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Article

Facile construction of $\text{Bi}_2\text{Mo}_3\text{O}_{12}@\text{Bi}_2\text{O}_2\text{CO}_3$ heterojunctions for enhanced photocatalytic efficiency toward NO removal and study of the conversion process

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ABSTRACT

Charge separation and transformation are some of the key requirements for high-efficiency photocatalysis. The photocatalytic reaction mechanism provides a guideline for the development and commercialization of high-efficiency photocatalysts. In this study, we designed and favorably synthesized BMO@BOC heterojunctions via a facile solvothermal route and applied the heat treatment method for application in high-efficiency photocatalytic NO removal. More importantly, both continuous stream and intermittent stream methods with *in situ* diffuse reflectance infrared Fourier transform spectroscopy were applied to intuitively and dynamically investigate the adsorption process and oxidation process of NO removal over the photocatalyst surface. The intermediate products (NO^- , NO_2^- , and NO_2) were explicitly detected in both the adsorption process and oxidation process, whilst the final product (NO_3^-) appeared only in the oxidation process, owing to the separation, migration, and conversion of photoinduced electron-hole pairs.

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1. Introduction

Photocatalytic semiconductor technology has attracted tremendous research interests for its application in NO_x re-

moval owing to its low energy consumption, low cost, and eco-friendliness. NO_x pollutant gases result in photochemical smog, haze, and acid rain, which are detrimental to human health and the environment [1–5]. Generally, semiconductor

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materials, which act as photocatalysts, are one of the determinant factors in semiconductor photocatalytic technology. Among various photocatalysts, Bi-based alternative materials such as $\text{Bi}_2\text{O}_2\text{CO}_3$ [6], Bi_2WO_6 [7,8], Bi_4MoO_9 [9], and BiOX ($X = \text{Br}, \text{I}, \text{Cl}$) [3,10–12] have shown great potential for application in photocatalytic NO removal, due to their suitable bandgaps, outstanding stabilities, and non-toxic features.

However, the photocatalytic activity exhibited by the high-profile Bi-based photocatalysts could not meet the requirements for commercialization owing to the deficient light response ability, rapid recombination of photoinduced electron-hole pairs, and sluggish surface reaction kinetics [13–15]. Therefore, intensive efforts have been devoted to further enhance the activity of the photocatalysts. For example, Huang et al. [16] found that the $\text{Bi}_2\text{O}_3/(\text{BiO})_2\text{CO}_3$ nanoplate heterojunctions constructed by *in situ* thermal treatment shows excellent improvement in activity toward the photocatalytic NO removal under solar light illumination, and the enhanced performance can be ascribed to the improved light absorption ability and facilitated charge separation. Shi et al. [3] reported that the ultrathin BiOBr/BiOI heterostructure synthesized via *in situ* growth routes exhibited enhanced photocatalytic NO removal efficiency, and the photocatalytic reaction process over the surface of the heterojunction consists of nonselective and selective oxidation processes. Therefore, constructing a heterojunction can dramatically enhance the photocatalytic activity by modulating the light response range, accelerating the charge separation, and retarding the recombination of carriers. In addition, although studies have been done to investigate the reactive oxygen species (ROS) and photocatalytic NO oxidation process, it is still a challenge due to the diversiform oxynitrides serving as intermediate products of the NO oxidation. Besides, it is difficult to reveal the conversion process of photocatalytic NO oxidation through an intuitive and dynamic detection method.

In this study, a $\text{Bi}_2\text{Mo}_3\text{O}_{12}@\text{Bi}_2\text{O}_2\text{CO}_3$ heterojunction ($\text{BMO}@\text{BOC}$) has been favorably synthesized by a facile solvothermal method followed by the calcination process. The as-prepared heterostructure delivered an excellent photocatalytic NO removal activity, owing to the receded recombination of electron-hole pairs. More importantly, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were used to intuitively and dynamically monitor the conversion process of the photocatalytic NO oxidation. The results of the *in situ* DRIFTS indicated that NO^- , NO_2^- , and NO_2 would be produced on the surface of the photocatalysts during the adsorption process and that NO_3^- appeared in the oxidation process. In addition, NO^- and NO_2^- , as intermediate products, could be oxidized by ROS to form NO_3^- , while NO_2 could be the toxic byproduct. This work provides an intuitive and dynamic method for understanding the NO oxidation process, which provides essential guidance for the development of photocatalytic technology.

