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ABSTRACT

Bi_2WO_6 is a typical visible-light-responsive semiconductor photocatalyst with a layered structure. However, the relatively large bandgap (2.6–2.8 eV) and quick recombination of photo-generated carriers result in its low quantum efficiency. In this paper, Bi-nanospheres-modified flower-like Bi_2WO_6 was successfully prepared by solvothermal treatment of Bi_2WO_6 powders in $\text{Bi}(\text{NO}_3)_3$ solution using ethylene glycol as reductant. The photoreactivity of this photocatalyst was evaluated by the oxidation of NO in a continuous-flow reactor under irradiation by a visible LED lamp ($\lambda > 400$ nm). It was found that both Bi nanospheres and flower-like Bi_2WO_6 precursor exhibit very poor photocatalytic activity with NO removal rates of only 7.7% and 8.6%, respectively. The photoreactivity of Bi/ Bi_2WO_6 was found to steadily increase from 12.3% to 53.1% with increase in the amount of Bi nanospheres from 0 to 10 wt%. However, with further increase in the loading amount of Bi nanospheres, the photoreactivity of Bi/ Bi_2WO_6 hybridized photocatalyst begins to decrease, possibly due to the light filtering by the Bi nanospheres. The enhanced visible photoreactivity of Bi/ Bi_2WO_6 towards NO abatement was attributed to surface plasmon resonance driven interfacial charge separation. The excellent stability of Bi/ Bi_2WO_6 hybridized photocatalyst towards NO oxidation demonstrates its potential for applications such as air purification.

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1. Introduction

In this era of rapid economic development with an ever-increasing use of fossil fuels, environmental pollution is fast

becoming one of the most challenging issues faced by mankind. One of the hazardous gaseous pollutants generated by fossil fuel combustion is NO, which not only causes acid rains but also affects the human respiratory system [1–7]. In recent times,

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semiconductor photocatalysis has attracted a lot of attention since it provides sustainable solutions to the problems surrounding environmental pollution [7–13] and energy crisis [14–17]. TiO_2 has been considered as the most important semiconductor photocatalyst owing to its strong oxidative power, cost effectiveness, excellent biocompatibility and long-term stability against photochemical corrosion [18,19]. However, TiO_2 can only be excited by UV light (bandgap of 3.2 eV), which only accounts for 3%–5% of the energy in the solar spectrum [20,21]. Therefore, exploration of a novel semiconductor photocatalyst which can harvest visible or IR light is both imperative and extremely challenging [13].

Recently, considerable attention has been given to Bi-based semiconductor photocatalysts such as BiOBr [22], BiOCl [12], $\text{Bi}_2\text{O}_2\text{CO}_3$ [23], Bi_4MoO_9 [11], BiPO_4 [7] and Bi_2WO_6 [24]. One of these materials, Bi_2WO_6 , has a bandgap of 2.6–2.8 eV and consists of perovskite-like slabs of WO_6 and $(\text{BiO}_2)^{2+}$ layers [25–28]. This unique layered structure of Bi_2WO_6 makes it an important visible-light-responsive photocatalyst. Despite this attractive property, the visible photoreactivity of Bi_2WO_6 is not high enough for practical applications [24,29]. According to literature, the apparent quantum efficiency of Bi_2WO_6 at 420 nm is less than 5% [30]. Up to now, many strategies have been used to improve the photocatalytic activity of Bi_2WO_6 such as controlling the morphology [26,29], surface modification [27,29,31], ion doping [32], introducing defects [33] and forming heterojunctions [34]. For example, it has been reported that flower-like Bi_2WO_6 microspheres exhibit improved photocatalytic activity compared to plate-like Bi_2WO_6 [35].

Very recently, surface plasmon resonance (SPR) effect of noble metals such as gold [36] and silver [37] has been used to enhance the visible photocatalytic activity of semiconductor photocatalysts [38]. Huge local electric field enhancement was observed at the surface of gold nanoparticles (NPs) due to the interaction with the electric and magnetic field of light [36]. Similarly, the excitation of electron-hole (e^-h^+) pairs was boosted in TiO_2 with the enhanced near-field of silver NPs [37], improving the photocatalytic activity of TiO_2 .

