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Construction of $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ Z-scheme heterogeneous photocatalyst for the remediation of organic pollutants

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ABSTRACT

Hole/electron separation and charge transfer are the key processes for enhancing the visible-light photocatalysis performance of heterogeneous photocatalytic systems. To better utilize and understand these effects, binary $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid materials were fabricated by a facile solution-phase reaction and characterized systematically by X-ray diffraction (XRD), energy-dispersive spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, field-emission scanning electron microscopy and ultraviolet-visible diffuse-reflectance spectroscopy. Under visible-light illumination, a heterogeneous $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ photocatalyst was constructed and demonstrated enhanced photocatalytic activity and photostability compared with pristine Ag_3PO_4 toward the remediation of the organic dye rhodamine B. The $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid catalyst with 8% mole fraction of Ag_2MoO_4 exhibited the highest photocatalytic activity toward the removal of typical dye molecules, including methyl orange, methylene blue and phenol aqueous solution. Moreover, the mechanism of the photocatalytic enhancement was investigated via hole- and radical-trapping experiments, photocurrent measurements, electrochemical impedance spectroscopy and XRD measurements. The XRD analysis revealed that metallic Ag nanoparticles formed initially on the surface of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composites under visible-light illumination, leading to the generation of a $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ Z-scheme tandem photocatalytic system. The enhanced photocatalytic activity and stability were attributed to the formation of the $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ Z-scheme heterojunction and surface plasmon resonance of photo-reduced Ag nanoparticles on the surface. Finally, a plasmonic Z-scheme photocatalytic mechanism was proposed. This work may provide new insights into the design and preparation of advanced visible-light photocatalytic materials and facilitate their practical application in environmental issues.

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1. Introduction

Semiconductor-based photocatalysis is a promising, environmentally friendly strategy to address current energy and environmental issues by using solar light [1–9]. Among the numerous photocatalysts, TiO_2 has proven one of the best-per-

forming materials, owing to its non-toxicity, low cost, relatively high chemical stability and strong oxidizing power [10–15]. However, because of its large band gap (3.0 eV for rutile and 3.2 eV for anatase), TiO_2 can only be activated under ultraviolet light (which accounts for about 5% of solar light) [16–18]. The poor light-harvesting ability of TiO_2 in the visible-light region

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makes it difficult to realize efficient solar-driven photocatalysis for energy and environmental applications.

To address this issue, extensive efforts have been focused on the exploration and fabrication of novel semiconductor catalysts with improved visible-light-driven photocatalytic performances during the past decades [19–21]. Recently, Ag-based photocatalysts, such as AgX (X = Cl, Br or I) [22–24], Ag₂O [25], Ag₂CO₃ [26], Ag₂WO₄ [27], Ag₂MoO₄ [28,29], Ag₆Si₂O₇ [30] and Ag₃PO₄ [31,32], have been developed for photocatalytic degradation of pollutants in waste water. Among the various Ag-based photocatalysts, Ag₃PO₄ is extremely attractive because of its remarkable quantum efficiency of up to 90% in the evolution of O₂ by photooxidation of water as well as the photodecomposition of organic dyes under visible-light irradiation [33,34]. Therefore, Ag₃PO₄ has been envisioned as one of the most promising photocatalysts in harvesting solar energy for environmental purification and clean energy production. Moreover, the photocatalytic activity of Ag₃PO₄ can be further enhanced by controlling the shape [35], particle size [36] and crystal face [37] of the Ag₃PO₄ crystals. However, there still exist some shortcomings inherent in Ag₃PO₄ photocatalytic systems. For instance, it is well known that Ag₃PO₄ is slightly soluble in aqueous solution, which reduces its stability under working conditions [38]. Furthermore, photo-decomposition of Ag₃PO₄ during the photocatalytic process generates Ag particles as by-products on the surface, which affects visible-light absorption by Ag₃PO₄ and decreases its photocatalytic activity [38]. As such, a number of methods, including doping with metals [33], coupling with other semiconductors [39] or forming P-N heterojunctions [40] or Z-scheme systems [41,42], have been reported to enhance the photocatalytic activity and stability of Ag₃PO₄. Among the various heterojunction photocatalysts, the Z-scheme photocatalytic system has shown the potential to achieve superb photocatalytic performances and photo-stabilities [43–46]. For example, Fang et al. [38,42] prepared visible-light-driven Ag₃PO₄/Ag/SiC and Ag₃PO₄/AgI hybrid photocatalysts with superior photocatalytic activity and stability. They found that the Z-scheme present in the Ag₃PO₄-based systems not only facilitated charge separation, but also retained the high reducing and oxidizing powers of the remaining electrons and holes, respectively, for the corresponding photocatalytic reactions. However, there are still only a few reports of the development of Ag₃PO₄-based Z-scheme systems, and the formation of efficient Z-scheme visible-light photocatalysts remains a challenge. To this end, it is important to explore novel visible-light-active components to construct and develop photocatalysts of this kind.

