively.

The adsorption energy ΔE of molecule A on the substrate surface is defined as

$$\Delta E = E_{*A} - (E_{*} + E_A) \quad (2)$$

where E_{*A} , E_A , and E_{*} denote the energies of surface-adsorbed molecule A, free molecule A, and the bare substrate, respectively.

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) Bi₅O₇Br-80 and (e) Bi₅O₇Br-100 samples, with a side length of 20–30 nm. This structural evolution suggests that water-assisted self-assembly at low temperatures led to the formation of nanotubules,¹⁹ which became ruptured into flaky structures at higher temperatures. Nevertheless, in high-resolution TEM measurements (right insets to panels a–e), all samples show clearly defined lattice fringes with an interplanar spacing of 0.32 nm, which can be assigned to the (312) crystalline facets of Bi₅O₇Br,^{27,32} consistent with the patterns of selected-area electron diffraction (SAED, left insets to panels a–e).

The porosity of the samples was then examined by nitrogen adsorption–desorption measurements. From the adsorption isotherms in Figure 2a, the BET specific surface area was found to vary among the series of samples: 45 m² g⁻¹ for Bi₅O₇Br-20,

101 m² g⁻¹ for Bi₅O₇Br-40, 30 m² g⁻¹ for Bi₅O₇Br-60, 22 m² g⁻¹ for Bi₅O₇Br-80, and 13 m² g⁻¹ for Bi₅O₇Br-100. That is, the sample prepared at 40 °C exhibited the largest surface area among the series.³³ From the pore size distributions (Figure 2a inset), one can see that the pores primarily fall into two size ranges (1.5 to 3 nm and 4 to 5 nm), and with increasing synthesis temperature, the fraction of the larger pores 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 Bi₅O₇Br was further confirmed by XRD measurements. From Figure S1, a series of diffraction peaks can be identified at $2\theta = 24.46, 30.18, 32.64, 46.76, 51.18,$ and 56.62° , which can be readily indexed to the (312), (004), (600), (604), (314), and (912) facets of the tetragonal phase of Bi₅O₇Br (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 Bi₅O₇Br 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 In UV-vis diffuse reflectance measurements (Figure 2b), the Bi₅O₇Br samples can be seen to exhibit a rather well-defined absorption edge, which red-shifted from 430 to 530 nm when the sample was prepared at increasing temperature. In fact, from the Tauc plot in the Figure 2b inset, the band gap can be estimated to be 2.44 eV for Bi₅O₇Br-20, 2.22 eV for Bi₅O₇Br-40, 2.38 eV for Bi₅O₇Br-60, 2.51 eV for Bi₅O₇Br-80, and 2.63 eV for Bi₅O₇Br-100. That is, the Bi₅O₇Br-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 Bi₅O₇Br 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 Bi₅O₇Br-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 Bi₅O₇Br-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

