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Article

Novel indirect Z-scheme g-C₃N₄/Bi₂MoO₆/Bi hollow microsphere heterojunctions with SPR-promoted visible absorption and highly enhanced photocatalytic performance

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ABSTRACT

The surface plasmonic resonance (SPR) effect of Bi can effectively improve the light absorption abilities and photogenerated charge carrier separation rate. In this study, a novel ternary heterojunction of g-C₃N₄/Bi₂MoO₆/Bi (CN/BMO/Bi) hollow microsphere was successfully fabricated through solvothermal and *in situ* reduction methods. The results revealed that the optimal ternary 0.4CN/BMO/9Bi photocatalyst exhibited the highest photocatalytic efficiency toward rhodamine B (RhB) degradation with nine times that of pure BMO. The DRS and valence band of the X-ray photoelectron spectroscopy spectrum demonstrate that the band structure of 0.4CN/BMO/9Bi is a z-scheme structure. Quenching experiments also provided solid evidence that the •O₂^{•-} (at −0.33 eV) is the main species during dye degradation, and the conduction band of g-C₃N₄ is only the reaction site, demonstrating that the transfer of photogenerated charge carriers of g-C₃N₄/Bi₂MoO₆/Bi is through an indirect z-scheme structure. Thus, the enhanced photocatalytic performance was mainly ascribed to the synergetic effect of heterojunction structures between g-C₃N₄ and Bi₂MoO₆ and the SPR effect of Bi doping, resulting in better optical absorption ability and a lower combination rate of photogenerated charge carriers. The findings in this work provide insight into the synergism of heterostructures and the SPR absorption ability in wastewater treatment.

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1. Introduction

In recent years, development of methods to handle water pollution in a simple way has become an important research topic of practical concern. Semiconductor-based photocatalysis

is a promising green chemical technique, using sunlight as an energy source for pollutant degradation and hydrogen production from water splitting. Numerous visible-light active photocatalysts have been developed, including Bi-based and Ag-based ones, such as Ag₃PO₄ [1], BiVO₄ [2], Bi₂WO₆ [3], and

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Bi_2MoO_6 [4].

Among various bismuth-based materials, Bi_2MoO_6 , as a novel complex semiconductor, is suitable for a visible-light active photocatalyst owing to its fascinating physicochemical properties, such as an appropriate bandgap (2.58 eV) [5]. However, Bi_2MoO_6 has a poor photocatalytic property because of its relatively poor quantum yield, which limits the possibility of practical application [6]. Designing a heterostructure with other materials is a useful method to solve the problem. Graphitic carbon nitrides (g- C_3N_4) are recognized as the most stable allotrope of carbon nitride. Because of its high nitrogen content and facile synthesis procedure, g- C_3N_4 may provide more active reaction sites than other N-carbon materials [7]. Use of g- C_3N_4 can improve the photocatalytic activity of many semiconductors [8], such as g- $\text{C}_3\text{N}_4/\text{MoO}_3$ [9], g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{MoO}_6$ [10], g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ [11], g- $\text{C}_3\text{N}_4/\text{C-TiO}_2$ [12], $\text{TiO}_2/\text{g-C}_3\text{N}_4/\text{RGO}$ [13], and $\text{WS}_2/\text{g-C}_3\text{N}_4$, because of the z-scheme heterostructure systems. Considering that the bandgap edge of Bi_2MoO_6 ($E_{\text{CB}} = -0.32$ eV, $E_{\text{VB}} = 2.34$ eV) is well-matched with g- C_3N_4 ($E_{\text{CB}} = -1.06$ eV, $E_{\text{VB}} = +1.52$ eV), g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{MoO}_6$ is a particularly suitable candidate for forming a z-scheme system, which can effectively promote the separation of photogenerated charge carriers to exhibit excellent photocatalytic performance [14].

