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Article

Porous Defective Bi/Bi₃NbO₇ Nanosheets for Efficient Photocatalytic NO Removal under Visible Light

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1. Introduction

As a kind of typical air pollution, nitrogen oxides (NO_x) are generated from the combustion of fossil energy. NO_x mainly consist of NO and NO₂, which can cause acid rain, photochemical smog and other environmental issues [1]. Hence, it is highly important to protect the atmosphere around the world from increasingly emissions of NO through developing effective technologies to relieve NO_x pollution [2]. Up to now, many studies have revealed that conventional NO removal technologies, e.g., biofiltration, physical adsorption and thermal catalysis, perform well at high NO_x concentration levels but are not much efficient for the treatment of low concentrations in practical applications [3].

Recently, researchers have found that photocatalysis could be sufficiently promising for removing NO_x at ppb levels and thus appears as a sustainable, energy-effective and ecologically friendly method to purify the environment [3–6]. TiO₂, the pioneer photocatalyst, has been widely used in NO pollution treatment. However, given its large band gap (~3.0 eV for rutile and ~3.2 eV for anatase), TiO₂ can only absorb ultraviolet light photons during the catalytic reactions, which makes its practical application restricted. In order to overcome this obstacle, many efforts have been made to develop visible light-driven

photocatalysts, including doping impurities [7,8], sensitization [9], and heterojunctions construction [10]. However, these modification techniques suffer from issues including thermal instability, rapid electron-hole recombination, high cost of metal sources, and so on [11,12]. To address these issues, developing novel semiconducting materials is always demanded.

Bi_3NbO_7 ($E_g \sim 2.9$ eV), an n-type semiconductor, has attracted a lot of interest because of its superior interaction with visible light photons and good photocatalytic performance [13,14]. The valence band of Bi_3NbO_7 is formed by the hybridization of Bi 6s and O 2p orbitals, resulting in high oxidation activity and charge separation efficiency. Interestingly, Bi_3NbO_7 possesses a layered structure which justifies its high specific surface area for heterogeneous photocatalytic reactions. However, the traditional methods of Bi_3NbO_7 preparation always are accompanied by some drawbacks such as the tough two-step synthesis, the use of toxic solvents such as hydrofluoric acid during the preparation, and poor chemical stability of the structure under irradiation [15]. Therefore, it is urgent to develop well-modified niobate photocatalysts that are easy to prepare, non-hazardous, and highly stable.

Noble metal-loaded semiconductors can improve the separation of photogenerated charge carriers and the visible light harvesting properties by surface plasmon resonance (SPR) effects, but their high costs limit the technology's development toward practical applications [16,17]. Interestingly, the cheaper metallic bismuth (Bi), aluminum (Al) and titanium nitride (TiN) have been shown to act well as effective alternatives to noble metals due to their intense SPR effect [18–20]. Moreover, porous defects insertion into the bulk structure is indicated to be a reliable strategy to ameliorate the photocatalytic performance of various kinds of semiconductors [21,22]. The aforementioned defects can increase the specific surface area, improve the substrates' adsorption on the surface and act as remarkable catalytic active sites to promote the subsequent oxidation of pollutants [23]. Based on previous works, urea, a low-cost, environmentally friendly and easily available porogenic agent, can serve to control the pore size of solid materials [24,25]. For instance, Wang et al. successfully fabricated porous Bi_3NbO_7 nanosheets by adjusting the urea content towards the photodegradation of dye compounds under visible light [13]. Overall, metallic Bi and porous defects show incredible synergetic effects to ameliorate the photocatalytic performance of pristine semiconductors under visible light irradiation.

In this work, 2D pore-defective Bi/ Bi_3NbO_7 nanomaterials were successfully prepared from niobium oxalate, as the raw niobium source, and urea in the presence of a Bi source via solvolysis. With the change of the urea content, the morphology of Bi_3NbO_7 gradually showed the growth of porous defects in the structure, which occurred along with the enhancement of visible light photoactivity. Meanwhile, the pore-defective Bi/ Bi_3NbO_7 exhibited a much more efficient photocatalytic performance for NO conversion when an appropriate amount of Bi nanoparticles was introduced. The synergistic interaction of metallic Bi and porous defects was shown to serendipitously affect the electronic properties, leading to the better light-harvesting capacity and charge carriers separation. Interestingly, NO_2 formation was significantly inhibited compared to that of observed for the other photocatalysts, which is of great importance to minimize the harmful effects of intermediates. The mechanism of enhanced photoactivity compared to that of pore-defective Bi/ Bi_3NbO_7 nanosheets is also discussed based on the EPR analysis and trapping tests.

2. Experimental Methods

2.1. Chemicals

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$), niobium oxalate ($\text{C}_{10}\text{H}_5\text{NbO}_{20}$), potassium hydroxide (KOH), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and potassium iodide (KI) were purchased from Shanghai Macklin Biochemical Co., Ltd. Acetic acid was obtained from Sinopharm Chemical Reagent Co., Ltd. Ethanol was obtained from Tianjin Fuyu Fine chemical Co., Ltd. Ethylene glycol, tert-butyl acrylate (TBA) and P-benzoquinone (PBQ) were obtained from Shanghai Rhawn Chemical Technology Co., Ltd.

Methanol and benzyl alcohol were obtained from Aladdin Reagent Co., Ltd. All chemicals in this work were of analytical grade and used without further purification.

