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Communication

Molecular oxygen activation enhancement by BiOBr_{0.5}I_{0.5}/BiOI utilizing the synergistic effect of solid solution and heterojunctions for photocatalytic NO removal

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ABSTRACT

To improve the photocatalytic oxidation reaction activity for NO removal, photocatalysts with excellent activity are required to activate molecular oxygen. Solid solution and heterojunction were suggested as effective strategies to enhance the molecular oxygen activation via exciton and carrier photocatalysis. In this study, a solid solution and heterojunction containing BiOBr_{0.5}I_{0.5}/BiOI catalyst was synthesized, and it showed improved photocatalytic activity for removing NO. The photocatalytic NO removal mechanism indicated that synergistic effects between the solid solution and heterojunction induced the enhanced activity for molecular oxygen activation. The photogenerated holes, superoxide, and singlet oxygen generated by the carrier and exciton photocatalysis supported the high photocatalytic NO removal efficiency. This study provides new ideas for designing efficient Bi-O-X (X = Cl, Br, I) photocatalysts for oxidation reactions.

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Nitric oxide (NO) has been confirmed as a main source of atmospheric pollution, which is harmful to water sources and soil due to formation of acid rain [1,2]. Moreover, long-term inhalation of NO can damage the respiratory tract of humans and cause serious diseases. In recent decades, the concentration of NO in the atmosphere increased considerably because of the rapid development of the modern industrial civilization. The situation is of concern and requires effective methods to remove NO or oxidize it to final harmless or non-hazardous

products [3–5]. The products of NO oxidation are NO₃[−] or NO₂, which are commonly converted into useful industrial materials. Recently, many researchers have demonstrated that photocatalytic technologies are efficient methods for atmospheric pollution remediation [6–9]. The photocatalytic NO removal is still an oxidation process. The core of this technology, the oxidation efficiency of the catalysts, is of significant importance for the photocatalytic NO removal.

Because of the outstanding oxidation capability under visi-

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ble light, layered bismuth oxyhalide (BiOX , $X=\text{Br}$, I and Cl) photocatalysts displayed efficient photocatalytic activity for NO removal [10–13]. In order to further strengthen its photocatalytic property, some modified structural bismuth oxyhalide catalysts were designed and showed enhanced photocatalytic activity [14–16]. The combination of solid solution and heterojunction was suggested as effective strategy to enhance the molecular oxygen activation via exciton and carrier photocatalysis. For example, the solid solution $\text{BiOX}_x\text{Y}_{1-x}$ (X and Y are the different halogens) and the heterojunction BiOX/BiOY (X and Y are the different halogen) were most commonly synthesized and researched [17–19]. However, the synergistic effect of solid solution and heterojunctions is usually applied to the photocatalytic production of hydrogen, using sulphided catalysts such as $\text{Zn}_{1-x}\text{Cd}_x\text{S}/\text{CdS}$ [20,21] and $\text{Fe}_{1-x}\text{Pt}_x/\text{ZnCdS}$ [22]. It is rarely applied for photocatalytic NO removal. In our previous work, we demonstrated that the solid solution $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and heterojunction BiOBr/BiOI have enhanced photocatalytic activity for molecular oxygen activation due to their special structures [23]. When irradiated by visible light, the excitation initiates different photocatalytic molecular oxygen activation reactions for $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOBr/BiOI . Singlet oxygen ($^1\text{O}_2$) and superoxide ($\bullet\text{O}_2^-$) are generated by $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOBr/BiOI via exciton and carrier photocatalysis, respectively. The enhanced molecular oxygen activation capacity supports their superior photocatalytic ability under visible light [23,24]. However, it was uncertain whether the synergistic effect of solid solution and heterojunctions can be used for photocatalytic NO removal.