In the current work, Ag₂MoO₄, a semiconductor with a band gap of around 3.24 eV [47], was combined with Ag₃PO₄ for the first time to form a high-efficiency Ag₃PO₄/Ag₂MoO₄ hybrid photocatalyst. The photocatalytic activities of the Ag₃PO₄/Ag₂MoO₄ hybrid photocatalysts with different molar ratios of Ag₂MoO₄ were evaluated by degradation of rhodamine B (RhB) under visible light (>420 nm), from which the optimal mole fraction of Ag₂MoO₄ was determined. Furthermore, the photocatalytic mechanism of the Ag₃PO₄/Ag₂MoO₄ hybrid photocatalyst was investigated via reactive-species-trapping experi-

ments, photocurrent measurements and EIS measurements. It was found that Ag nanoparticles were generated on the surface of Ag₃PO₄/Ag₂MoO₄ in the early stage of the photocatalytic oxidation and formed a Z-scheme system with Ag₃PO₄ and Ag₂MoO₄, contributing to the enhanced photocatalytic activity. Finally, the stability of the Ag₃PO₄/Ag₂MoO₄ hybrid photocatalyst was examined.

2. Experimental

2.1. Materials

All reagents were of analytical purity and were used without further purification. Silver nitrate (AgNO₃), molybdenum trioxide (MoO₃), disodium hydrogen phosphate dodecahydrate (Na₂HPO₄·12H₂O), ammonia (NH₃·H₂O), RhB, methyl orange (MO), methylene blue (MB), phenol, *p*-benzoquinone (BZQ), disodium ethylenediamine tetraacetate (Na₂-EDTA) and butyl alcohol were obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout this study.

2.2. Preparation of Ag₃PO₄/Ag₂MoO₄ photocatalyst

In a typical procedure, a specified amount of AgNO₃ was dissolved in 50 mL of distilled water and stirred for 10 min. A 10% ammonia solution was dropped into this solution to obtain a silver/ammine complex. Meanwhile, 1 mmol Na₂HPO₄·12H₂O was dissolved in 50 mL deionized water and stirred for 10 min, after which a specified amount of MoO₃ was added into this solution and ultrasonicated for 15 min. Finally, the as-prepared silver/ammine complex was added into the Na₂HPO₄·12H₂O/MoO₃ mixture drop-by-drop and stirred continuously for 6 h. The obtained precipitates were washed several times with distilled water and then dried at room temperature overnight. The samples prepared at MoO₃ mole ratios of 3 mol%, 8 mol% and 25 mol% were named 3%Ag₂MoO₄/Ag₃PO₄, 8%Ag₂MoO₄/Ag₃PO₄ and 25%Ag₂MoO₄/Ag₃PO₄, respectively. For comparison, pure Ag₃PO₄ and Ag₂MoO₄ particles were prepared under the same conditions but without adding the MoO₃ and Na₂HPO₄, respectively.

2.3. Characterization

The crystal phases of the obtained products were analyzed by a Bruker D8 Advance X-ray diffractometer (XRD, Cu K_α radiation, λ = 0.15406 Å) in a 2θ range from 10° to 80° at room temperature. The X-ray photoelectron spectroscopy (XPS) measurement was carried out in a PHI ESCA-5000C electron spectrometer. The morphologies and structures of the products were characterized by scanning electron microscopy (SEM, JEOL JXA-840A) with energy dispersive X-ray spectroscopy (EDS). Fourier transform infrared (FT-IR) spectra of all the products (in KBr pellets) were recorded on a Nicolet Model Nexus 470 FT-IR instrument. Raman experiments were performed with a DXR spectrometer using the 532 nm laser line, the measurements being made in backscattering geometry. UV-vis diffuse-reflectance spectra of the products were ob-

tained from dry-pressed disk samples using a UV-vis spectrophotometer (UV2550, Shimadzu, Japan), with BaSO₄ as the reflectance standard. The Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of the powders were analyzed by nitrogen adsorption in an ASAP2020 surface area and porosity analyzer (Micromeritics, USA). All the samples were degassed at 180 °C prior to the nitrogen adsorption measurements. S_{BET} was determined by the multipoint BET method using the adsorption data in the relative pressure (p/p_0) range of 0.05–0.25. Desorption isotherms were used to determine the pore size distribution via the Barrett-Joyner-Halenda (BJH) method, assuming cylindrical pores. The nitrogen adsorption volume at a relative pressure (p/p_0) of 0.994 was used to determine the pore volumes and average pore sizes.