Table 1. Summary of the Fitting Results of Impedance Data of the Bi₅O₇Br Series

	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	15 140

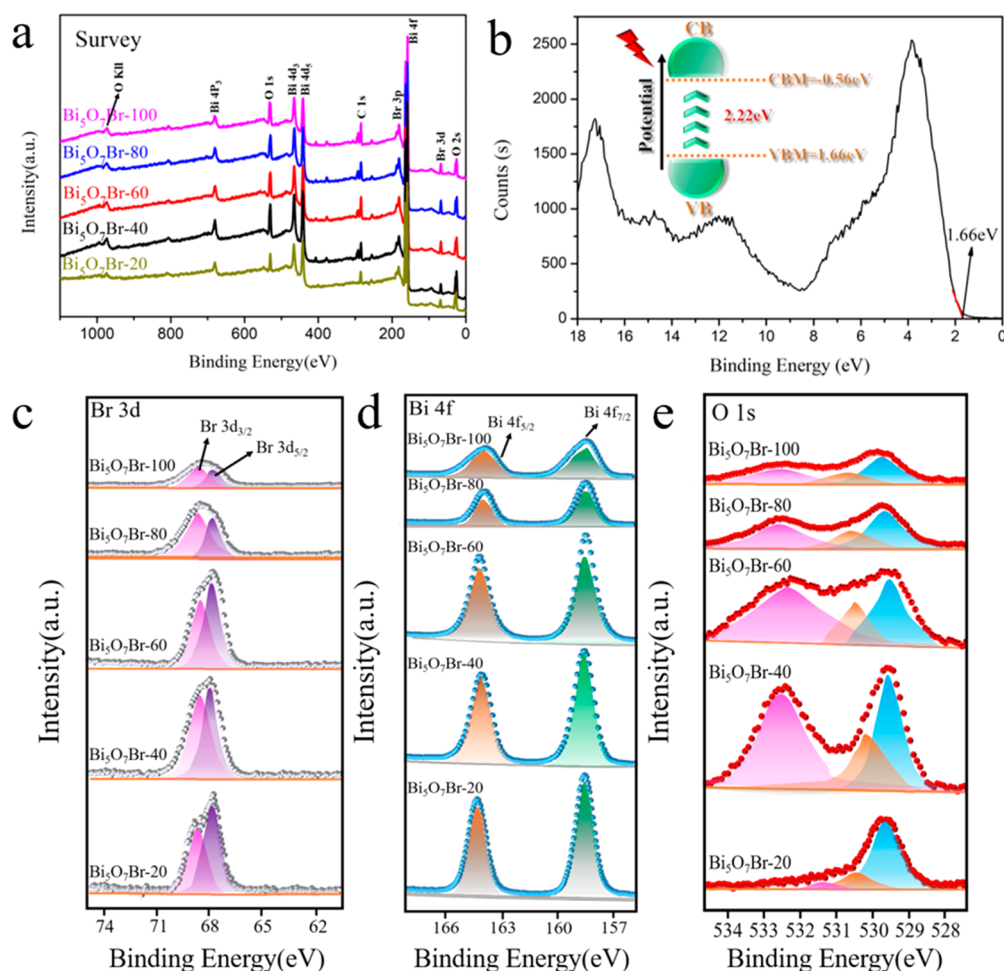


Figure 3. (a) XPS survey spectra of the series of $\text{Bi}_5\text{O}_7\text{Br}$ samples. (b) Valence-band (VB) analysis of the $\text{Bi}_5\text{O}_7\text{Br}$ -40 sample. The inset is a diagram of the electronic energy levels. High-resolution scans of the (c) Br 3d, (d) Bi 4f, and (e) O 1s electrons of the $\text{Bi}_5\text{O}_7\text{Br}$ samples. Dotted curves are experimental data, and shaded peaks are deconvolution fits.

seen that $\text{Bi}_5\text{O}_7\text{Br}$ -40 exhibited the lowest charge-transfer resistance (R_{CT} , 6537 Ω) among the series. This correlates well with the highest photocurrents observed in Figure 2c.⁴⁰ In addition, one can see that $\text{Bi}_5\text{O}_7\text{Br}$ -40 also exhibited the lowest internal resistance (R_s , 4.0 Ω) and interfacial resistance (R_{SC} , 54.2 Ω).

The elemental composition and valence state of the $\text{Bi}_5\text{O}_7\text{Br}$ samples were then studied and compared by XPS measurements. Figure 3a shows the full survey spectra of the $\text{Bi}_5\text{O}_7\text{Br}$ 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 $\text{Bi}_5\text{O}_7\text{Br}$. Results from XPS measurements can also be used to determine the energy of the valence band (VB).³⁹ From Figure 3b, the VB of the $\text{Bi}_5\text{O}_7\text{Br}$ -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 $3d_{3/2}$ and $3d_{5/2}$ 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), OV (530.5 eV), and adsorbed oxygen on the sample surface (532.2 eV).^{36,37} On the basis of the integrated peak areas, the OV concentration was found to vary among the series of samples: $\text{Bi}_5\text{O}_7\text{Br}$ -40 (14.6%) > $\text{Bi}_5\text{O}_7\text{Br}$ -60 (14.2%) > $\text{Bi}_5\text{O}_7\text{Br}$ -100 (11.9%) > $\text{Bi}_5\text{O}_7\text{Br}$ -80 (10.6%) > $\text{Bi}_5\text{O}_7\text{Br}$ -20 (9.5%). That is, $\text{Bi}_5\text{O}_7\text{Br}$ -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 $\text{Bi}_5\text{O}_7\text{Br}$ -40 upon photoirradiation were significantly higher than those in the dark. Consistent behaviors can be seen with other samples in the series, where $\text{Bi}_5\text{O}_7\text{Br}$ -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.^{38,39} Note that the production of a large number of OVs was conducive to N_2 adsorption and fixation (vide infra).^{13,27,40,41} By contrast, no obvious hydroxyl radical signal was detected with the $\text{Bi}_5\text{O}_7\text{Br}$ -40 and $\text{Bi}_5\text{O}_7\text{Br}$ -100 samples in the dark or under photoirradiation (Figure S5).⁴²

