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Fabrication of a monoclinic/hexagonal junction in WO₃ and its enhanced photocatalytic degradation of rhodamine B

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ABSTRACT

A series of WO₃ samples with different crystalline phases were prepared by the thermal decomposition method from ammonium tungstate hydrate. X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy, and N₂ adsorption-desorption were used to characterize the crystalline phase, morphology, particle size, chemical composition, and surface area of the WO₃ samples. The formation of hexagonal (h-WO₃) and monoclinic (m-WO₃) crystal structures of WO₃ at different temperatures or different times was confirmed by XRD. m-WO₃ is formed at 600 °C, while m-WO₃ starts to transform into h-WO₃ at 800 °C. However, h-WO₃, which forms at 800 °C, may transform into m-WO₃ by increasing the calcination temperature to 1000 °C. SEM results indicate that m-WO₃ particles exhibit a bulky shape with heavy aggregates, while h-WO₃ particles exhibit a rod-like shape. Moreover, m-WO₃ crystals are sporadically patched on the surface of the h-WO₃ rod-like particles, resulting in the exposure of both m-WO₃ and h-WO₃ on the surface. It is observed that the monoclinic phase (m-WO₃)/hexagonal phase (h-WO₃) junction was fabricated by tuning the calcination temperature and calcination time. The relative ratios between m-WO₃ and h-WO₃ in the phase junction can readily be tailored by control of the calcination time. The photocatalytic activities of WO₃ with different crystalline phases were evaluated by the photocatalytic degradation of rhodamine B as a model pollutant. A higher photocatalytic activity was observed in the WO₃ sample with the m-WO₃/h-WO₃ junction as compared with the sample with only m-WO₃. The improvement of photocatalytic activity can be attributed to the reduction of the electron-hole recombination rate owing to the formation of the phase junction, whose presence has been confirmed by HRTEM and photoluminescence spectra.

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1. Introduction

Photocatalysis has been intensively investigated as it has

potential for exploitation in environmental remediation (pollutant degradation) and clean energy production (H₂ production, CO₂ reduction) [1–3]. The metal oxide semiconductors, such as

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TiO₂, tungsten oxide (WO₃), Bi₂O₃, and ZnO, have been shown to be efficient as photocatalysts in different processes [4–6]. Among these metal oxides, WO₃ is of great interest because of its attractive properties such as small energy band gap (from 2.4 to 2.8 eV), stable physicochemical properties, non-toxicity, and resistance to photocorrosion [7].

However, a high charge recombination rate of photo-induced electron-hole pairs is a critical drawback in the development of WO₃ as an efficient photocatalyst [8]. Several methods have been developed to improve the photocatalytic activity of WO₃. Zhang et al. [9] synthesized monoclinic WO₃ nanoplates by a one-step template-free hydrothermal route through a topochemical conversion process of H₂WO₄ nanoplates. The as-prepared m-WO₃ nanoplate exhibited a superior photocatalytic activity for the degradation of rhodamine B (RhB) under visible light irradiation. Lin et al. [10] modified WO₃ with an ionic liquid [Bmim]I through a facile impregnation method. The presence of a surface-bound imidazolium ring was demonstrated to effectively suppress the recombination of photoexcited electron-hole pairs.

Additionally, it has been shown that proper junctions formed in semiconductor-based photocatalysts could lead to enhanced activity. Oh et al. [11] prepared WO₃/MWCNT-TiO₂ composites using a modified sol-gel method. It is found that the WO₃/MWCNT-TiO₂ photocatalyst showed efficient charge separation during UV irradiation. Our previous work [12] indicated that the phase junction formed between the anatase and rutile TiO₂ could greatly enhance photoexcited charge migration between the two phases that, in turn, enhanced the charge separation. Recently, Jaroniec et al. [13] proposed a new “sur-

face heterojunction” concept to explain the difference in the photocatalytic activity of anatase TiO₂ with co-exposed (001) and (101) facets. The phase junction enhanced charge separation and thus improved photocatalytic efficiency, and has been demonstrated for a variety of materials. α -Ga₂O₃/ β -Ga₂O₃ [14], α -Bi₂O₃/ β -Bi₂O₃ [15], and WO₃/WO₃·H₂O [16] phase junction structures have been successfully synthesized and exhibit high photocatalytic activity for H₂ production and RhB degradation. Therefore, the formation of the phase junction becomes an efficient way to produce semiconductor metal oxides exhibiting high photocatalytic activity.