2. Experimental

2.1. Chemicals

Sodium molybdate dehydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$), sodium carbonate (Na_2CO_3 , $\geq 98.0\%$), and bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 98.0\%$) were purchased from Alfa Aesar. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, Grade AR 96.0%) and ethylene glycol (EG, $\geq 99.0\%$) were purchased from Chongqing Chuandong Chemical (Group) Co. Ltd., China. All chemical reagents used in this work were of analytical grade and were used as received.

2.2. Synthesis of photocatalysts

$\text{Bi}_2\text{Mo}_3\text{O}_{12}@\text{Bi}_2\text{O}_2\text{CO}_3$ heterostructures with different composition proportions were favorably composited by a facile solvothermal method followed by the heat treatment method. In a typical procedure, solution A: 3 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added into 20 mL of EG solution under rapid stirring. Solution B: Na_2CO_3 and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were mixed into 10 mL of EG solution under vigorous stirring with different reactant ratios ($\text{Na}_2\text{CO}_3:\text{Na}_2\text{MoO}_4 = 4:1, 2:1, 1:1$, and $0.5:1$, and the total molar mass was 1.5 mmol). After A and B completely dissolved and formed homogeneous clear solutions, B was dropped into A under drastic magnetic stirring for 1 h. Subsequently, the mixture was transferred into a 50 mL Teflon-lined autoclave and heated at 160°C for 18 h. After the reaction, the precipitates were washed and dried at 60°C for 6 h. In addition, the collected products were calcined at 350°C for 2 h under ambient conditions. Finally, the products, corresponding with the different reactant ratios, were named as $\text{BMO}@\text{BOC}-4$, $\text{BMO}@\text{BOC}-2$, $\text{BMO}@\text{BOC}-1$, and $\text{BMO}@\text{BOC}-0.5$.

2.3. Materials characterization

Focused ion beam scanning electron microscopy (Zeiss Auriga, FIB/SEM), high-resolution transmission electron microscopy (HRTEM, ThermoFisher Scientific, Talos F200S), X-ray diffraction (XRD, $\text{Cu K}\alpha$, Rigaku D/max 2500), and Raman spectroscopy (LabRAM HR Evolution) were used to characterize the morphologies, chemical composition, and crystal structures of the prepared samples. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, $\text{Al K}\alpha$) was employed to survey the surface chemical state. UV-Vis spectroscopy (UV-2700, Japan) and fluorescence spectroscopy (PL, Hitachi F4600) were applied to investigate the light absorption and recombination of the carriers, respectively, with BaSO_4 as the reference. Electron spin resonance (ESR) spectroscopy (Bruker JES FA200) was used to test the hydroxyl ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$), with DMPO (5,5'-dimethyl-1-pyrroline-N-oxide) as a spin-trap reagent. *In situ* DRIFTS was employed to dynamically monitor the reaction pathway of the photocatalytic NO oxidation. In this work, we employed two test methods to investigate the photocatalytic NO oxidation process: continuous stream and intermittent stream methods. The continuous stream method involves the continual passage of the mixture gas (50% NO and 50% O_2) through the detection chamber of the *in situ* DRIFTS instrument during the adsorption and oxidization processes, where the adsorption process occurs before light on, and the oxidization process, after light on. This method could dynamically detect the reaction process and allow the investigation of

the accumulation of intermediate and final products on the surface of the photocatalysts. The intermittent stream method involves the continual passage of the mixed gas through the detection chamber only in the adsorption process, while the oxidation process has no gas stream. Thus, this method is used to reveal the conversion process of the adsorption species into final products.