2.2. Photocatalyst Preparation

2.2.1. Synthesis of Bi_3NbO_7

We dissolved 3 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.46 g) in 10 mL of acetic acid, obtaining solution A. To prepare solution B, 1 mmol of niobium oxalate (0.54 g) was added to 20 mL of methanol. Under vigorously swirling, solution A was slowly drizzled into solution B. Then, urea (0, 0.8, 1.6 and 3.2 g) was added to the mixed solution, obtaining the solutions called BNO, 1-BNO, 2-BNO and 3-BNO, respectively. The pH of all mixtures was adjusted to 13 with a KOH solution. Each suspension was then transferred to a 100 mL polytetrafluoroethylene reaction tank and kept at 180 °C for 24 h. After cooling to room temperature, the samples were washed repeatedly with deionized water and ethanol, and then dried at 60 °C for 6 h.

2.2.2. Synthesis of $\text{Bi}@\text{Bi}_3\text{NbO}_7$

We dispersed 0.4 g of the as-obtained Bi_3NbO_7 powder in 60 mL of ethylene glycol to form a homogeneous suspension. A certain amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was then added to the suspension, which was stirred for 30 min. The suspension was transferred to a 100 mL polytetrafluoroethylene reaction tank and kept at 180 °C for 8 h. After the completion of the reaction, the suspension was repeatedly washed and centrifuged (8 times) to obtain a precipitate which was finally dried at 60 °C for 6 h, yielding the pore-defective $\text{Bi}@\text{Bi}_3\text{NbO}_7$ nanosheets. Three samples with different Bi nanodot loadings, labeled as 1% Bi-2-BNO, 2% Bi-2-BNO and 4% Bi-2-BNO, were prepared from 0.04, 0.1 and 0.2 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, respectively.

2.3. Characterization

A Bruker D8 Advance X-ray diffractometer ($\lambda = 0.15406$ nm) at 127.40 kV and 40 mA over a 2θ range from 10 to 80° (Bruker, Karlsruhe, Baden-Württemberg, Germany) was utilized to provide XRD patterns. A FEI Talos F200X (Thermo Fisher Scientific, Hillsboro, OR, USA) microscope was used to perform high-resolution transmission electron microscopy (HRTEM) and morphological analyses. The sample powder was dispersed in ethanol before being placed as a very diluted suspension onto a copper grid. Using 3–5 kV accelerating voltage, a scanning electron microscope (ZEISS Sigma 300, Carl Zeiss, Jena, Thuringia, Germany) was used to examine the samples' microstructure and average size. Using BaSO_4 as the background, a Shimadzu UV-2550 spectrophotometer (Shimadzu, Kyoto, Japan) was used to examine the diffuse reflectance spectra (DRS) in the UV–Vis range. Under Al K α radiation as the excitation source, X-ray photoelectron spectroscopy (XPS) data were supplied to a VG Multilabel 2000 (Thermo Fisher Scientific, Waltham, MA, USA) photoelectron spectrometer. Using the contaminant carbon's (C 1s 284.8 eV) binding energy as the reference, all binding energies were calibrated. A Micromeritics ASAP 2460 (Micromeritics, Norcross, GA, USA) gas adsorption–desorption device, the Brunauer–Emmett–Teller (BET) specific surface areas were determined through the nitrogen adsorption–desorption isotherms. Using DMPO as the trapping agent, the Bruker E500 (Bruker, Karlsruhe, Baden-Württemberg, Germany) instrument was used to conduct electron paramagnetic resonance (EPR) investigations, while the suspensions were prepared in a 40 mM DMPO solution using water as a solvent for $\text{DMPO} \cdot \text{OH}$ and methanol for $\text{DMPO} \cdot \text{O}_2^-$. A 5 mol·L⁻¹ aqueous solution of Na_2SO_4 , as the reference electrolyte, was used in the photoelectrochemical (PEC) measurements over a CHI660E electrochemical workstation (Chenhua Instruments, Inc., Shanghai, China).

2.4. Photocatalytic NO Removal

The photocatalytic setup consisted of a gas supply system, an airflow meter, the main reactor, a light source and the NO_x analyzer. The gas supply system provided NO gas with a concentration of 100 ppm and clean dry air. The gases from the gas supply system

were well mixed in the airflow meter at a gas flow rate of $300 \text{ mL}\cdot\text{min}^{-1}$, adjusting the NO concentration level at 700 ppb. The photocatalytic reactor was made from a cylindrical quartz reactor with the volume of 150 mL. The light source was a xenon lamp with a 420 nm cut-off filter, which was operated at 300 W and 20 mA to keep the light density and intensity consistent throughout the study. The NO_x analyzer was able to track the concentration of both NO and NO₂ continuously. First of all, 50 mg of the powder sample was uniformly dispersed in a Petri dish with 6.0 cm of diameter (Figure 1). A drying device was added prior to NO_x analysis to remove water vapor from the inlet gas. All devices in the photocatalytic efficiency evaluating system were connected to polytetrafluoroethylene hoses, and each interface was sealed by sealing tape to ensure that there were no leaks in the system. The obtained coated dish was placed in the center of the photocatalytic reactor. The above-described setup for photocatalytic NO removal is schematically displayed in Figure 2. The photocatalytic efficiency, η , was calculated using the following equation:

$$\eta = \frac{C}{C_0} \times 100\% \quad (1)$$

$$\eta = \frac{C}{C_0} \times 100\% \quad (2)$$

where C and C_0 correspond to the concentrations of NO before and after the photocatalytic test. The concentration of the toxic by-product NO₂ was calculated according to the following equation:

$$C_{\text{NO}_2} (\text{ppb}) = C_{\text{NO}_x} - C_{\text{NO}} \quad (3)$$

where C_{NO_x} and C_{NO} stand for the concentrations of NO_x and NO, respectively.