WO₃ exists mainly in four polymorphs, which are monoclinic, triclinic, orthorhombic, and tetragonal, along with a hexagonal phase [17]. Among these crystalline phases, the monoclinic phase has been reported as the most stable phase [18]. The monoclinic (m-WO₃) and hexagonal (h-WO₃) phases of WO₃ have attracted the most attention because the m-WO₃ is an attractive candidate for photocatalytic applications and h-WO₃ exhibits an open-tunnel structure and rich intercalation chemistry [19]. We are interested in determining if we can fabricate the phase junction formed between m-WO₃ and h-WO₃ by a simple method, as well as understanding if the phase junction in WO₃ enhances its photocatalytic activity. However, the relationship between the phase junction in WO₃ and the photocatalytic activity is not well understood.

Generally, a material with different crystalline phases possesses a different band gap and flat band. Therefore, a phase junction could be built between different crystal phases given the two phases are in close contact, which will lead to efficient electron-hole separation and higher catalytic reactivity [20].

Jing Zhang (born in 1980) is currently a Professor in College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University. Supervised by Prof. Can Li, Jing Zhang obtained her PhD degree in physical chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2007. During the PhD, she has been investigating the effect of surface crystalline phase of TiO₂ on its photocatalytic activity and firstly presented that the phase junction in TiO₂ which is beneficial for improving the efficiency of the charge separation of photoexcited electrons and holes in photocatalysis. Rational design and fabrication of phase junctions is therefore demonstrated to be an attractive strategy for the development of efficient photocatalysts. The corresponding results were published in *J. Phys. Chem. B* with 410 citations and *Angew. Chem. Int. Ed.* with 525 citations, and also highlighted by *Chemical & Engineering News (C&E NEWS)*. With the accomplishments of above research work, she was awarded as the Second Prize of National Natural Science Award (ranking the 3rd).

In 2007, she joined Liaoning Shihua University, where her research interest includes UV Raman spectroscopy, control and tunes the surface crystalline phase of metal oxides, fabrication of homojunction and heterojunction materials in photocatalysis. She extended postdoctoral research on biomass conversion (developing the effective catalyst for the conversion of fructose in water phase and delineating the critical molecular level reactions involved in the catalytic breakdown of glucose, fructose to produce feedstock chemicals) at Northwestern University. Jing Zhang was promoted as full professor in 2014 and was selected as distinguished professor of Liaoning Province in 2015. After that, she is launching project of constructing Key Laboratory of Advanced Clean Energy Materials Chemistry enrolling 8–10 young teaching staff upon the university policy support. She has published more than 30 peer reviewed journal articles in *Angew. Chem. Int. Ed.*, *Appl. Catal. B*, *ACS Catal.*, *J. Phys. Chem. C*, etc., with over 1500 citations and one book chapter, and delivered over 20 presentations in scientific meetings and congresses. In recognition of her achievements in phase junction in photocatalysis and biomass conversion research, **she was granted as a Young Scientists of the 15th International Congress on Catalysis and the Catalysis Rising Star Award in 2012 presented by The Catalysis Society of China.**

According to Ref. [21], the valence band position and conduction band position of h-WO₃ are lower than those of m-WO₃, which implies that a phase junction could be established between m-WO₃ and h-WO₃.

Therefore, this study attempts to fabricate a phase junction in a WO₃ photocatalyst, and then to investigate the effect of the phase junction in the WO₃ photocatalyst on its photocatalytic activity. The thermal decomposition method was used to fabricate a phase junction in WO₃ by tuning the calcination temperature and the calcination time, and the phase junction (m-WO₃/h-WO₃) formed between hexagonal and monoclinic WO₃ demonstrated an enhanced photocatalytic activity for RhB degradation.