In this study, in order to improve the photocatalytic property of BiOX ($X = \text{Br}$ and I) for NO removal, we used a one-pot solvothermal method to design and prepare the solid solution and heterojunction containing $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ catalyst. The

basic structure of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ has been confirmed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The molecular oxygen activation enhanced by the synergistic effect of solid solution and heterojunction resulted in the ameliorative NO removal capacity of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$. In addition, the mechanism for photocatalytic NO removal, including the intermediate processes and products, was also explored and confirmed. To the best of our knowledge, this work should be the first to report on the synergistic effect of solid solution and heterojunction for photocatalytic NO removal. It provides a constructive thought to enhance the photocatalytic activity of BiOX ($X = \text{Br}$, I and Cl) to remove NO.

The characteristic diffraction peaks of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$, $\text{BiOBr}_{0.5}\text{I}_{0.5}$, BiOBr , and BiOI were determined by XRD. As is shown in Fig. 1(a), consistency was observed between the characteristic peaks of BiOBr and BiOI and the referenced values (BiOBr : PDF: 01-078-0348; BiOI : PDF: 01-073-2062) [25]. The diffraction peaks of $\text{BiOBr}_{0.5}\text{I}_{0.5}$ located between those of BiOI and BiOBr confirmed its solid solution structure [26,27]. All diffraction peaks of $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOI appeared also in the $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ sample, which implied that the solid solution and heterojunctions were successfully formed [28–30]. The amplified XRD information (Fig. 1(b) and (c)) also confirmed the co-existing structure. Fig. 1(d) shows UV-Vis diffuse reflectance spectra (DRS) comparing the maximum absorption wavelengths. The maximum absorption wavelengths of $\text{BiOBr}_{0.5}\text{I}_{0.5}$, BiOI and $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ were 701.5, 679.5 and 691.5 nm, respectively. This indicated that these three samples all responded to visible light [31,32] and that visible light supports NO removal. Physical nitrogen adsorption determined the specific surface area of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$, $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOI . Figure 1(e) shows that the

Fig. 1. XRD patterns of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$, $\text{BiOBr}_{0.5}\text{I}_{0.5}$, BiOBr and BiOI : (a) 5°–70°; (b) 5°–15° and (c) 26°–35°; (d) DRS patterns of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$, $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOI ; BET curves (e) and pore size distribution (f) of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$, $\text{BiOBr}_{0.5}\text{I}_{0.5}$ and BiOI .

Fig. 2. XPS spectra of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI. (a) Survey; (b) Bi 4f; (c) I 3d; (d) Br 3d; (e) O 1s.

N₂ adsorption and desorption curves all correspond to type IV adsorption isotherms [33]. The specific surface area of BiOBr_{0.5}I_{0.5}/BiOI (35.0 m²·g^{−1}) was larger than that of BiOBr_{0.5}I_{0.5} (8.2 m²·g^{−1}) and BiOI (14.4 m²·g^{−1}). Figure 1(f) shows the pore distribution curves of the samples. The peak pore diameters of the three samples were all close to 2.47 nm. The high surface area and abundant pore structure of BiOBr_{0.5}I_{0.5}/BiOI favor the photocatalytic NO removal [34].

