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Article

Preparation of Z-scheme $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites with enhanced photocatalytic activity and durability

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ABSTRACT

Ag_3PO_4 is widely used in the field of photocatalysis because of its unique activity. However, photo-corrosion limits its practical application. Therefore, it is very urgent to find a solution to improve the light corrosion resistance of Ag_3PO_4 . Herein, the Z-scheme $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites are successfully prepared through microwave hydrothermal and simple stirring. The $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites are characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and UV-Vis spectroscopy. In the degradation of organic pollutants, $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites exhibit excellent performance under visible light. This is mainly attributed to the synergy of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . Especially, the photocatalytic activity of 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ is the highest, and the methylene blue can be completely degraded in 4 min. In addition, the stability of the composites is also greatly enhanced. After five cycles of testing, the photocatalytic activity of 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ is not obviously decreased. However, the degradation efficiency of Ag_3PO_4 was only 20.2%. This indicates that adding $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ can significantly improve the photoetching resistance of Ag_3PO_4 . Finally, Z-scheme photocatalytic mechanism is investigated.

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1. Introduction

Photocatalytic technology is widely considered to be one of the most effective ways to manage pollution [1–5]. For many years, researchers have been looking for efficient photocatalysts. Many photocatalysts have been found, such as TiO_2 [6,7], CeO_2 [8,9], BiOX ($X = \text{Br}, \text{Cl}, \text{I}$) [10,11], BiPO_4 [12,13] and ZnO [14,15]. These photocatalysts have many advantages, such as

high efficiency, low harm and low price [16,17]. However, these photocatalysts can only absorb light in the ultraviolet (UV) region because of their relatively large band gap. To achieve high-efficiency photocatalysis, the use of semiconductors that are capable of absorbing a broad spectrum of solar light is desirable [18,19]. Recently, various photocatalysts with visible light response have been developed, such as Ag_3PO_4 [20,21], Bi_2MoO_6 [22,23], SnNb_2O_6 [24,25], $\text{g-C}_3\text{N}_4$ [26–28], BiVO_4

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[29–31], CdSe [32,33] and CdS [34,35]. These semiconductor photocatalysts have excellent photocatalytic activity in the visible light region. For example, Wang et al. [36] successfully prepared Ag_3PO_4 as a highly recyclable photocatalyst. Ying et al. [37] fabricated hierarchical Bi_2MoO_6 nanosheet-built frameworks with excellent photocatalytic properties. Jiang et al. [38] synthesized BiOCl single-crystalline nanosheets with facet-dependent photoreactivity.

Among these semiconducting materials, Ag_3PO_4 has attracted considerable attention because of its excellent photocatalytic activity [39–41]. Its efficiency is highly sought after by researchers. However, the photocatalytic performance of Ag_3PO_4 decreased significantly after several cycles, because the photo-generated electrons and holes are likely to recombine rapidly [42]. The instability of Ag_3PO_4 largely limits its practical application [43,44]. Therefore, it is very urgent and essential to design some novel composite photocatalysts to inhibit the recombination of electron-hole pairs [45–47].

Z-scheme composites have many advantages in improving the photocatalytic activity [48,49]. For example, Zhang et al. [50] found that the Z-scheme $\text{Bi}_{12}\text{GeO}_{20}/\text{g-C}_3\text{N}_4$ composite photocatalyst could efficiently degrade organic pollutants. Tang et al. [51] demonstrated Z-scheme C_3N_4 -based systems for pure water splitting. The Z-scheme composite photocatalysts can combine the advantages of different photocatalysis and overcome the shortcomings of a single photocatalyst. In fact, besides the spatial separation of redox reactions, the other important advantage over single-catalyst systems is that Z-scheme systems replace a wide band gap photocatalyst by two narrow ones, thus harvesting more photons from light. Consequently Z-scheme systems have a theoretically higher efficiency than single-catalyst systems [52,53]. In this way, the redox reactions take place separately, which can effectively prevent the recombination of electrons and holes [54,55], so the performance of the composite photocatalyst is greatly improved. Moreover, the Z-scheme composites can give full play to the redox ability of single photocatalyst and further enhance the photocatalytic activity [56,57]. Nevertheless, after comprehensive consideration of many factors, such as the band gap and band alignment, finding the right semiconductor is still a formidable challenge.