2. Experimental

2.1. Sample preparation

Ammonium tungstate hydrate (H₄₀N₁₀O₄₁W₁₂·xH₂O, APT) was of analytical grade and used without further purification. For the thermal decomposition method, the white APT powder was calcined at 600–1000 °C for 4 h in a static atmosphere of air, and then was naturally cooled to room temperature. The obtained samples were labeled as WO₃-*T*, where *T* represents the calcination temperature (°C) used to obtain the samples. APT powders were also calcined at 800 °C for different times from 8 to 30 h and were denoted as WO₃-*t*, where *t* represents calcination time (*h*).

2.2. Sample characterization

Thermogravimetry and differential thermal analysis (TG-DTA) was performed using a TG/DTA-6300 thermal analyzer at the rate of 10 °C/min under air atmosphere (60 mL/min). The structure characterization was carried out by powder X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with a Cu K_α radiation source. The morphologies of the samples were investigated using scanning electron microscopy (SEM, Quanta 200 F) and high-resolution transmission electron microscopy (HETRM, JEOL, JEM-2100). X-ray photoelectron spectra (XPS) were obtained using a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer. The BET surface area was determined by N₂ adsorption-desorption isotherms using a NOVA 4200e surface area and pore size analyzer from Quantachrome. A Hitachi F-4500 spectrophotofluorometer was used to record the photoluminescence spectra (PL) using an excitation wavelength of 350 nm.

2.3. Photocatalytic reaction

A set of photocatalytic degradation experiments were performed with the following procedure. Photodegradation of RhB was carried out in a 100-mL Pyrex reactor filled with de-ionized water (60 mL) containing RhB (10 mg/L) and the WO₃ sample. The suspension was stirred for 30 min in the dark to obtain adsorption-desorption equilibrium of the dye before illumination. After irradiation with a 125-W Hg lamp (λ = 365

nm, Shanghai Feilipu Yaming Lighting Co.), a 3-mL aliquot was taken every 30 min and immediately centrifuged. The RhB concentration in the clear solution was analyzed by optical characteristic absorption (22PC spectrophotometer, Shanghai Lengguang Technology Co., Ltd.) at a wavelength of 553 nm for a RhB solution. The blank experiments without a mercury lamp and without catalysts in the RhB solution under the same conditions are also compared. The blank study shows that mere photolysis can be ignored for RhB.

3. Results and discussion

Fig. 1 shows TG-DTA curves of APT in a dynamic atmosphere of air. The TG curve shows five main mass-loss steps with a total of 11.8% loss of the original mass of APT. Four mass-loss steps totaling 10.6% (2.2% + 2.1% + 1.2% + 5.1% = 10.6%) and four main endothermic peaks at 84, 130, 208, and 275 °C could be observed in the DTA curve, which are attributed to the loss of absorbed water, crystal water, structural water, and loss of ammonia. In addition, two exothermic peaks are observed at 355 and 440 °C. The peak at 440 °C can be attributed to crystallization of the amorphous phase of WO₃ [22]. In this study, calcination temperatures higher than 600 °C were chosen to prepare WO₃, which facilitated a high degree of crystallinity.

Fig. 2 shows the XRD patterns of APT calcined at different temperatures. When the WO₃ sample was calcined at 600 °C, diffraction peaks at 2θ = 23.1°, 23.6°, 24.3°, and 34.1° were observed, which represent the indices of the (002), (020), (200), and (202) planes of m-WO₃ (PDF #43-1035), respectively. These results indicate that the WO₃-600 °C sample is in the monoclinic phase. Moreover, the XRD peaks are strong and sharp, indicating that the WO₃-600 °C sample exhibits high crystallinity. The XRD pattern of the WO₃-700 °C sample is almost the same as that for the WO₃-600 °C sample. On heating to 800 °C, three weak peaks appear at 2θ = 14.0°, 28.2°, and 36.6°, which arise from h-WO₃ (PDF #33-1387), in addition to the typical peaks of the monoclinic phase. This implies the co-existence of hexagonal and monoclinic phases in the WO₃-800 °C sample, while m-WO₃ is the main constituent in the crystalline phase.

Fig. 1. TG-DTA curves of APT in a dynamic atmosphere of air.

Fig. 2. XRD patterns of APT calcined at different temperatures.

