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Fabrication of Z-scheme MoO₃/Bi₂O₄ heterojunction photocatalyst with enhanced photocatalytic performance under visible light irradiation

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ABSTRACT

Constructing Z-scheme heterojunction to improve the separation efficiency of photogenerated carriers of photocatalysts has gained extensive attention. In this work, we fabricated a novel Z-scheme MoO₃/Bi₂O₄ heterojunction photocatalyst by a hydrothermal method. XPS analysis results indicated that strong interaction between MoO₃ and Bi₂O₄ is generated, which contributes to charge transfer and separation of the photogenerated carriers. This was confirmed by photoluminescence (PL) and electrochemical impedance spectroscopy (EIS) tests. The photocatalytic performance of the as-synthesized photocatalysts was evaluated by degrading rhodamine B (RhB) in aqueous solution under visible light irradiation, showing that 15% MoO₃/Bi₂O₄ (15-MB) composite exhibited the highest photocatalytic activity, which is 2 times higher than that of Bi₂O₄. Besides, the heterojunction photocatalyst can keep good photocatalytic activity and stability after five recycles. Trapping experiments demonstrated that the dominant active radicals in photocatalytic reactions are superoxide radical (•O₂⁻) and holes (h⁺), indicating that the 15-MB composite is a Z-scheme photocatalyst. Finally, the mechanism of the Z-scheme MoO₃/Bi₂O₄ composite for photo-degrading RhB in aqueous solution is proposed. This work provides a promising strategy for designing Bi-based Z-scheme heterojunction photocatalysts for highly efficient removal of environmental pollutants.

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1. Introduction

Organic pollutants are harmful to human health, such as dyes and volatile organic compounds (VOCs), which come from leather, textile, printing industries, and construction and decoration materials [1–4]. Especially, organic dyes containing various refractory organic compounds were discharged into natural water without any treatment because of the waste in the production process, which affects the safety of water quality [5,6]. Even though the concentration of organic dyes in the water is low, the water quality has been affected. The organic dyes in waste water are difficult to be degraded completely by traditional technologies, which poses a grave threat to human health and their production activities. Therefore, it is highly desirable to explore novel technologies for degradation of dye waste water. Advanced oxidation processes have been developed and applicated for organic pollutant degradation [7,8]. Especially, semiconductor photocatalytic technology can remove and de-

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grade organic pollutants by catalytic reaction driven by solar energy, which has been considered as a promising technology for environmental purification because of the advantages of its highly efficiency and environmental friendliness [9,10]. The common photocatalysts, such as TiO₂ and ZnO, which can be excited by UV-light to generate electron-hole pairs and finally involved in the redox reaction, have been studied for solving problems of environmental pollution and energy shortage [11–13]. However, the visible-light excited photocatalysts can utilize solar energy more efficiently, which have wider application prospect. Therefore, it is desirable to explore novel visible-light excited photocatalysts.

In recent years, many visible light responsive Bi-based photocatalysts with highly hole mobility and fantastic optical properties have been reported. Typical Bi-based photocatalysts such as BiO_{2-x} [14-16], Bi₂WO₆ [17-20], and BiOX (X = Cl, Br, I) [21-29] have been developed and applied for degradation of organic pollutants, hydrogen generation, CO2 reduction, and NO_x removal. However, single-phase photocatalyst usually suffers from quick recombination of charge carriers, affecting their photocatalytic efficiency seriously [30,31]. Especially, fabrication of hybrid semiconductor photocatalysts with staggered band alignments has been identified as one of the most promising ways for boosting their photocatalytic performance, benefiting from the faster interfacial charge transfer [32-34]. Recently, constructing Z-scheme photocatalysts to widen the range of light absorption and increase the redox ability of photocatalysts has drawn much attention [35-37]. Wang et al. [38] have successfully synthesized Bi3TaO7/g-C3N4 Z-scheme composites, and this Z-scheme photocatalyst shows higher visible light catalytic activity for degrading antibiotics. Nie et al. [39] have fabricated Z-scheme g-C₃N₄/ZnO composites, and the obtained composites showed higher photocatalytic performance for CO₂ reduction, benefiting from the high separation efficiency of charge. Therefore, developing novel Z-scheme photocatalysts for environment remediation is promising.

