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Synthesis of nano-sized $Ag_3PW_{12}O_{40}/ZnO$ heterojunction as a photocatalyst for degradation of organic pollutants under simulated sunlight



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KEYWORDS

Ag₃PW₁₂O₄₀/ZnO; Nanoheterojunction; Photocatalyst; Organic pollutant **Abstract** With the rapid development of the world economy, water pollution has become increasingly serious. The photocatalytic degradation of pollutants is one of the most promising environmental treatment techniques. In this study, novel $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction was successfully constructed via a chemical process and was then characterized using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, diffuse reflectance spectroscopy, Brunauer-Emmett-Teller analysis, and photoluminescence measurements. The synthesized nanoheterojunction exhibited good crystallinity and dispersity. The particle diameter of the composite was approximately 800 nm, the bandgap was 2.92 eV, and the specific surface area was approximately 10.5 m².g⁻¹. Under optimum conditions, the photocatalyst degraded 82.1% RhB in 60 min. Moreover, the novel $Ag_3PW_{12}O_{40}/ZnO$ heterojunction also exhibited an excellent recycling stability. Hydroxyl radicals, superoxide radicals, and holes played important roles in the photocatalytic degradation process. A

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possible mechanism for the enhanced photocatalytic performance of the nanoheterojunction was proposed. This work provides a strong foundation for the application of $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction for treating environmental organic pollutants.

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1. Introduction

The rapid development of modern industrialization has led to severe environmental pollution because of the discharge of industrial wastewater, which contains a variety of organic pollutants, into the environment (Nguyen Quoc, Sabbah et al., 2021; Ren, Lv et al., 2021). Some organic pollutants are highly toxic, chemically stable and difficult to biodegrade (Huo, Yang et al., 2021; Tufail, Price et al., 2021). Once they enter the aquatic ecosystem, they can cause serious harm to the ecological environment. The commonly used wastewater treatment methods are physical adsorption, microbial methods, chemical redox methods, etc. (Ganiyu, Martinez-Huitle et al., 2020; Rojas and Horcajada, 2020). These methods can remove organic dyes from wastewater to a certain extent, but cannot completely remove these pollutants. Moreover, the removal efficiency of these methods is not high for some pollutants. Sometimes, these treatment methods cause secondary environmental pollution. In addition, some methods involve complex operations and are expensive. Therefore, it is imperative to explore new technologies for degrading the organic dyes in wastewater with high efficiency and low cost (Hasanpour and Hatami, 2020; Yu et al., 2020a). It is of great significance for the further development of industrial production, protecting the environment, and maintaining the ecological balance.

Photocatalytic degradation is based on the redox process of a photocatalyst under illumination, which leads to the effective decomposition of the pollutants (Zhang, Tang et al., 2010; Zare, Iftekhar et al., 2021). This method has many advantages, such as high reaction speed, mild reaction conditions, no secondary pollution, and complete catalytic degradation, and hence has been widely used in the treatment of wastewater (Chakrabarti and Dutta, 2004; Zangeneh, Zinatizadeh et al., 2015). ZnO is a widely used n-type semiconductor photocatalyst with a bandgap of approximately 3.2 eV. It has the unique advantages of high efficiency, stability, low price, and nontoxicity. However, owing to its high energy band and low sunlight utilization efficiency, its application as a photocatalyst is limited (Danwittayakul, Jaisai et al., 2015; Ani, Akpan et al., 2018). It has been demonstrated that fabricating composites of ZnO with other nanomaterials is an effective approach to improve its photocatalytic performance.

Polyoxometalates are inorganic anionic metal oxygen clusters formed by connecting high valent transition metals M (M = W(VI), Mo(VI), V(V), Nb(V), Ta(V), etc.) through oxygen bridge bonds, also known as polyacids or metal-oxygen clusters (POMs) (Long, Tsunashima et al., 2010). Noble metals can replace the coordination atoms of POMs and change the electronic structure, shape, and size of polyacid materials (Putaj and Lefebvre, 2011; Izarova, Pope et al., 2012). With the replacement of Ag, the properties of POMs change, but their redox state stability and electron transfer properties remain constant (Zhang, Liu et al., 2021). Silver phosphomolybdate ($Ag_3PW_{12}O_{40}$) combines the advantages of polyacids and Ag and is generally insoluble in water (Tadjarodi, Zad et al., 2015; Hua, Yuan et al., 2020). Therefore, Ag_3PW_{12} - O_{40} shows huge potential for application in catalysis, especially photocatalysis. A composite of ZnO and $Ag_3PW_{12}O_{40}$ can construct a new nanoheterojunction photocatalyst. Such nanoheterojunctions are expected to expand the spectral response range of the photocatalyst, promote its photoexcited carrier separation efficiency, and further improve the photocatalytic activity of the composite material.