Martínez-de la Cruz et al. [23] prepared m-WO₃ particles by the precipitation method using APT as the starting material and PEG as the template and steric stabilizer. It was also found that a long calcination time promoted the formation of the hexagonal structure of WO₃ in addition to m-WO₃. The XRD peaks of h-WO₃ hardly changed for the WO₃ sample calcined at temperatures up to 900 °C. However, the intensities of the typical peaks of h-WO₃ were decreased for the WO₃-1000 °C sample (Fig. 2(b)).

The morphologies and particle sizes of the WO₃-*T* samples were investigated by SEM (Fig. 3). As shown in Fig. 3(a) and (b), the WO₃-600 °C sample consists of dispersed large and fine particles with irregular polyhedral shapes. Bulky components with dimensions up to 10 μm were observed, and the sizes of the fine particles were approximately 200–500 nm for the WO₃-600 °C sample. It is obvious that the rod-like components (circled by a dashed line in Fig. 3), assigned to the hexagonal phase, appear in the WO₃-800 °C sample (Fig. 3(c) and (d)). This shows the co-existence of the monoclinic and hexagonal phases in the WO₃-800 °C sample, which is in agreement with the results from XRD (Fig. 2). Moreover, it can be seen that m-WO₃ and h-WO₃ particles are in close contact, and m-WO₃ particles are located on the surface of h-WO₃ particles with a rod-like shape.

Crucial information on the spatial distribution of the h-WO₃ and m-WO₃ particles was further provided by HRTEM (Fig. 4). The HRTEM image of WO₃-800 °C shows an example of the intimate contact between m-WO₃ and h-WO₃ phases. As shown in Fig. 4, the small particles and rod-like particles exhibit fringes with a lattice spacing of 3.779 and 6.361 Å, respectively, which can be indexed into the (020) atomic plane of m-WO₃ and (100) atomic plane of h-WO₃, respectively. HRTEM and SEM results (Fig. 3) reveal that the phase junction can be built between the m-WO₃ particles and h-WO₃ nanorods.

From Fig. 3, no apparent changes in the morphology of the m-WO₃ particles were observed in the WO₃-1000 °C sample, as

Fig. 3. SEM images of WO₃-600 °C (a, b), WO₃-800 °C (c, d), and WO₃-1000 °C (e, f).

Fig. 4. HRTEM image of WO₃-800 °C.

compared with the WO_3 -800 °C sample. However, the samples obtained after calcination at 1000 °C showed a minor tendency to form large agglomerates, as shown in Fig. 3(e). Moreover, it should be noted that it is not easy to observe rod-like particles in the WO_3 -1000 °C sample, and the number of rod-like particles decreased for WO_3 -1000 °C as compared with the WO_3 -800 °C sample, from the SEM image. This result is in agreement with that from XRD (Fig. 2).

It is reported that triangular and hexagonal channels are formed along the structure in h-WO_3 bronzes owing to the special arrangement of corner-sharing WO_6 octahedra [24]. Alkaline (Na^+ , K^+ , Cs^+ and so forth) or NH_4^+ ions are thought to be located in hexagonal channels [25]. Szilágyi et al. [24] studied the formation of h-WO_3 during the annealing of hexagonal ammonium tungsten bronze (HATB), which is obtained by heating APT ($(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$) in H_2 . They proposed that, in general, some ions or molecules were needed in the hexagonal channels to maintain a hexagonal tungsten oxide structure. Moreover, residual NH_4^+ and NH_3 (from APT) in the hexagonal channels seemed to be vital for stabilizing h-WO_3 : when NH_4^+ and NH_3 were completely released, the hexagonal framework collapsed in an exothermic reaction into m-WO_3 . Thus, combined with the results from previous studies, h-WO_3 , which forms at 800 °C, may transform into m-WO_3 by increas-

ing the calcination temperature to 1000 °C because of the release of NH_4^+ ions and NH_3 molecules (from APT starting material) in the hexagonal channels at high temperature. Thus, the amount of rod-like h-WO_3 decreased for WO_3 -1000 °C from Fig. 2. Further work is in progress to study the mechanism of the phase transformation between h-WO_3 and m-WO_3 in our lab.