2.4. Evaluation of the photocatalytic activity

The photocatalytic activities of the prepared samples were assessed by testing their efficiencies toward NO removal under visible light irradiation. In detail, 0.20 g of the photocatalysts were mixed into ethyl alcohol, uniformly dispersed, and covered on two 12.0 cm diameter glass culture dishes, followed by drying at 60 °C. After the dishes cooled naturally, they are placed at the 4.5 L (30 × 15 × 10 cm) rectangular reactor center with continuous flow. The original NO (100 ppm, balance N₂) provided from the gas cylinder was diluted to about 550 ppb by an air stream. After reaching adsorption-desorption equilibrium in the reactor, the tungsten halogen lamp (150 W) with a UV cutoff filter ($\lambda \geq 420$ nm) was turned on. Moreover, the variation in the NO concentration was detected by the NO_x analyzer (Thermo Scientific, model 42c-TL), which recorded every minute of the process. The NO removal efficiency (η) was calculated using the following expression: $\eta = (1 - C/C_0) \times 100\%$, where C_0 and C are the NO concentrations in the inlet and outlet, respectively.

3. Results and discussion

The Bi₂Mo₃O₁₂@Bi₂O₂CO₃ (BMO@BOC) heterostructures were successfully synthesized by a facile solvothermal route followed by the heat treatment method. In addition, the com-

position proportions of Bi₂Mo₃O₁₂ (BMO) and Bi₂O₂CO₃ (BOC) were well-tuned. The typical synthesis process is described in the Methods section. The geometrical morphologies of the as-prepared heterostructures were investigated by FIB/SEM. As shown in Fig. 1, the morphologies of different samples are significantly different. In detail, BMO@BOC-4 consists of nanoparticles, while BMO@BOC-2, which is a nano/micro-sphere, consists of ultrafine nanoparticles/nanosheets. More importantly, both BMO@BOC-1 and BMO@BOC-0.5 are shaped as spherical nanoflowers constructed by nanosheets. The difference between them is that the nanosheets of BMO@BOC-1 are ultra-thinner than those of BMO@BOC-0.5. These distinct features of BMO@BOC-1 could provide more reactive sites for facilitating the photocatalytic reactions. In addition, the corresponding TEM images of BMO@BOC-4 show the 100–200 nm sized nanoparticles, while the ultrafine nanosheets appear in the TEM images of BMO@BOC-2, BMO@BOC-1, and BMO@BOC-0.5, which agrees with the results of SEM. Simultaneously, the HRTEM image of BMO@BOC-4 indicates the lattice spacing of BMO (-221) and BOC (161). Similarly, the (-221) facets of BMO emerged in BMO@BOC-2, BMO@BOC-1, and BMO@BOC-0.5. The lattice spacing of (002) indexed to BOC is exhibited in BMO@BOC-2, BMO@BOC-1, and BMO@BOC-0.5, rather than the (161) lattice spacing, which also confirms the existence of BOC and generates the heterojunction between BMO and BOC. Notably, based on the morphology characterization, we could not identify the precise morphologies of BMO and BOC, which could be due to the synthesis methods. Firstly, the precursors were synthesized by solvothermal method; thereafter, the samples were obtained by a one-step calcination process. Therefore, the products would inherit the morphology of the precursors to some extent, and BMO and BOC would be uniformly confined in the morphology.

