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Article

Preparation, characterization and photocatalytic performance of heterostructured AgCl/Bi₂WO₆ microspheres

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ABSTRACT

Bi₂WO₆ microspheres with a diameter of 1.5–2 μm were prepared by a hydrothermal method, and then coated with different contents of AgCl to form heterostructured AgCl/Bi₂WO₆ microspheres. The prepared Bi₂WO₆ and AgCl/Bi₂WO₆ photocatalysts were characterized by X-ray diffraction, N₂ physical adsorption, scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and ultraviolet-visible diffuse reflectance spectroscopy. The photocatalytic activity of the catalysts was evaluated by photocatalytic degradation of rhodamine B under ultraviolet and visible light irradiation. Results showed that the deposition of AgCl had no obvious effect on the light absorption and surface properties of Bi₂WO₆. However, the heterostructured AgCl/Bi₂WO₆ photocatalysts exhibited considerably higher activity than the pure AgCl and Bi₂WO₆ catalysts. With the optimal AgCl content of 20 wt%, the photocatalytic activity of the heterostructured AgCl/Bi₂WO₆ catalyst was increased under both ultraviolet and visible light compared with that of Bi₂WO₆. The main reason for the enhanced photocatalytic activity is attributed to the formation of AgCl/Bi₂WO₆ heterostructures effectively suppressing the recombination of photo-generated electrons and holes.

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1. Introduction

Semiconductor photocatalysts can rapidly degrade persistent organic pollutants in wastewater. Moreover, the photocatalytic process does not produce secondary pollution, and is relatively simple. Therefore, semiconductor photocatalysts show great potential for use in environmental management [1–6]. Bismuth tungstate (Bi₂WO₆) is an n-type semiconductor with a small band gap of 2.7 eV that can absorb visible light and exhibit certain visible-light activity [7]. The activity of Bi₂WO₆ is

closely related to its crystal properties and morphology.

Various Bi₂WO₆ nanomaterials with different shapes and morphologies have been reported, such as nanofilms [8], nanoflowers [9], nanobelts [10], microspheres [11], and microrods [12]. Zhu et al. [13] found that the photocatalytic activity and photoelectric conversion efficiency of porous Bi₂WO₆ films were far superior to those of solid Bi₂WO₆ films. Meanwhile, Zhang et al. [14] reported that under visible light irradiation, 3D Bi₂WO₆ microspheres assembled on nanofilms showed much higher activity toward degradation of rhodamine B (RhB)

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than Bi_2WO_6 nanofilms.

Microsphere photocatalysts assembled from units like nanoparticles, nanorods, or nanolayers possess advantages such as large surface area, easy separation, rich interfaces and good stability [15–17]. These microspheres not only inherit the characteristics of the structural units in them, but also have the synergistic effects from the interactions between the units, which benefit the adsorption of reactants and light harvesting. The construction of heterostructure is an effective strategy to improve photocatalytic performance. For example, Li et al. [18] found that the formation of an anatase/rutile heterojunction on a TiO_2 surface and CdS/MoS_2 heterojunction on a CdS surface can greatly increase hydrogen production. Additionally, a $\text{BiOI}/\text{Bi}_5\text{O}_7\text{I}$ heterojunction in BiOI [19] and WO_3/ZnO heterojunction in ZnO [20] obviously improved the photocatalytic performance of the main photocatalyst. We also found that the formation of well-defined junctions between Ag_2O and Ag_2CO_3 effectively facilitated charge transfer between Ag_2O and Ag_2CO_3 and suppressed the recombination of photogenerated electrons and holes, resulting in extremely high activity and stability toward photocatalytic degradation of pollutants. As a result, the activity and stability of structure of Ag_2CO_3 and Ag_2O were 73 and 20 times, respectively, higher than those of Ag_2CO_3 alone [21].

In this paper, Bi_2WO_6 microspheres are first prepared by a hydrothermal route. Then, different contents of AgCl are deposited on the Bi_2WO_6 microspheres to produce a series of $\text{AgCl}/\text{Bi}_2\text{WO}_6$ composite microspheres. The influence of AgCl content on the texture and photocatalytic activity of Bi_2WO_6 in the composites is then investigated.