Figure 1. Optical images of BNO (a), 2-BNO (b) and 2% Bi-2-BNO (c).

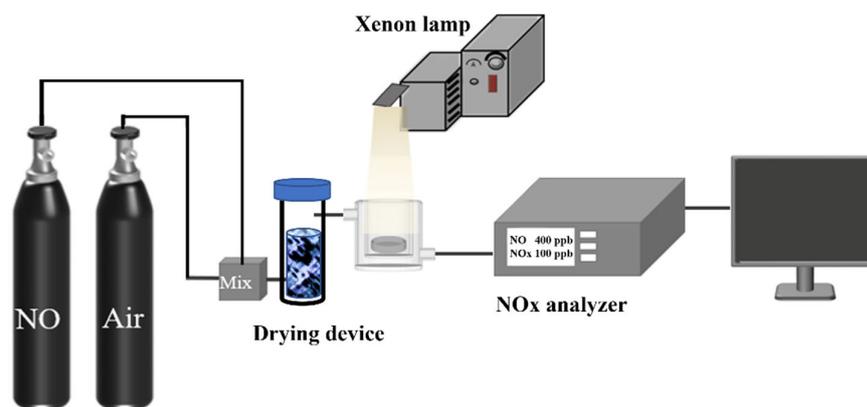


Figure 2. Experimental setup for the real-time monitoring and testing of photocatalytic NO removal.

2.5. Trapping Test

PBQ, TBA, $\text{K}_2\text{Cr}_2\text{O}_7$ and KI were used as effective scavengers to trap $\bullet\text{O}_2^-$, $\bullet\text{OH}$, e^- and h^+ , respectively [26]. Using an ultrasonic mixer, samples (50 mg) and 1 mmol of the trapping agents were uniformly mixed in 10 mL of deionized water. A homogenous film was then created by treating these combined suspensions at 60°C in an oven.

3. Results and Discussion

3.1. Photocatalytic Efficiency

Under visible-light illumination ($\lambda > 420$ nm), the photocatalytic activity of the as-prepared samples was investigated for NO removal. The findings are shown in Figure 3. The best photocatalyst was determined based on the composition of the samples, and their catalytic activities under the default operational conditions. The NO content was kept constant following the dark adsorption equilibrium. The photocatalytic efficiency curves for the samples with different urea content are exhibited in Figure 3a. After 14 min of irradiation, BNO showed poor photocatalytic activity, with a 17.0% of NO removal efficiency. The surface of BNO was smooth and lacked pore defects, which led to a limited of NO adsorption. After 11 min of illumination, the NO adsorption efficiency gradually decreased owing to the fact that the adsorption active sites were occupied by the photocatalytic reaction product NO_3^- . When urea was added, Bi_3NbO_7 photoactivity improved in the following order: 2-BNO (37.5%) > 3-BNO (27.7%) > 1-BNO (32.5%). According to the obtained results, the urea content drastically influenced the Bi_3NbO_7 photocatalytic activity towards NO removal, and the best performance was recorded with 1.6 g of urea. We speculate that the porosity of Bi_3NbO_7 structures was improved in the presence of urea, which could improve the absorption capacity of NO, ameliorating the photocatalytic performance. The photocatalytic activity of the samples with different Bi contents were also tested under the same operational conditions, and the results are presented in Figure 3b. The NO removal efficiency for these samples followed the sequence: 2% Bi-2-BNO (60.3%) > 1% Bi-2-BNO (56.5%) > 4% Bi-2-BNO (43.3%) > 2-BNO (37.5%). It is worth noting that the C/C_0 ratio of 4% Bi-2-BNO increased after 9 min of irradiation, which was due to the fact that the generated NO_3^- ions accumulated around the Bi nanoparticles, resulting in the decrease of the catalytic active sites on the surface and a reduction of NO removal efficiency. The results showed that increasing the Bi content from 0 to 2% improved the NO removal efficiency. However, as the concentration increased to above 2%, the photocatalytic efficiency began to decline, with a 17% decrease for the sample with 4% Bi. This could be due to the improvement of the light-harvesting properties via the SPR effect exerted by an appropriate amount of Bi, whereas excessive Bi nanodots hindered the photocatalytic activity via decreasing the contact area between Bi_3NbO_7 active sites and incident photons during the photocatalytic process.