Surface plasmonic resonance (SPR) provides an effective way to improve light absorption abilities and the photogenerated charge carrier separation rate [15]. Precious metal, such as Au [16] and Pd [17], is used to absorb visible light because of the strong SPR and is introduced to construct semiconductors [18]. Pt-decorated g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ was reported as an effective method to extend the photoabsorptivity of g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ to visible light because of the localized SPR of Pt [16]. However, because of the high price, inexpensive Bi alloy with an SPR effect is a good substitute. For the construction of $\text{Bi}/\text{Bi}_4\text{MoO}_9$, both the SPR of Bi metal and the defect states induced by oxygen vacancies contribute to optimizing the photoabsorption, charge separation efficiency, and generation of oxidative radical [19].

In the present work, to improve the light-harvesting ability and accelerate the separation rate of photogenerated charge carriers of Bi_2MoO_6 , novel ternary heterojunctions of

g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{MoO}_6/\text{Bi}$ (CN/BMO/Bi) hollow microspheres were fabricated through g- C_3N_4 coupling via solvothermal precipitation calcination and a reduction method to deposit Bi metal cocatalyst *in situ* on Bi_2MoO_6 microspheres. The novel ternary heterojunctions of g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{MoO}_6/\text{Bi}$ photocatalysts displayed excellent photocatalytic performance in rhodamine B (RhB) degradation under visible-light irradiation, while those of g- $\text{C}_3\text{N}_4/\text{Bi}_2\text{MoO}_6$ and $\text{Bi}_2\text{MoO}_6/\text{Bi}$ were poor. The chemical composition, morphology structures, optical properties, photocatalytic activities, and photostability were fully investigated to understand the photocatalytic mechanism.

2. Experimental

All experimental conditions are provided in the Supporting Information.

3. Results and discussion

3.1. Morphology and structure characterization

To identify the crystal phases of CN, BMO, xCN/BMO, and 0.4CN/BMO/9Bi samples, their X-ray diffraction (XRD) patterns are illustrated in Fig. 1. The XRD pattern of CN shows two intrinsic peaks at 13.2° and 27.6° , which is consistent with the standard g- C_3N_4 (JCPDS 87-1526), representing in-plane packing and interfacial stacking of g- C_3N_4 nanosheets, respectively [20]. All diffraction peaks of Bi_2MoO_6 are well indexed to orthorhombic bismuth molybdate (JCPDS 72-1524) [21]. For xCN/BMO and 0.4CN/BMO/9Bi composites, there are only diffraction peaks of Bi_2MoO_6 and no diffraction peaks of CN and metallic Bi, which are possibly caused by the low contents of g- C_3N_4 and Bi on the surface of Bi_2MoO_6 .

To investigate the composite and structure further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) spectra were analyzed. The pure Bi_2MoO_6 consists of three-dimensional hollow flowerlike microspheres, as in Figs. 2(a)–(c), with the lattice fringe (approximately 0.316 nm) on the (131) plane of Bi_2MoO_6 (JCPDS 72-1524) [22]. As shown

Fig. 1. XRD patterns of BMO, CN, xCN/BMO, and 0.4CN/BMO/9Bi composites.

Fig. 2. (a) SEM image of BMO, (b) and (c) TEM/high-resolution TEM (HRTEM) images of BMO, (d) TEM image of 0.4CN/BMO and TEM image of g- C_3N_4 in the inset, and (e) TEM image and (f) HRTEM image of 0.4CN/BMO/9Bi sample.

Fig. 3. Mapping images of 0.4CN/BMO/9Bi composite.

in Fig. 2(b), the microspheres of BMO are assembled by many irregular particles. As shown in Fig. 2(d) inset, the pure g-C₃N₄ displays thin nanosheet structures. For 0.4CN/BMO composite, the Bi₂MoO₆ nanoparticles are dispersed in the g-C₃N₄ nanosheet, and g-C₃N₄ nanosheets are attached to the surface of Bi₂MoO₆, as shown in Fig. 2(d), forming some tight bonds. Fig. 2(e) shows the TEM image of 0.4CN/BMO/9Bi, which has a similar construction to that of 0.4CN/BMO. Fig. 2(f) shows three kinds of lattice fringe: 0.324 and 0.244 nm were detected for the lattice fringes on the (012) plane and the (110) plane of Bi(JCPDS 44-1246) [23], except for the (110) plane of Bi₂MoO₆, exhibiting metallic Bi anchored on 0.4CN/BMO composite.