2. Experimental

2.1. Catalyst synthesis

Bi_2WO_6 microspheres were prepared by a hydrothermal route. Under vigorous stirring, 0.005 mol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (AR grade, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and 0.01 mol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (AR grade, Sinopharm Chemical Reagent Co. Ltd) were separately dissolved in deionized (DI) water (40 mL). The Na_2WO_4 solution was added to the $\text{Bi}(\text{NO}_3)_3$ solution. Then 0.01 g of hexadecyltrimethylammonium bromide (AR grade, Sinopharm Chemical Reagent Co. Ltd) was added to the above solution, which was subsequently stirred for 60 min. The suspension was transferred into a Teflon-lined stainless steel autoclave with a volume of 100 mL. The autoclave was sealed and maintained at 160 °C for 12 h under self-generated pressure and then allowed to cool to room temperature naturally. The product was filtered, washed several times with absolute alcohol and DI water, and finally dried at 60 °C for 5 h.

$\text{AgCl}/\text{Bi}_2\text{WO}_6$ composite microspheres were prepared by a precipitation method. Stoichiometric amounts of NaCl and AgNO_3 were separately dissolved in DI water (20 mL). The Bi_2WO_6 microspheres were dispersed in the NaCl solution by ultrasonic irradiation for 10 min. The AgNO_3 solution was then added dropwise to the stirred Bi_2WO_6 suspension. After stir-

ring for a further 2 h, the produced composite was filtered, washed with DI water and absolute alcohol, and finally dried at 60 °C for 10 h. The final content of AgCl in the $\text{AgCl}/\text{Bi}_2\text{WO}_6$ microspheres was 5 wt%, 10 wt%, 20 wt% or 30 wt%.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Bruker D8 Advance, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm) at a scan rate of 0.05 °/s. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained from N_2 adsorption-desorption isotherms measured at liquid N_2 temperature using an automatic analyzer (Micromeritics, ASAP 2020). The samples were degassed for 2 h under vacuum at 120 °C prior to adsorption measurements. The microstructures of the samples were determined by a scanning electron microscope (SEM, XL30, Philips, the Netherlands). Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) measurements were performed on an electron microscope (Tecnai 20, FEG) coupled with an energy-dispersive X-ray spectrometer (Oxford Instruments). Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Nicolet 470 USA) using KBr disk. Ultraviolet-visible (UV-Vis) diffuse reflectance spectra (DRS) were measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

2.3. Photocatalytic activity

The photocatalytic activities of the samples were determined by measuring their ability to degrade RhB in aqueous solution. Each photocatalyst (50 mg) was suspended in an aqueous solution of RhB (10 mg/L, 100 mL). Before light irradiation, each suspension was stirred in the dark for 40 min to attain physical adsorption-desorption equilibrium between dye and photocatalyst. In visible-light activity tests, a 300-W iodine tungsten lamp was used as the light source, and in UV tests, a 7-W lamp with a wavelength of 254 nm was substituted for the visible lamp. Each suspension was magnetically stirred during the degradation process, and the reaction temperature was maintained at 20 °C by circulation of water. After fixed intervals of illumination, an aliquot of each suspension was taken out and centrifuged. The upper clear solution was analyzed by a spectrophotometer (UV-2550). The degradation percentage $D = (C_0 - C)/C_0 \times 100\%$, where C_0 is the initial dye concentration and C is the final dye concentration.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows the XRD patterns of pure Bi_2WO_6 and $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples with different AgCl contents. Pure Bi_2WO_6 displays obvious diffraction peaks at $2\theta = 28.3^\circ$, 32.9° , 47.2° , 55.9° and 58.6° that can be indexed to the (113), (200), (220), (313) and (226) planes, respectively, of orthorhombic structure.

Fig. 1. XRD patterns of the prepared Bi_2WO_6 and $\text{Ag}/\text{Bi}_2\text{WO}_6$ samples.

bic-phase Bi_2WO_6 (JCPDS 73-2020). The lattice constants calculated for Bi_2WO_6 are $a = 0.5457$ nm, $b = 0.5436$ nm, and $c = 1.6427$ nm. For $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples with >5 wt% AgCl , new and weak diffraction peaks appeared at $2\theta = 27.9^\circ$, 32.3° , and 46.3° that corresponded to the (111), (200), and (220) planes of AgCl (JCPDS 31-1238). The intensity of these new peaks increased with AgCl content.

We used the Scherrer equation, $D = 0.89\lambda/(\beta\cos\theta)$, where β is the full width at half-maximum of the diffraction peak, λ is the wavelength of incident light (0.154 nm), and θ is the diffraction angle, to calculate the average crystallite size of the samples (Table 1). The average crystallite size of Bi_2WO_6 was around 16 nm, and the deposition of AgCl did not affect the

Table 1

Average grain size and specific surface area of Bi_2WO_6 samples with different AgCl contents.