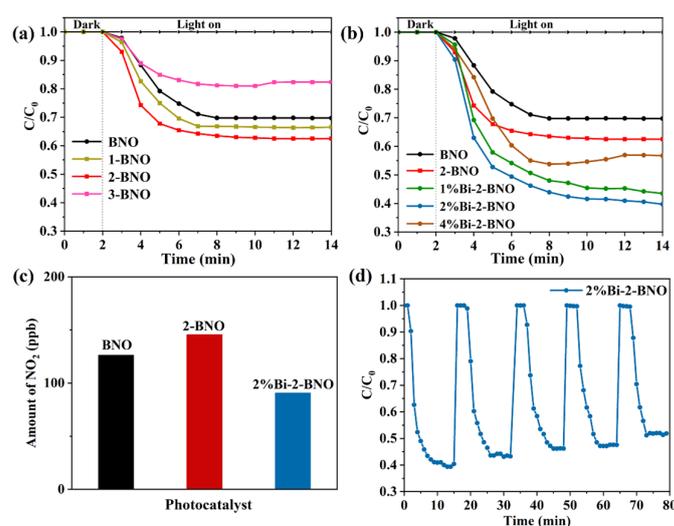


Figure 3. Photocatalytic activity of Bi_3NbO_7 with different contents of urea (a) and with different contents of Bi (b); NO_2 generation over the BNO, 2-BNO and 2% Bi-2-BNO samples under visible light (c); results of the recycling experiments with the 2% Bi-2-BNO photocatalyst (d).

Toxic by-products such as NO_2 are prone to be produced during the photocatalytic NO conversion process, which should be avoided as far as possible. In Figure 3c, NO_2 concentration for the BNO, 2-BNO and 2% Bi-2-BNO samples was 126, 146, and 91 ppb, respectively, which implied that the 2% Bi-2-BNO sample showed the best performance for converting NO and inhibiting NO_2 generation. The porous structure promoted the photocatalytic NO removal while increasing NO_2 production. However, the introduction of Bi nanodots in the pore-defective Ba_3NbO_7 significantly inhibited NO_2 production, indicating that metallic Bi was beneficial to enhance the photocatalytic oxidation capacity of the aforementioned photocatalyst, resulting in the complete conversion of NO. In real-world NO_x removal, photocatalyst stability is of major concern. From the recycling experiments with the 2% Bi-2-BNO photocatalyst, it was seen that the photocatalytic yield decreased slightly (12% of reduction) after five run cycles (Figure 3d). This can be attributed to the formation of NO_3^- on the surface, which damaged the catalytic active sites. As shown in the SEM images before and after the stability test (Figure S1), there was no significant difference in the phase and morphology of 2% Bi-2-BNO, indicating that its stability was satisfactory.

3.2. Structural and Surface Characterizations

The XRD patterns of the prepared BNO, 1-BNO, 2-BNO and 3-BNO are shown in Figure 4a. The diffraction peaks of all samples could be well indexed as Bi_3NbO_7 crystalline phases (JCPDS PDF No.50-50078). Five typical diffraction peaks at $2\theta = 28.16, 32.74, 46.73, 55.60$ and 58.27° , were assigned to the (1 1 1), (200), (220), (311) and (222) planes, respectively. It is evident that pristine Bi_3NbO_7 was successfully synthesized in the presence of urea, and no other impurity peak appeared. As shown in Figure 4b, Bi displayed unique peaks at 2θ of $27.16, 37.95$ and 39.62° , attributed to the planes (102), (104) and (110), respectively, according to the JCPDS Card No. 44-1246 [14]. The diffraction peaks of 1% Bi-2-BNO, 2% Bi-2-BNO and 4% Bi-2-BNO could be indexed as Bi and Bi_3NbO_7 , indicating that Bi nanodots were successfully introduced in the pore-defective Bi_3NbO_7 .

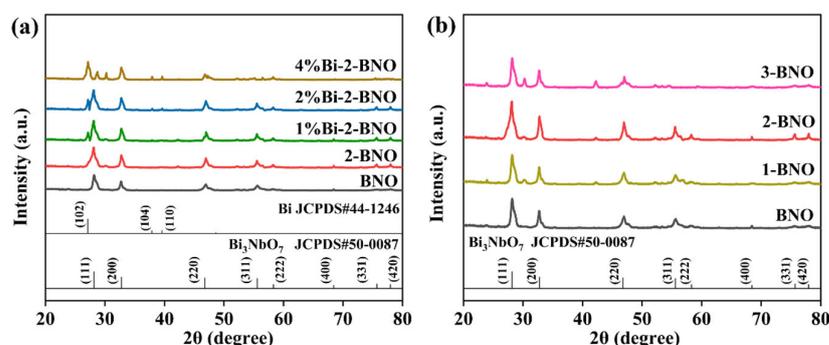


Figure 4. XRD patterns of the BNO photocatalyst with different amounts of urea (a) and of the 2-BNO sample with different amounts of Bi (b).

The optical properties of the samples were compared as shown in Figure 5a. The Bi nanoparticles-containing sample exhibited the highest optical absorption compared with the others. It was seen that the absorption edge of the 2-BNO sample showed a slight red shift compared with that of BNO, implying that the promotion of light absorption by the porous defects was small. In comparison with 2-BNO, an obvious increase of light absorption was achieved by the 2% Bi-2-BNO sample in the range of 300–800 nm, indicating that the presence of Bi nanoparticles was beneficial to the light absorption capacity of the pore-defective Bi_3NbO_7 . Moreover, the formula $\alpha h\nu = A(h\nu - E_g)^{1/2}$ was used to estimate the band gap energy, where α is the absorption coefficient close to the absorption edge, h is the Planck constant, A is a constant, and E_g is the band gap energy (Figure 5b) [27]. The band gaps of BNO, 2-BNO and 2% Bi-2-BNO were calculated and shown to be 2.46, 2.42 and 2.05 eV, respectively. This decreasing band gap tendency for the samples was caused

by alterations in the electrical structure due to the combination of the pore defects and the SPR effect of Bi, which could facilitate visible light photoactivity.