Bi₂O₄ is a novel visible light responsive photocatalyst with narrow band gap and wide absorption region. Wang et al. [40] synthesized Bi₂O₄ for application in bacterial inactivation and decomposition of organic pollutants. To enhance catalytic performance of single phase Bi₂O₄ photocatalyst, Xia et al. [41] fabricated Z-scheme C₃N₄/Bi₂O₄ heterojunction photocatalysts, which have better and stable photocatalytic performance. Besides, many studies on Bi₂O₄ have also been reported [42-46]. MoO₃ is a noticeable material for environmental treatment due to its chemical stability and non-toxicity. MoO₃ is a promising material to construct heterostructures with other semiconductors because of its energetically electrical properties [47]. He et al. [48] synthesized Z-scheme MoO₃/C₃N₄ composites by a mixed calcination method and evaluated their photocatalytic activities by degrading methyl orange (MO), and the obtained composites exhibited higher visible-light photocatalytic performance than C₃N₄. Therefore, it is meaningful to fabricate a novel MoO₃/Bi₂O₄ heterojunction photocatalyst for highly efficient photocatalysis.

Herein, we successfully synthesized MoO_3/Bi_2O_4 Z-scheme composites by a hydrothermal method. The structure, mor-

phology, and surface chemical properties of the as-synthesized composites were studied by a series of characterizations. Subsequently, the photocatalytic activity of the composites was evaluated by using RhB as the target pollutant. Chemical trapping experiments were conducted to determine the participation of active radicals in photocatalytic reactions. Finally, the possible Z-scheme photocatalytic mechanism was proposed and discussed in detail.

2. Experimental

2.1. Photocatalyst preparation

Preparation of MoO₃ is similar to the pioneer's reported work [49]. 2 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added to the crucible and heated for 4 h in a muffle furnace at 500 °C (the rate of heating was set as 5 °C/min). When the muffle furnace was cooled, the obtained sample was washed four times with water and dried at 70 °C for 12 h.

 MoO_3/Bi_2O_4 photocatalysts were synthesized by a hydrothermal process. Typically, 1.58 g of NaBiO_3·2H_2O was added into 60 mL ultrapure water, and then a certain amount of MoO_3 was dispersed in NaBiO_3 solution and stirred for 1 h. After that, the mixture was transferred into a PPL-lined stainless autoclave and heated at 160 °C for 6 h. After the autoclave was cooled naturally, the precipitation was washed with ultrapure water and ethanol five times, and dried at 70 °C for 6 h. A series of MoO_3/Bi_2O_4 composites were prepared by changing the amount of MoO_3. According to the MoO_3 and Bi_2O_4 molar ratios of 0.05:1, 0.15:1, 0.2:1, and 0.3:1, these samples were named 5-MB, 15-MB, 20-MB, and 30-MB, respectively. Besides, pure Bi_2O_4 was synthesized by the same method without adding MoO_3.

2.2. Characterization

Chemical compositions of the photocatalysts were analyzed by X-ray diffraction (XRD) on a D/MAX-RB diffractometer. Scanning electron microscopy (SEM, JSM-5610LV) and transmission electron microscopy (TEM, JEM 2100 F) were applied to examine the morphology and microstructure of the samples. X-ray photoelectron spectroscopy (XPS, VG Multilab2000) was used to analyze the surface properties of obtained samples, and the binding energies of the elements in the samples were calibrated by 284.6 eV of C 1*s*. The optical properties of the samples were tested with an UV-Vis spectrophotometer (UV-3600 plus). Photoluminescence (PL) measurements were performed on a fluorescence spectrophotometer (RF-5301), and the excitation wavelength was 312 nm.

2.3. Photoelectrochemical measurements

The photoelectrochemical properties of the as-obtained samples were analyzed on an electrochemical workstation (CHI660E) using 0.5 mol/L Na₂SO₄ aqueous solution as the electrolyte. The working electrodes were made as follows. A 10 mg sample was suspended in 1 mL mixed solution (prepared with 1 mL Nafion dispersion and 24 mL ethyl alcohol), and then the mixed solution was sonicated for 1 h until forming uniform solution. The above solution was slowly dropped onto the ITO glass and dried in an ambient environment. Bi₂O₄-ITO, MoO_3 -ITO, or Bi₂O₄/MoO₃-ITO were used as working electrode, and platinum wire and Ag/AgCl electrode was used as counter electrode and reference electrode, respectively.