2.4. Photocurrent and EIS measurements

To investigate the dynamics of the photogenerated electrons in the Ag₃PO₄/Ag₂MoO₄ hybrid materials, modified electrodes were prepared by a simple casting method: 20 μL Ag₃PO₄/Ag₂MoO₄ aqueous solution (5.0 mg/mL) was dropped onto a pretreated ITO substrate and these electrodes were dried at 50 °C for 8 h. The photocurrents of these electrodes were measured with an electrochemical analyzer (CHI660B) in a standard three-electrode system, which employed a platinum wire as counter electrode, Ag/AgCl as reference electrode and ITO as working electrode. A 500 W Xe arc lamp ($\lambda > 420$ nm) was utilized as the light source. A Na₂SO₄ aqueous solution (0.1 mol/L) was used as the electrolyte. All the above electrochemical measurements were taken at room temperature.

2.5. Evaluation of photocatalytic activity

The photocatalytic activities of the Ag₃PO₄/Ag₂MoO₄ hybrid materials were evaluated by degrading RhB, MO and MB aqueous solutions with a concentration of 10 ppm under visible-light irradiation. The optical system for the photocatalytic reactions was composed of a 350 W Xe lamp (with a light intensity of 120 $\mu\text{W}/\text{cm}^2$) and a cut-off filter (excluding light of $\lambda > 420$ nm). In each experiment, a 100 mL dye solution containing 40 mg of sample (2×10^{-5} mol/L) was put in a sealed glass beaker and ultrasonicated for 10 min, and then stirred in the dark for 30 min to ensure absorption-desorption equilibrium. During the irradiation, a 5 mL sample of the reaction suspension was taken every 1 min and centrifuged at 10000 r/min for 5 min. The supernatants were collected and analyzed by measuring the variations of the absorption band maxima in the UV-vis spectra using a Lambda 25UV/Vis spectrophotometer.

3. Results and discussion

3.1. Characterization of Ag₃PO₄/Ag₂MoO₄ photocatalysts

The crystal structure and phase composition of the Ag₃PO₄/Ag₂MoO₄ hybrid photocatalysts were determined by XRD. Fig. 1(a) shows the XRD patterns of the pure Ag₃PO₄, Ag₂MoO₄ and 8%Ag₂MoO₄/Ag₃PO₄ samples. It can be observed that both Ag₃PO₄ and Ag₂MoO₄ are in the cubic phase (JCPDS 06-0505 and 08-0473, respectively). The intensities of the diffraction peaks of Ag₃PO₄ in the Ag₃PO₄/Ag₂MoO₄ composites decreased with increasing content of Ag₂MoO₄. No obvious

Fig. 1. XRD patterns (a), EDS (b), XPS (c), FTIR (d), and Raman spectra (e) of 8%Ag₂MoO₄/Ag₃PO₄ hybrid materials.

peaks of the Ag_2MoO_4 phase are found in the patterns of $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ because of the low content and good dispersion of Ag_2MoO_4 . EDS analysis was employed to investigate the presence and distribution of elements (Fig. 1(b)), wherein the observed peaks confirmed that the product was composed of Ag, P, O and Mo. Fig. 1(c) shows the XPS spectrum of the $8\%\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ sample, in which peaks derived from Ag, P, O and Mo are all evident. FT-IR and Raman spectroscopy were further carried out to confirm the presence of Ag_2MoO_4 in the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composites. Fig. 1(d) shows a comparison of the FT-IR spectra of pure Ag_3PO_4 , pure Ag_2MoO_4 and the $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composite. For pure Ag_3PO_4 , the peaks at 540, 856, 1073 and 1402 cm^{-1} are attributed to the stretching and bending vibrations of PO_4^{3-} [48]. The peaks at about 991, 848 and 694 cm^{-1} in the spectrum of pure Ag_2MoO_4 correspond to the stretching vibrations of O–Mo–O [47]. For the $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composite, the characteristic bands for Ag_3PO_4 remain, but two characteristic peaks emerge at around 848 and 694 cm^{-1} , which match well with the stretching vibration peaks of Ag_2MoO_4 , indicating the existence of Ag_2MoO_4 in the composite [47]. Fig. 1(e) shows the Raman spectra of Ag_3PO_4 , Ag_2MoO_4 and the related hybrid photocatalysts. In the case of pure Ag_3PO_4 , the sharp peak centered at about 910 cm^{-1} is attributed to the PO_4^{3-} symmetric stretching vibration [48]. The pure Ag_2MoO_4 shows four sharp peaks at 763, 819, 873 and 995 cm^{-1} , which are attributed to the MoO_4^{2-} symmetric and antisymmetric stretching vibrations [49]. For the $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composite, its Raman spectrum contains peaks from both Ag_3PO_4 and Ag_2MoO_4 , further confirming the presence of Ag_2MoO_4 in the composite. Based on the EDS, FT-IR and Raman analysis, we can conclude that $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composite photocatalysts were successfully synthesized.