$\text{WO}_3(\text{H}_2\text{O})_{0.333}$ is a kind of semiconductor materials with a visible light responsive band gap (2.78 eV), which is similar to WO_3 and has been widely applied in fields of photocatalysis, and the band gap is matched with Ag_3PO_4 . Compared to previously reported [58], the traditional form of WO_3 is lumpy or rod like with the size of 200–300 nm. $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ shows a linear shape, its size is about 50 nm, and it can be fully combined by Ag_3PO_4 . $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ was successfully fabricated by a simple microwave hydrothermal method followed by annealing. Herein, we successfully prepared $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites by in-situ synthesis. The constituent elements of the photocatalysts are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive spectroscopy (EDS). The morphology of photocatalyst was observed by SEM. The absorption light spectrum was determined by UV-Vis diffuse

reflectance spectroscopy (DRS). From the photoluminescence (PL) measurements, we know that the separation efficiency of the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite is the highest. This indicates that the composites can largely reduce the recombination rates of electrons and holes. Through the degradation of methylene blue (MB), it is confirmed that the photocatalytic activity of $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ was much higher than that of pure $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . In addition, after repeated testing, the 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ almost completely degraded organic pollutants in 4 min under visible light irradiation. After five cycles, the degradation ability of the composites has almost no decay, suggesting it has good stability. This work may provide the possibility of efficient and stable decomposition of organic pollutants in a practical environment.

2. Experimental

2.1. Materials

Silver nitrate (AgNO_3), ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$), dibasic sodium phosphate (Na_2HPO_4), nitric acid (HNO_3), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4\cdot\text{H}_2\text{O}$), sodium chloride (NaCl), and hydrogen chloride (HCl) were bought from the Shanghai Chemical Reagent Co. Ltd. (China). L-ascorbic acid, isopropanol (IPA), triethanolamine (TEOA), and MB were bought from Sinopharm Chemical Reagent Corp. (China).

2.2. Preparation of the $\text{WO}_3(\text{H}_2\text{O})_{0.333}$

$\text{Na}_2\text{WO}_4\cdot\text{H}_2\text{O}$ (0.28 g) and NaCl (0.04 g) were mixed in solution of 30 mL deionized water (DW) and stirred for 30 min. Then, HCl was added to the mixed solution to adjust $\text{pH} = 2$ and stirred for another 2 h. The mixture was transferred into a reaction kettle and the autoclave reacts at 453 K for 30 min in the microwave digestion apparatus and then cooled to room temperature and then washed with DW repeatedly. The product was finally obtained by centrifugation and dried in a freeze dryer for 12 h to obtain the $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ nanowires.

2.3. Preparation of $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites

A certain amount of AgNO_3 was added in 20 mL DW and stirred for 10 min. Then, $\text{NH}_3\cdot\text{H}_2\text{O}$ of $\text{pH} = 10$ was added dropwise to the AgNO_3 solution, which first became turbid and then clear. After that, a certain amount of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ was added and stirred for 5 min, and the mixed solution was sonicated for 10 min. Then, an appropriate amount of Na_2HPO_4 solution was added dropwise to the mixed solution and stirred for 10 min. Then, 1.0 mol/L HNO_3 was dropped into the mixed solution until the pH of the solution was 7. The mixed solution was washed several times with 18.2 M Ω DW, and the washed precipitation was frozen in a refrigerator for several hours. Finally, the precipitation was placed in the freeze dryer for 12 h, and the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ complex was obtained. The preparation process of the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites is shown in Fig. 1.

Fig. 1. Schematic diagram for the synthesis of $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites.

2.4. Characterization

XRD patterns of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites were recorded on a DX-2000 diffractometer with the 2θ range from 10° to 80° . SEM (FE-SEM Hitachi S5500) was implemented to examine the granularity and structure of the samples. XPS was performed on a Thermo ESCALAB 250 spectrometer. The UV-Vis DRS measurements were surveyed with a PerkinElmer Lambda 950 UV-Vis spectrophotometer. The specific surface area of the samples was measured by N_2 adsorption using the multipoint Brunauer-Emmett-Teller (BET) method (ASAP 2010). The photoelectrochemical measurements were carried out on a Shanghai Chenhua CHI-660D electrochemical system. The electrolyte solution was 1.0 mol/L Na_2SO_4 . A 0.05 g catalyst sample was mixed with 50 μL 5% nafion and 0.5 mL ethyl alcohol absolute to make slurry. The slurry was then injected onto a 1.0 cm^2 ITO conductive glass electrode and these electrolytes were dried at 333 K for 30 min.