2.4. Photocatalytic experiments

RhB was chosen to evaluate photocatalytic performance of the obtained MoO₃/Bi₂O₄ composites. Typically, 50 mg photocatalysts were added in RhB solution (10 mg/L, 100 mL). The suspensions were continuously stirred for 30 min in the dark to establish adsorption equilibrium. The 100 W LED lamps with the wavelength of 420 nm as the visible light source. During visible-light irradiation, 5 mL of the suspensions were withdrawn at different regular time intervals of 10 min from the photocatalytic system, then centrifuged to obtain liquid supernatant, and analyzed on a UV-visible spectrophotometer (UV-1100) at its characteristic peak of 554 nm. The calculated degradation is expressed by C_t/C_0 , where C_t and C_0 are the concentration of RhB at each irradiated time (t) and after adsorption/desorption equilibrium, respectively.

In the cycle experiments of degrading RhB solution, the used 15-MB photocatalyst was washed with ultrapure water and ethanol and then dried at oven for next photocatalytic reaction.

3. Results and discussion

The XRD patterns of pure MoO₃, Bi₂O₄, and MoO₃/Bi₂O₄ composites were shown in Fig. 1. The main peaks of pure MoO₃ are at 12.8°, 23.4°, 25.7°, 25.8°, 27.3°, and 29.7°, relating to the (020), (110), (040), (120), (021), and (130) planes, respectively. This pattern is consistent with the standard JCPDS No.05-0508 well. The XRD pattern of Bi₂O₄ corresponds to Bi₂O₄ (JCPDS No. 50-0864). The characteristic diffraction peaks at 26.8° and 29.5° are attributed to (111) and (31-1) planes of Bi₂O₄. The XRD pattern of the 20-MB composite indicates the



Fig. 1. XRD patterns of as-synthesized samples.

coexistence of MoO_3 and Bi_2O_4 . However, this pattern is similar to that of pure Bi_2O_4 due to the low content of MoO_3 in the composite. It is obvious that no characteristic peaks of other impurities existed in the as-obtained photocatalysts, indicating that the synthesized samples are pure.

The morphologies of the as-obtained Bi₂O₄, MoO₃, and 15-MB composite were observed by SEM and TEM. SEM images of the representative photocatalysts are shown in Fig. 2. Pure Bi₂O₄ is made up of massive nanorods (Fig. 2a and 2b). For MoO₃, it is grain-like morphology with a glazed surface (Fig. 2c and 2d), which is consistent with previous study [49]. As for the MoO₃/Bi₂O₄ composite, large numbers of Bi₂O₄ nanorods are coated on the surface of MoO₃ (Fig. 2e and 2f). This structure allows the surface between Bi₂O₄ and MoO₃ with large contact area, which is beneficial to the transfer of photogenerated carries. The HRTEM image of the Bi₂O₄ is exhibited in Fig. 3a, and the lattice fringes of 0.295 nm correspond to the (400) planes of Bi₂O₄ [43]. Fig. 3b is the HAADF-STEM image of the 15-MB sample. The EDS analysis are showed in Fig. 3c-e, proving that 15-MB composite is only composed of Bi, Mo, and O elements, these elements uniformly distributed on the surface of 15-MB sample. These results indicate that the structures of MoO3 and Bi₂O₄ are not changed after synthesis, and the interactions between MoO₃ and Bi₂O₄ may lead to different chemical states and optical properties.

The surface chemical states of Bi_2O_4 , MoO_3 , and 15-MB composite were investigated by XPS analysis. The survey spectra in Fig. S1 show the existence of Bi and O elements in the Bi_2O_4 catalyst and the presence of Mo and O elements in the MoO_3 sample, while the 15-MB composite consists of Bi, O, and Mo elements without other elements detected. Fig. 4 presents



Fig. 2. SEM images of (a, b) Bi₂O₄, (c, d) MoO₃, and (e, f) 15-MB samples.