The morphology and microstructure of the as-prepared samples were characterized by SEM analysis. Fig. 2 shows the SEM images of the pure Ag_3PO_4 , pure Ag_2MoO_4 and $3\%\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$, $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ and $25\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ hybrid materials. Fig. 2(a) and (b) shows that the Ag_3PO_4 particles had irregular sphere-like shapes with sizes of about $0.1\text{--}1\text{ }\mu\text{m}$

while the Ag_2MoO_4 particles had polyhedral-like block shapes. The $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composites (Fig. 2(c)–(e)) exhibited Ag_2MoO_4 nanoparticles and irregular sphere-like Ag_3PO_4 particles. We also found that the size of the Ag_3PO_4 particles gradually decreased as the Ag_2MoO_4 content increased from 3% to 8%, which is consistent with the XRD analysis. However, further increasing the Ag_2MoO_4 content to 25% led to large particles. These observations indicate that an optimal Ag_2MoO_4 amount is important for controlling the morphology and size of the final product.

The optical absorption properties of the photocatalysts were studied by UV-vis DRS spectroscopy, and the results are shown in Fig. 3. The pure Ag_2MoO_4 had an absorption edge at about 400 nm, while the pure Ag_3PO_4 showed absorption at wavelengths shorter than 530 nm, both of which are in agreement with previously reported results [50,51]. More remarkably, compared with the other samples, $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ showed notably enhanced absorption intensities across the whole spectral range. Similar observations of enhanced absorption in previous reports were attributed to strong electronic coupling between two semiconductors [52]. Therefore, in the present system, the absorption enhancement implies strong electronic coupling between Ag_3PO_4 and Ag_2MoO_4 , which is beneficial for enhanced photocatalytic activity.

The band gap energy of a semiconductor can be calculated by the following formula [51]: $\alpha(h\nu) = A(h\nu - E_g)^{n/2}$, where α , h , ν , E_g and A are the absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. n is determined by the type of optical transition of the semiconductor ($n = 1$ for a direct transition and $n = 4$ for an indirect transition) [51]. Ag_3PO_4 and Ag_2MoO_4 are direct-band-gap semiconductors, so the value of n is 1 [29,51]. Therefore, the band gap energies (E_g values) of Ag_3PO_4 and Ag_2MoO_4 can be estimated by plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (Fig. 3(b)); in this way, they were determined to be ~ 2.40 and $\sim 3.24\text{ eV}$, respectively.

The nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of the

Fig. 2. SEM images of Ag_3PO_4 (a), Ag_2MoO_4 (b), $3\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ (c), $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ (d) and $25\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ (e).

Fig. 3. (a) UV-visible absorption spectra of Ag_3PO_4 , Ag_2MoO_4 and $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ hybrids with various molar ratios of Ag_2MoO_4 to Ag_3PO_4 ; (b) Plots of $(ah\nu)^2$ versus energy $(h\nu)^2$ for the band gap energy of Ag_3PO_4 and Ag_2MoO_4 .

as-obtained samples are shown in Fig. 4. The tested Ag_3PO_4 and 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ materials exhibited type IV isotherms with H3 hysteresis loops, which is characteristic of mesoporous materials. The corresponding BJH analyses (inset in Fig. 4) showed that most of the pores fell into the size range from 2 to 30 nm, which further revealed the mesoporosity of the photocatalyst. The specific surface areas of the pure Ag_3PO_4 and 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ were calculated to be 17.34 and 19.2 m^2/g , respectively.

3.2. Evaluation of photocatalytic activity

The photocatalytic activity of the as-prepared samples was first evaluated by the degradation of RhB. Fig. 5(a) shows the photocatalytic activities of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid photocatalysts with different ratios of Ag_2MoO_4 under visible-light irradiation. The blank test showed that RhB was only slightly degraded in the absence of catalysts, indicating that the photolysis of RhB can be ignored. The photocatalytic degradation efficiency of the prepared samples followed the order: 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4 > 3\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4 > 25\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4 > \text{Ag}_3\text{PO}_4$. This result clearly demonstrates that all the

$\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid photocatalysts exhibited higher photocatalytic activities than pure Ag_3PO_4 , which suggests that the coupling between Ag_2MoO_4 and Ag_3PO_4 is an efficient route to enhance the photocatalytic activity of Ag_3PO_4 . In the presence of 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$, about 95% of the RhB molecules were decomposed within 5 min under visible light.