To further change the phase composition in the WO_3 sample, the APT powder was calcined at 800 °C for different times. Fig. 5 displays the XRD patterns of the WO_3 - t samples. It can be seen that the mixed phases of m-WO_3 and h-WO_3 were obtained for all the WO_3 - t samples. WO_3 -8 h sample is mainly composed of m-WO_3 with a small amount of h-WO_3 . More intense peaks of h-WO_3 appeared when the annealing time was increased from 8 to 12 h (Fig. 5(b)), suggesting an increase of h-WO_3 content in the mixed phases. However, the diffraction peaks of h-WO_3 gradually decreased in intensity after calcination for 12 h. With a further increase of the calcination time up to 24–30 h, WO_3 samples were again mainly composed of m-WO_3 with a small amount of h-WO_3 .

The XPS technique was used to determine the chemical states of WO_3 samples. The overview XPS spectrum of the WO_3 -12 h sample in Fig. 6(a) shows the corresponding peaks of O 1s, C 1s, and W 4f, confirming the existence of W and O elements in the WO_3 -12 h sample. The fine spectrum in Fig. 6(b)

Fig. 5. XRD patterns of APT calcined at 800 °C for different times.

Fig. 6. XPS spectra of the WO_3 -12 h sample. (a) Survey spectrum; (b) W 4f; (c) O 1s.

displays two peaks at 35.4 and 37.5 eV, which suggests that the W exists in the W^{6+} form [26]. These two peaks are attributed to the spin-orbit splitting of the W 4f components (W 4f_{7/2} and W 4f_{5/2}). For O 1s XPS (Fig. 6(c)), a peak at 530.6 eV was found, which can be assigned to lattice oxygen O²⁻ of WO₃ [27]. According to XPS studies, the W/O atomic ratio was estimated to be 1:3, which is consistent with tungsten(VI) trioxide. Therefore, the XPS results agree well with the results from the XRD pattern of the WO₃-12 h sample.

The morphologies of the WO₃-*t* samples were determined by the SEM analysis and are shown in Fig. 7. The m-WO₃ particles exhibit a bulky shape with heavy aggregates, while h-WO₃ particles exhibit a rod-like shape. Therefore, substances containing m-WO₃ and h-WO₃ can be identified simply by the particle morphology. The WO₃-8 h sample (Fig. 7(a)) is composed of m-WO₃ particles and some h-WO₃ particles. As compared with the WO₃-8 h sample, the number of rod-like particles obviously increases for the WO₃-12 sample, which is in accord-

ance with the XRD results (Fig. 5). It is shown that h-WO₃ particles can be easily observed in the WO₃-16 h sample although the number of h-WO₃ particles decreases with an increase of the calcination time to 16 h. With a further increase in the calcination time to 30 h, the WO₃ products are composed of a large number of m-WO₃ particles coupled with a small number of h-WO₃ particles, as shown in Fig. 7(g).

The results from XRD, SEM, and HRTEM demonstrate that well-defined m-WO₃/h-WO₃ phase junctions of WO₃ can be fabricated by the phase transformation between m-WO₃ and h-WO₃. It is observed that the ratio of m-WO₃ and h-WO₃ in the WO₃ products is mainly controlled by the calcination time. Moreover, from SEM and HRTEM images, it can be seen that m-WO₃ crystals are sporadically patched on the surface of the h-WO₃ rod-like particles, resulting in the exposure of both m-WO₃ and h-WO₃ on the surface.

RhB was used as a representative organic substance to investigate and compare the photocatalytic activity of the WO₃ samples (Fig. 8). The degradation of RhB could be described by the first-order kinetics of $\ln(C_t/C_0)$ versus reaction time (*t*): $-\ln(C_t/C_0) = k_{ap}t$, where k_{ap} is the apparent reaction rate constant, and C_0 and C_t are the initial concentration and the concentration at reaction time *t* of RhB, respectively.