In this study, SPR effect was used to stimulate the excitation of photo-generated e^-h^+ pairs in Bi_2WO_6 by deposition of Bi nanospheres on the surface of flower-like Bi_2WO_6 . The photocatalytic activity of Bi_2WO_6 microspheres was evaluated by the oxidation of NO in ppb level under irradiation by an LED lamp ($\lambda > 400$ nm). We systematically studied the effect of Bi loading amount on the properties and performance of Bi_2WO_6 microspheres. Although SPR effect of Bi has been used to improve the

visible photoreactivity of some semiconductor photocatalysts such as BiOBr [22,39], Bi_4MoO_9 [11], and BiPO_4 [7], the present work is the first report on the SPR effect of Bi on Bi_2WO_6 photocatalyst, to the best of our knowledge.

2. Experimental

2.1. Synthesis

Microspheric Bi_2WO_6 precursor was synthesized according to the procedure detailed in Ref. [40]. Typically, 2.0 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 2.0 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and 0.1 mmol of sodium dodecyl sulfate were dissolved in 30 ml of water, which was first sonicated for 10 min and then stirred for 20 min to form a uniform solution. The resulting solution was transferred to a 100-ml Teflon-lined stainless steel autoclave and heated in an oven at 180 °C for 24 h. After cooling down to room temperature, the light-yellow precipitates were collected by centrifugation, washed several times with ethanol and *n*-hexane, and dried in an oven at 80 °C for 4 h.

Bi-nanospheres-modified Bi_2WO_6 microspheres ($\text{Bi}/\text{Bi}_2\text{WO}_6$) were prepared by reduction of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ using ethylene glycol as reductant. Following this, 0.42 g of the prepared Bi_2WO_6 was added to 80 ml of ethylene glycol solution, in which 0.2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ had been dissolved. After ultrasonication for 10 min and stirring for 2 h, the suspensions were transferred to Teflon-lined stainless-steel autoclave and heated at 180 °C for 10 h. The obtained grey precipitates thus were separated by centrifugation and washed with distilled water. The resulting cake was dried at 80 °C for 4 h.

By varying the amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, a series of $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalysts with different mass ratios of Bi to Bi_2WO_6 were obtained (Table 1). For simplicity, the prepared samples are named as S_x, where x% represents the calculated mass ratio of Bi to Bi_2WO_6 . For example, sample S10 refers to the $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst with a Bi to Bi_2WO_6 mass ratio of 10%. Note that sample S0 was also prepared in an ethylene glycol medium, but without the addition of any $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ during the treatment of Bi_2WO_6 precursor.

For comparison, pure Bi sample (denoted as S_{Bi}) was also prepared under identical conditions except for the addition of Bi_2WO_6 precursor.

2.2. Characterization

The crystalline structure of the samples was investigated by

Table 1
Physical properties of the photocatalysts based on the nitrogen sorption.

Sample	Starting materials		Nitrogen sorption		
	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (mmol)	Bi_2WO_6 (g)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore size (nm)
Precursor	—	—	45.1	0.09	8.3
S0	0	0.42	43.0	0.12	10.9
S1	0.02	0.42	47.3	0.12	10.0
S2	0.04	0.42	48.9	0.11	9.3
S5	0.1	0.42	44.1	0.11	9.9
S10	0.2	0.42	40.9	0.10	9.7
S20	0.4	0.42	42.2	0.09	8.4

X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microscopic morphology of the catalyst was observed by transmission electron microscopy (TEM, Tecnai G20) and field emission scanning electron microscopy (SEM, Hitachi, Japan), with the acceleration voltages set to 200 and 20 kV for the TEM and SEM, respectively. UV-Vis diffuse reflectance spectrum (DRS) was measured using a spectrophotometer (Shimadzu UV-2550, Japan) using BaSO_4 as the reference. Photoluminescence (PL) spectra were obtained on a fluorescence spectrophotometer (F-7000, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was performed using a Multilab 2000 XPS system. A nitrogen-adsorption instrument (ASAP 2020, USA) was used to obtain information regarding the surface area and pore structure of the photocatalyst.

2.3. Detection of radicals

Electron spin resonance (ESR) spectroscopy (JES FA200 spectrometer) was used to record free radicals by mixing the photocatalysts in a 40 mmol/L 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) solution tank (methanol dispersion for $\text{DMPO}\cdot\text{OOH}/\text{O}_2\cdot$ and aqueous dispersion for $\text{DMPO}\cdot\text{OH}$), illuminated with a visible LED lamp ($\lambda = 420$ nm).