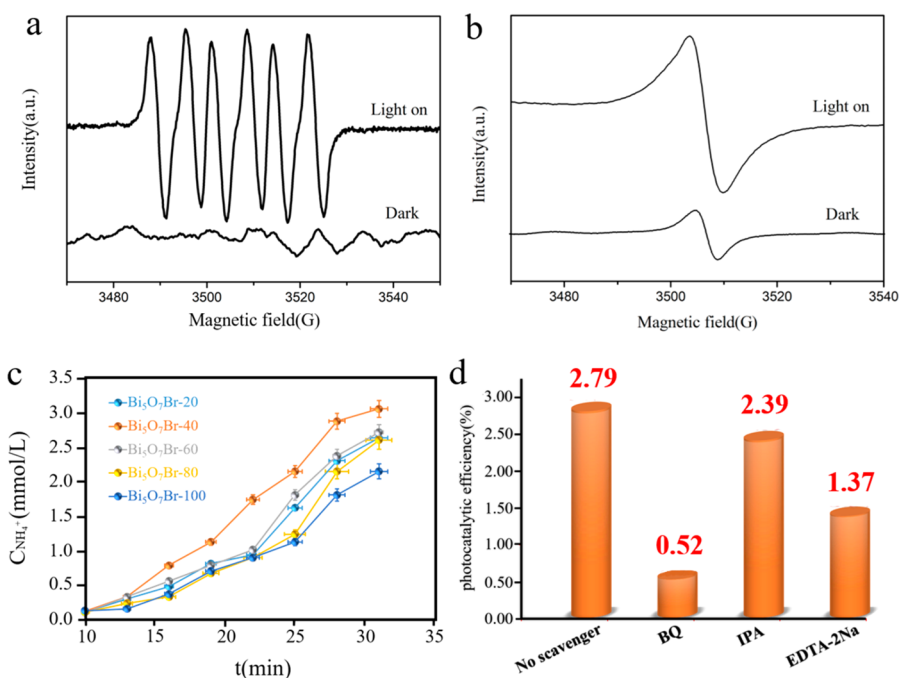


Figure 4. ESR spectra of (a) O_2^- radicals and (b) OV radicals produced by $\text{Bi}_5\text{O}_7\text{Br}$ -40 in the dark and under visible light photoirradiation. (c) Amount of nitrogen fixation catalyzed by different $\text{Bi}_5\text{O}_7\text{Br}$ samples with time. (d) Photocatalytic performance of nitrogen fixation by $\text{Bi}_5\text{O}_7\text{Br}$ -40 ($0.5 \text{ g}\cdot\text{L}^{-1}$) in the absence and presence of various radical scavengers after visible light photoirradiation for 30 min.