For further confirming the elemental compositions and distributions of 0.4CN/BMO/9Bi, the results of elemental mapping are displayed in Fig. 3. Sections A and B are the g-C₃N₄ nanosheet and BMO hollow sphere, which are the same as in Fig. 2(e). The distribution of Bi, Mo, and O, in Section A shows that many irregular particles of BMO are distributed on the

surface of g-C₃N₄, and the distribution of C and N in Section B shows that g-C₃N₄ nanosheets are dispersed on the surface of the BMO hollow sphere, which is consistent with the TEM analysis. The analysis demonstrates that the g-C₃N₄/Bi₂MoO₆/Bi composite formed successfully.

X-ray photoelectron spectroscopy (XPS) spectra were obtained to investigate further the elemental composition, the surface chemical state, and the interaction between g-C₃N₄ and Bi₂MoO₆ in the 0.4CN/BMO/9Bi composite. As outlined in Fig. 4(a), C, N, Bi, Mo, and O were clearly detected in the full survey spectrum of the 0.4CN/BMO/9Bi composite. In Fig. 4(b), the deconvoluted XPS peaks of the C 1s spectrum demonstrate two deconvoluted peaks at 284.7 and 288.2 eV, which were ascribed to C–C from graphitic or amorphous carbons adsorbed on the g-C₃N₄ sheet, and C–(N)₃ in the g-C₃N₄ lattice, respectively [24]. In Fig. 4(c), three peaks of high-resolution N 1s located at 399.35, 400.09, and 401.34 eV are identified as C–N=C, N–(C)₃, and N–H, separately [25]. For the Bi species shown in Fig. 4(d), the peaks at 159.00 and 164.32 eV of pure BMO are in agreement with Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, confirming the existence of Bi³⁺ ions [26]. The peaks of Bi 4f in 0.4CN/BMO/9Bi shifted to 158.64 and 163.96 eV, approximately 0.36 eV lower than those of BMO [27]. Similar results were found in the Mo 3d and O 1s spectra. However, there are no metallic Bi peaks in the XPS spectra, which was possibly caused by a small amount of Bi. For Mo 3d shown in Fig. 4(e), the two strong peaks at 232.28 and 235.41 eV in pure BMO are consistent with Mo 3d_{5/2} and Mo 3d_{3/2} of Mo⁶⁺, while the peaks of 0.4CN/BMO/9Bi composite were at 231.97 and 235.10 eV, which were 0.31 eV lower than those of BMO [28]. The O 1s spectrum of BMO can be divided into three peaks at 529.65, 530.17, and 531.07 eV, corresponding to Bi–O, Mo–O, and O–H bands of Bi₂MoO₆ and adsorbed H₂O on the Bi₂MoO₆ surface [29], which also are 0.29 eV higher than those of

Fig. 4. XPS spectra of BMO and 0.4CN/BMO/9Bi. (a) Survey; (b) C 1s; (c) N 1s; (d) Bi 4f; (e) Mo 3d; (f) O 1s.

0.4CN/BMO/9Bi at 530.0, 530.6, and 531.4 eV (Fig. 4(f)). These are attributed to the close integration between Bi, the Bi_2MoO_6 and g- C_3N_4 [30].