The elemental compositions of the BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI were confirmed by XPS. Figure 2(a) shows that the surfaces of BiOBr_{0.5}I_{0.5}/BiOI and BiOBr_{0.5}I_{0.5} consist of the same elements Bi, O, Br, and I, while those of BiOI were Bi, O and I. The Bi 4f_{5/2} binding energies of BiOBr_{0.5}I_{0.5} and BiOI were 164.56 eV, and the Bi 4f_{7/2} binding energy was 159.27 eV (Fig. 2(b)). The binding energies of BiOBr_{0.5}I_{0.5} and BiOI at 630.73 and 619.20 eV were assigned to I 3d_{3/2} and I 3d_{5/2} (Fig. 2(c)), respectively. However, the Bi 4f and I 3d binding energies of BiOBr_{0.5}I_{0.5}/BiOI deviated by 0.1–0.2 eV compared to the single components which indicated that there were interactions between BiOBr_{0.5}I_{0.5} and BiOI. The Br 3d_{3/2} and Br 3d_{5/2} binding energies of BiOBr_{0.5}I_{0.5}/BiOI and BiOBr_{0.5}I_{0.5} were 68.4 and 69.4 eV (Fig. 2(d)). Figure 2(e) shows the O 1s pattern whose binding energies were 530.0 and 530.8 eV for BiOBr_{0.5}I_{0.5}, 530.1 and 531.0 eV for BiOI, and 529.8 and 530.7 eV for BiOBr_{0.5}I_{0.5}/BiOI, respectively. It was crystal lattice O atoms (Bi–O) and surface hydroxyl groups that caused the two energy bands [35,36]. The binding energy of 532.3 eV for BiOBr_{0.5}I_{0.5}/BiOI indicated adsorbed surface water on BiOBr_{0.5}I_{0.5}/BiOI [35,36]. Based on the XPS valence band and plots of $(\alpha(h\nu))^{1/2}$ versus energy ($h\nu$) of BiOBr_{0.5}I_{0.5} and BiOI, the band structure of BiOBr_{0.5}I_{0.5}/BiOI is shown in Fig. S1. In Fig. S1(a), the valence band of BiOBr_{0.5}I_{0.5} and BiOI were 1.37 and 1.64 eV. The band gap values of BiOBr_{0.5}I_{0.5} and BiOI were 1.90 and 1.99 eV (Fig. S1(b)). It was calculated that the conduction

band values of BiOBr_{0.5}I_{0.5} and BiOI were −0.53 and −0.35 eV. Combining the above experimental results, the band structure of BiOBr_{0.5}I_{0.5}/BiOI is shown in Fig. S1(c).

High-angle annular dark field (HAADF) image, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and element mapping of BiOBr_{0.5}I_{0.5}/BiOI are presented in Fig. 3. HAADF (Fig. 3(a)) and TEM (Fig. 3(b)) images show that BiOBr_{0.5}I_{0.5}/BiOI aggregated in the form of nanosheets. In the HRTEM image of BiOBr_{0.5}I_{0.5}/BiOI (Fig. 3(c)), there was an obvious boundary at the junction, which implied the heterostructure formed by coupling BiOI with BiOBr_{0.5}I_{0.5}. In addition, two interplanar distances of 0.18 and 0.29 nm were observed. Based on the crystal structure parameters of bismuth oxyhalide [37–39], 0.18 and 0.29 nm were attributed to the {202} plane of BiOI and {012} plane of BiOBr_{0.5}I_{0.5}. It validated the formation of the heterojunction between BiOI and BiOBr_{0.5}I_{0.5}. Another HRTEM image of BiOBr_{0.5}I_{0.5}/BiOI also confirmed it. As shown in Fig. S2, the distances of 0.27 and 0.33 nm were attributed to the {111} plane

Fig. 3. HAADF (a), TEM (b), HRTEM (c), and element mapping (d) of BiOBr_{0.5}I_{0.5}/BiOI.

Fig. 4. Photocatalytic results for BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI: (a) NO removal rates; (b) cyclic experiments for NO removal over BiOBr_{0.5}I_{0.5}/BiOI; (c) generated NO₂ amounts of cycling experiments over BiOBr_{0.5}I_{0.5}/BiOI.

of BiOI and {011} plane of BiOBr_{0.5}I_{0.5}. In addition, comparing the corresponding element mapping, it was observed that the signal of Br is relatively weak in the elliptic marked region (Fig. 3(d)). It indicated that this region corresponds to BiOI, and the other regions are related to BiOBr_{0.5}I_{0.5}. It was concluded that the binary solid-heterostructural BiOBr_{0.5}I_{0.5}/BiOI was formed successfully.