2.5. Photocatalytic activity evaluation

The photocatalyst (30 mg) was mixed with MB solution (30 mL, 20 mg/L). Light-emitting diode (LED) arrays (active power 50 W, $\lambda = 410$ nm) were used as a solar model. The irradiation time intervals were set at 2 min and the process was repeated five times. After each light irradiation, the absorbance of the MB solution was determined using the clear liquid obtained after centrifuging the mixture. The dominant reactive species affecting MB photodegradation were identified using IPA, L-ascorbic acid, and TEOA as scavengers for $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and holes, respectively. In a typical process, either L-ascorbic acid (150 mg), IPA (20 mmol/L, 5.4 mL), or TEOA (10 mmol/L, 6.1 mL) was added to a mixture of the photocatalyst and MB solution. Radical-trapping experiments were performed using the same method as for the photodegradation experiments.

3. Results and discussion

Fig. 2 shows the XRD patterns of the samples. The strong

Fig. 2. XRD patterns of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites and Ag_3PO_4 .

diffraction peaks centered at $2\theta = 14.17^\circ, 18.18^\circ, 23.05^\circ, 24.28^\circ, 27.12^\circ, 28.23^\circ, 33.72^\circ, 36.68^\circ, 50.25^\circ$, and 55.68° match the (020), (111), (002), (200), (022), (220), (202), (222), (260), and (224) crystal planes of cubic $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ (PDF No. 87-1203), respectively. The strong diffraction peaks located at $2\theta = 20.99^\circ, 29.82^\circ, 33.46^\circ, 36.73^\circ, 47.96^\circ, 52.84^\circ, 55.18^\circ$, and 57.47° are assigned to the (110), (200), (210), (211), (310), (222), (320), and (321) crystal planes of orthorhombic Ag_3PO_4 (PDF No. 84-0510), respectively. All strong diffraction peaks in 5%, 15% and 25% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ corresponded to Ag_3PO_4 , indicating that Ag_3PO_4 is present in the composites. There is no peak relative to $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ in 5% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$, and the $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ content may be too small to be detected. The XRD pattern of 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ shows that a small peak corresponds to the (220) crystal face of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, suggesting that the composite contains $\text{WO}_3(\text{H}_2\text{O})_{0.333}$. The XRD pattern of 25% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ shows two small peaks corresponding to the $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ (002) and (220) planes, indicating that the composite contains $\text{WO}_3(\text{H}_2\text{O})_{0.333}$.

As shown in Fig. 3a, $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ presents a linear shape with the size of about 50 nm. In Fig. 3b, Ag_3PO_4 exhibits a cubic shape with the size of about 1 μm . The $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite retains the shape of Ag_3PO_4 , and a small amount of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ is deposited on Ag_3PO_4 . Fig. 3d–3f show that all the elements in $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites can be detected. The origin of the C element can be ascribed to the conductive adhesive material, and no other impurities were observed, indicating that the samples are pure. The elemental mapping shows homogeneous distribution of Ag, P, O, and W in the as-prepared $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites (Fig. 3g).

XPS was used to study the elemental composition and chemical state of each catalyst. From Fig. 4a, it can be seen that the 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite contains all elements of pure $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 , which is consistent with the EDS results in Fig. 3. Fig. 4b shows the binding energy of O 1s in $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, with 532.92 and 530.63 eV corresponding to hydroxyl oxygen and lattice oxygen [47,59], respectively. The

Fig. 3. SEM images of (a) $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, (b) Ag_3PO_4 , and (c) $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$, EDS spectra of (d) $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, (e) Ag_3PO_4 , and (f) $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$, and (g) SEM image with corresponding elemental mapping images for $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$.