2.4. Photoelectrochemical measurements

Photocurrent and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode configuration on an electrochemical station (CHI760e, China), using $\text{Bi}_2\text{WO}_6/\text{ITO}$ as the working electrode, Pt plate as the counter electrode, and Ag/AgCl as the reference electrode, in a aqueous solution (0.4 mol L^{-1}) of Na_2SO_4 (as the electrolyte). During the photocurrent measurements, an LED lamp which emitted mainly at 420 nm (3 W, Shenzhen LAMPLIC) was used as the light source to excite the $\text{Bi}_2\text{WO}_6/\text{ITO}$ electrode.

2.5. Visible photocatalytic oxidation of NO

The photocatalytic activity of the system was evaluated by oxidation of NO at room temperature. The reaction was carried out in a 4.5-L stainless steel rectangular reactor which was covered by quartz glass in the upper layer. A visible LED lamp (150 W) with a cut-off filter ($\lambda > 400$ nm) was used as the light source. The photocatalyst powders (0.3 g) were deposited on the surface of a watch glass (diameter of about 11.5 cm). The NO gas was supplied from a compressed gas cylinder having 50 ppm of NO (diluted with N_2) in line with the standards recommended by the U.S. National Institute of Standards and Technology. An air stream produced by a zero-air generator (Advanced Pollution Instrumentation, A Teledyne Technologies Co., Model 701) was used for diluting the initial NO concentration to approximately 600 ppb. When the gas system reached adsorption-desorption balance, the lamp was turned on. A chemiluminescence NO_x analyzer (Advanced Pollution Instrumentation, Teledyne Technologies, Model T200) was used for monitoring the concentrations of NO continuously at a gas-flow rate of $1.0 \text{ L}\cdot\text{min}^{-1}$.

3. Results and discussion

3.1. Phase structure and morphology

XRD was used to identify the phase structure and crystallinity of the photocatalyst. It can be seen from Fig. 1 that the diffraction peaks of Bi_2WO_6 precursor are in good agreement with those of the pure orthorhombic Bi_2WO_6 (JCPDS card no. 39-0256), where the diffraction peaks appearing at 28.3° , 32.8° , 47.1° and 55.8° correspond to the (131), (002), (202) and (133) planes, respectively [26,29]. After further solvothermal treatment of Bi_2WO_6 precursor in $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ /ethylene glycol solution, a sharp diffraction peak appears at $2\theta = 27.2^\circ$ due to the formation of metallic Bi (JCPDS card no. 44-1246) [41,42]. This indicates that Bi/ Bi_2WO_6 hybridized photocatalyst has been successfully prepared. Note that the diffraction peaks for metallic Bi cannot be observed for samples S0, S1 and S2, possibly due to the smaller particle sizes of Bi nanoparticles.

Fig. 2 compares the SEM and TEM images of Bi_2WO_6 precursor (Figs. 2(a)–(c)) and S0 sample (Figs. 2(d)–(f)). It can be seen that both samples have a similar flower-like morphology, and the diameter of the flower-like Bi_2WO_6 assembly from nanosheets is about $2 \mu\text{m}$. This indicates that ethylene glycol has little effect on the Bi_2WO_6 precursor. Similar to sample S0, sample S10 maintains the flower-like morphology. However, several smooth nanospheres with diameters 200–500 nm were also observed on the surface of sample S10. These are most likely to be Bi nanospheres (see discussion below) [42]. Therefore, we can conclude that Bi nanospheres are produced as a result of the reduction of $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, and not of the Bi_2WO_6 precursor itself.

Sample S10 was further characterized by elemental mapping using energy dispersive X-ray spectroscopy (EDX). From Fig. 3, it can be clearly seen that the density of Bi is higher at the place indicated by the arrow, while the densities of elements W and O in this area are lower than average. This indicates that the nanospheres are composed of metallic Bi. The molar ratio of Bi to W on the surface of flower-like Bi_2WO_6 (area A) is 1.61, while the ratio increases to 6.27 (by a factor of 3.90) on the surface of nanosphere (area B) as shown in Fig. 4. This sharp increase in the concentration of Bi from area A to B in sample

Fig. 1. XRD patterns of the photocatalysts, together with the expected diffraction peaks for Bi_2WO_6 and Bi.

Fig. 2. SEM and TEM images of Bi_2WO_6 precursor (a–c), S0 (d–f) and S10 (g–i) photocatalysts. Arrows indicating the presence of Bi nanospheres.