Figure 4 displays the results of the photocatalytic NO removal experiments of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI. Comparing their photocatalytic NO removal efficiency (Fig. 4(a)), the enhanced photocatalytic NO oxidation properties of BiOBr_{0.5}I_{0.5}/BiOI were obvious, where 36.2% NO was removed after a 20-min irradiation under visible light. The activity was higher than most of the reported results (Table 1). At the same conditions, the NO removal efficiency of BiOBr_{0.5}I_{0.5} and BiOI was just 22.3% and 7.0%, respectively. The BET specific surface areas were also determined. The comparison of BiOX based NO removal photocatalysts is presented in Table 1. The BiOBr_{0.5}I_{0.5}/BiOI photocatalyst displayed a better activity than reported BiOX based photocatalysts. The BET areas of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI were 9.4, 3.5 and 2.8 m²·g⁻¹, respectively. Noticeably, the samples with higher specific surface area display better activity. It implied that there is a significant influence of BET specific surface area on photocatalytic activity. The stability of BiOBr_{0.5}I_{0.5}/BiOI was confirmed after repeating experiments three times (Fig. 4(b)). The results established that the considerable photocatalytic NO removal stability of BiOBr_{0.5}I_{0.5}/BiOI of approximately 36% NO remained in cyclic experiments. In addition, the recorded TEM image (Fig.

S2) of BiOBr_{0.5}I_{0.5}/BiOI after three cycles did not show obvious changes. NO degradation products could affect the photocatalytic process. Figure 4(c) shows the amount of NO₂ generated from NO degradation during the three cycles. It was observed that NO degradation and NO₂ generation was stable during the cycling experiments. Moreover, the NO degradation amount was approximately equal to the generated NO₂ amount, which implied that the main product of photocatalytic NO removal with BiOBr_{0.5}I_{0.5}/BiOI was NO₂. This is also in agreement with previous reports, where NO reacted with reactive oxygen species (ROS) to yield NO₂ by the selective oxidation process [40].

According to our previous work, heterojunction and solid solution structures efficiently improve molecular oxygen activation carrier and exciton photocatalytic process [20,21]. In order to confirm that the synergistic effect of solid solution and heterojunction of BiOBr_{0.5}I_{0.5}/BiOI leads to molecular oxygen activation enhancement, we verified the carrier and exciton photocatalytic processes separately. The separation efficiency of holes and photogenerated electrons should be improved in order to obtain a better photocatalysis of carriers from heterostructures. Photoluminescence (PL) is a method to assess the photo-generated electron-hole pair efficiency. Figure S5 shows PL spectra of BiOBr_{0.5}I_{0.5}/BiOI with a weaker intensity than those of BiOBr_{0.5}I_{0.5} and BiOI, which indicated that the carrier photocatalysis could be enhanced at a lower electron-hole recombination rate by BiOBr_{0.5}I_{0.5}/BiOI [46]. Compared with BiOBr_{0.5}I_{0.5} and BiOI, the higher photocurrent intensity (Fig. 5(a)) and smaller diameter semicircle arc (Fig. 5(b)) of BiOBr_{0.5}I_{0.5}/BiOI was consistent with the enhanced carrier photocatalysis [47,48]. It was also in agreement with the PL results.

The typical ROS measurements were the most direct evidence to confirm the molecular oxygen activation in the photocatalytic process. It was reported that there are two typical main products in the processes of exciton and carrier photocatalysis, singlet oxygen (¹O₂) and the superoxide radical (•O₂⁻) [49,50]. A higher generation of ¹O₂ and •O₂⁻ implies the enhanced ability of molecular oxygen activation. ESR spectroscopy together with the compounds, 3',3',5',5'-tetramethylbenzidine (TMB) and nitrobluetetrazolium (NBT) were used to evaluate the generation of ¹O₂ and •O₂⁻ [51,52]. As is shown in Fig. 5(c), for •O₂⁻, BiOBr_{0.5}I_{0.5}/BiOI displayed stronger ESR signals than BiOBr_{0.5}I_{0.5} and BiOI. It indicated that BiOBr_{0.5}I_{0.5}/BiOI produced more •O₂⁻ under visible light irradiation via enhanced carrier photocatalysis due to the heterostructure. With

Table 1

Photocatalytic activity of BiOX based photocatalysts for NO removal (Light: λ > 420 nm).