To expressly verify the crystal structure and composition

Fig. 1. SEM ($x = a, b, c, d$), TEM ($x-1$) and the corresponding HRTEM ($x-2$) images of the BMO@BOC-4 (a), BMO@BOC-2 (b), BMO@BOC-1 (c) and BMO@BOC-0.5 (d).

information of the as-prepared photocatalysts, XRD and Raman spectroscopy were employed, and the corresponding curves are shown in Fig. 2(a) and Fig. 2(b), respectively. The diffraction peaks of all the samples observed in Fig. 2(a) are well matched with the monoclinic phase, $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (PDF# 78-2420), and orthorhombic phase, $\text{Bi}_2\text{O}_2\text{CO}_3$ (PDF# 84-1752), suggesting the favorable synthesis of the BMO@BOC heterojunctions. In addition, the peaks indexed to $\text{Bi}_2\text{O}_2\text{CO}_3$ are gradually weakened; moreover, some peaks disappeared as the carbonate content decreased during the preparation process, which implied that the proportions of BMO and BOC in the heterostructure could be easily modulated, and the proportion of BOC in the heterojunctions decreased in the order of $\text{BMO@BOC-4} > \text{BMO@BOC-2} > \text{BMO@BOC-1} > \text{BMO@BOC-0.5}$. Meanwhile, the vibration modes of the as-prepared products, presented in Fig. 2(b), could be attributed to the lattice vibrations of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ and $\text{Bi}_2\text{O}_2\text{CO}_3$, suggesting the successful construction of the heterojunction. Specifically, the bands at 300–325 and 715–850 cm^{-1} could be assigned to the bending vibrations of the Bi–O bonds and the stretching motions of Mo–O bonds, respectively [17–19]. The bands at 356 cm^{-1} could be ascribed to the bending motions of O–Mo–O bonds [17]. Moreover, the bands located at 433, 877, and 885 cm^{-1} could be attributed to the stretching variations of C–O bonds [20–22]. Significantly, the band intensity of the C–O bonds in BMO@BOC-0.5 is very weak, while the signal of Mo–O did not appear in BMO@BOC-4. In addition, both fingerprints are clearly presented in the curves of BMO@BOC-1, suggesting the appropriate proportion of BOC in BMO@BOC-1. These features are consistent with the XRD analysis results.

Furthermore, XPS was used to further analyze the composition and surface chemical state. In the full scan spectrum of all the as-prepared samples (Fig. S1(a)), C 1s, O 1s, Bi 4f, and Mo 3d can be clearly observed, indicating the presence of these ele-

ments in the hybrids. Based on the high-resolution spectra of C 1s (Fig. 2(c)), the spectra of all the as-prepared heterostructures can be deconvoluted into three peaks, where the peaks at 284.80–284.90 and 286.30–286.60 eV could be assigned to the C–C and C–O bonds, respectively [23]. These two peaks were contributed by the adventitious C [6]. Interestingly, the peaks at 288.60–288.90 eV could be indexed to the carbonate species, suggesting the existence of carbonate in the heterostructures [6]. Similarly, the high-resolution spectra of O 1s can be divided into three peaks (Fig. 2(d)). The peaks at 529.30–529.80, 530.00–530.30, and 529.90–530.10 eV can be ascribed to Bi–O, Mo–O (and/or carbonate), and adsorbed oxygen, respectively [6,13,23]. In addition, the double peaks of Bi 4f at 158.90–159.30 and 164.20–164.70 eV can be attributed to Bi 4f_{7/2} and Bi 4f_{5/2} of the Bi³⁺ state, respectively (Fig. S1(b)) [23,24]. Additionally, the double peaks of Mo 3d_{5/2} and Mo 3d_{3/2} are respectively located at 232.00–232.60 and 235.10–235.70 eV, corresponding to the Mo⁶⁺ state (Fig. S1(c)) [23].