hydroxyl oxygen and lattice oxygen in Ag_3PO_4 are 532.54 and 530.80 eV, respectively. The hydroxyl oxygen and lattice oxygen of $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ are 532.25 and 530.86 eV, which are between $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 , indicating that the composites contain $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . In Fig. 4c, the binding energies of $\text{W } 4f_{5/2}$ and $\text{W } 5f_{7/2}$ in $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ correspond to 37.92 and 35.83 eV [60,61], respectively. In $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$, the binding energies of $\text{W } 4f_{5/2}$ and $\text{W } 5f_{7/2}$ are 38.29 and 36.21 eV [62,63], respectively. Compared to $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, the peak value of $\text{W } 4f$ in $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ shifts 0.38 eV to a high position. This may be due to the fact that the reconstitution of atoms between $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 has resulted in mutual interaction in the process of combination with each other. It is further explained that $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 are composited rather than simply mixed. In Fig. 4d, the binding energies of $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$ of Ag_3PO_4 are 374.17 and 368.16 eV

[64,65], respectively. The binding energies of $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$ in $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ are 374.20 and 368.18 eV, respectively, and there is almost no change in binding energy with respect to $\text{WO}_3(\text{H}_2\text{O})_{0.333}$. In Fig. 4e, the $\text{P } 2p$ binding energies of Ag_3PO_4 and $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ are 133.03 and 133.13 eV, respectively.

Fig. 5 shows the N_2 adsorption-desorption isotherms and the BET surface area of different samples. The S_{BET} values of Ag_3PO_4 and $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ are 0.63 and 16.71 $\text{m}^2 \text{g}^{-1}$, respectively. When Ag_3PO_4 and $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ were composited, the S_{BET} of $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites grows with increasing content of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$.

Fig. 6a shows UV-Vis DR spectra of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites. $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 have absorption edges at 473 and 540 nm, respectively. The absorption edge of the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites is 553 nm. There is a significant blue shift in the absorption

Fig. 4. (a) All XPS scanned spectra of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$, and high-resolution XPS of (b) O 1s, (c) W 4f, (d) Ag 3d, and (e) P 2p.

Fig. 5. (a) N_2 adsorption-desorption isotherms and (b) S_{BET} for $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 and $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites.

edge in the composites, and the blue shift increases with the increase of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ ratios. Therefore, the $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites exhibit better capture of visible light than $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 , which can be ascribed to the synergistic reaction of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . This result indicates that the composites have a potential application in visible light photocatalysis. In Fig. 6b, the energy band gaps (E_g) of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 are 2.78 and 2.38 eV, respectively. E_g is calculated as follows [66]:

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (1)$$

where α and $h\nu$ represent the absorbance and energy of radiation, respectively. Valence band (VB) energy (E_{VB}) and conduction band (CB) energy (E_{CB}) of photocatalyst are determined using the following formula [67]:

$$E_{\text{VB}} = X - E^c + 0.5E_g \quad (2)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (3)$$

where X is the electronegativity of semiconductor, and the X

values of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 are 6.49 and 5.96 eV, respectively. E^c is 4.5 eV. Therefore, E_{VB} of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 is 3.38 and 2.65 eV, respectively, and E_{CB} of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 is 0.6 and 0.27 eV, respectively.

In order to further explore the separation efficiency of photogenerated electrons and holes, the transient photocurrent-time curves of different photocatalysts are measured. As shown in Fig. 7, the photocurrent densities of $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites are higher than that of pure $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . Among them, $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ has the highest photocurrent density. This result indicates that addition of $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}$ can greatly enhance the separation efficiency of photogenerated electrons and holes in Ag_3PO_4 . This result further suggests that the heterojunction formed between $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 is the key to promote the separation of photogenerated electrons and holes.

Fig. 6. (a) UV-Vis DR spectra of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites; (b) Linear transformation $h\nu - (\alpha h\nu)^2$ curves for UV-Vis DRS spectra.

The photocatalytic activity of the photocatalysts was evaluated by the degradation of MB solution. As shown in Fig. 8a, we first added various photocatalysts into the MB solution and stirred it under dark conditions, and tested every 60 min. After three tests, the pollutants were hardly degraded. However, under visible light, the degradation ability of the composites is significantly enhanced relative to pure $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and Ag_3PO_4 . The photocatalytic ability of $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ was much higher than that of pure $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and a physical mixture of $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333} + 85\%\text{Ag}_3\text{PO}_4$. The MB solution was almost completely degraded in 4 min. Fig. 8b shows that there is a linear relationship between $\ln C_0/C$ and t , and the photodegradation reaction conforms to the pseudo-first-order kinetic equation. The equation is shown as follows:

$$\ln C_0/C = k_{\text{app}} t \quad (4)$$

where C_0 is the absorbance of the initial MB solution, C is the absorbance of the dye solution after t min light irradiation time, and k_{app} is a rate constant of pseudo-first-order. According to Eq. (4) and Fig. 8b, the Fig. 8c shows the k_{app} constants of different photocatalysts. The k_{app} of $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ is 0.969 min^{-1} , which is 161.5 and 2.9 times higher than that of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ (0.006 min^{-1}) and Ag_3PO_4 (0.329 min^{-1}), respec-

tively.

The stability of a catalyst determines whether it can be applied in practice. In order to further study the stability of the $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite, five cycle experiments on composites and pure Ag_3PO_4 were carried out under the same conditions. As shown in Fig. 9, the degradation efficiency of the composites can still retain 88.2% after five cycles, but the degradation efficiency of pure Ag_3PO_4 is only 20.2% after five cycles. This result indicates that the addition of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ greatly enhances the stability of Ag_3PO_4 . The higher stability enables $15\%\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ have a wide range of practical applications.

Fig. 10 shows the Z-scheme photocatalytic mechanism. From Fig. 6, we know that the CB and VB values of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ are 0.6 and 3.38 eV, respectively. Ag_3PO_4 has CB and VB values of 0.27 and 2.65 eV, respectively. Under the visible light irradiation, electron-hole pairs are generated on the surfaces of Ag_3PO_4 and $\text{WO}_3(\text{H}_2\text{O})_{0.333}$. The photogenerated electrons of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ first transfer to the CB of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ and then migrate to the VB of Ag_3PO_4 to combine with holes. Therefore, the photo-induced electrons and holes of Ag_3PO_4 are separated effectively, and the photoelectrons are continuously transferred to the CB interface of Ag_3PO_4 . In this way, a large amount of electrons are accumulated on the CB interface of Ag_3PO_4 , and a large number of holes are accumulated in the VB interface of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$. Under the action of holes, $-\text{OH}$ reacts with h^+ to produce $\cdot\text{OH}$, and $\cdot\text{OH}$ reacts with contaminants to form CO_2 and H_2O . Meantime, a great deal of H^+ and O_2 react with electrons to generate H_2O_2 at the conduction band interface of Ag_3PO_4 . After that, H_2O_2 reacts with electrons to generate $\cdot\text{OH}$, and $\cdot\text{OH}$ reacts with MB to form CO_2 and H_2O [59,68]. In this way, the photogenerated electrons and holes are separated continuously, which largely increases photocatalytic reaction rate speed [69], and finally the photocatalytic activity of the catalyst is greatly improved.

4. Conclusions

We have successfully prepared a novel Z-scheme $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite photocatalysts, which exhibits excellent photocatalytic activity and good stability under

Fig. 7. Photocurrent-time curves of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$, Ag_3PO_4 , and $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites.

Fig. 8. (a) MB degradation curves under dark and visible light irradiation, (b) Linear transform of MB degradation curves, (c) The apparent pseudo-first-order rate constant k_{app} with different catalysts.

visible light irradiation. The $15\%WO_3(H_2O)_{0.333}/Ag_3PO_4$ composite has the best ability to degrade pollutants and can almost completely degrade methylene blue within 4 min, which is 161.5 and 2.9 times higher than that of $WO_3(H_2O)_{0.333}$ and Ag_3PO_4 , respectively. Moreover, after five cycles, the photodegradation ability of the $15\%WO_3(H_2O)_{0.333}/Ag_3PO_4$ composite hardly changed. Therefore, is novel $WO_3(H_2O)_{0.333}/Ag_3PO_4$ composite might provide an effective and feasible route for

environmental pollution control.

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Fig. 9. Five cycles of photocatalytic test for $15\%WO_3(H_2O)_{0.333}/Ag_3PO_4$ and Ag_3PO_4 .

Fig. 10. The photocatalytic mechanism of $WO_3(H_2O)_{0.333}/Ag_3PO_4$ composites under visible light.