Photocatalysts	Activity (%)	Ref.
BiOBrMicrospheres	30	[11]
Bi/BiOCl	35	[41]
BiOBr/C ₃ N ₄	32.7	[42]
BiOI	6.0	[43]
BiOI _{1.5}	32	[44]
BiOBr/BiOI	10	[45]
Bi/BiOI	40.8	[56]
BiOBr _{0.5} I _{0.5} /BiOI	36.2	This work
BiOBr _{0.5} I _{0.5}	22.3	
BiOI	7.0

Fig. 5. Photocurrent (a) and electrochemical impedance spectra (b) of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI; ESR for •O₂⁻ (c) and ¹O₂ (d) of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI; TMB oxidation rate (e) and NBT reduction rate (f) of BiOBr_{0.5}I_{0.5}/BiOI, BiOBr_{0.5}I_{0.5} and BiOI.

regards to the ¹O₂ generation, Fig. 5(d) reveals a stronger ESR signal for BiOBr_{0.5}I_{0.5}/BiOI than for BiOBr_{0.5}I_{0.5} and BiOI. The experimental results suggested that the solid solution structure leads to more ¹O₂ produced by BiOBr_{0.5}I_{0.5}/BiOI under visible light via the enhanced exciton photocatalysis. In addition, the ROS quantitative experiments also support these results. Figs. 5(e) and S6 show that BiOBr_{0.5}I_{0.5}/BiOI decreased the NBT (53%) in the absorption spectra more than BiOBr_{0.5}I_{0.5} (28%) or BiOI (13%). Figures 5(f) and S7 reveal a higher TMB oxidation rate for BiOBr_{0.5}I_{0.5}/BiOI (65%) compared to BiOBr_{0.5}I_{0.5} (27%) and BiOI (10%). This suggested that the solid solution structure leads to more ¹O₂ produced by BiOBr_{0.5}I_{0.5}/BiOI under visible light via the enhanced exciton photocatalysis. The ROS quantitative experiments further supported that the synergistic effect of heterojunction and solid solution via exciton and carrier photocatalysis leads to an enhancement of the molecular oxygen activation of BiOBr_{0.5}I_{0.5}/BiOI. Therefore, the photocatalytic NO removal efficiency of BiOBr_{0.5}I_{0.5}/BiOI was enhanced by the improved molecular oxygen activation capacity due to the synergistic effect of solid solution and heterojunction.

Trapping experiments with different trapping agents during the photocatalytic NO removal process were conducted to explore the photocatalytic NO removal process of BiOBr_{0.5}I_{0.5}/BiOI further. As is shown in Fig. 6(a) and (b), compared to the NO removal efficiency (36.2%) without trapping agents, adding triethanolamine (13.2%), 2,2,2,6,6,6-tetramethylpiperidine nitrogen oxide (TEMPO, 10.2%) and benzoquinone (BQ, 7.1%) reduced the efficiency [53]. It indicated that the holes (h⁺), ¹O₂ and •O₂⁻ generated by BiOBr_{0.5}I_{0.5}/BiOI were all efficient ROS generated by the photocatalytic NO removal process. Based on the molecular orbital of NO (Fig. 6(c)), there was an unpaired electron present in the anti-bonding molecu-

lar orbital, which could be easily removed due to its instability [54]. We determined that the heterojunction structure of BiOBr_{0.5}I_{0.5}/BiOI resulted in more h⁺ to capture unpaired NO electrons (Fig. 6(d)), which transformed NO into NO⁺. Then ROS (¹O₂ and •O₂⁻) oxidized NO⁺ to NO₂.