Furthermore, to investigate the light harvesting and carrier recombination characteristics of the BMO@BOC heterojunctions, UV-Vis spectroscopy and fluorescence spectroscopy (PL) were performed; the relevant curves were recorded and are shown in Figs. 2(e) and (f). Noticeably, BMO@BOC-4 exhibits the best light absorption performance, while that of BMO@BOC-1 is slightly superior to that of BMO@BOC-0.5. However, the PL spectra intensity of BMO@BOC-1 is lower than those of other heterostructures, suggesting the low recombination rate of the photoinduced electron-hole pairs, which contributes to enhancing the photocatalytic activity. In this work, the photocatalytic efficiency was evaluated by removing the NO pollution gas under visible light irradiation. The visible light derived NO removal efficiency of the as-prepared heterojunctions are presented in Fig. 3(a). Noticeably, BMO@BOC-1 pos-

Fig. 2. XRD patterns (a), Raman spectra (b), high-resolution XPS spectra of C 1s (c) and O 1s (d), UV-vis diffuse reflectance spectra (e) and PL spectra (f) of the BMO@BOC-4, BMO@BOC-2, BMO@BOC-1 and BMO@BOC-0.5.

sesses the preferable photocatalytic activity, approximately 37% better than those of the others, which can be attributed to the constructed BMO@BOC heterojunction with suitable component proportions and receding recombination of the electron-hole pairs. Moreover, the stability and durability of BMO@BOC-1 were certified by testing for five cycles, and the tested curves are shown in Fig. 3(b). Noticeably, the NO removal efficiency did not significantly degrade after five cycles, and an efficiency retention of ~35% was achieved, which indicates the excellent stability and durability of the photocatalyst. During the photocatalytic NO oxidation process, the reactive oxygen radicals played a very vital role, which warrants investigation. Therefore, ESR spectroscopy was applied to analyze the formation of hydroxyl ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) with DMPO assistance. As shown in Fig. 3(c), four signals with an intensity ratio of 1:2:2:1 emerged under visible light illumination, and they were assigned to photoinduced $\bullet\text{OH}$ [1]. Similarly, the four strong fingerprint peaks with an intensity ratio of 1:1:1:1 were ascribed to the $\bullet\text{O}_2^-$ species, while the other two faint shoulder peaks were attributed to the DMPO^+ species (Fig. 3(d)) [25]. These results demonstrate the presence of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ as reactive oxygen radicals in the photocatalysis.

The analysis and investigation of the elementary reaction (or reaction process) have far-reaching significance for the development of high-efficiency photocatalysts. Therefore, to intuitively reveal the photocatalytic NO oxidation process over the surface of BMO@BOC-1, *in situ* DRIFTS measurements were employed, and the corresponding recorded curves are shown in Fig. 4. In this work, we adopted two methods to dynamically monitor the reaction process, namely the continuous stream method and intermittent stream method, of which the detailed description is provided in the Methods section. Firstly, the adsorption processes of the two methods on the surface of

BMO@BOC-1 are identical; the curves measured by the continuous stream method are shown in Fig. 4(a), whilst those of the intermittent stream method are shown in Fig. 4(d). Although the adsorption curves detected by the two methods are not completely in agreement, the characteristic peaks of the adsorption species are identical, suggesting the equivalence of the adsorption process monitored by two different methods. The fingerprint signals of the adsorption species at 1075, 1076, 1156, 1159, 1612, and 1621 cm^{-1} can be clearly observed. The signals at 1156 and 1159 cm^{-1} could be attributed to the NO-species [26], which are generated from the adsorption of gaseous NO on the BMO@BOC-1 surface. Meanwhile, the bands at 1075 and 1076 cm^{-1} could be assigned to linear nitrite (NO_2^-) [27], which could have originated from the mild oxidation of the adsorbed NO on the surface of the photocatalyst. In addition, the remaining two peaks at 1612 and 1621 cm^{-1} could be ascribed to the adsorbed gaseous NO_2 [28,29], which could have been formed from the moderate oxidation of NO. More importantly, all the distinct signals that emerged in the adsorption process under dark ambient conditions gradually increased until reaching the adsorption-desorption equilibrium point, and the variations in the NO^- , NO_2^- , and NO_2 contents are shown in Figs. 4(c, f) and Fig. S2(a), implying the generation and aggregation of the adsorbed species (intermediate products) on BMO@BOC-1.