Fig. 3. (a) HRTEM image of the Bi_2O_4 , (b) HAADF-STEM image of the 15-MB sample, and (c–e) elemental EDS-mapping images of the 15-MB sample.

the high-resolution spectra of Bi 4f, 0 1s, and Mo 3d. The Bi $4f_{5/2}$ (or Bi $4f_{7/2}$) spectrum of Bi₂O₄ is shown in Fig. 4a, the binding energies located at 163.5 and 164.0 eV (or 158.2 and 158.7 eV) correspond to Bi3+ and Bi5+ [43]. However, for the 15-MB composite, the characteristic peaks of Bi $4f_{5/2}$ (or Bi 4f7/2) respectively shift to 163.6 and 164.1 eV (or 158.3 and 158.8 eV), which might be due to the interactions between Bi₂O₄ and MoO₃. The asymmetric O1s peaks of 15-MB composite appeared at 529.4 and 530.8 eV (Fig. 4b). The peak at 529.4 eV belongs to the lattice oxygen of Bi-O bonds, and the peak at 530.8 eV can be assigned to 0^{2-} in molybdenum oxide. As for the Mo 3d peaks of MoO₃, the binding energy located at 232.9 and 236.1 eV (Fig. 4c), respectively. These two peaks were attributed to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ [49], but the Mo 3d peaks of 15-MB were shifted to 232.6 and 235.8 eV. The XPS results demonstrate that MoO₃/Bi₂O₄ composites were successfully synthesized, which might lead to distinct optical and electrochemical properties.

Fig. 5a shows the UV-vis diffuse reflectance spectra of pure Bi_2O_4 , MoO_3 , and MoO_3/Bi_2O_4 composites. It is obvious that the absorption wavelengths of Bi_2O_4 and MoO_3 are approximately 647 and 435 nm. After combining MoO_3 with Bi_2O_4 , the absorption edge red-shifted, and the absorption ability of visible light

is improved. The results of UV-vis diffuse reflectance spectroscopy analysis indicate that the UV-vis absorption properties of MoO₃/Bi₂O₄ composites are impacted, because the intermolecular interaction occurs between Bi₂O₄ and MoO₃. The band gaps of Bi₂O₄ and MoO₃ can be estimated by the formula [43] E_g = 1240/ λ_g , where E_g is the band gap energy, and λ_g is the absorption threshold wavelength of catalysts. The band gaps of Bi₂O₄ and MoO₃ are about 1.9 and 2.8 eV, respectively. These results matched well with the previous reports [41,49].

The Mott-Schottky plot measurement was conducted to determine the energy band structure of Bi₂O₄ and MoO₃, and the results are shown in Fig. 5b. Generally, the conduction band of semiconductor is close to its flat-band potential. The flat-band potentials of Bi₂O₄ and MoO₃ were at -0.59 and 0.29 V (vs Ag/AgCl, pH = 7), respectively. And they were determined to be -0.39 and 0.49 V (vs NHE, pH = 7), respectively. The VB positions of Bi₂O₄ and MoO₃ were, respectively, determined to be 1.51 and 3.29 V (vs NHE, pH = 7) according to the empirical formula $E_{VB} = E_{CB} + E_g$ [50,51].

The photocatalytic activity of Bi₂O₄, MoO₃, and MoO₃/Bi₂O₄ heterojunction photocatalysts was evaluated by degrading RhB solution under visible light (λ = 420 nm). The photocatalytic degradation experiments were carried out after the adsorption experiments. The degradation results are presented in Fig. 6a. As we can see, about 2% RhB was decomposed under visible light irradiation without photocatalyst, and pure MoO₃ photocatalyst had neglected photocatalytic performance for RhB degradation. After irradiating for 40 min by visible light, about 73% of RhB were eliminated over pure Bi₂O₄. By comparison, degradation rate of RhB was determined to be 67%, 99.6%, 92.5%, and 75.2% for 5-MB, 15-MB, 20-MB, and 30-MB composites, respectively. Obviously, the MoO₃/Bi₂O₄ composite exhibits enhanced photocatalytic performance. With increasing the MoO₃ content, the photocatalytic activity of as-obtained composites increased firstly and then decreased. It is obvious that the content of MoO₃ in the composites exerted an influence on



Fig. 4. XPS spectra of Bi₂O₄, MoO₃, and 15-MB composite. (a) Bi 4f; (b) O 1s; (c) Mo 3d.