3.2. Optical properties

The optical properties play an important role in calculating the band structures of the composite. As illustrated in Fig. 5(a), the optical absorption edge of pure Bi_2MoO_6 was approximately 556 nm, which shifted to 486.7 nm for 0.4CN/BMO and 576 nm for BMO/9Bi. After BMO was coupled with g- C_3N_4 , its visible harvesting ability improved a little, while BMO/9Bi showed a significantly visible harvesting ability in the range of 250–800 nm after single modifying by Bi nanoparticles, exhibiting that Bi can enhance the light absorption. This was possibly caused by the SPR effect of Bi [31]. As previously reported, the SPR absorption of bismuth nanospheres showed camellike shapes located at 200–600 nm, which depended on the nanosize of Bi [32]. To explore the SPR absorption of Bi, the absorption spectra of Bi_2MoO_6 and $\text{Bi}_2\text{MoO}_6/\text{Bi}$ were tested. In Fig. 5(c), a slight rise appeared at approximately 350–450 nm, which could be the result of the SPR and light scattering [33]. When g- C_3N_4 and Bi were both modified on Bi_2MoO_6 , the ternary 0.4CN/BMO/9Bi composite also exhibited a further red shift of E_g , as in Fig. 5(c), and a stronger absorption ability in the visible range in Fig. 5(a). The Kubelka–Munk equation was used to identify the bandgap energies (E_g) of g- C_3N_4 and Bi_2MoO_6 ,

which were 2.64 and 2.48 eV. The potentials of E_{VB} and E_{CB} of Bi_2MoO_6 and g- C_3N_4 can be calculated according to the following empirical equations [34].

$$E_{\text{VB}} = X - E_e + 0.5E_g \quad (1)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (2)$$

where X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, and E_e is the energy of free electrons on the hydrogen scale (approximately 4.5 eV). The values of X for CN and BMO are 4.72 and 5.54 [35]. Using Eqs. (1) and (2), the E_{VB} and E_{CB} potentials of Bi_2MoO_6 were determined to be 2.28 and –0.20 eV, respectively. The E_{VB} and E_{CB} of g- C_3N_4 were defined as 1.54 and –1.10 eV, separately. As Fig. 5(b) shows, the XPS valence bands (VBs) of CN, BMO, and 0.4CN/BMO/9Bi were 2.5, 2.04, and 1.5 eV, which are relative to the Fermi level. Therefore, the values of E_f for CN and BMO were –0.96 and 0.24 eV, which demonstrated that the electrons can transfer from BMO to CN. Based on the calculated band parameters, the band structures of the CN and BMO in Fig. 5(d) can be estimated, and they have a tendency to form a z-schemed heterojunction [36].

3.3. Photocatalytic activity

The photocatalytic performances of the CN, BMO, xCN/BMO, and 0.4CN/BMO/mBi samples were measured by the RhB degradation during 60 min of visible-light irradiation, as displayed in Fig. 6(a) (where C_0 and C_t are the equilibrium concentrations

Fig. 5. (a) UV-Vis DRS spectra of CN, BMO, 0.4CN/BMO, BMO/9Bi, and 0.4CN/BMO/9Bi and the E_g of CN and BMO; (b) XPS VB spectra for Bi_2MoO_6 , CN, and 0.4CN/BMO/9Bi; (c) Absorption spectra of BMO, BMO/9Bi, and 0.4CN/BMO/9Bi; and (d) Estimated band structures of BMO and CN.

Fig. 6. (a) RhB degradation efficiency of CN, BMO, xCN/BMO, and 0.4CN/BMO/mBi samples; (b) first-order kinetic equations of all samples; (c) Cycling tests of the 0.4CN/BMO/9Bi composite toward RhB degradation.

of RhB at times 0 and t , respectively). After 60 min of irradiation, CN and BMO had relatively low photocatalytic efficiencies of approximately 20% and 10%, respectively. All the xCN/BMO composites exhibited better photocatalytic activities than pure BMO. 0.4CN/BMO emerged with the highest efficiency of 60%. When the g-C₃N₄ content was relatively low (<40%), the photocatalytic activity increased with the increasing increment of g-C₃N₄. Additionally, when the g-C₃N₄ content was relatively high (>40%), the photocatalytic activity decreased with the increasing content of g-C₃N₄, which may be because of reaching the limitation of the coupled heterojunction [37]. After Bi doping, the photocatalytic activities of 0.4CN/BMO/mBi composites further improved, among which 0.4CN/BMO/9Bi displayed the highest activity, reaching as much as a 90% degradation rate, nine times that of pure BMO. This is thought mainly to be because Bi nanoparticles distributed on BMO improve the visible-light-harvesting ability as a result of the SPR effect. The results suggest that the synergistic effect of g-C₃N₄ and metallic Bi can obviously enhance the photocatalytic activity of Bi₂MoO₆, in view of its higher separation efficiency of photogenerated charge carriers and the enhanced visible-light-harvesting ability [38].