In this work, a $Ag_3PW_{12}O_{40}/ZnO$ composite was successfully constructed through a chemical process and was then characterized using various analytical techniques. The organic dye used to evaluate the photocatalytic performance of the composite was Rhodamine B (RhB) (Fig. 1). The composite showed excellent photocatalytic degradation performance. Moreover, a possible mechanism for the enhanced photocatalytic performance of the composite of the composite was proposed. This work provides a solid theoretical foundation and strong experimental support for the application of Ag_3PW_{12} - O_{40}/ZnO photocatalysts in wastewater treatment.

2. Experimental section

2.1. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized using a hydrothermal method as follows. First, a solution of 15 mL water and 1.36 g ZnCl₂ was added to 20 mL of a 1 mol/L NaOH solution under vigorous stirring. Then, the mixture was transferred to a stainless-steel autoclave lined with 50 mL polytetrafluoroethylene and was heated at 120 °C for 12 h. After the autoclave was naturally cooled to room temperature, the precipitate was washed three times with deionized water and ethanol and dried at 80 °C to obtain the ZnO nanoparticles.

2.2. Preparation of $Ag_3PW_{12}O_{40}$

 $Ag_3PW_{12}O_{40}$ was prepared according to a previously reported method (Zhang, Zhao et al., 2020). First, 1 mmol $H_3PW_{12}O_{40}$ was dissolved in 10 mL of deionized water under stirring and then 50 mL of a 3 mmol AgNO₃ solution was added dropwise to the mixture. After 60 min, $Ag_3PW_{12}O_{40}$ was formed in the solution. The prepared samples were washed with water and alcohol. After the sample was dried in air, the desired product was obtained.

2.3. Fabrication of the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction photocatalysts

The nanoheterojunction photocatalyst was synthesized as follows. ZnO (0.5 g) was evenly dispersed in 50 mL deionized



Fig. 1 Schematic for the construction and photocatalytic performance of the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction.

water under ultrasonication for 10 min. To the resulting solution, $Ag_3PW_{12}O_{40}$ was added (in different amounts) under vigorous stirring for 24 h. Then, the resulting mixture was centrifuged and the precipitate was collected. Finally, the precipitate was alternately washed three times with water and ethanol and dried overnight at 80 °C to obtain the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction photocatalyst. Different $Ag_3-PW_{12}O_{40}/ZnO$ mass ratios (10%, 20%, 30%, 40%, and 50%) were used.

2.4. Characterization

The samples used for the characterization were ZnO, Ag₃- $PW_{12}O_{40}$, and the Ag₃PW₁₂O₄₀/ZnO composite with a Ag₃-PW₁₂O₄₀ to ZnO mass ratio of 30%. The morphologies of the samples were examined using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The X-ray diffraction (XRD) analysis of the samples was performed using an X-ray diffractometer with Cu Ka radiation as the X-ray source operating at 60 kV and 80 mA (Bruker AXS, D8, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed on an electron spectrometer (VG, EscaLab 250Xi, Britain) with Al Ka X-ray radiation at 300 W. All the binding energies were calibrated using the C 1 s peak at 284.8 eV. The Fourier transform infrared (FT-IR) spectra of the samples were recorded using a Fourier transform infrared spectrophotometer (PE, USA) over the wavenumber range of 400-4000 cm⁻¹ with KBr discs. The absorbance of the samples was evaluated using an ultraviolet-visible (UV-Vis) dual-beam spectrophotometer (Persee, TU-1900, China) manufactured by Beijing General Electric Co., Ltd. The pore diameters of the catalysts were determined from their N₂ absorption-desorption isotherms (Quantachrome Nova Win2, American Kang Tai Company). The photoluminescence (PL) spectra of the samples were recorded on an F-7000 FL spectrophotometer (Hitachi, Japan) with an excitation wavelength of 315 nm.