Sample	D (nm)	S_{BET} (m^2/g)
Bi_2WO_6	16.50	22.59
5 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$	15.06	26.59
10 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$	16.81	24.53
20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$	15.95	21.03
30 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$	16.61	16.83

crystalline properties of Bi_2WO_6 . Therefore, the average crystallite size of $\text{AgCl}/\text{Bi}_2\text{WO}_6$ is similar to that of Bi_2WO_6 .

3.2. BET surface area analysis

The BET surface areas of the samples are listed in Table 1. The specific surface area of the $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples depends on AgCl content. Deposition of 5 wt%–10 wt% AgCl slightly increased the surface area of the catalysts. Further increasing the content of AgCl to 20 wt%–30 wt% decreased the specific surface area of the samples. A possible reason for this could be that a small amount of AgCl is well dispersed over the Bi_2WO_6 crystallites, which increases the BET surface area. However, when a large amount of AgCl is deposited on the Bi_2WO_6 crystallites, AgCl could aggregate into big particles, which decreases the surface area of the sample. A higher surface area should promote the adsorption of dye and increase the photocatalytic activity of the samples.

3.3. SEM analysis

Figure 2 displays typical SEM images of the samples. Fig. 2(a) shows that the fabricated Bi_2WO_6 is composed of flower-like microspheres with a diameter of around 1.5–2 μm . The

Fig. 2. SEM images of Bi_2WO_6 (a), and $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples with an AgCl content of 5 wt% (b), 10 wt% (c), 20 wt% (d), and 30 wt% (e). (f) Enlarged image of 30 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$.

Fig. 3. (a) TEM image of Bi_2WO_6 , low- (b) and high-resolution (c) TEM images of 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$.

microspheres are composed of many small nanoplates. The surface of the nanoplates is smooth without defects or holes. The deposition of AgCl did not change the overall morphology of the Bi_2WO_6 microspheres. However, we can observe that numerous AgCl nanoparticles were deposited over the smooth surface of the Bi_2WO_6 nanoplates. Fig. 2(f) is an enlarged SEM image of the 30 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ sample. It reveals that although $\text{AgCl}/\text{Bi}_2\text{WO}_6$ retains the microspherical morphology, there are a large number of AgCl nanoparticles deposited on the Bi_2WO_6 nanoplates.

3.4. TEM and EDX analysis

Figure 3 depicts low- and high-resolution TEM images of Bi_2WO_6 and 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples. The Bi_2WO_6 particles are nanoplates with square morphology. The particle size determined from the TEM image is 15–25 nm, which is consistent with the XRD results. The surface of each Bi_2WO_6 nanoplate is very smooth. The 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ sample consists of numerous spherical particles with a size of 2–5 nm deposited over the surface of the Bi_2WO_6 nanoplates. The high-resolution TEM image of the 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ sample (Fig. 3(c))

clearly shows the characteristic lattice fringes of AgCl and Bi_2WO_6 , with a lattice spacing of AgCl of 0.32 nm, which corresponds to the (111) plane, and lattice spacing of Bi_2WO_6 of 0.31 nm, which corresponds to the (113) plane.

Selected-area elemental analysis of a spherical particle from the 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ sample was also carried out by EDX, as shown in Fig. 4. The particle contains O, W, Bi, Ag, and Cl, with contents of 11.34 wt%, 21.58 wt%, 48.00 wt%, 14.85 wt%, and 4.23 wt%, respectively. These values almost correspond to the composition of 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$.

3.5. FT-IR analysis

Figure 5 displays the FT-IR spectra of all of the samples. All spectra contain a peak at 3433 cm^{-1} that is assigned to the stretching and bending vibrations of surface $-\text{OH}$ groups on the catalyst particles. The peak at 716 cm^{-1} is attributed to the stretching vibration of the $\text{W}-\text{O}-\text{W}$ bond. The peaks at both 1110 and 440 cm^{-1} are assigned to the stretching vibration of the $\text{Bi}-\text{O}$ bond, while that at 578 cm^{-1} is attributed to the stretching vibration of the $\text{W}-\text{O}$ bond. These peaks indicate the high crystallinity of Bi_2WO_6 . The deposition of AgCl does not

Fig. 4. Survey EDX obtained for the 20 wt% $\text{AgCl}/\text{Bi}_2\text{WO}_6$ sample.