In order to elucidate the process of photocatalytic NO removal further, in situ FT-IR spectra were recorded, which are shown in Fig. 7, demonstrating the photocatalytic NO oxidation on the BiOBr_{0.5}I_{0.5}/BiOI surface with irradiation of visible light. After 30 min of adsorption, it was observed that NO (1245 cm⁻¹), NO + O₂ (1533 and 1614 cm⁻¹), and NO⁺ (1373 cm⁻¹) peaks appeared [55]. When the light was switched on, the curves changed obviously. There was a trend of increasing intensity of the characteristic NO peaks. At longer irradiation, the NO⁺ peaks increased while the NO₂ peaks increased initially and then decreased. The NO₂ peaks increased at first because NO₂

Fig. 6. (a, b) Trapping experimental results of BiOBr_{0.5}I_{0.5}/BiOI for NO removal; (c) the molecular orbital diagram of NO; (d) transformation of NO into NO⁺.

Fig. 7. In situ infrared spectra of BiOBr_{0.5}I_{0.5}/BiOI for photocatalytic NO removal.

was produced through the photocatalytic oxidation of NO by BiOBr_{0.5}I_{0.5}/BiOI. With the continuous increase in NO₂, NO₂ was partly desorbed, which agrees with the above photocatalytic results. The in-situ FT-IR results further confirmed the selective NO removal process of BiOBr_{0.5}I_{0.5}/BiOI.

Based on the experimental results, we proposed the photocatalytic NO removal process that is shown in Scheme 1. The first step, the transfer of photogenerated electrons and holes via carrier photocatalysis is promoted by the electric field caused by the heterojunction. Then, NO⁺ was generated as an intermediate product by the reaction between h⁺ and NO. Moreover, O₂ combined with e⁻ and •O₂⁻ was produced. The BiOBr_{0.5}I_{0.5} solid solution had a unique layered structure, exhibiting an intensive electron-hole interaction, which promoted ¹O₂ generation via an energy transfer process. Furthermore, •O₂⁻ and ¹O₂ supported the superior photocatalytic oxidation activity of BiOBr_{0.5}I_{0.5}/BiOI to oxidize NO to NO₂. Finally, NO₂ reacted with water to produce nitric and nitrous acid. According to our findings, the synergistic effect of the solid solution and heterojunction induced the enhanced photocatalytic NO removal process of BiOBr_{0.5}I_{0.5}/BiOI and is presented as follows.

- (1) BiOBr_{0.5}I_{0.5}/BiOI + visible light → h⁺ + e⁻
- (2) NO + h⁺ → NO⁺

Scheme 1. Photocatalytic NO removal mechanism of BiOBr_{0.5}I_{0.5}/BiOI.

- (3) e⁻ + O₂ → •O₂⁻
- (4) O₂ + visible light → ¹O₂
- (5) NO⁺ + •O₂⁻ → NO₂; NO⁺ + ¹O₂ → NO₂
- (6) 2NO₂ + H₂O → HNO₃ + HNO₂

In this study, the solid solution and heterojunction containing photocatalyst BiOBr_{0.5}I_{0.5}/BiOI was prepared and characterized. The molecular oxygen activation capacity was enhanced by the heterojunction and solid solution structures and induced the exciton and carrier photocatalysis, which was confirmed by •O₂⁻ and ¹O₂ generation. The superior photocatalytic oxidation activity of BiOBr_{0.5}I_{0.5}/BiOI promoted the effective NO oxidation to NO₂ under visible light irradiation. The photocatalytic mechanism for NO removal was revealed by trapping experiments and in situ infrared spectroscopy. The intermediate product NO⁺, generated from NO reacting with h⁺, was oxidized to NO₂ by •O₂⁻ and ¹O₂. The NO₂ was finally converted into NO₃⁻ and NO₂⁻ by the reaction with water.

Supporting Information

Bandgap structure, TEM images, PL, TMB and NBT adsorption spectra were described in the supplementary information.

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Graphical Abstract

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Molecular oxygen activation enhancement by $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ utilizing the synergistic effect of solid solution and heterojunctions for photocatalytic NO removal

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The synergistic effect of solid solution and heterojunction was used to enhance the ability of $\text{BiOBr}_{0.5}\text{I}_{0.5}/\text{BiOI}$ to removal NO under visible light.