2.5. Photocatalytic performance

2.5.1. Photocatalytic activity evaluation

In this study, RhB was chosen as a representative organic pollutant. The photocatalytic degradation experiment was carried out as follows. In a 50 mL quartz tube, 15 mg of the photocatalyst was dispersed in 50 mL of a 50 mg/L RhB solution. The quartz tube was placed in a reactor equipped with a cooling water jacket. The mixture was stirred in the dark for 30 min to achieve the adsorption saturation of RhB on the photocatalyst. Then, the reaction system was irradiated with a 500 W xenon lamp with light intensity of 800 W/m² and photon flux of 650 lm (DY500G, Guangzhou Xingchuang Electron Co. Ltd, China). At 10 min intervals, 5 mL of the mixture was removed and centrifuged. The absorbance of the supernatant at 554 nm was measured using a UV spectrophotometer.

2.5.2. Scavenging photogenerated carriers

To identify the reactive species that played an important role in the photocatalytic degradation process, scavenger experiments were carried out. For this purpose, p-benzoquinone, isopropanol, and methanol were used as the trapping agents for superoxide radicals (\cdot O₂), hydroxyl radicals (\cdot OH), and holes (h⁺), respectively in the photocatalytic process. The rest of the experimental process was the same as that for the photocatalytic degradation reaction.

3. Results and discussion

3.1. Crystal structure analysis

XRD was used to analyze the crystal structures of Ag₃PW₁₂-O₄₀, ZnO, Ag₃PW₁₂O₄₀/ZnO, and the diffraction patterns are shown in Fig. 2. As can be observed from the figure, Ag₃- $PW_{12}O_{40}$ showed diffraction peaks at $2\theta = 21.0^{\circ}, 23.5^{\circ}, 25.8^{\circ}, 25.8^{\circ}$ 29.9°, 31.8°, 33.5°, 35.2°, 38.4°, 41.4°, 42.8°, 45.5°, 46.9°, 49.4°, 54.3°, 61.1°, and 63.28°. These peaks are consistent with those reported by Matachowski et al. and Liu et al. (Matachowski, Zimowska et al., 2012; Liu, Zhang et al., 2014). The ZnO nanoparticles showed diffraction peaks at $2\theta = 31.7^{\circ}$, 34.4° , 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, and 69.08° corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) diffraction planes of wurtzite, respectively (No. 65-3411). All the diffraction peaks of ZnO were observed in the XRD pattern of the Ag₃PW₁₂O₄₀/ZnO composite. The composite showed a weak diffraction peak at $2\theta = 26.2^{\circ}$ (inset of Fig. 2), which is a characteristic peak of $Ag_3PW_{12}O_{40}$ nanomaterials. In addition, because of the low amount of Ag₃PW₁₂- O_{40} in the composite, the intensity of its diffraction peak was weak. These results indicate the successful fabrication of the Ag₃PW₁₂O₄₀/ZnO composite.

3.2. Morphology

The morphologies of the ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3PW_{12}O_{40}/ZnO$ samples were observed using TEM and SEM, and the TEM and SEM images of the samples are shown in



Fig. 2 XRD patterns of ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3PW_{12}O_{40}/ZnO$; the inset shows the magnified diffraction pattern of $Ag_3-PW_{12}O_{40}/ZnO$ over the 2 θ range of 20–32°.

Fig. 3. As can be observed from Fig. 3a and 3d, the ZnO nanoparticles were flake-shaped with an average diameter of approximately 200 nm. The $Ag_3PW_{12}O_{40}$ particles were polyhedral in shape and had an average diameter of approximately 700 nm, as shown in Fig. 3b and 3e. Fig. 3c and 3f show the TEM and SEM images of the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction composite, respectively. As can be observed from the images, the morphology of the composite material was different from those of ZnO and $Ag_3PW_{12}O_{40}$. The $Ag_3PW_{12}O_{40}/ZnO$ composite showed agglomerated $Ag_3PW_{12}O_{40}$ nanoparticles, which were surrounded by ZnO nanoparticles. The diameter of the $Ag_3PW_{12}O_{40}/ZnO$ composite nanoparticles was



Fig. 4 $\;$ FT-IR spectra of ZnO, $Ag_3PW_{12}O_{40},$ and $Ag_3PW_{12}O_{40}/$ ZnO.

approximately 800 nm. In addition, the $Ag_3PW_{12}O_{40}/ZnO$ composite showed good dispersity.