Fig. 5. FT-IR spectra of the Bi_2WO_6 and $\text{AgCl}/\text{Bi}_2\text{WO}_6$ samples.

Fig. 6. UV-Vis absorption spectra of the AgCl, Bi₂WO₆ and AgCl/Bi₂WO₆ samples.

have a marked effect on the FT-IR spectrum of the Bi₂WO₆ microspheres.

3.6. UV-Vis DRS results

UV-Vis DRS of the Bi₂WO₆, AgCl and AgCl/Bi₂WO₆ samples are shown in Fig. 6. Bi₂WO₆ strongly absorbs light from 200 to 360 nm, with weak absorption in the visible range. The absorption edge of Bi₂WO₆ is around 450 nm, while that of AgCl is about 490 nm, indicating that it has the ability to absorb visible light. With respect to Bi₂WO₆, the absorption edge of the AgCl/Bi₂WO₆ samples shifts to longer wavelength. The band-gap energy (E_g) for the catalysts was determined from the equation $E_g = 1240/\lambda_g$ (eV) [22], where λ_g is the absorption edge, which was obtained from the intercept between the tangent of the absorption curve and abscissa. The calculated E_g for the samples are given in Table 2. E_g of Bi₂WO₆ and AgCl were 2.84 and 2.07 eV, respectively. The presence of AgCl did not change the band gap of Bi₂WO₆ because AgCl was only deposited on the surface of Bi₂WO₆, so it does not affect the crystal structure and energy level of Bi₂WO₆.

3.7. Photocatalytic activity

The photocatalytic activities of the samples were evaluated by measuring their ability to decompose RhB in aqueous solution under UV- or visible-light irradiation. Fig. 7 shows the change in concentration of RhB under UV-light irradiation in solutions containing different catalysts. Both AgCl and Bi₂WO₆

Fig. 7. Photocatalytic performance of AgCl, Bi₂WO₆ and AgCl/Bi₂WO₆ samples under UV light.

show low activity toward photocatalytic degradation of RhB. The deposition of 5 wt% AgCl on Bi₂WO₆ obviously increased its photocatalytic activity. As the content of AgCl was increased from 5 wt% to 20 wt%, the degradation rate of RhB gradually increased. When the content of AgCl was 20 wt%, the highest activity was obtained, and about 62% of RhB was degraded during 15 min of light irradiation. After 75 min of irradiation, the degradation percentages of RhB over AgCl, Bi₂WO₆, 5 wt% AgCl/Bi₂WO₆, 10 wt% AgCl/Bi₂WO₆, 20 wt% AgCl/Bi₂WO₆ and 30 wt% AgCl/Bi₂WO₆ were 48%, 60%, 63%, 82%, 98% and 92%, respectively. The stability of 20 wt% AgCl/Bi₂WO₆ was examined using a recycling test, which showed that the degradation percentage decreased as the number of cycles increased (data not shown).

Figure 8 illustrates the photocatalytic performance of the samples under visible-light irradiation. Under visible-light irradiation for 150 min, the degradation percentages of RhB over

Fig. 8. Photocatalytic performance of AgCl, Bi₂WO₆ and AgCl/Bi₂WO₆ samples under visible-light irradiation.

Table 2

Band gap energies (E_g) of the AgCl, Bi₂WO₆ and AgCl/Bi₂WO₆ samples.

Sample	E_g /eV
AgCl	2.07
Bi ₂ WO ₆	2.84
5 wt% AgCl/Bi ₂ WO ₆	2.80
10 wt% AgCl/Bi ₂ WO ₆	2.78
20 wt% AgCl/Bi ₂ WO ₆	2.82
30 wt% AgCl/Bi ₂ WO ₆	2.81

Table 3

Absolute electronegativity (X), band gap (E_g), and conduction and valence band potentials (E_{CB} and E_{VB} , respectively) of AgCl and Bi_2WO_6 .

Sample	X/eV	E_g/eV	E_{VB}/eV	E_{CB}/eV
AgCl	6.08	2.07	2.61	0.54
Bi_2WO_6	6.09	2.84	3.01	0.17

pure AgCl and Bi_2WO_6 were 52% and 47%, respectively. However, the deposition of AgCl markedly increased the visible-light photocatalytic activity of the catalysts. When the content of AgCl was 20 wt%, 99% of RB was degraded after 150 min of light irradiation.