S10 further confirms the composition of the nanospheres.

3.2. UV-visible absorption and nitrogen sorption

The photocatalytic activity of the photocatalyst depends on the efficiency of the following sequential processes [43]: (1) separation of the photo-generated carriers after light absorption, (2) migration of photo-generated electrons and holes from the bulk to the surface of the photocatalyst, and (3) capture of

Fig. 3. SEM image (a) and corresponding maps for Bi (b), W (c) and O (d) elements of S10 sample. Arrows indicating the place for the deposition of Bi nanospheres.

electrons and holes to initiate redox reaction with adsorbed substrates. Therefore, light-harvesting ability is of great importance to the photoreactivity of the photocatalyst [44]. Here, UV-visible diffuse reflectance spectrum was used to evaluate the light-harvesting ability of the photocatalyst. From Fig. 5, it can be seen that the optical absorption edge of the yellowish Bi_2WO_6 (sample S0) is about 436 nm corresponding to a bandgap of 2.84 eV, consistent with earlier reports [26,30].

After the deposition of Bi nanospheres, we can clearly see

Fig. 4. Comparison of the EDX spectra of S10 sample between selected area A (a and b) and area B (c and d).

Fig. 5. UV-visible diffuse reflectance spectra of the photocatalysts.

that the light-harvesting ability of Bi_2WO_6 microspheres are conspicuously enhanced, which can be attributed to a charge-transfer transition between the Bi spheres and Bi_2WO_6 microspheres. A distinct SPR peak centered at 533 nm can be observed for pure Bi nanospheres. When compared to the pristine Bi_2WO_6 microspheres, the $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst exhibits an additional broad absorption peak around 530 nm, which is the characteristic SPR peak of Bi nanospheres. The SPR effect of Bi nanospheres can boost the excitation of e^-h^+ pairs of Bi_2WO_6 microspheres under visible-light irradiation, improving the photoreactivity of Bi_2WO_6 .

Fig. 6 compares the nitrogen adsorption-desorption isotherms of pristine Bi_2WO_6 microspheres (sample S0) and Bi-nanospheres modified Bi_2WO_6 microspheres (sample S10). It can be seen that the isotherms of both photocatalysts are type IV with one hysteresis loop at a relative pressure range of 0.5–1.0. This indicates the presence of mesopores (type H3), corresponding to slit-shaped pores that are generally associated with plate-like particles, consistent with their sheet-like morphology [45,46]. The isotherms of samples S0 and S10 almost coincide, indicating their similar structures. Table 1 summarizes the BET surface areas and pore structures of the photocatalysts. It can be seen that all samples have comparable BET surface area (40–50 m^2/g), pore volume (0.09–0.12 cm^3/g) and average pore size diameter (8–10 nm). Therefore, BET surface area and pore structure are not critical factors affecting the photoreactivity of Bi_2WO_6 microspheres.

Fig. 6. Comparison of the nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves (inset) between pristine Bi_2WO_6 (S0) and $\text{Bi}/\text{Bi}_2\text{WO}_6$ (S10) samples.

3.3. XPS analysis

XPS was used to characterize the elemental composition and the chemical state of Bi_2WO_6 precursor, pristine Bi_2WO_6 (S0) and $\text{Bi}/\text{Bi}_2\text{WO}_6$ (S10). From the XPS survey spectra, it can be seen that all samples contain Bi, W, O and small amounts of C. The C contained in the samples arises from the residual organic solvent or from the hydrocarbons present in the XPS instrument itself [47].

The high resolution XPS spectra in Bi 4f, W 4f and O 1s regions are shown in Fig. 7(B), Fig. 7(C) and Fig. 7(D), respectively. It can be seen that Bi_2WO_6 precursor and sample S0 have similar peak positions in Bi 4f, W 4f and O 1s regions which further confirm that ethylene glycol has little effect on Bi_2WO_6 , consistent with the XRD (Fig. 1) and SEM/TEM (Fig. 2) characterization results. The two peaks with binding energies of 159.4 and 164.7 eV correspond to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively (Fig. 7(B)) [26,48,49]. The peaks with binding energies of 35.7 and 37.8 eV originate from W 4f_{7/2} and W 4f_{5/2}, respectively (Fig. 7(C)) [26,50]. The peak with binding energy of 530.5 eV can be attributed to O 1s (Fig. 7(D)) [26,48]. When compared with those of Bi_2WO_6 microspheres (sample S0), the binding energies for all the Bi 4f, W 4f and O 1s peaks of sample S10 reduced by 0.3–0.5 eV. The reduction in binding energy implies a corresponding increase of electron cloud density. This indicates that electrons have a tendency to be transferred from Bi nanospheres to Bi_2WO_6 due to the built-in Mott-Schottky effects at the interface between Bi metal and Bi_2WO_6 [42].