3.3. Chemical bond analysis

Fig. 4 shows the FT-IR spectra of ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3PW_{12}O_{40}/ZnO$. All the samples showed IR peaks at approximately 3450 cm⁻¹, which can be ascribed to the surface hydroxyl group (Wang et al., 2019). The FT-IR spectrum of ZnO showed IR absorption peaks at 571 and 432 cm⁻¹, which can be attributed to the asymmetric and symmetric stretching vibrational peaks of Zn-O, respectively. $Ag_3PW_{12}O_{40}$ exhibited



Fig. 3 TEM images of (a) ZnO, (b) $Ag_3PW_{12}O_{40}$, and (c) $Ag_3PW_{12}O_{40}/ZnO$; SEM images of (d) ZnO, (e) $Ag_3PW_{12}O_{40}$, and (f) $Ag_3PW_{12}O_{40}/ZnO$.

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IR absorption peaks at 1080, 985, 889, 806 cm⁻¹, which can be attributed to the stretching vibrational peaks of P-O_a, W-O_d, W-O_b-W, and W-O_c-W, respectively. Here, O_a is the oxygen in the central PO₄ tetrahedron, O_d is the end oxygen bonded with the W atom, O_b is the edge-shared oxygen connected with W, and O_c is the angle shared oxygen connected with W₃O₁₃ (Zhu, Gao et al., 2013; Holclajtner-Antunovic, Bajuk-Bogdanovic et al., 2015; Zhang, Zhao et al., 2020). The Ag₃-PW₁₂O₄₀/ZnO composite showed IR peaks corresponding to ZnO and Ag₃PW₁₂O₄₀ at 1080, 985, 889, 806, 571, and 432 cm⁻¹. This further confirms the successful fabrication of the Ag₃PW₁₂O₄₀/ZnO nanoheterojunction.

3.4. Element state analysis

XPS analysis was carried out to investigate the elemental states of the Ag₃PW₁₂O₄₀/ZnO nanoheterojunction. As shown in Fig. 5, the survey XPS profile of the composite showed peaks corresponding to (a), Zn (b), Ag (c), W (d), and O (e), indicating the presence of these elements in the composite. The Zn 2p (Fig. 5b) XPS profile of the composite showed two peaks at 1044.6 and 1021.6 eV corresponding to the $Zn2p_{3/2}$ and Zn2p_{1/2} states of the ZnO crystal lattice. However, these two peaks shifted slightly to 1044.9 and 1021.9 eV, respectively. This is because the chemical environment of Zn ions changed after the incorporation of Ag₃PW₁₂O₄₀ into the ZnO lattice. Ag₃PW₁₂O₄₀ showed Ag XPS peaks at 373.1 and 367.1 eV in Fig. 5c, which can be attributed to the Ag $3d_{3/2}$ and Ag 3d_{5/2} states of Ag(I), respectively (Zhang, Hu et al., 2016). The Ag 3d XPS profile of Ag₃PW₁₂O₄₀/ZnO could be fitted by multiple Gaussians into four peaks. The peaks at 373.5 and 367.6 eV correspond to the $3d_{3/2}$ and Ag $3d_{5/2}$ states of Ag(I), respectively. As compared to the Ag(I) peaks of Ag₃-PW₁₂O₄₀, the Ag(I) peaks Ag₃PW₁₂O₄₀/ZnO shifted to higher binding energies. This can be attributed to the change in the chemical environment of the Ag ions in the composites. The peaks at 374.5 and 368.5 eV can be ascribed to the Ag $3d_{3/2}$ and Ag $3d_{5/2}$ states of Ag(0), respectively. This indicates that Ag(0) was formed during the synthesis process. This can be attributed to the reduction of Ag(I) in the solution environment.

Fig. 5d shows the W XPS profiles of $Ag_3PW_{12}O_{40}$ and $Ag_3PW_{12}O_{40}/ZnO$. In the case of $Ag_3PW_{12}O_{40}$, W XPS peaks were observed at 37.1 and 35.0 eV, which can be attributed to W (VI) (Cai, Shi et al., 2018). The W XPS profile of $Ag_3PW_{12}O_{40}/ZnO$ showed peaks at 38.2 and 36.1 eV. This is probably because the chemical environment of W in the composite material changed after the formation of the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction through the reaction between ZnO and $Ag_3PW_{12}O_{40}$. By fitting with the Gaussian function, the O 1 s XPS peak of the $Ag_3PW_{12}O_{40}/ZnO$ composite could be deconvoluted into two components, as shown in Fig. 5e. The peak at 531.8 eV can be attributed to the O^{2-} ions in the ZnO crystal lattice, while that at 530.6 eV corresponds to the O^{2-} ions in the crystal lattice of Keggin structure (W-O-W).