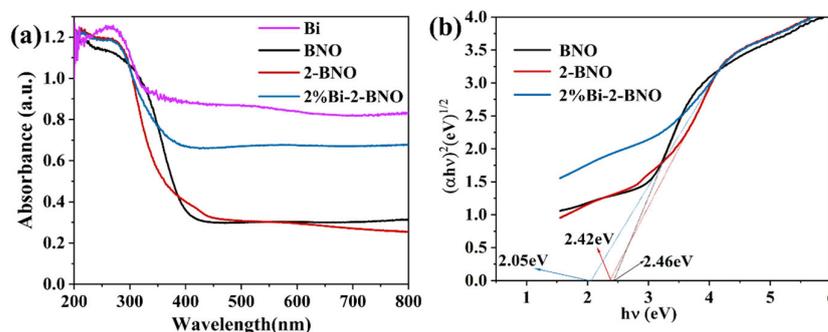


Figure 5. (a) Optical absorption spectra of the BNO, 2-BNO and 2% Bi-2-BNO samples and (b) the corresponding plots of $(\alpha hv)^{1/2}$ vs. energy ($h\nu$).

SEM images served to examine the morphology and microstructure of the photocatalysts. As illustrated in Figure 6a,b, the BNO sample exhibited a smooth nanosheet morphology, and the average diameter and thickness of the nanoflowers were about $1\ \mu\text{m}$ and $50\ \text{nm}$, respectively. The 2-BNO sample exhibited a dense cluster morphology, and the diameter and thickness were similar to those of BNO (Figure 6c,d). The surface of the 2-BNO sample appeared rough and showed a porous structure, with pores having an average diameter of $50\ \text{nm}$, indicating that 2-BNO had successfully acquired porous defects after adding urea. The SEM images of 2% Bi-2-BNO are indicated in Figure 6e,f, which shows that the diameter and thicknesses were also similar to those of BNO and 2-BNO, but the 2% Bi-2-BNO morphology seemed looser than that of 2-BNO. As shown in the SEM images of 4% Bi-2-BNO (Figure S2), the structure of this sample was more compact, with more a clustered texture appearing on the surface, filling the porous defects. These observations imply that excess Bi would occupy the porous structure channels leading to a decrease in porous defects. As shown in Figure S3, the elemental mapping images indicated that Bi, Nb and O were uniformly distributed throughout the 2% Bi-2-BNO nanosheets. The weight percentages of the Bi, Nb and O elements were 75.36, 11.12, and 13.46%, respectively. More detailed information on the porous structure of the 2% Bi-2-BNO nanosheets could be deduced from the TEM images, Figure 6g, in which the Bi nanoparticles can be observed with the lattice space of $0.3210\ \text{nm}$ and $0.3710\ \text{nm}$, corresponding to the (012) and (101) planes [28]. Additionally, the lattice fringes with a spacing of $0.2780\ \text{nm}$ were attributed to the (200) facet of the Bi_3NbO_7 nanosheets [28]. Figure 6h depicts four crystalline planes, (111), (220), (200) and (400), for the BNO sample. It demonstrates that the synthesized BNO was in nanoscale. As displayed in Figure 6i, 2% Bi-2-BNO showed the (101) crystalline plane of Bi near the (200) plane of BNO, which corresponded to the TEM image, while this concentric circle was smaller than the concentric rings of BNO diffraction spot, indicating that the Bi nanoparticles were partly available in smaller sizes [28].

The nitrogen adsorption–desorption isotherms of the samples were type IV with typical hysteresis loops, as shown in Figure 7a. The hysteresis loops were of the H3 type at the relative pressure of $0.5\text{--}1.0\ P/P_0$, which is characteristic of nanosheet materials. Among all samples, 2% Bi-2-BNO had the highest specific surface area (S_{BET}), $47.22\ \text{m}^2\ \text{g}^{-1}$, which facilitated NO adsorption on its surface. The S_{BET} values of the BNO and 2-BNO composites were found to be 18.24 , and $27.45\ \text{m}^2\ \text{g}^{-1}$, respectively. After the addition of urea and the insertion of Bi nanodots, the S_{BET} increased significantly, which was caused by increased surface roughness and the appearance of porous defects and a loose structure. As can be seen from the pore size distribution curves in Figure 7b, these samples contained mesopores ($2\text{--}50\ \text{nm}$) and macropores ($>50\ \text{nm}$). We inferred that the 2-BNO photocatalyst had higher photocatalytic activity than the nonporous BNO nanosheets due to its significantly porous structure. Moreover, the photocatalytic activity of 2% Bi-2-BNO

was higher than that of 2-BNO, resulting from the more active sites provided by the SPR effect due to the Bi nanoparticles.