According to literature, the XPS characteristic peaks for the Bi-Bi bonds of elemental Bi are centered at 156.8 and 162.1 eV [3]. However, in the present study, the XPS peaks for Bi-Bi bond were not found in the $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybrid (sample S10), which is possibly due to the oxidization of the surface of Bi nanospheres.

3.4. Photocatalytic oxidation of NO

Fig. 8(A) compares the photocatalytic oxidation curves of NO in presence of the different photocatalysts under visible irradiation. It can be seen that pure Bi nanospheres, Bi_2WO_6 precursor and pristine Bi_2WO_6 (sample S0) exhibit poor photocatalytic activity with NO removal rate of 7.7%, 8.6% and 12.3%, respectively. This is due to the quick recombination of photo-generated carriers [28]. Upon modification with Bi metal, the photocatalytic activity of Bi_2WO_6 microspheres improves steadily, with the highest NO removal rate (53.1%) achieved for sample S10. However, with further increase in the loading amount of Bi nanospheres to 20 wt%, the photoreactivity of $\text{Bi}/\text{Bi}_2\text{WO}_6$ begins to decrease. The NO removal rate for S20 reduces to 44.5%.

To further determine the surface interaction between Bi nanospheres and Bi_2WO_6 microspheres, we measured the photoreactivity of the physically mixed $\text{Bi}/\text{Bi}_2\text{WO}_6$ sample (Smix) which contains 10 wt% Bi nanospheres. It was found that the NO removal rate of Smix is only 16.9%, much smaller than that of sample S10 (53.1%). This indicates the strong interaction between Bi nanospheres and Bi_2WO_6 microspheres exists only in the $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst.

Fig. 7. XPS survey spectra (A) and high resolution XPS spectra in Bi 4f (B), W 4f (C) and O 1s (D) regions for Bi_2WO_6 precursor, S0 and S10 samples.

Not only the photocatalytic activity, but also the stability of the photocatalyst is of great importance from the viewpoint of practical applications [51]. Therefore, the catalytic activity of the S10 photocatalyst was tested during repeated use, and the experimental results are shown in Fig. 8(B). It can be seen that the NO removal rate only slightly decreases after cycling the catalyst 5 times, indicating excellent stability of the Bi/ Bi_2WO_6 hybridized photocatalyst.

3.5. Photo(electro)chemical measurements

To account for the enhanced photocatalytic activity of Bi/ Bi_2WO_6 hybridized photocatalyst, we performed PL, photocurrent measurements, and EIS of the photocatalyst.

PL spectrum is commonly used to analyze the recombination rate of photo-generated carriers of the photocatalyst [49].

Fig. 9(A) shows the PL spectra of pristine Bi_2WO_6 (sample S0) and Bi_2WO_6 modified with different amounts of Bi metal (samples S10 and S20). It can be seen that pure Bi_2WO_6 sample shows the highest PL peak intensity, indicating that the recombination rate of photo-generated carriers in pure Bi_2WO_6 is the highest, and the deposition of Bi nanospheres can retard the recombination process. Therefore, it is not hard to understand the positive effect of Bi nanospheres on the photoreactivity of Bi_2WO_6 (Fig. 8).

Photocurrent is a measure of the ability of the photocatalyst to generate and transfer of photo-generated charge carriers after excitation [52]. From Fig. 9(B), it can be seen that the photocurrent in Bi/ Bi_2WO_6 hybridized photocatalyst (samples S10 and S20) is much higher than that of pristine Bi_2WO_6 photocatalyst (sample S0).

Fig. 9(C) compares the EIS spectra of the photocatalysts. It

Fig. 8. Visible photocatalytic oxidation curves of NO in the presence of different photocatalysts (A) and the photocatalytic stability test for Bi/ Bi_2WO_6 (S10 sample).