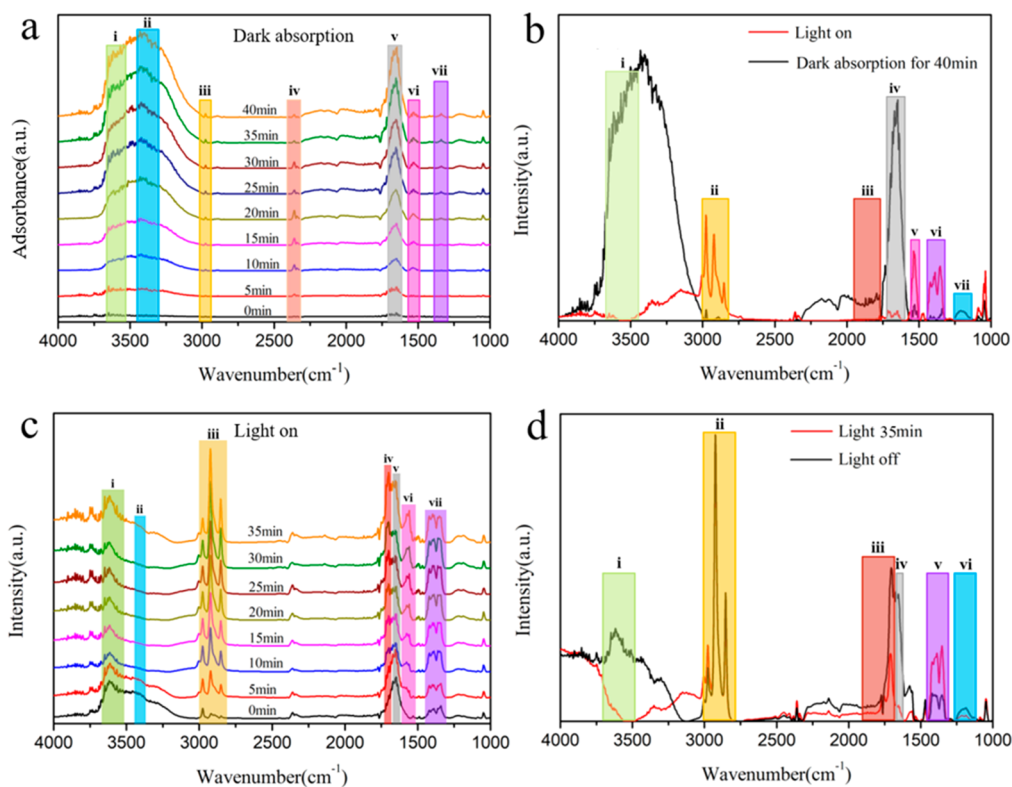


Figure 5. (a) In situ infrared spectra of $\text{Bi}_5\text{O}_7\text{Br}$ -40 after the adsorption of N_2 in the dark for up to 40 min. (b) In situ infrared spectra of $\text{Bi}_5\text{O}_7\text{Br}$ -40 after adsorption in the dark for 40 min and then visible light photoirradiation being turned on. (c) In situ infrared spectra of $\text{Bi}_5\text{O}_7\text{Br}$ -40 under visible light photoirradiation for up to 35 min. (d) In situ infrared spectra of $\text{Bi}_5\text{O}_7\text{Br}$ -40 after visible light photoirradiation for 35 min, after which the light is turned off.

Consistent behaviors were observed in photoluminescence measurements. From Figure S6, all $\text{Bi}_5\text{O}_7\text{Br}$ samples can be seen to exhibit a prominent emission peak at ca. 473 nm, and

the $\text{Bi}_5\text{O}_7\text{Br}$ -40 sample displayed the lowest peak intensity among the series. Because electron–hole recombination is responsible for the photoluminescence emission, a low

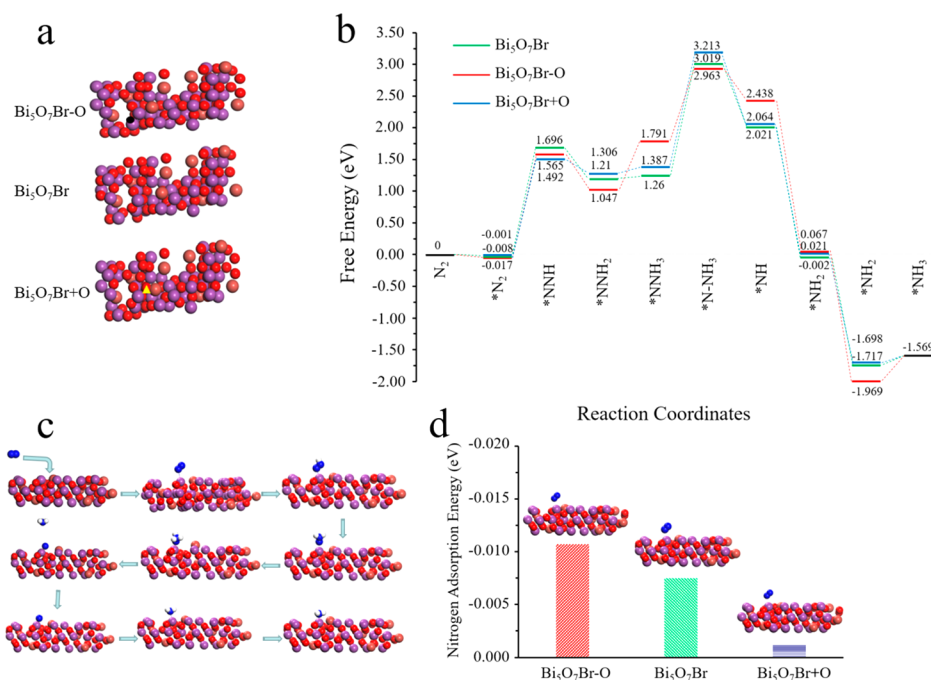


Figure 6. (a) Structural models of anoxic Bi₅O₇Br-O, pristine Bi₅O₇Br, and oxygen-enriched Bi₅O₇Br (Bi₅O₇Br+O). The black circle represents the site of an oxygen vacancy, and the yellow triangle refers to the site of the additional oxygen. (b) Reaction energy diagram of nitrogen fixation catalyzed by Bi₅O₇Br-O, Bi₅O₇Br, and Bi₅O₇Br+O. (c) Schematic pathway of nitrogen fixation. (d) Nitrogen adsorption energy (eV) on the surfaces of Bi₅O₇Br-O, Bi₅O₇Br, and Bi₅O₇Br+O.