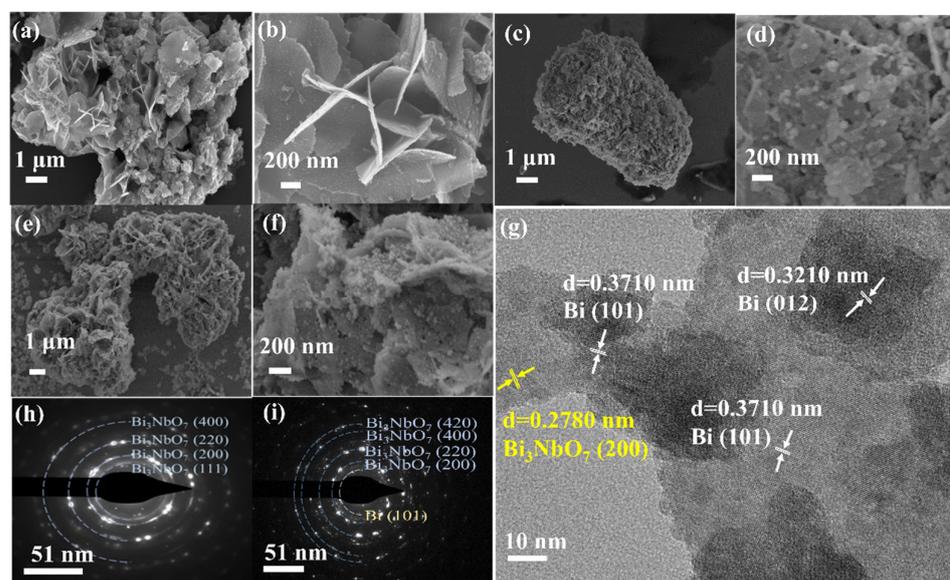


Figure 6. SEM images of (a,b) BNO, (c,d) 2-BNO and (e,f) 2% Bi-2-BNO; TEM images of 2% Bi-2-BNO nanosheets (g); SAED images of BNO (h) and 2% Bi-2-BNO (i).

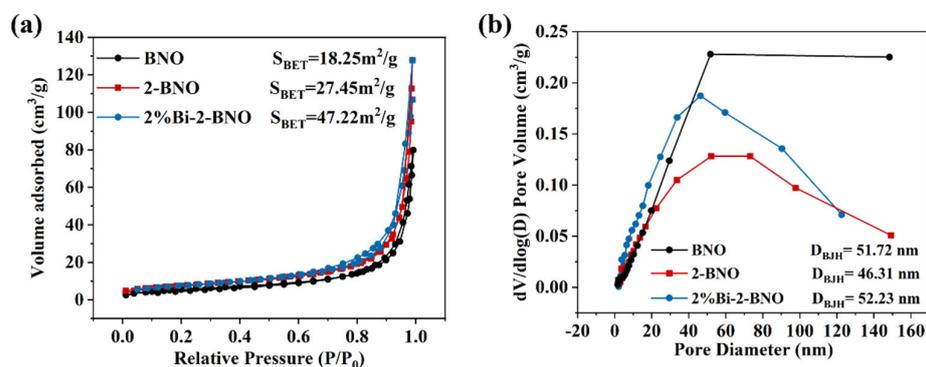


Figure 7. (a) N_2 adsorption–desorption isotherms for the photocatalytic samples, as well as (b) their pore size distribution curves.

Using X-ray photoelectron spectroscopy (XPS), the chemical state and composition of the BNO and 2% Bi-2-BNO photocatalysts were investigated. As shown in Figure 8a, the survey spectra revealed that the aforementioned samples contained Bi, Nb and O elements. As seen in the high-resolution Bi 4f spectra of BNO, the peaks of Bi 4f_{7/2} and 4f_{5/2} were positioned at about 158.7 and 164.01 eV and attributed to the Bi³⁺ chemical state [29]. In the Bi 4f spectra of 2% Bi-2-BNO (Figure 8b), two characteristic peaks were located at 158.97 and 164.34 eV, corresponding to Bi³⁺ 4f_{7/2} and 4f_{5/2} [30]. Metallic Bi was observed at 158.00 and 163.57 eV, demonstrating the existence of zero-valent Bi in 2% Bi-2-BNO [31]. The Nb 3d XPS spectrum for BNO displayed two peaks located at binding energy values of 206.43 and 209.18 eV, which were assigned to Nb 3d_{3/2} and 3d_{5/2}, respectively [32]. In Figure 8c, the peaks positioned at about 206.57 and 209.34 eV correspond to Nb⁵⁺ [33]. The high-resolution scan of the O 1s spectrum of BNO showed some peaks located at about 529.30 and 531.03 eV, which were attributed to the Bi–O and Nb–O bonds, respectively [14]. Compared with BNO, three peaks could be observed in the O 1s XPS spectra of 2% Bi-2-BNO (Figure 8d), with an additional peak at the lattice oxygen’s binding energy of 531.03 eV [34]. The binding energies of Bi, Nb and O were shifted to the high binding

energy side after the growth of metallic Bi, which might be the result of a partial electron transfer to it [27].

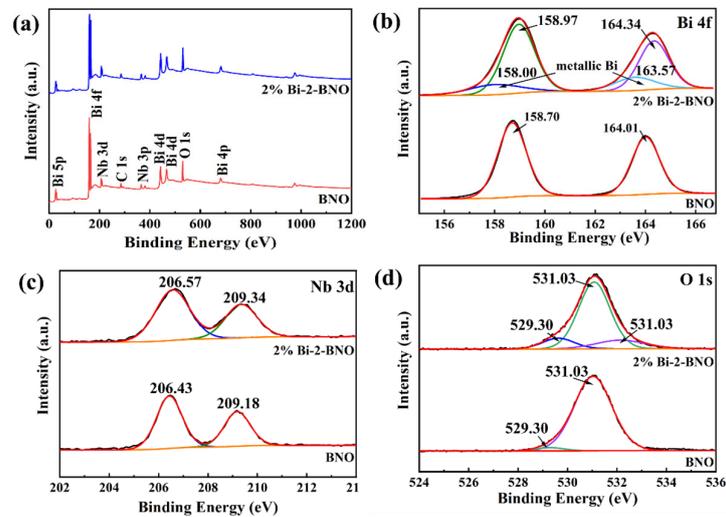


Figure 8. XPS analysis of the BNO and 2% Bi-2-BNO samples: (a) survey spectra, (b) Bi 4f, (c) Nb 3d and (d) O 1s.