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利用固溶体和异质结的协同效应增强BiOBr_{0.5}I_{0.5}/BiOI分子氧活化能力 光催化去除NO

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摘要: 层状卤氧化铋(BiOX, X=Br, I和Cl)光催化剂在可见光下具有优异的分子氧活化性, 因而对NO的去除具有较好的光催化活性. 为了进一步增强其光催化性能, 人们设计了一些改性结构的卤氧化铋光催化剂, 并显示出了较强的光催化活性. 固溶体和异质结是通过提高激子和载流子的分离效率来增强分子氧活化的有效策略. 我们前期工作表明, 固溶体BiOBr_{0.5}I_{0.5}和异质结材料BiOBr/BiOI因其特殊的结构而提高了分子氧活化的光催化活性. 然而, 固溶体和异质结的协同效应是否可以用于光催化去除NO尚不确定.

因此, 本文采用一锅热法设计和制备了固溶体和异质结共存的催化剂BiOBr_{0.5}I_{0.5}/BiOI, 运用X射线衍射(XRD), X射线光电子能谱(XPS)和透射电镜(TEM)表征了其基本结构. BiOBr_{0.5}I_{0.5}/BiOI与BiOBr_{0.5}I_{0.5}和BiOI的光致发光光谱(PL)结果表明, BiOBr_{0.5}I_{0.5}/BiOI较弱的电子空穴复合能力及其增多的光催化载流子, 与其较高的光电流强度和较小的阻抗结果相符合. 活性氧的测定是证实光催化过程中分子氧活化的最直接证据. 据报道, 在激子和载流子光催化过程中存在两种主要的典型产物: 单线态氧(¹O₂)和超氧自由基(•O₂⁻). 更多的¹O₂和•O₂⁻的产生意味着分子氧活化能力的增强. 我们用ESR光谱与化合物3',3',5,5'-四甲基联苯胺(TMB)和硝基蓝四氮唑(NBT)一起评价了¹O₂和•O₂⁻的生成. 对于¹O₂和•O₂⁻, BiOBr_{0.5}I_{0.5}/BiOI比BiOBr_{0.5}I_{0.5}和BiOI具有更强的ESR信号. 结果表明, 由于固溶体结构光催化增强的激子和异质结的存在, BiOBr_{0.5}I_{0.5}/BiOI在可见光照射下产生更多的¹O₂和•O₂⁻. 另一方面, ROS定量实验也支持该结果. 因此, 固溶体和异质结的协同作用提高了分子氧活化能力, 从而提高了BiOBr_{0.5}I_{0.5}/BiOI的光催化NO去除效率.

采用不同诱捕剂的实验探索了BiOBr_{0.5}I_{0.5}/BiOI光催化NO去除过程. 与无捕获剂的NO去除效率(36.2%)相比, 加入三乙醇胺(13.2%), 2,2',6',6'-四甲基哌啶氮氧化物(TEMPO, 10.2%)和苯醌(BQ, 7.1%)时, 光催化NO去除效率明显下降. 通过傅里叶红外光谱(FT-IR)进一步证实光催化NO的去除过程. 基于上述实验结果, 我们提出了光催化NO的去除过程. 第一步, 由异质结引起的电场将促进光生电子和空穴分离, 通过载流子光催化转移. 然后, h⁺与NO反应生成NO⁺作为中间产物. 同时, O₂与e⁻结合产生•O₂⁻. 另一方面, BiOBr_{0.5}I_{0.5}固溶体具有独特的层状结构, 因此具有强烈的电子空穴相互作用, 通过能量转移过程促进了¹O₂的产生. 第二步, ¹O₂和•O₂⁻促进了BiOBr_{0.5}I_{0.5}/BiOI对NO氧化至NO₂的良好光催化氧化活性. 最后, NO₂可以与水反应生成硝酸和亚硝酸.

这是首次报道固溶体和异质结的协同光催化去除NO. 它为提高BIOX (X=Br, I和Cl)的光催化活性提供了一个建设性的思路.

关键词: BiOBr_{0.5}I_{0.5}/BiOI; 去除NO; 分子氧活化; 载流子; 激子

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