Fig. 5. (a) UV-vis diffuse reflectance spectra of the as-obtained samples; (b) Mott-Schottky plots of Bi₂O₄ and MoO₃.



Fig. 6. (a) Photocatalytic degradation curves of RhB solution over different photocatalysts; (b) UV-vis absorption spectra of RhB solution over the 15-MB composite; (c) Degradation percentage of RhB solution by the 15-MB composite in cycle experiments; (d) XRD patterns of the 15-MB composite before and after five cycles of photocatalytic degradation process.

degradation activity. A suitable content of MoO₃ can promote the absorption of visible light for MoO₃/Bi₂O₄ composites, which accelerates the transfer and separation of photo-generated carriers, and finally improves the photocatalytic efficiency. However, when MoO₃ was over-loaded, the photocatalytic activity decreased, which is probable that MoO₃ provided more recombination centers. The 15-MB composite with moderate MoO₃ content has the best photocatalytic activity among the as-synthesized samples by RhB degrading experiments. In addition, the adsorption experiments of the as-synthesized photocatalysts toward RhB solution were carried out, and the results are shown in Fig. S2. As we can see, less than 10% of RhB was adsorbed by different photocatalysts. To quantify the photocatalytic ability of the as-synthesized samples, the reaction kinetic was analyzed. As shown in Fig. S3, the k value of 15-MB is 2 times as that of Bi₂O₄, implying the best photocatalytic activity of the 15-MB composite. In Fig. 6b, it is apparent that the UV-vis adsorption peaks of RhB solution at 554 nm decreased rapidly, indicating that the molecular structure of RhB was destroyed.

The stability of photocatalyst is essential for its practical application. A cycle experiment of degrading RhB in aqueous solution over the 15-MB heterojunction composite was conducted, and the results are shown in Fig. 6c. 15-MB still held high photocatalytic activity after five cycles, and the degradation ratio of RhB declined a little because of the loss of the catalyst during the recovery process. The XRD pattern of the 15-MB sample after recycle is nearly the same as that of the fresh sample, as can be seen from Fig. 6d. The results confirmed that the photocatalyst is stable and effective during the process of degrading RhB.

To display the charge transfer efficiency and the separation of photogenerated hole-electron of as-obtained samples, the EIS and photocurrent tests were performed. Fig. 7a shows the Nyquist plots of the pure MoO₃, Bi₂O₄, and 15-MB composite under dark. In general, the smaller arc radius means a lower resistance of charge transfer [52,53]. The circle size of as-obtained samples follows the order: 15-MB composite < Bi₂O₄ < MoO₃. This result suggested that the 15-MB composite has the lowest resistance, which would enhance photocatalytic performance. Fig. 7b displays the photocurrent response curves of MoO₃, Bi₂O₄, and 15-MB composite. The 15-MB composite exhibits the highest photocurrent intensity, indicating that the photogenerated hole-electron separated more efficiently [54,55]. Furthermore, PL was used to analyze the excitation and transfer of charge carriers. In general, higher intensity of PL spectra indicates lower separation efficiency of carriers [56-59]. Fig. 7c shows the PL spectra of MoO₃, Bi₂O₄, and

the 15-MB heterojunction photocatalyst. It is apparent that 15-MB shows the weakest intensity of PL spectra, which indicates that the formation of MoO₃/Bi₂O₄ heterojunction contributes to separation of photogenerated electrons and holes. This result means that 15-MB might have the best photocatalytic performance compared with pure MoO₃ and Bi₂O₄.