Fig. 9. Comparison of the photoluminescence spectra (A), photocurrents (B) and EIS spectra (C) between Bi_2WO_6 (S0) and Bi modified Bi_2WO_6 photocatalysts (S10 and S20).

can be seen that: (1) all samples have only one arc/semicircle on the EIS plane display, which indicates that only the surface-charge-transfer step is involved in the photocatalytic reaction, and (2) sample S10 possesses the smallest arc radius on the EIS Nyquist plot. The smaller the radius of the arc, the more effective is the separation of the photogenerated electron-hole pair and faster the interfacial charge transfer to the electron donor/electron acceptor [53]. Therefore, the loading of Bi metal can stimulate the generation and transfer of photo-generated electrons and holes, enhancing the photocatalytic activity.

3.6. Radical trapping experiment

Reactive oxygen species (ROSs) such as hydroxyl radicals ($\cdot\text{OH}$) and super oxygen radicals ($\cdot\text{O}_2^-$) are important radicals responsible for the oxidation of NO [3,54]. Therefore, radical trapping experiment was also performed in the present study, and the experimental results are shown in Fig. 10. It can be seen that hardly any $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals can be detected from pristine Bi_2WO_6 (sample S0) or Bi/ Bi_2WO_6 hybridized photocatalyst (sample S10) in the dark. However, after irradiation for 10 min, signals originating from $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals were observed for pristine Bi_2WO_6 and Bi/ Bi_2WO_6 hybridized photocatalyst, and the intensities of the signals for $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals in Bi/ Bi_2WO_6 suspensions were much stronger than in pristine Bi_2WO_6 . These results suggest that more electrons and holes present in the Bi/ Bi_2WO_6 hybridized photocatalyst produce ROSs (instead of undergoing quick recombination) when compared to pristine Bi_2WO_6 , consistent with the observed

trend in photocatalytic activity (Fig. 8).

Since all the photocatalysts have similar BET surface areas and pore structures (Table 1), the enhanced photocatalytic activity of Bi_2WO_6 microspheres can be attributed to the introduction of Bi nanospheres. The conduction band (CB) position of Bi_2WO_6 flowers was reported to be -0.32 eV (vs. NHE) [29], which is higher than the flatband position of Bi nanospheres (-0.17 eV) [3,55]. Therefore, the photo-generated electrons prefer to migrate from the CB of Bi_2WO_6 microspheres to Bi nanospheres, which are then captured by adsorbed oxygen to form superoxide radicals ($E^{\circ}_{\text{O}_2/\cdot\text{O}_2^-} = -0.046$ V vs. NHE) [56]. As the bandgap of pristine Bi_2WO_6 sample is 2.84 eV (Fig. 5), the valence band (VB) potential of Bi_2WO_6 microspheres can be calculated as $+2.52$ eV. This value of the VB potential is high enough to oxidize H_2O to produce hydroxyl radicals ($E^{\circ}_{\text{H}_2\text{O}/\cdot\text{OH}} = 2.3$ V vs. NHE) [57]. Both $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals are important ROSs that are responsible for the oxidation of NO. However, the concentrations of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals over pristine Bi_2WO_6 microspheres are very low (Fig. 10), mainly due to the quick recombination of carriers. After modification of Bi_2WO_6 microspheres with Bi nanospheres, the photo-generated carriers can transfer from the CB of Bi_2WO_6 microspheres to Bi nanospheres, retarding the recombination. In addition, the near-field enhancement produced on Bi nanospheres by the SPR effect can significantly enhance energy of electrons, which then consequently boosts the separation and migration of photo-generated carriers [25]. Then, highly concentrated ROSs such as $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals are produced in Bi/ Bi_2WO_6 to oxidize NO (Figs. 10 and 11).

Fig. 10. ESR signals of the DMPO- $\cdot\text{OH}$ (A) and DMPO- $\cdot\text{O}_2^-$ (B) adducts as a function of irradiation time in the dark and under visible irradiation.

Fig. 11. Proposed mechanism on the enhanced photoreactivity of Bi_2WO_6 towards NO oxidation after loaded with Bi nanospheres.

However, the photoreactivity of $\text{Bi}/\text{Bi}_2\text{WO}_6$ begins to decrease when the concentration of Bi is high, which may be due to the light-filtering effect of Bi nanospheres, as excessive Bi can block the visible-light irradiation on Bi_2WO_6 microspheres (Fig. 5) [3].