To investigate the kinetics of RhB degradation by the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid photocatalysts, a pseudo-first-order reaction model was applied to describe the experimental data, as follows: $-\ln(C/C_0) = k_{\text{ap}}t$, where k_{ap} is the apparent reaction rate constant, C_0 is the adsorption equilibrium concentration of RhB, t is the reaction time, and C is the concentration of RhB at time t [53]. In Fig. 5(b), it can be seen that all of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composite photocatalysts exhibited higher photocatalytic degradation rates than the pure Ag_3PO_4 sample under visible-light irradiation. The photocatalytic degradation rate first gradually increased with the content of Ag_2MoO_4 , and then decreased. The 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ hybrid sample exhibited the highest degradation rate, 0.6347 min^{-1} , which is about 2.95 times higher than that of the pure Ag_3PO_4 sample (0.2151 min^{-1}). With the further increase of the Ag_2MoO_4 content to 25%, the photocatalytic performance clearly decreased, with a

Fig. 4. Nitrogen adsorption-desorption isotherms of pure Ag_3PO_4 (a) and 8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ hybrid materials (b).

Fig. 5. (a) Photocatalytic degradation of RhB in the presence of pure Ag_3PO_4 and Ag_2MoO_4/Ag_3PO_4 hybrid materials under visible light irradiation; (b) The kinetic fit for the degradation of RhB with the pure Ag_3PO_4 and Ag_2MoO_4/Ag_3PO_4 hybrid materials; (c) Photocatalytic degradation of RhB in the presence of pure Ag_3PO_4 , pure Ag_2MoO_4 , 8% Ag_2MoO_4/Ag_3PO_4 hybrid material and the sum of Ag_3PO_4 and Ag_2MoO_4 material.

rate constant of 0.2689 min^{-1} , although this sample still exhibited greater photocatalytic activity than pure Ag_3PO_4 .

To further verify the close relationship between the improved photocatalytic activity and the presence of hetero-interfaces between Ag_3PO_4 and Ag_2MoO_4 , a mechanically blended sample of Ag_3PO_4 and Ag_2MoO_4 was also prepared. The amounts of Ag_3PO_4 and Ag_2MoO_4 in the mechanical-mixture sample were the same as in the 8% Ag_2MoO_4/Ag_3PO_4 composite. It can be clearly seen from Fig. 5(c) that the photocatalytic activity of the Ag_3PO_4/Ag_2MoO_4 hybrid composites (with a degradation percentage of about 98%) was higher than that of the mechanical mixture (with a degradation percentage of about 80%). These results confirmed that the formation of a heterojunction between Ag_3PO_4 and Ag_2MoO_4 was crucial for

the improved photocatalytic performance.

To confirm the versatile degradation capability of the as-prepared photocatalysts, their photocatalytic activities toward MB and MO under the same conditions were also evaluated. Fig. 6(a) shows the photocatalytic degradation of MB, RhB and MO in the presence of the 8% Ag_2MoO_4/Ag_3PO_4 hybrid material. The degradation percentages of RhB, MB and MO reached 95%, 97% and 90% after being irradiated for 5 min, respectively. Therefore, we can conclude that the Ag_3PO_4/Ag_2MoO_4 composite exhibited universally high photocatalytic activity for the degradation of RhB, MB and MO, which suggests its potential application to degrading different organic pollutants in waste water. RhB, MB and MO may have exerted a certain dye-sensitization effect on the photocatalyst, which can

Fig. 6. Photocatalytic degradation (a) and the color change photographs (b) of MB, RhB and MO; (c) Phenol in the presence of 8% Ag_2MoO_4/Ag_3PO_4 hybrid materials; (d) Cycle runs of 8% Ag_2MoO_4/Ag_3PO_4 for the degradation of RhB under visible light irradiation (>420 nm).

lead to the self-degradation of the dye under visible light [54]. In order to prevent this process, the colorless compound phenol was selected as the target degradation substance, and the results are shown in Fig. 6(c). The 8%Ag₂MoO₄/Ag₃PO₄ sample exhibited excellent photocatalytic activity in the degradation of phenol under visible light, confirming its inherent visible-light photocatalytic properties.