Fig. 6(b) illustrates that the photodegradation of RhB follows the first-order kinetics. The rate constant value of k was determined by using the formula, $-\ln(C_t/C_0) = kt$ [39]. The rate constants were estimated to be 0.00157, 0.0047, 0.01112, 0.01213, 0.01206, 0.0172, 0.01015, 0.01438, 0.04006, 0.02596, and 0.00302 min⁻¹ for BMO, CN, 0.1CN/BMO, 0.2CN/BMO, 0.3CN/BMO, 0.4CN/BMO, 0.5CN/BMO, 0.4CN/BMO/6Bi, 0.4CN/BMO/9Bi, 0.4CN/BMO/12Bi, and BMO/9Bi, respectively. The rate constants' order is consistent with the photocatalytic activity result. To identify the stability and reusability of the photocatalysts, five consecutive cycles were conducted by using the 0.4CN/BMO/9Bi sample. As shown in Fig. 6(c), no evident deactivation was observed during the degradation of RhB in the five consecutive cycles. This proved that no light corrosion occurred during the reaction.

3.4. Photocatalytic mechanism

The improved photocatalytic property must be caused by the high utilization of photogenerated carrier charges. First, the transfer and separation efficiency of photoinduced elec-

tron-hole pairs in the composites were elucidated by photoluminescence (PL) measurements, as in Fig. 7. All the samples had a main emission peak at approximately 485 nm, while those of BMO and BMO/Bi can be neglected. The emission intensity of 0.4CN/BMO was obviously weaker than that of CN, which further demonstrated that 0.4CN/BMO can significantly hinder the recombination of photogenerated electron-hole pairs [33]. Compared to that of 0.4CN/BMO, the emission intensity of 0.4CN/BMO/9Bi exhibited no decrease, but an increase occurred at approximately 450 nm with a blue shift to higher energy, which could be because metallic Bi can promote higher recombination between photogenerated electrons in the conduction band (CB) of BMO and photoexcited holes in the VB of CN on the interface [40]. The recombined electrons mainly come from the emission peak at approximately 450 nm. The results not only indicate that the low recombination efficiency of photogenerated charge carriers in 0.4CN/BMO/9Bi is caused by the crucial roles of the z-scheme heterostructure between g-C₃N₄ and Bi₂MoO₆ in facilitating the separation of the photoinduced carriers, but they also demonstrate that Bi has the ability to transfer electrons and holes to recombine.

To understand further the photocatalytic mechanism, the effects of different active species scavengers on the photocatalytic degradation in 0.4CN/BMO/9Bi samples were studied. The main active species, including $\bullet\text{O}_2^-$, $\bullet\text{OH}$, e^- , and h^+ , were trapped via the addition of 1,4-benzoquinone (BQ), isopropanol

Fig. 7. PL spectra for CN, BMO, 0.4CN/BMO, BMO/9Bi, and 0.4CN/BMO/9Bi composite.

Fig. 8. Trapping experiments with 0.4CN/BMO/9Bi composite.

(IPA), silver nitrate (AgNO_3), and disodium ethylenediamine tetraacetic acid (EDTA-2Na), respectively [41]. As shown in Fig. 8, the photocatalytic activity of 0.4CN/BMO/9Bi had a decreasing trend because of the addition of different active species scavengers. The catalytic performance of 0.4CN/BMO/9Bi was significantly reduced after the addition of BQ and EDTA-2Na. However, after the introduction of IPA and AgNO_3 , the photocatalytic activity slightly decreased. The above analysis indicates that $\bullet\text{O}_2^-$ is the most active species in the reaction, and h^+ is the main active species in the photocatalytic reaction, followed by $\bullet\text{OH}$ and e^- in decomposing RhB dye [42].