4. Conclusions

$\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst was successfully fabricated by solvothermal treatment of Bi_2WO_6 in $\text{Bi}(\text{NO}_3)_3$ solution using ethylene glycol as reductant. The photocatalytic NO removal rate of Bi_2WO_6 increased from 12.3% to 53.1% after loading 10 wt% of Bi nanospheres under visible LED lamp irradiation. This sharp increase in visible photocatalytic activity of $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst was attributed to the SPR

effect of Bi nanospheres. This SPR effect not only facilitates the transfer of photo-generated electrons, but also boosts the separation and migration of photo-generated carriers, enhancing the production of ROSs such as $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals that are responsible for the oxidation of NO. $\text{Bi}/\text{Bi}_2\text{WO}_6$ hybridized photocatalyst also exhibits excellent photocatalytic stability, making it a potential candidate to be used in air purification systems.

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Graphical Abstract

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SPR effect of bismuth enhanced visible photoreactivity of Bi_2WO_6 for NO abatement

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In-situ formed Bi nanospheres stimulates the production of ROSs such as $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals to oxidize NO under visible irradiation of flower-like Bi_2WO_6 microspheres due to the SPR effect of metal Bi.

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利用Bi的SPR效应增强Bi₂WO₆的可见光催化NO氧化去除性能

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摘要: 作为大气中的典型污染物之一, 化石燃料燃烧产生的NO不仅会引起酸雨, 还会影响人体呼吸系统. 半导体光催化技术可以利用太阳能和空气中的氧气来分解环境污染物, 因而得到了国内外学者的广泛关注. 作为最具代表性的半导体光催化材料, TiO₂虽然具有较强的氧化能力和优异的生物相容性, 但是其禁带宽度较大(3.2 eV)而只能被紫外光激发, 无法充

分利用太阳能。因此,开发新型可见光响应的半导体催化材料具有重要意义。 Bi_2WO_6 是一种独特的具有层状结构半导体光催化材料,因其具有可见光响应性能而受到了广泛关注;但是可见光响应范围窄(禁带宽度2.6–2.8 eV)以及其较快的光生载流子复合,导致 Bi_2WO_6 其光催化效率不高,迫切需要采取有效措施对 Bi_2WO_6 进行改性。

贵金属(诸如金和银)纳米粒子可见光区的表面等离子体效应(SPR),可以用来增强半导体材料的可见光催化性能。但是,贵金属的价格昂贵,难以满足实际需求。近来的研究发现,非贵金属Bi同样具有类似的表面等离子体效应。因此,本文选用以乙二醇为还原剂,通过低温还原 $\text{Bi}(\text{NO}_3)_3$ 的方式,在花球 Bi_2WO_6 表面,成功制备了沉积了Bi纳米球复合光催化材料。本文用NO的可见光催化氧化来评价Bi/ Bi_2WO_6 复合材料的光催化性能的可见光催化性能,所使用的光源为可见光LED灯($\lambda > 400 \text{ nm}$)。结果发现:(1)单一组分的Bi金属和 Bi_2WO_6 前驱体花球均表现出非常差的光催化活性,NO去除率分别仅为7.7%和8.6%;(2)随着Bi纳米球的负载量从0增加至10 wt%,复合材料Bi/ Bi_2WO_6 的NO去除效率从12.3%稳定增加至53.1%至20 wt%时开始降低。这可能是由于Bi纳米球阻碍了 Bi_2WO_6 对光的吸收;(3)改性后的Bi/ Bi_2WO_6 具有良好的可见光催化稳定性,循环使用在五次后其活性变化不大。

光催化机理研究结果显示,Bi/ Bi_2WO_6 增强的可见光NO去除性能归因于Bi纳米球的SPR效应。在可见光照射下,Bi纳米球的SPR效应产生的电场可以显著促进 Bi_2WO_6 的光生载流子分离效率。同时,Bi纳米球可以快速转移 Bi_2WO_6 导带上的光生电子,生成超氧游离基($\cdot\text{O}_2^-$),从而抑制了光生电子和空穴的复合。 Bi_2WO_6 表面的空穴可以被表面吸附水捕获,产生羟基自由基($\cdot\text{OH}$)。在活性氧物种 $\cdot\text{OH}$ 和 $\cdot\text{O}_2^-$ 的不断进攻作用下,NO最终被氧化。本文为宽禁带半导体的非贵金属敏化,提升其可见光催化性能解决环境问题提供了新思路。

关键词: 铋; Bi_2WO_6 ; 表面等离子体; 光催化; 氧化氮

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