3.8. Enhancement mechanism

The mechanism for the enhanced activity of AgCl/ Bi_2WO_6 compared with those of AgCl and Bi_2WO_6 is now considered. The XRD and UV-Vis DRS analyses revealed that the deposition of AgCl had no marked effect on the surface area, crystal structure and light absorption of Bi_2WO_6 . Therefore, the formation of an AgCl/ Bi_2WO_6 heterojunction could be the main reason for the enhanced photocatalytic performance. When two semiconductors with suitable E_g are combined, a heterojunction can be produced. A potential difference is generated on the two sides of the heterojunction because of the different potential levels of the two conductors. Such an electric potential difference can promote the separation of photogenerated electrons (e^-) and holes (h^+), improving the photocatalytic activity of the semiconductor [23].

The positions of the valence band (VB) and conduction band (CB) for the samples were calculated by the electronegativity principle [24]. According to the empirical formulae $E_{VB} = X - E_e + 0.5 E_g$ and $E_{CB} = E_{VB} - E_g$ (here, E_{VB} , X , and E_e , are the energies of the VB edge potential, the absolute electronegativity, and free electrons on the hydrogen scale (4.5 eV), respectively) we calculated the potentials of the VB and CB of the samples; the results are shown in Table 3. The CB position of AgCl (0.54 eV) is more anodic than that of Bi_2WO_6 (0.17 eV). Therefore, an excited electron in the CB of Bi_2WO_6 can transfer to the CB of AgCl. As a result, the recombination of photogenerated e^- and h^+ over Bi_2WO_6 could be suppressed. Therefore, more e^- and h^+ could be available to produce active free radicals like $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$ because e^- can be captured by the surface-adsorbed O_2 to produce $\text{O}_2^{\cdot-}$, and the $-\text{OH}$ groups can capture photogenerated h^+ to form reactive $\cdot\text{OH}$ radicals. According to the literature [25, 26], in photodegradation of RhB over Bi_2WO_6 , $\cdot\text{OH}$ radical oxidation is not the dominant photooxidation pathway, $\text{O}_2^{\cdot-}$ are the main radicals to decompose RhB. The proposed mechanism of the AgCl/ Bi_2WO_6 photocatalyst heterojunction is outlined in Fig. 9.

4. Conclusions

Bi_2WO_6 microspheres with a diameter of 1.5–2 μm were fabricated using a hydrothermal method and then coated with AgCl. The effects of deposition of different contents of AgCl on the photocatalytic performance of the Bi_2WO_6 microspheres

Fig. 9. Mechanism for the enhanced photocatalytic activity of the AgCl/ Bi_2WO_6 heterostructure.

were investigated. Although the deposition of AgCl had no obvious effect on the crystal structure, surface area, and light absorption of Bi_2WO_6 , the UV- and visible-light photocatalytic activity of the AgCl/ Bi_2WO_6 samples was substantially promoted. The main reason for this activity increase was attributed to the formation of an AgCl/ Bi_2WO_6 heterojunction that facilitates the separation of photogenerated e^- and h^+ .

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Graphical Abstract

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The formation of AgCl/Bi₂WO₆ heterostructures could effectively separate its photo-generated electron (e⁻) and hole (h⁺) pairs, then increasing its photocatalytic activity.

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异质结构AgCl/Bi₂WO₆微米球制备、表征及其光催化性能

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摘要: 首先利用水热法制备了由纳米片组装的粒径为1.5–2 μm的Bi₂WO₆微球, 然后在微球表面沉积了不同含量的AgCl (5 wt%, 10 wt%, 20 wt%, 30 wt%), 制备了异质结构AgCl/Bi₂WO₆微球光催化剂. 利用X射线粉末衍射、扫描电镜、透射电镜、红外光谱、紫外-可见漫反射吸收等手段对所制的光催化剂进行表征, 并以紫外光和可见光分别为光源, 罗丹明B为降解对象测试了其光催化活性, 考察复合不同含量的AgCl对Bi₂WO₆光催化剂的性能影响. 结果表明, 沉积AgCl对Bi₂WO₆的晶体结构、表面性能和光吸收性能没有产生明显影响, 但大幅度提高了Bi₂WO₆的紫外和可见光催化活性. 当复合20 wt%AgCl时, AgCl/Bi₂WO₆光催化活性最佳, 紫外光下比纯Bi₂WO₆提高了2.2倍, 可见光下提高了1倍. 这主要是由于形成的AgCl/Bi₂WO₆异质结能有效抑制光生电子和空穴的复合, 从而提了其光催化性能.

关键词: 纳米微球; 氯化银; 钨酸铋; 异质结构; 光催化; 罗丹明B

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