Graphical Abstract

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Preparation of Z-scheme $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composites with enhanced photocatalytic activity and durability

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A Z-scheme $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ composite with enhanced photocatalytic activity and durability is successfully constructed. Under visible light irradiation, electron-hole pairs are generated on the surfaces of Ag_3PO_4 and $\text{WO}_3(\text{H}_2\text{O})_{0.333}$. The photo-induced electrons of $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ are transferred to the CB interface of Ag_3PO_4 . Under the action of holes, $\cdot\text{OH}$ reacts with h^+ to produce $\cdot\text{OH}$, and $\cdot\text{OH}$ reacts with contaminants to form CO_2 and H_2O . Meantime, a great deal of H^+ and O_2 react with electrons to generate H_2O_2 at the conduction band interface of Ag_3PO_4 . After that, H_2O_2 reacts with electrons to generate $\cdot\text{OH}$, and $\cdot\text{OH}$ reacts with MB to form CO_2 and H_2O .

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Z-机制 $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 复合材料的制备及其增强光催化活性和稳定性

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摘要: Ag_3PO_4 由于具有独特的活性而被广泛应用于光催化领域。然而, 由于其光生电子和空穴的快速复合, Ag_3PO_4 的光催化性能在几个循环之后显著下降, 光腐蚀限制了它的实际应用。因此, 亟需设计一种新型的复合光催化剂来抑制电子空穴对的快速复合。而Z型复合光催化剂可综合不同光催化剂的优点, 克服单一光催化剂的缺点。Z方案体系使用两个窄带隙的催化剂取代宽带隙的光催化剂, 从而可以捕获更多的光子。并且光催化剂的氧化还原反应分开进行, 可以有效地防止电子和空穴的复合, 从而大大提高复合光催化剂的性能。

本文通过微波水热法和简单搅拌法成功地制备了Z机制 $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 复合材料。采用X射线衍射、扫描电子显微镜、X射线光电子能谱、 N_2 吸附-解吸等温线、比表面积测定、紫外-可见光谱和光电流曲线等方法对 $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 复合材料进行了表征。通过这些表征, 我们确定了所研究的光催化剂物相高度匹配; 确定了光催化剂的形貌; 确定了复合光催化剂是复合物, 而不是简单的混合物; 确定了光催化剂中光生电子和空穴的结合、分离效率; 研究了光催化剂的吸收边以及带隙。光催化降解测试发现, $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 复合材料在可见光下表现出优异的催化性能, 这主要归因于 $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 的协同作用。其中15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 的光催化活性最高, 在4 min内几乎将30 mL 20 mol/L的次甲基蓝完全降解。并且, 复合材料的稳定性也得到很大提升。经过5次循环反应后, 15% $\text{WO}_3(\text{H}_2\text{O})_{0.333}/\text{Ag}_3\text{PO}_4$ 的降解效率仍可以维持在88.2%。相比之下, 纯 Ag_3PO_4 的降解效率仅为20.2%。这表明添加 $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ 可以显著提高 Ag_3PO_4 的耐腐蚀性。

最后, 我们详细研究了Z-机制机理。在可见光照射下, Ag_3PO_4 和 $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ 的表面产生电子-空穴对。 $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ 的光生电子首先转移到其导带, 然后迁移到 Ag_3PO_4 的价带中与空穴结合。因此, Ag_3PO_4 的光生电子和空穴被有效分离, 光生电子连续转移到 Ag_3PO_4 的导带界面。这样, Ag_3PO_4 的导带界面上积累了大量的电子, 并且在 $\text{WO}_3(\text{H}_2\text{O})_{0.333}$ 的价带界面中积累了大量的空穴。在空穴的作用下, $-\text{OH}$ 与 h^+ 反应生成 $\cdot\text{OH}$, $\cdot\text{OH}$ 与污染物甲基蓝反应生成 CO_2 和 H_2O 。同时, 大量的 H^+ 和 O_2 与电子反应, 在 Ag_3PO_4 的导带界面处产生 H_2O_2 。之后, H_2O_2 与电子反应产生 $\cdot\text{OH}$, $\cdot\text{OH}$ 与甲基蓝反应形成 CO_2 和 H_2O 。这样, 光生电子和空穴连续分离, 大大提高了光催化反应速度, 最终催化剂的光催化活性得到极大的提高。

关键词: 光催化; Ag_3PO_4 ; $\text{WO}_3(\text{H}_2\text{O})_{0.333}$; 复合材料; Z-机制

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