Electron spin resonance (ESR) was adopted to explore the

active groups in the degradation process further. TEMP is the radical scavenger of e^- and is commonly used to detect the number of free electrons in ESR. When 0.4CN/BMO/9Bi was exposed under light irradiation, no signal of TEMP was revealed, as shown in Fig. 9(a), which means that light irradiation results in a large number of electrons that convert TEMP into TEMPO.

It has been proposed that photogenerated electrons usually participate in a two-electron reduction process with the assistance of active molecular oxygen (Eqs. (3) and (4)) [43].

The signals of h^+ , $\bullet\text{O}_2^-$, and $\bullet\text{OH}$ were checked in 0.4CN/BMO/9Bi by ESR, as in Figs. 9(b)–(d), to verify the transfer route of photogenerated electrons. No signal of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ can be seen under a dark condition, while both of the ESR peaks can be observed in 0.4CN/BMO/9Bi under visible illumination. The results suggest that $\bullet\text{OH}$, and $\bullet\text{O}_2^-$ are produced in the catalytic system.

Based on the above results, a possible photocatalytic mechanism is illustrated in Fig. 10. A Z-scheme system consists of an oxidation photocatalyst with low VB position and a reduction photocatalyst with high CB position [44]. When exposed to visible light, the electrons on the CB of the oxidation photocatalyst transfer and then recombine with the holes on the VB of the reduction photocatalyst, leaving more electrons in the reduction photocatalyst and more holes in the oxidation photocatalyst to participate in reduction and oxidation reactions [45]. The band structures of CN and BMO are shown in Fig.

Fig. 9. ESR spectra record of (a) e^- , (b) h^+ , (c) $\bullet\text{O}_2^-$, and (d) $\bullet\text{OH}$ at ambient temperature with 0.4CN/BMO/9Bi photocatalyst.

Fig. 10. Schematic photocatalytic mechanism of 0.4CN/BMO/9Bi composite during RhB degradation.

5(d). CN has a high CB position with a high reduction ability, and BMO has a low VB position with a strong oxidation ability. E_f of CN at -0.96 eV is more negative than that of BMO at 0.24 eV, which demonstrates that the electrons can transfer from BMO to CN in a z-scheme structure. Meanwhile, $\bullet\text{O}_2^-$ are the main active species, and BMO cannot produce $\bullet\text{O}_2^-$, because of the more negative CB position of BMO than E_0 ($\text{O}_2/\bullet\text{O}_2^- = -0.046$ eV) [46]. The accumulated holes on the VB of BMO can react with OH^- to generate $\bullet\text{OH}$ (E_0 ($\text{OH}^-/\bullet\text{OH}$) = 2.4 eV) [47]. Moreover, owing to the lower VB potentials, the enriched holes on the VB of g- C_3N_4 cannot react with H_2O or OH^- to produce $\bullet\text{OH}$, which can directly degrade RhB by oxidation [48]. The analysis further demonstrates that the photocatalytic mechanism is a z-scheme heterojunction.

When irradiated under visible light, the electrons are transferred from the CN to the BMO. When the Fermi level reaches equilibrium, an internal electric field at the interface of the composite formed to hinder the migration of the photoelectrons from the CB of CN to the CB of BMO [49]. With the help of the SPR effect of Bi, the light absorption properties of BMO significantly improved in the visible region. In addition, Bi has fine conductivity and can serve as an electron trap to promote separation of electrons and holes. Electrons are easily transferred from the CB of the BMO to the Bi. Meanwhile, the PL analysis also demonstrates that Bi makes the electrons of BMO and the holes of CN recombine.

As shown in Fig. 10, the electrons transfer by an indirect Z-scheme heterojunction from the CB of BMO to Bi to the VB of CN for recombination. The electrons staying on the CB of CN can reduce oxygen molecules absorbed on the surface of hybrids to produce O_2 radicals that directly oxidize RhB or indirectly oxidize via transforming to $\bullet\text{OH}$ radicals by a two-electron oxidation pathway. The holes located on the VB of BMO oxidize OH^- to $\bullet\text{OH}$. The analysis supports the indirect photocatalytic mechanism.