After reaching the adsorption-desorption equilibrium point, the lamp was turned on. Simultaneously, the visible light driven NO oxidation process was analyzed by *in situ* DRIFTS, and the curves, as a function of time, are presented in Figs. 4(b, e). Quite noticeably, two new fingerprint bands appeared in each figure, which were derived from the oxidation process. The new characteristic signals at 1270, 1273, and 1500 cm^{-1} could be assigned to the monodentate nitrate (M-NO_3^-) [27,30,31], whilst

Fig. 3. (a) NO removal curves of all samples under irradiation of visible light; (b) cycling runs for the photocatalytic NO removal over BMO@BOC-1 under visible light irradiation, the catalysts was not washed to remove the nitrate on the surface after each cycle; ESR spectra of $\text{DMPO} \cdot \bullet\text{OH}$ (c) and $\text{DMPO} \cdot \bullet\text{O}_2^-$ (d) for the BMO@BOC-1 in darkness and under visible light irradiation.

Fig. 4. In situ DRIFTS spectra of NO adsorption (a, d) and oxidation processes (b, e) under visible light illumination over the BMO@BOC-1. The content variation of the NO_2^- and NO^- over time are shown in (c, f), where (c) is tested by continuous stream method while that of intermittent stream method is (f). Continuous stream method (a, b, c) is the mixture gas (50% NO and 50% O_2) continuing through the detection chamber of In situ DRIFTS measurement during the adsorption and oxidation process, where the adsorption process is before light on while the oxidation process is after light on. Intermittent stream method (d, e, f) is the mixed gas continuing through the detection chamber just in the adsorption process, while the oxidation process has no gas stream. The data of (b, e) come from the in situ DRIFTS analysis. The M-NO_3^- and B-NO_3^- are the monodentate nitrate and bidentate nitrate, respectively.

the bands at 1549 cm^{-1} is attributed to the bidentate nitrate (B-NO_3^-) [26], suggesting that nitrate is the photocatalytic oxidation final products of gaseous NO. Similar to the case with the adsorbed species, the nitrate content gradually accumulates on the surface of BMO@BOC-1, as shown in Fig. S2(b, c). Although the final products detected by the continuous stream and intermittent stream methods remain the same, slight differences exist. The dynamic curves monitored by the continuous stream method exhibit only the characteristic signals of M-NO_3^- in the oxidation process, while the intermittent stream method presents those of M-NO_3^- and B-NO_3^- , which can be attributed to the presence or absence of a mixture gas flowing through the reaction chamber during the oxidation process. Significantly, the characteristic peaks of NO^- , NO_2^- , and NO_2 can still be observed in the oxidation process. The contents of these intermediate products detected by the continuous stream method increased dramatically after the lamp was turned on, as shown in Fig. 4(c) and Fig. S2(a). Interestingly, the contents of NO^- and NO_2^- decreased slightly after sharply reaching the maximum value at the moment the light was turned on, whilst that of NO_2 increased gradually, which indicates that visible light can improve the formation of these adsorbed species. Moreover, the NO^- and NO_2^- contents tested by the intermittent stream method exhibit a clear declining trend (Fig. 4(c)), suggesting that NO^- and NO_2^- are oxidized under visible light irradiation. Notably, the NO_2 content still increased gradually (Fig. S2(a)), as is the case in the continuous stream method, which indicates that some NO^- species might have been oxidized to form NO_2 . In addition, notwithstanding the detection method, NO_2 in-

creased continuously, implying that NO_2 is possibly a toxic by-product of the photocatalytic NO oxidation process.

Based on the aforementioned results and analyses, the adsorbed species (NO^- , NO_2^- , and NO_2) would form and accumulate on the surface of the photocatalysts when the mixture gas ($\text{NO}+\text{O}_2$) flows through the reaction chamber. NO^- and NO_2^- would be further oxidized to generate mainly nitrate under visible light irradiation, owing to the generation of photoinduced electron-hole pairs and the formation of ROS ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$). Therefore, the elementary reaction of photocatalytic NO oxidation can be described by the following equations (Eqs. (1)–(8)), and the corresponding schematic diagram is presented in Fig. 5.