After 180 min of irradiation, 41% and 30% of RhB were degraded by the WO₃-600 °C and WO₃-700 °C catalysts, respectively. The lower degradation ability may be ascribed to the decrease of the surface area from 1.216 to 0.867 m²/g with increasing calcination temperature from 600 to 700 °C. From Table 1, WO₃-600 °C, WO₃-700 °C, WO₃-800 °C, WO₃-900 °C, and WO₃-1000 °C samples exhibit a photocatalytic performance with k_{ap} determined as 0.00298, 0.00198, 0.00383, 0.00440, and 0.00232 min⁻¹. It is observed that the photocatalytic activity increases with increasing calcination temperature to 800 °C. The WO₃-900 °C sample exhibits the highest photocatalytic activity although the surface area of the WO₃-900 °C sample (0.779 m²/g) is lower than those of WO₃-600 °C and WO₃-700 °C. Therefore, we concluded that the enhancement in the photocatalytic activity of the WO₃-800 °C and WO₃-900 °C samples arose from the phase junction between m-WO₃ and h-WO₃, the presence of which is confirmed by SEM and HRTEM results.

Fig. 7. SEM images of WO₃-8 h (a, b), WO₃-12 h (c, d), WO₃-16 h (e, f), and WO₃-30 h (g, h).

Fig. 8. Photocatalytic activity of the degradation of RhB on the WO₃ calcined at different temperatures.

Table 1

First-order rate constants (k_{ap}) and relative coefficients (R^2) for the degradation of RhB under UV light irradiation for different calcination temperatures and different calcination times.

Catalyst	k_{ap} (min^{-1})	R^2
WO ₃ -600 °C	0.00298	0.96308
WO ₃ -700 °C	0.00198	0.99605
WO ₃ -800 °C	0.00383	0.97547
WO ₃ -900 °C	0.00440	0.99094
WO ₃ -1000 °C	0.00232	0.97461
WO ₃ -8 h	0.00818	0.99267
WO ₃ -12 h	0.01025	0.99569
WO ₃ -16 h	0.00853	0.99833
WO ₃ -24 h	0.00680	0.99614
WO ₃ -30 h	0.00672	0.99858

The formation of the phase junction may improve the charge separation efficiency of photoexcited electrons and holes in the WO₃-800 °C and WO₃-900 °C samples. Thus, WO₃-800 °C and WO₃-900 °C samples show a higher photocatalytic activity than WO₃-600 °C and WO₃-700 °C containing the monoclinic phase.

By further increasing the calcination temperature to 1000 °C, the photocatalytic activity of WO₃-1000 °C (surface area is 0.617 m²/g) decreased. However, the WO₃-1000 °C sample shows a comparable photocatalytic activity to WO₃-600 °C although the photocatalytic activity of WO₃-1000 °C decreases compared with that of WO₃-800 °C and WO₃-900 °C. From the above discussion, the decrease of the photocatalytic activity for WO₃-1000 °C arises from the decrease in the amount of h-WO₃ when the calcination temperature is raised to 1000 °C, which decreases the amount of the exposed m-WO₃/h-WO₃ phase junction.

To further confirm the phase junction effect of WO₃, the photocatalytic activities of WO₃-*t* samples that were calcined at 800 °C for different times were investigated (Fig. 9) because the m-WO₃ and h-WO₃ phase composition can be carefully controlled by calcination at 800 °C for different times. When the APT powder was calcined at 800 °C for 8–30 h, all samples are in the mixed phases of m-WO₃ and h-WO₃ from XRD results (Fig. 5), and all the above samples show higher photocatalytic

Fig. 9. Photocatalytic activity of degradation of RhB by the WO₃-*t* photocatalysts and WO₃-600 °C.

activities compared with WO₃-600 °C containing m-WO₃ (Fig. 9). Moreover, the photocatalytic activities were improved by gradually increasing the calcination time range from 8 to 12 h. The increase in the photocatalytic activity may mainly arise from the extent of the phase junction when the calcination time is increased from 8 to 12 h because the XRD results indicate that the amount of h-WO₃ increases gradually with increasing calcination time. From Table 1, the WO₃-12 h sample exhibits the highest photocatalytic activity with k_{ap} of 0.01025 min⁻¹. With further increases of the calcination time to 24 and 30 h, the photocatalytic activity decreases.