In addition to their photocatalytic activity, the stability and recyclability of photocatalysts are also very important criteria for their practical applications. To investigate the performance stability of the 8%Ag₂MoO₄/Ag₃PO₄ hybrid photocatalyst, recycling experiments of RhB decomposition were performed, and the corresponding results are shown in Fig. 6(d). The efficiency of the 8%Ag₂MoO₄/Ag₃PO₄ hybrid photocatalyst was nearly 100% for the first cycle and remained above 84% even after four cycles. In contrast, the efficiency of the pure Ag₃PO₄ hybrid photocatalyst was 80% for the first cycle and only 50% after four cycles. The excellent recyclability of the 8%Ag₂MoO₄/Ag₃PO₄ also implied that the final removal of RhB from the solutions was dominated by the photocatalytic process rather than the physical adsorption of the dye on the catalyst surface. The slight decrease of the photoactivity during the repeated runs is attributed to the loss of the catalyst during the photocatalytic trials. Nonetheless, the retained high performance of the Ag₃PO₄/Ag₂MoO₄ photocatalyst after several working cycles indicates its capacity for long-term continuous photocatalysis in aqueous media.

3.3. Separation of photogenerated electron/hole pairs and photocatalytic mechanism

The recombination of photogenerated electron/hole pairs is an important limiting factor for the performance of photocatalysts [55,56]. The transient photocurrent responses and electrochemical impedance spectra were measured to examine the separation efficiency of photogenerated electron/hole pairs for the as-prepared samples. The transient photocurrent responses of the pure Ag₃PO₄ and 8%Ag₂MoO₄/Ag₃PO₄ hybrid-material electrodes were recorded for several on/off cycles under visible-light irradiation, as shown in Fig. 7(a). As can be seen from the figure, a fast and uniform photocurrent response to each switch-on and switch-off event was observed for all the tested electrodes, indicating the good reproducibility of the tested samples. The 8%Ag₂MoO₄/Ag₃PO₄ sample showed a markedly higher photocurrent density than that of the pure Ag₃PO₄ sample. It is well known that the photocurrent is mainly determined by the efficiency of separation of photogenerated electron/hole pairs within a photoelectrode; holes are transferred at the photocatalyst/electrolyte interface, while electrons are transported to the back contact [57]. The higher photocurrent response recorded for the 8%Ag₂MoO₄/Ag₃PO₄ sample implies that the Ag₂MoO₄/Ag₃PO₄ heterojunction structure is favorable for charge separation and transfer to the electrolyte, thus enhancing the photo-response and improving the photocatalytic activity. Electrochemical impedance spectroscopy (EIS) of the

Fig. 7. Transient photocurrent response (a) and electrochemical impedance spectroscopy (b) of pure Ag₃PO₄ and 8%Ag₂MoO₄/Ag₃PO₄ hybrid materials; (c) Trapping experiment of active species during the photocatalytic degradation of RhB; (d) XRD patterns before and after recycling runs of 8%Ag₂MoO₄/Ag₃PO₄ hybrid materials.

pure Ag_3PO_4 and $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ samples was carried out to further investigate the charge transfer and recombination processes in the $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composites under visible-light irradiation, and the results are shown in Fig. 7(b). Compared with pure Ag_3PO_4 , a smaller arc radius can be observed on the EIS Nyquist plot of $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$, indicating that a more effective separation of the photogenerated electron/hole pairs and a faster interfacial charge transfer occurred on the surface of the $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composite. The EIS results are consistent with the photocurrent analysis, and further confirm that the formation of a heterojunction between Ag_2MoO_4 and Ag_3PO_4 is beneficial to the separation of electron/hole pairs, thus leading to improved photocatalytic activities.

On the basis of the above results, the superior photocatalytic activity of the $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ composite photocatalyst can be ascribed to two aspects: the increased light absorption and the enhanced separation of photogenerated electron/hole pairs. In addition, the specific surface areas of the pure Ag_3PO_4 and $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ are both relatively small (17.34 and 19.2 m^2/g), suggesting that the specific surface area is not a decisive factor in the photocatalytic degradation of organic dyes.

To study the photocatalytic mechanism of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid material in detail, the effects of different scavengers on the decolorization of dye molecules were investigated, in order to determine the predominant reactive oxygen species in the photocatalytic process (Fig. 7(c)). In this study, *p*-benzoquinone (BZQ) [58], disodium ethylenediamine tetraacetate ($\text{Na}_2\text{-EDTA}$) [18] and butyl alcohol [26] were used as scavengers for superoxide radicals, photogenerated holes and hydroxyl radicals, respectively, in the visible-light-driven photocatalytic systems. As shown in Fig. 7(c), the degradation efficiency of RhB under visible-light irradiation decreased significantly when BZQ and $\text{Na}_2\text{-EDTA}$ were used as scavengers for superoxide radicals and photogenerated holes, respectively. In contrast, the addition of butyl alcohol had only a slight negative effect on the photodegradation of RhB, implying that hydroxyl radicals do not play a predominant role in the improved photodegradation performance. Hence, it can be concluded that superoxide radicals and photogenerated holes are the main oxygen active species contributing to the oxidative degradation of organic dyes by the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid photocatalyst.