4. Conclusions

An indirect Z-scheme photocatalytic mechanism of Bi-decorated plasmonic g- C_3N_4 /Bi $_2$ MoO $_6$ was successfully developed. The introduced g- C_3N_4 greatly facilitated the separa-

tion of electron-hole pairs by forming an interfacial heterojunction. The metallic Bi distributed on the surface of BMO enhances the optical absorption ability caused by the SPR effect and acts as a mediator to promote the recombination of photo-generated electron-hole pairs between the CB of BMO and the VB of CN. The optimal 0.4CN/BMO/9Bi composite displayed the highest photocatalytic efficiency toward RhB degradation under visible-light irradiation. As a consequence, the excellent photocatalytic performance is ascribed to the synergetic effect of heterojunction and SPR-promoted Bi, providing new insights into the design of efficient photocatalytic materials for environmental protection.

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Graphical Abstract

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Novel indirect Z-scheme g-C₃N₄/Bi₂MoO₆/Bi hollow microsphere heterojunctions with SPR-promoted visible absorption and highly enhanced photocatalytic performance

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This work constructs a novel ternary heterojunction of g-C₃N₄/Bi₂MoO₆/Bi hollow microsphere with the synergetic effect of heterojunction structures and the surface plasmon resonance (SPR) effect of Bi, resulting in an enhanced photocatalytic performance.

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新型间接Z字结型g-C₃N₄/Bi₂MoO₆/Bi空心微球等离子共振增强光吸收和光催化性能

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摘要: 半导体光催化技术是目前最有前景的绿色化学技术, 可通过利用太阳光降解污染物或制氢。作为有潜力的半导体催化剂, 钼酸铋具有合适的带隙(2.58 eV)。但是, 由于低的量子产量, 钼酸铋的光催化性能并不理想。为了提高钼酸铋的光催化性能, 研究者多考虑采取构造异质结的方式。石墨相氮化碳(g-C₃N₄)能带位置合适, 与多种光催化半导体能带匹配, 是构造异质结的常用选择。因此, 本文选用g-C₃N₄与钼酸铋复合, 构造异质结结构。为了进一步提高光催化性能, 多采用负载贵金属(Pt, Au和Pd)作为助催化剂, 利用贵金属特有的等离子共振效应, 增加光吸收, 促进载流子分离, 但贵金属价格昂贵。Bi金属单质价格便宜, 具备等效的等离子共振效应, 是理想的贵金属替代物。钼酸铋可以采取原位还原的方式还原出Bi单质, 构造更紧密的界面结构, 更有利于载流子传输。Bi的等离子共振效应可以有效提高材料的光吸收能力和光生载流子分离率。

本文采用溶剂热和原位还原方法成功合成了一种新型三元异质结结构g-C₃N₄/Bi₂MoO₆/Bi (CN/BMO/Bi)空心微球。结果显示, 三元异质结结构的最佳配比为0.4CN/BMO/9Bi, 该样品表现出最好的光催化降解罗丹明B效率, 是纯钼酸铋的9倍。通过计算DRS和XPS的价带数据, 0.4CN/BMO/9Bi是一种Z字型异质结。牺牲试剂实验也提供了Z字型异质结的有力证据, 测试显示超氧自由基·O²⁻ (在-0.33 eV)是光催化降解的主要基团。但是, 钼酸铋的导带位置低于-0.33 eV, g-C₃N₄的导带高于-0.33 eV, 因此g-C₃N₄的导带是唯一的反应位点, 从而证明了光生载流子的转移是通过Z字型异质结结构实现的。TEM图显示金属Bi分散在钼酸铋表面。DRS和PL图分析表明金属Bi增加了材料的光吸收能力, 同时扮演了中介介质的角色, 促进钼酸铋导带的电子和g-C₃N₄价带的空穴快速复合。因此, g-C₃N₄/Bi₂MoO₆/Bi的优异光催化性能主要归功于Z字型异质结和Bi金属的等离子共振吸收效应, 提高了材料的光吸收能力和光生载流子分离率。

关键词: 钼酸铋; 石墨相氮化碳; 金属铋; Z字型异质结; 等离子共振效应; 罗丹明B; 可见光

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