A mechanism for electron-hole separation and transport of an m-WO₃/h-WO₃ phase junction is proposed and is shown in Fig. 10. The valence and conduction band potentials of h-WO₃ were found to be 3.18 and 0.41 eV [21], whereas these values for m-WO₃ were 3.37 and 0.80 eV, respectively [28]. The conduction band (CB) of h-WO₃ is lower than that of m-WO₃, thus the photo-induced electrons on the conduction band of h-WO₃ transfer easily to m-WO₃ through the well-developed interface, and the photogenerated holes move in the opposite direction from the electrons. Therefore, the phase junction of m-WO₃/h-WO₃ could act as an active center for hindering the rapid recombination of photo-induced electron-hole pairs. The electrons accumulated on the CB of m-WO₃ can be scavenged by O₂ to produce a superoxide radical ($\cdot\text{O}_2^-$) and hydrogen peroxide (H₂O₂), which can interact to produce a powerful oxidant (hydroxyl radical, $\cdot\text{OH}$) to decompose RhB. The holes accumulated in the VB of h-WO₃ take part in the oxidation process to make OH⁻ or H₂O species to produce reactive hydroxyl radicals [29–31].

To further investigate the effect of the phase junction, PL analysis was applied to reveal the diffusion and recombination process of photogenerated electron-hole pairs. Fig. 11 shows the PL spectra of WO₃-600 °C, WO₃-800 °C, and WO₃-12 h samples. A main peak at approximately 469 nm and several peaks in the range of 400–600 nm were observed in the PL spectrum of WO₃-600 °C, which is in agreement with the results from Ref. [32]. In the case of WO₃-800 °C and WO₃-12 h with an m-WO₃/h-WO₃ junction, the shape of the curves is similar to that of WO₃-600 °C, whereas the peak intensities significantly decrease.

Fig. 10. A proposed mechanism for the charge transfer and separation in the m-WO₃/h-WO₃ phase junction.

Fig. 11. PL emission of different photocatalysts under UV radiation.

Generally, a higher PL intensity indicates a higher recombination rate of photoexcited electron-hole, and a lower PL intensity expresses a lower recombination rate of photoexcited electrons and holes [33,34]. This indicates that the interaction between h-WO₃ and m-WO₃ in the WO₃-800 °C and WO₃-12 h samples is favorable for interfacial charge transfer, and thus reduces the recombination rate of electron-hole pairs under light irradiation. Moreover, it can be seen that the PL intensity of the peak at 469 nm of WO₃-12 h is weaker than that of the WO₃-800 °C sample. This result indicates that WO₃-12 h exhibits a lower electron-hole recombination rate than that of WO₃-800 °C. Thus, WO₃-12 h exhibits higher photocatalytic activity than WO₃-800 °C.

4. Conclusions

WO₃ photocatalysts with different crystalline phases were prepared by thermal decomposition of APT at 600–1000 °C for 4 h and 800 °C for 8–30 h. Characterization of crystal structure, morphology, chemical composition, surface area, and optical

properties of WO₃, together with their relationships with the photocatalytic degradation of RhB, reveal that a phase junction between m-WO₃ and h-WO₃ of WO₃ was fabricated by a thermal decomposition strategy to inhibit the recombination of carriers. The promotion of the photocatalytic performance is mainly ascribed to the enhanced charge separation originating from the phase junction between m-WO₃ and h-WO₃. This work provides a simple method to design and fabricate the effective WO₃-based photocatalyst.

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Graphical Abstract

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Fabrication of a monoclinic/hexagonal junction in WO₃ and its enhanced photocatalytic degradation of rhodamine B

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A monoclinic phase (m-WO₃)/hexagonal phase (h-WO₃) composite has been fabricated by tuning the calcination temperature and time in the thermal decomposition method. The m-WO₃/h-WO₃ phase junction demonstrates enhanced photocatalytic activity for RhB degradation.

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WO₃中单斜相/六方相异相结的构建及提高光催化降解罗丹明B活性

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摘要: 光催化技术被认为有可能成为解决环境污染和能源危机的有效手段之一, 引起了各国政府和科学家的极大兴趣. 以TiO₂, WO₃和Bi₂O₃等半导体为催化剂的光催化反应受到广泛关注. WO₃是一种典型的n型半导体材料, 具有电致变色、气敏和光催化等性能, 在电致变色器件、气敏传感器和光催化剂等方面有着广泛应用前景. 由于WO₃具有高的太阳能利用率、良好的可见光响应性和较强的抗光腐蚀性, 是一种极具开发潜力的半导体光催化材料, 所以在光解水制氢及催化降解有机污染物等领域中得到广泛应用. 然而, WO₃半导体表面上较高的光生电子-空穴复合效率是影响其光催化性能的主要因素之一, 从而限制了WO₃在光催化领域的工业应用.