The transient photocurrent responses for electrodes coated with BNO, 2-BNO and 2% Bi-2-BNO under visible light irradiation were investigated to better understand the behavior of photoinduced charges (Figure 9a). The corresponding pattern for 2-BNO appeared obviously at higher responses compared with that of BNO, indicating that the porous defects could improve the separation efficiency of the photogenerated electron-hole pairs. Furthermore, the photocurrent response of the 2% Bi-2-BNO sample was much higher than those of the others, as expected. The results suggest that the Bi SPR effect accelerated the migration of the charge carriers at the zero-dimensional/two-dimensional interfaces, which was highly favorable to charge separation, resulting in a better photocatalytic performance. The EIS Nyquist plots are shown in Figure 9b. The arc radius of BNO, 2-BNO and 2% Bi-2-BNO decreased sequentially, implying that the charge transfer resistance also decreased in a similar manner.

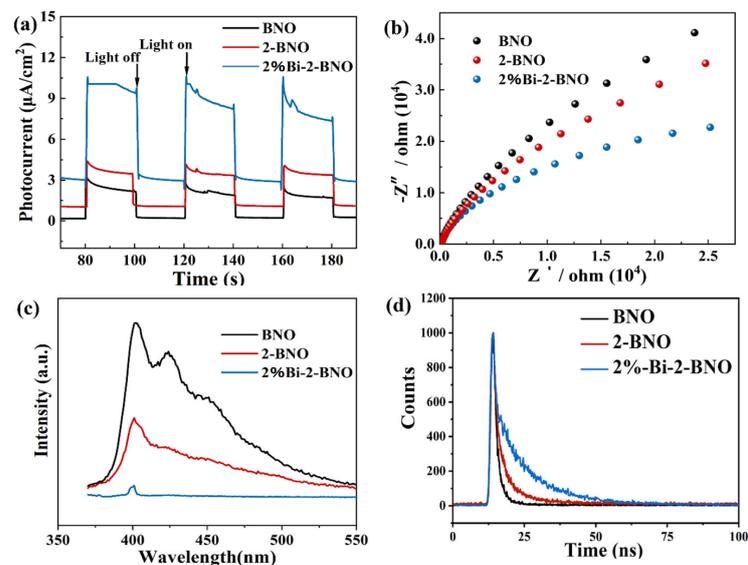


Figure 9. (a) Transient photocurrent responses; (b) EIS spectra of the as-prepared samples; (c) photoluminescence spectra; (d) time-resolved photoluminescence spectra of the photocatalysts.

Fluorescence spectroscopy and time-resolved transient fluorescence spectroscopy were used to explore the separation efficiency of the photogenerated charge carriers. A weaker PL intensity frequently indicates a lower charge carriers' recombination rate. The pristine BNO and the 2% Bi-2-BNO samples exhibited the strongest and the weakest PL emission intensity, respectively (Figure 9c). This quenching effect could be owed to the presence of more active sites because of the porous defects and metallic Bi, which raised the chance of charge separation and suppressed their recombination, thus improving the photocatalytic activity. As presented in Figure 9d, the average fluorescence lifetimes (τ_{ave}) of BNO, 2-BNO and 2% Bi-2-BNO were estimated to be 2.3, 5.02 and 5.28 ns, respectively. The prolonged τ_{ave} value of 2% Bi-2-BNO suggests that the porous flaws and metallic Bi promoted the effective separation of the photogenerated charge carriers.

3.3. Photocatalytic Mechanism

Electron paramagnetic resonance (EPR) measurements were carried out to detect the reactive oxygen species during photocatalysis. As shown in Figure 10a,b, no EPR signal was observed in the dark, but the superoxide radical ($\bullet\text{O}_2^-$) and the hydroxyl radical ($\bullet\text{OH}$) signals appeared after 5 min of light irradiation for the 2% Bi-2-BNO sample [35,36], indicating that both reactive oxygen species played a key role throughout the photocatalytic elimination of NO over the aforementioned photocatalyst. To further justify the results of the EPR analysis and the effectiveness of the mentioned primary active ingredients during the photocatalytic pathway, trapping tests were conducted for 2% Bi-2-BNO. PBQ, TBA, $\text{K}_2\text{Cr}_2\text{O}_7$ and KI were chosen to trap $\bullet\text{O}_2^-$, $\bullet\text{OH}$, e^- and h^+ , respectively. According to Figure 10c, the addition of PBQ, $\text{K}_2\text{Cr}_2\text{O}_7$ and KI clearly retarded the NO conversion, demonstrating that the photocatalytic conversion mechanism depended predominantly on $\bullet\text{O}_2^-$, e^- and h^+ . However, when TBA was used, the NO removal efficiency did not obviously decrease, suggesting that $\bullet\text{OH}$ rarely participated in the photocatalytic NO removal process.