To further understand the photocatalytic mechanism of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid photocatalyst, the $8\%\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ sample was characterized by XRD before and after one and four recycling runs (Fig. 7(d)). As can be seen, no obvious peaks of the Ag phase were evident before recycling. However, peaks of the Ag phase appeared after one cycle, and their intensity increased after four recycling runs. This implies that Ag nanoparticles were formed in the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ hybrid during the photocatalytic reaction process. These particles may have formed close contacts with the surface of Ag_2MoO_4 and Ag_3PO_4 because of the photosensitization of $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ [38]. Therefore, the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ may have transformed to a ternary $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4/\text{Ag}$ heterostructure during the photocatalytic reaction.

The possible transfer routes of the photogenerated elec-

trons and holes will also be discussed to explain the enhanced photocatalytic activity, based on the conduction band minimum (CBM) and valence band maximum (VBM) potentials of Ag_3PO_4 and Ag_2MoO_4 . For a semiconductor, according to the empirical equation $E_{\text{VB}} = X - E^e + 0.5 E_g$, where E_{VB} is the VB edge potential, X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (~ 4.5 eV), E_g is the band gap energy of the semiconductor, and E_{CB} (the CB edge potential) can be determined by $E_{\text{CB}} = X - E^e - 0.5E_g$ [38]. The X values for Ag_3PO_4 and Ag_2MoO_4 are 6.16 eV and 5.92 eV, respectively [38,47]. The conduction band (CB) and valence band (VB) energy levels of Ag_2MoO_4 were calculated to be ca. -0.2 and $+3.04$ eV (vs SHE), respectively; hence, Ag_2MoO_4 cannot be excited under visible-light irradiation due to its large band gap. Meanwhile, the CB and VB potentials of Ag_3PO_4 are ca. $+0.46$ and $+2.86$ eV (vs SHE), respectively. Because the CB level of Ag_3PO_4 is less negative than the $\cdot\text{O}_2^-/\text{O}_2$ potential (-0.04 eV vs SHE) [59], it is thermodynamically unfavorable for Ag_3PO_4 to reduce the adsorbed O_2 to produce $\cdot\text{O}_2^-$. However, the reactive-species-trapping experiments demonstrated that $\cdot\text{O}_2^-$ radicals played an important role in the photocatalytic process. These observations imply that the photo-generated electrons in the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composite photocatalyst are not transferred directly from Ag_3PO_4 to O_2 .

On the basis of the above experimental results and band structure analysis of Ag_3PO_4 and Ag_2MoO_4 , a plasmonic Z-scheme photocatalytic mechanism for the observed superior photocatalytic performance of the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ composite photocatalyst is proposed, as illustrated in Fig. 8. $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ transforms to $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4/\text{Ag}$ in the early stage of the photocatalytic reaction. Under visible-light irradiation, Ag_3PO_4 can absorb photons to produce photogenerated electrons and holes [42]. Because of the surface plasmonic resonance effect and dipolar character of metallic Ag, metallic Ag can also absorb visible light, and each absorbed photon induces the efficient separation of an electron and a hole [60]. The plasmon-induced electrons in the Ag nanoparticles are transported to the CB of Ag_2MoO_4 to react with oxygen, forming $\cdot\text{O}_2^-$ active species, which further oxidize the organic pollutants, while the holes remain in the Ag nanoparticles [59]. Simulta-

Fig. 8. Schematic illustration of the charge separation and transfer in the $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4/\text{Ag}$ composites under visible light irradiation.

neously, the photogenerated electrons in the conduction band of Ag_3PO_4 transfer to the Ag nanoparticles to recombine with the plasmon-induced holes produced by plasmonic absorption in the Ag nanoparticles, while the photogenerated holes of Ag_3PO_4 remain on the VB to directly oxidize the dye molecules [59]. This effectively corresponds to a Z-scheme in the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4/\text{Ag}$ ternary heterostructure, which promotes the separation of the photogenerated electrons and holes, reducing their probability of recombination, and thus improving the activity and stability of the photocatalyst. This Z-scheme photocatalytic mechanism has also been demonstrated in other hybrid systems reported previously [59–62]. The simultaneous transfer of photogenerated electrons and holes at the $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4/\text{Ag}$ heterojunction increases both the yield and lifetime of the charge carriers by spatially separating the photogenerated electrons and holes into different domains in the hybrid photocatalyst. Furthermore, the photocorrosion of the pure Ag_3PO_4 material is further suppressed by coupling with Ag_2MoO_4 , because the photogenerated electrons are accepted by the metallic Ag produced in the photocatalytic process rather than being transferred to the Ag^+ ions of the Ag_3PO_4 lattice. As a result, the ternary $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4/\text{Ag}$ photocatalysts exhibit improved photocatalytic activity and stability.