研究发现, TiO₂材料在从锐钛矿向金红石转变的过程中, 通过精细调变焙烧温度, 可以在两种晶相的界面形成TiO₂异相结. 形成的锐钛矿-金红石异相结能有效促进电子-空穴分离. 目前, 构建异相结已成为改善光催化剂电子-空穴分离效率的有效方法之一. 近年来, 人们先后成功构建了 α -Ga₂O₃/ β -Ga₂O₃, α -Bi₂O₃/ β -Bi₂O₃和WO₃/WO₃·H₂O等异相结, 这些异相结催化剂在光催化降解水产氢和降解污染物反应中显示了比单一晶相更高的光催化活性.

WO₃是一种多晶相材料, 具有正交、六方、单斜和四方等多种晶体结构, 其中六方晶相(h-WO₃)由于具有开放结构而在气体传感器和电池电极等领域显示了突出性能, 而单斜晶相(m-WO₃)具有合适的带宽和良好的可见光响应性, 因而广泛应用于光催化领域. 而且, h-WO₃的导带和价带均低于m-WO₃的导带和价带, 所以在WO₃材料中有可能通过构建单斜/六方异相结(m-WO₃/h-WO₃)来提高WO₃的光催化性能.

本文借鉴半导体异相结概念, 采用固相热分解法, 试图通过调节焙烧温度和焙烧时间以构建m-WO₃/h-WO₃异相结催化剂. 利用X射线衍射(XRD)、高分辨透射电镜(HRTEM)、扫描电镜(SEM)、X射线光电子能谱仪(XPS)和N₂吸附-脱附等方法对WO₃样品的晶相结构、形貌和元素组成等进行了表征. 以光催化降解罗丹明B(RhB)为模型, 研究了不同晶相WO₃材料的光催化性能, 考察了WO₃晶相和异相结对其光催化性能的影响, 从而为WO₃材料中异相结的构建提供思路、方法和理论指导.

结果表明, 采用偏钨酸铵固相热分解制备WO₃的过程中, 焙烧温度为600–700 °C时, 样品为单斜晶相, 随着焙烧温度升高至800 °C时, 样品中开始出现六方晶相. 随着焙烧温度升高, h-WO₃的含量没有明显变化, 当温度升至1000 °C时, h-WO₃的含量有所减少. SEM和HRTEM结果验证了m-WO₃/h-WO₃异相结的形成, 小的m-WO₃粒子分布在棒状h-WO₃上, 并且两者紧密接触. 为了进一步证实WO₃的异相结效应, 将偏钨酸铵在800 °C焙烧不同时间(8–30 h). 结果表明, 通过改变焙烧时间可有效控制m-WO₃和h-WO₃混合晶相比例, 800 °C焙烧8 h时m-WO₃为主要晶相, 焙烧12 h时h-WO₃含量明显增加, 当焙烧时间延长至24 和30 h时h-WO₃含量减少. SEM结果同样显示, 在800 °C焙烧12 h样品中棒状h-WO₃显著增多, 与小的m-WO₃

粒子接触几率增大, 即m-WO₃/h-WO₃异相结数量增加。

不同晶相WO₃样品光催化降解RhB的结果表明, 具有m-WO₃/h-WO₃异相结结构的WO₃催化剂具有较高光催化活性。荧光光谱结果表明, 单斜相/六方相异相结的形成提高了电子-空穴分离效率, 从而提高了其光催化降解RhB的活性。而在具有m-WO₃/h-WO₃异相结结构的WO₃催化剂中, 随着焙烧温度升高或焙烧时间延长, h-WO₃含量有所减少, 从而导致暴露的m-WO₃/h-WO₃异相结数量减少, 因而使得活性有所降低。本文采用固相热分解法通过调变焙烧温度构建了m-WO₃/h-WO₃异相结光催化剂, 显著提高了光催化降解RhB的活性, 这对设计合成高效WO₃基光催化剂具有一定借鉴。

关键词: 氧化钨; 异相结; 热分解法; 光催化; 罗丹明B

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