The electrons and holes would be generated in photocatalysts during the degradation process, and then migrate to the surface of photocatalysts to produce •OH (hydroxyl radicals), h^+ , and $\bullet O_2^-$ radical species, which play a significant role in photocatalytic reactions. To investigate the mechanism of the 15-MB composite for photocatalytic degradation of RhB solution under visible light and evaluate the role of radical species, trapping experiments were performed. Isopropyl alcohol (IPA), sodium oxalate (Na₂C₂O₄), and benzoquinone (BQ) were respectively used to capture the generated \bullet OH, h⁺, and \bullet O₂⁻ during the RhB degradation [60-62]. The results are shown in Fig. 7d. After IPA was introduced, the degradation rates of RhB declined a little. When BQ or Na₂C₂O₄ was introduced, 10% and 20% of RhB were degraded. The results of trapping experiments demonstrate that h^+ and $\bullet O_2^-$ play an important role, and •OH is also involved in the degradation process.

Based on the above results, two possible mechanisms of organic pollutant degradation over MoO_3/Bi_2O_4 heterojunction



Fig. 7. (a) EIS spectra of Bi₂O₄, MoO₃, and 15-MB photocatalysts; (b) Photocurrent response curves of Bi₂O₄, MoO₃, and 15-MB photocatalysts; (c) Photoluminescence spectra of Bi₂O₄, 15-MB, and MoO₃ photocatalysts; (d) Photocatalytic degradation curves of RhB solution over the 15-MB sample with different scavengers.



Fig. 8. Possible photocatalytic degradation mechanism on the 15-MB composite under visible light irradiation. (a) Type-II heterojunction mechanism; (b) Direct Z-scheme mechanism.

photocatalyst are predicted and shown in Fig. 8. Upon visible light irradiation, electrons in valence band (VB) of Bi₂O₄ and MoO₃ can be activated [41,49], and then transfer to their conduction band (CB), the photogenerated holes are left in VB, respectively. If the separation and recombination process of photogenerated carriers follows the Type-II photocatalytic mechanism like Fig. 8a, the photoexcited electrons in CB of Bi₂O₄ can easily transfer to CB of MoO₃, and photogenerated holes transfer from VB of MoO3 to VB of Bi2O4 simultaneously because of the more negative band potential of MoO₃. However, the CB potential of MoO_3 (0.49 V vs NHE, pH = 7) is more positive than the potential of $O_2/\bullet O_2^-$ (-0.046 V vs NHE, pH = 7) [63,64], so the photoexcited electrons on the CB of MoO₃ cannot react with oxygen to produce •O₂⁻. Meanwhile, the holes on VB of Bi₂O₄ could not oxide H₂O to •OH because the VB potential of Bi_2O_4 (1.51 V vs NHE, pH = 7) is lower than the redox potential of $H_2O/\bullet OH$ (2.27 V vs NHE, pH = 7) [65]. In this case, only holes can oxidize dyes, which is not consistent with the result that $\bullet O_2^-$ is one of the dominant reactive species for 15-MB composite photocatalytic degradation of RhB. Thus, the process of separation and recombination of photogenerated carriers in 15-MB composite followed a direct Z-scheme mechanism. As shown in Fig. 8b, the photogenerated electrons would transfer from CB of MoO₃ to VB of Bi₂O₄ fleetly and recombine with the photogenerated holes of Bi2O4, leading to accumulation of electrons on the CB of Bi2O4 and holes on the VB of MoO3. The electrons on the CB of Bi_2O_4 can react with O_2 to form $\bullet O_2^-$ because the CB potential of Bi₂O₄ is more negative than the potential of $O_2/\bullet O_2^-$ (-0.046 V vs NHE, pH = 7) [63,64]. The holes retained in VB of MoO3 could directly oxidize dyes and part of holes can oxidize the adsorbed H₂O to form •OH, because the VB potential of MoO₃ is much positive than the redox potential of $H_2O/\bullet OH$ (2.27 V vs NHE, pH = 7) [65]. Therefore, MoO₃ and Bi₂O₄ form a direct Z-scheme photocatalytic system and thus significantly increase the photocatalytic activity of MoO₃/Bi₂O₄ composites. $\bullet O_2^-$, h⁺, and $\bullet OH$ produced in the photocatalytic reaction can oxidize RhB to CO2 and H2O or other intermediate products.