4. Conclusions

A novel, high-efficiency visible-light-driven $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ system was successfully prepared by a facile solution reaction method, and the as-prepared hybrid materials exhibited excellent photocatalytic activity in the degradation of typical dyes (RhB, MO and MB), superior to that of pure Ag_3PO_4 under visible light. Ag nanoparticles form in situ on the surface of $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ in the early stage of the photocatalytic reaction and then act as a Z-scheme charge-transmission bridge. The excellent photocatalytic activity of $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ may originate from the efficient separation of photogenerated electron/hole pairs through the Z-scheme system composed of Ag_3PO_4 , Ag and Ag_2MoO_4 . Moreover, $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ exhibited good stability in the photocatalytic process

under visible-light irradiation. On the basis of their efficient and stable photocatalytic activity, $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ systems show promise for use in environmental purification via the removal of organic pollutants.

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Graphical Abstract

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Construction of $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ Z-scheme heterogeneous photocatalyst for the remediation of organic pollutants

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A novel $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ Z-scheme heterojunction photocatalytic system was constructed, giving rise to excellent photocatalytic activity on the degradation of typical dyes.

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Z型Ag₃PO₄/Ag₂MoO₄异质结光催化剂构建和光催化降解有机污染物

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摘要: 作为一种绿色技术, 半导体光催化氧化广泛应用于环境污染治理和太阳能转化领域. 高效、稳定、可回收利用催化剂的开发是光催化技术发展的一个重要方向. Ag系半导体光催化剂因在可见光分解水制氢及降解有机污染物等方面表现出优异的催化性能而广受关注. 然而, 该催化剂失活快, 制约了其应用. 因此, 提高Ag系半导体材料的光催化稳定性成为近年研究热点. 在各种Ag基光催化剂中, Ag₃PO₄光催化剂因其在可见光下光氧化水产生O₂以及有机染料的光催化分解中有着高的量子效率, 引起了人们广泛关注. 如何进一步提升Ag₃PO₄光催化剂性能及在光催化过程中的稳定性成为研究焦点, 包括Ag₃PO₄光催化剂的特殊形貌和晶体结构控制生长以及复合材料控制制备. 但是Z型Ag₃PO₄基可见光催化剂的构筑仍然是一个挑战.

本文利用Ag₂MoO₄和Ag₃PO₄的溶液相反应法合成了Z型Ag₃PO₄/Ag₂MoO₄复合光催化剂, 通过Ag₃PO₄/Ag₂MoO₄异质结

光催化剂在可见光下降解罗丹明B(RhB)、亚甲基橙(MO)、亚甲基蓝(MB)和苯酚研究了其光催化性能,采用X射线衍射(XRD)、能谱、傅立叶变换红外光谱(FT-IR)、拉曼光谱、场发射扫描电子显微镜(FE-SEM)以及紫外可见漫反射光谱(UV-vis)等手段表征了该催化剂。

XRD, FTIR 和拉曼光谱结果表明,复合材料由 Ag_3PO_4 , Ag_2MoO_4 和单质银组成,表面成功合成了Z构型 $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ 复合材料。SEM结果发现纯 Ag_3PO_4 是规则的球状,纯 Ag_2MoO_4 则是多面体状块的颗粒,在 $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ 复合材料中可以看到规则的球状体 Ag_3PO_4 和 Ag_2MoO_4 纳米颗粒,并且随着 Ag_2MoO_4 含量的增加, Ag_3PO_4 颗粒的尺寸逐渐减小。UV-vis结果发现 Ag_2MoO_4 的加入拓展了复合材料对可见光的吸收范围。光催化性能测试结果表明,8% $\text{Ag}_2\text{MoO}_4/\text{Ag}_3\text{PO}_4$ 在可见光下具有优异的光催化性能:可见光照射5 min, RhB, MO和MB的降解效率分别可达95%, 97%和90%。复合材料样品经过4个循环实验后,其降解RhB的效率仍然保持在84%,证明了其具有较高的稳定性。

为了进一步研究 $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{MoO}_4$ 的光催化机理,我们用对苯醌、乙二胺四乙酸二钠和丁醇进行了捕捉剂实验。结果表明,超氧自由基和光生空穴在降解有机染料过程中起主要作用。通过光电流测试、复合材料价带导带位置计算以及循环过程样品XRD分析并结合文献结果认为,Z构型 $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{Ag}_2\text{MoO}_4$ 异质结光催化体系以及可见光照射初期金属Ag纳米颗粒的生成是其具有高光催化活性和稳定性的原因。

关键词: Z型异质结; 磷酸银; 杂化材料; 电荷转移; 光催化

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