4. Conclusions

In summary, the BMO@BOC heterostructures constructed by a facile solvothermal procedure followed by the calcination process exhibited enhanced photocatalytic efficiency toward NO removal, attributed to the suitable light response ability and inhibited charge recombination. Significantly, the *in situ*

Fig. 5. The schematic of photocatalytic NO oxidation reaction pathway.

DRIFTS applied to intuitively and dynamically explore the elementary reaction of photocatalytic NO oxidation certified that NO^- and NO_2^- , as adsorbed species, could be further oxidized by ROS to produce NO_3^- . In this study, we systematically investigated the photocatalytic NO oxidation process via an intuitive and dynamic method, which has far-reaching significance for the development and commercialization of photocatalytic technology.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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Facile construction of $\text{Bi}_2\text{Mo}_3\text{O}_{12}@\text{Bi}_2\text{O}_2\text{CO}_3$ heterojunctions for enhanced photocatalytic efficiency toward NO removal and study of the conversion process

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The in situ DRIFTS was applied to intuitively and dynamically investigate the NO oxidation process over the surface of BMO@BOC heterojunction. And the NO^- and NO_2^- could be oxidized by ROS to form the nitrate.

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简易构筑Bi₂Mo₃O₁₂@Bi₂O₂CO₃异质结增强光催化脱除NO性能及其转化过程

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摘要: 电荷分离及转移是影响光催化效率的重要因素之一。本文采用简易的水热焙烧法, 设计并构筑了Bi₂Mo₃O₁₂@Bi₂O₂CO₃(BMO@BOC)异质结, 促进了光生载流子的分离与迁移, 并优化了异质结构中的BMO与BOC的组分比例, 其中BMO@BOC-1样品展现了最高的光催化脱除NO效率(~35%), 且具有优异的循环稳定性。SEM与TEM结果表明, BMO@BOC-1样品是由超薄纳米片构成, 可以提供丰富的反应活性位点, 从而促进光催化反应的发生。HRTEM, XRD及Raman充分证明已成功合成不同组分比例的BMO@BOC异质结。同时, Raman与XPS结果表明, BMO@BOC异质结由Bi, O, C及Mo组成, XPS图谱中拟合峰位置的偏移是由异质结组分不同所致。值得注意的是, UV-vis DRS结果表明, BMO@BOC-4具有最好的光谱吸收性能, 但它与BMO@BOC-2和BMO@BOC-1样品的吸收带边相近, 而PL结果则表明BMO@BOC-1具有更好的电荷分离性能, 以及合适的组分比例, 在一定程度上可以促进光吸收, 并能最大限度的促进光生载流子的分离。BMO@BOC-1样品的ESR测试结果说明, •OH与•O₂⁻的含量随着光照时间的延长而增加, 证实了它们是光催化NO氧化的活性中间物种。另外, 光催反应机制的研究在高效光催化剂的研发及其商业化应用中具有深远意义。本文还利用原位红外实时动态监测手段, 采用“连续流测试法”与“间歇流测试法”直观动态地研究了BMO@BOC异质结催化剂表面光催化NO脱除反应过程。结果表明, 在开灯前的吸附阶段于催化剂表面形成了NO⁻, NO₂⁻以及NO₂等中间产物, 开灯后的氧化阶段出现终产物(NO₃⁻)。进一步深入分析, 中间产物NO⁻和NO₂⁻在氧化阶段会被氧化活性物种进一步氧化成NO₃⁻, 而中间产物NO₂可能作为一种毒副产物影响NO的完全氧化。综上所述, 本文为理解NO氧化过程提供直观且动态的研究方法, 对光催化技术的发展具有重要的指导意义。

关键词: 异质结; NO脱除; 光催化; 原位红外; 反应过程

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