photoluminescence intensity implies a low recombination rate of photogenerated charge carriers.⁴³ Taken together, one can see that the Bi₅O₇Br-40 sample displays the highest charge separation efficiency among the series, a unique feature that can facilitate the photocatalysis of nitrogen fixation.

Remarkably, the Bi₅O₇Br samples prepared above indeed exhibited apparent photocatalytic activity toward nitrogen fixation to ammonia under visible light illumination. The quantity of NH₄⁺ generated was quantified by using Nessler's reagent as a chromogenic probe (Figure S7). From Figure 4c, one can see that Bi₅O₇Br-40 produced the largest quantity of NH₄⁺ after 30 min of photoirradiation at 3.18 mM·L⁻¹, and the rate of nitrogen fixation was estimated to be 12.72 mM·g⁻¹h⁻¹, which was 9.8 times those of other Bi₅O₇Br 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 O₂⁻. 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 O₂⁻ 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 Bi₅O₇Br samples was then tested by cycling voltammetric measurements.^{47,48} From Figure S8, one can see that after 500 cycles, the Bi₅O₇Br-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 Bi₅O₇Br-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 Bi₅O₇Br catalysts, in situ infrared spectroscopic measurements were carried out using a synchrotron radiation source. Figure 5a shows the IR spectra of N₂ adsorption on Bi₅O₇Br-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-OH, peak iii (2874 cm⁻¹) due to the NH₄⁺ stretching vibration, peak iv (2359 cm⁻¹) due to adsorbed CO₂, peak v (1624 cm⁻¹) due to adsorbed N₂, and peak vi (1557 cm⁻¹) due to adsorbed NH₃. 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 N₂ and the conversion of N-H to NH₃.^{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 N₂) was obviously weakened, suggesting the effective cleavage of the N≡N bond and the subsequent formation of NH₄⁺. In fact, the N-H bending vibrations (peaks iv and vii) increased in intensity after prolonged photoirradiation.^{27,52-54} Figure 5d compares

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 OVVs in the sample (Figure 3), as manifested below in DFT calculations.

In order to examine the influence of OVVs 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 *N₂ → *NNH → *NNH₂ → *NNH₃ → *N + NH₃ → *NH → *NH₂ → *NH₃ → NH₃ (Figure 6b,c), 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 (*N₂), 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 *N–NH₂ → *N–NH₃ step exhibits the greatest energy barrier (Figure 6b), suggesting that this is the rate-determining step in the reaction pathway (Figure 6c),⁵⁴ 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 *NH₂ 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 (H₂NNH₂) 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, N₂ + 6H⁺ + 6e[–] → 2NH₃, 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 OVVs; (ii) N₂ is chemisorbed and activated on the OVVs; (iii) the photoexcited

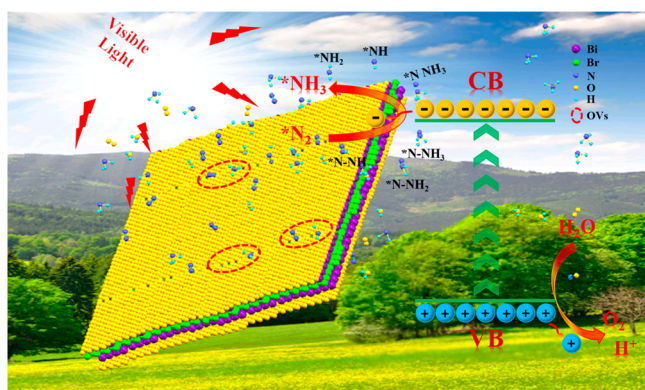


Figure 7. Schematic diagram of photocatalytic nitrogen fixation catalyzed by Bi₅O₇Br.

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 OVVs are refilled by capturing O from water, leading to a good recovery to the original stable OV-free composition.^{27,57,58}

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 OVVs under photoirradiation. 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.^{59–62}

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

The authors declare no competing financial interest.

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