4. Conclusions

A novel MoO₃/Bi₂O₄ heterojunction has been fabricated by a hydrothermal method and used as a Z-scheme photocatalyst for highly efficient degradation of RhB in aqueous solution. The degradation rate of the optimized MoO₃/Bi₂O₄ photocatalyst is higher than that of pure MoO₃ and Bi₂O₄ samples, approximately 2 times that of pure Bi₂O₄. Trapping experiments demonstrated that h⁺, \bullet O₂⁻, and \bullet OH participate in the degradation of RhB solution. The PL and photoelectrochemical analysis revealed a Z-scheme charge transfer path between the MoO₃ and Bi₂O₄. This work A the Z-scheme photocatalytic mechanism of the Bi-based heterojunction system was proposed, which can help design highly efficient photocatalysts for organic pollutants degradation.

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Graphical Abstract

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 $Fabrication \ of \ Z-scheme \ MoO_3/Bi_2O_4 \ heterojunction \ photocatalyst \ with \ enhanced \ photocatalytic \ performance \ under \ visible \ light \ irradiation$

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 $Novel \ Z-scheme \ MoO_3/Bi_2O_4 \ heterojunction \ photocatalyst \ exhibited \ excellent \ photocatalytic \ activity \ under \ visible \ light \ irradiation \ benefiting \ from \ efficiently \ charge \ transfer \ and \ photogenerated \ hole-electron \ separation.$

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增强可见光催化活性的Z型MoO₃/Bi₂O₄复合光催化剂的制备

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摘要: 全球工业化进程的加快使人们饱受环境污染问题的困扰. 半导体光催化技术作为一种高效、绿色、有潜力的新技术, 在环境净化方面有着广阔的应用前景. Bi₂O₄是近年来新开发出的一种铋基光催化剂,在环境净化方面已有一些研究. 但 是,单体光催化剂通常存在光响应范围窄、光生载流子复合率高等问题,这些不足限制了Bi₂O₄的进一步应用. 因此,需要通 过适当的改性来拓宽其光响应范围和提高其载流子的分离效率,从而提高其光催化活性. 构建Z型异质结被认为是提高光 催化剂光生载流子分离效率并进一步提高光催化活性的有效方法. MoO₃是一种宽禁带的n型半导体,具有独特的能带结 构、光学特性和表面效应,是一种非常有前景的半导体光催化剂. 虽然MoO₃材料的光生载流子复合率高,带隙(2.7–3.2 eV) 大,不利于其参与光催化反应,但MoO₃与其他合适的半导体配位形成复合材料后能够有效提高其光生载流子的分离效率, 从而提高其光催化活性.

本研究采用简单的水热法制备了一种新型Z型MoO₃/Bi₂O₄复合光催化剂, SEM和TEM分析结果表明, MoO₃和Bi₂O₄紧 密结合在一起.X射线光电子能谱分析表明, MoO₃和Bi₂O₄之间存在很强的界面相互作用, 这有助于电荷转移和光生载流子 的分离.光致发光光谱、电阻抗和光电流测试也证明了MoO₃/Bi₂O₄复合光催化剂的光生载流子分离效率更高, 形成了更强 的光电流.通过在可见光下降解RhB溶液评价了所合成光催化剂的光催化性能.15% MoO₃/Bi₂O₄ (15-MB)复合光催化剂表 现出了最佳的可见光催化活性, 在40 min内对10 mg/L RhB溶液的降解率达到了99.6%, 其降解速率是Bi₂O₄的2倍.此外, 15-MB复合光催化剂在经过五次循环降解RhB溶液后仍保持良好的光催化活性和稳定性, 表明MoO₃/Bi₂O₄复合光催化剂 具有较强的应用潜力.通过自由基捕获实验确定了光催化反应中主要的活性自由基为•O₂⁻⁻和h⁺.通过莫特-肖特基测试和 带隙计算得到MoO₃和Bi₂O₄的价带和导带位置.最后, 根据实验和分析结果提出了Z型MoO₃/Bi₂O₄复合光催化剂在可见光 下降解RhB溶液的机理.本研究为设计铋基Z型异质结光催化剂用于高效去除环境污染物提供了一种有前景的策略. 关键词:氧化钼; 四氧化二铋; Z型; 异质结; 可见光; 降解

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