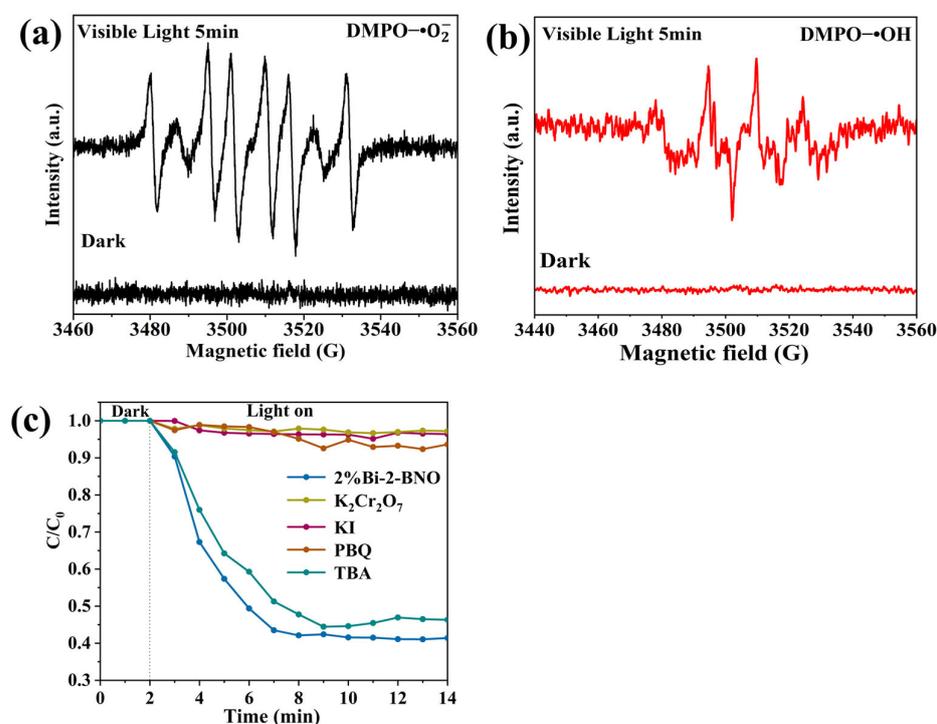
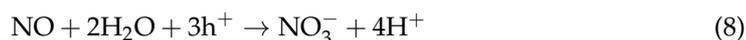
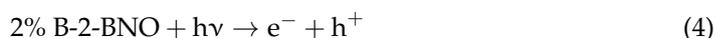


Figure 10. EPR spectra of the (a) DMPO- $\bullet\text{O}_2^-$ and (b) DMPO- $\bullet\text{OH}$ adducts under dark and irradiation; (c) effect of different radical scavengers on NO removal using 2% Bi-2-BNO.

According to the abovementioned findings, a plausible mechanism for the photocatalytic NO removal using 2% Bi-2-BNO is as follow:



This pathway is schematically illustrated in Figure 11.

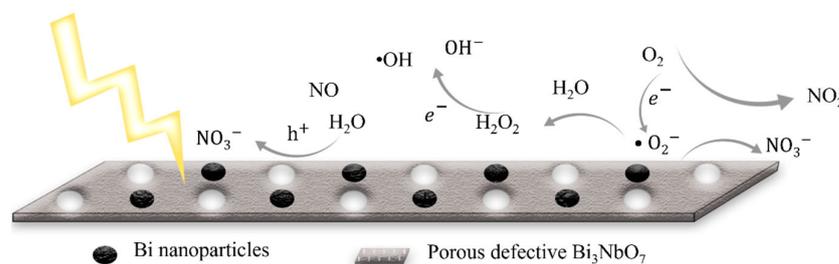


Figure 11. Reaction mechanism diagram of the photocatalytic NO removal by the 2% Bi-2-BNO photocatalyst.

4. Conclusions

Concisely, photocatalytic pore-defective Bi/Bi₃NbO₇ nanosheets were successfully synthesized via the solvothermal method. Using urea during the synthesis steps, the Bi₃NbO₇ microstructure and porosity were serendipitously affected, leading to a 20.5% improvement of the photocatalytic efficiency towards NO removal. Furthermore, it was demonstrated that the growth of Bi nanodots along with the increase in porosity enhanced the photocatalytic activity of the materials. The highest NO removal efficiency, 60.3%, was obtained over the pore-defective Bi@Bi₃NbO₇ when the molar ratios of urea and Bi(NO₃)₃•5H₂O to pristine Bi₃NbO₇ were 1:25 and 1:2, respectively, and was two times higher than that of BNO in the same conditions. In brief, the combination of porous defects and the SPR effect of the Bi nanoparticles ameliorated the visible light-harvesting properties, delayed the electron-hole recombination, and provided more efficient active sites on the surface, resulting in a better photocatalytic performance, while the generation of the toxic by-product NO₂ was significantly inhibited. More importantly, NO was predominantly converted to NO₃⁻, and •O₂⁻, e⁻ and h⁺ played a key role in the prepared photocatalysts, with a minor contribution of •OH radicals. The present work provides new insights for the removal of NO, especially for minimizing the generation of toxic byproducts during this process.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11010115/s1>, Figure S1: SEM images of 2% Bi-2-BNO (a) before and (b) after the stability test, Figure S2: SEM images of 4% Bi-2-BNO, Figure S3: Elemental mapping of (a) 2% Bi-2-BNO corresponding to (b) Bi, (c) Nb and (d) O.

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