3.5. UV–Vis diffuse reflectance spectroscopy (DRS) analysis of the nanoheterojunction

DRS is used to analyze the optical absorption properties of solid nanoheterojunctions that cannot be characterized in the

transmission mode (Nanda, Sapra et al., 2000; Zhang, Shi et al., 2000). The DRS profiles of ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3-PW_{12}O_{40}/ZnO$ are shown in Fig. 6. As shown in Fig. 6a, the absorption onsets for ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3PW_{12}O_{40}/ZnO$ were approximately 393, 398, and 425 nm, respectively.

Although the absorption onset was used to evaluate the bandgap of the as-synthesized composite, the bandgap could be determined from the Tauc plot of its DRS profile. The following expression proposed by Tauc et al. and Davis and Mott (Tauc, Grigorovici et al., 1966; Davis and Mott, 1970) was used.

$$(hv\alpha)^2 = A(hv - E_g) \tag{1}$$

where α is the absorption coefficient, v is the frequency of vibration, A is a proportional constant, E_g is the bandgap, and h is the Planck's constant. The hv- $(\alpha hv)^2$ (tangent) curves of the samples are shown in Fig. 6b. The bandgap E_g values of ZnO, Ag₃PW₁₂O₄₀, Ag₃PW₁₂O₄₀/ZnO were found to be 3.15, 3.12, and 2.92 eV, respectively. The results revealed that the spectrum response of the Ag₃PW₁₂O₄₀/ZnO composite extended to the visible region. This can broaden the utilization of the solar spectrum by nanoheterojunctions and further improve the photocatalytic performance of photocatalysts.

3.6. Specific surface area and pore size distribution of the nanoheterojunction

 N_2 adsorption-desorption isotherms were recorded to investigate the BET surface area and Barrett-Joyner-Halenda pore size distribution of the Ag₃PW₁₂O₄₀/ZnO nanoheterojunction. The results are shown in Fig. 7. The composite showed a type-IV isotherm with a type-H3 hysteresis loop and a relatively wide pore size distribution in the mesoporous region (Yu et al., 2020b; Lu et al., 2020).

The specific surface areas of ZnO, Ag₃PW₁₂O₄₀, and Ag₃-PW₁₂O₄₀/ZnO were calculated to be 7.8, 2.1, and 10.5 m². g⁻¹, respectively. Interestingly, the Ag₃PW₁₂O₄₀/ZnO composite exhibited the largest BET specific surface area among all the samples investigated in this study. According to the pore size distribution results (inset in Fig. 7), the average pore sizes of ZnO, Ag₃PW₁₂O₄₀, and Ag₃PW₁₂O₄₀/ZnO were approximately 27.8, 18.4, and 12.9 nm, respectively. The Ag₃PW₁₂O₄₀/ZnO heterojunction catalyst showed smaller average pore diameter (12.9 nm) than ZnO and Ag₃PW₁₂O₄₀. The large specific surface area of the composite provided numerous surface active centers and facilitated the separation of the photogenerated electron and hole pairs, which improved the photocatalytic performance of the composite.

3.7. Evaluation of photocatalytic activity and recycling stability

3.7.1. Optimum photocatalytic conditions

The photocatalytic activity of the composites was evaluated by carrying out the photocatalytic degradation of RhB on them. The $Ag_3PW_{12}O_{40}$ to ZnO mass ratio, photocatalyst amount, initial dye concentration, and solution pH were found to be the four key factors that remarkably affected the photocatalytic activity of the composites.

The $Ag_3PW_{12}O_{40}/ZnO$ composites with different mass ratios (10%, 20%, 30%, 40%, and 50%) were used for the photocatalytic degradation experiments and their photocatalytic



Fig. 5 XPS profiles of ZnO and the $Ag_3PW_{12}O_{40}/ZnO$ composite (a) survey, (b) Zn 2p, (c) Ag 3d, (d) W 4f, and (e) O 1 s.

activity was evaluated. As shown in Fig. 8a. the RhB photocatalytic degradation rates of the 10%, 20%, and 30% Ag₃PW₁₂-O₄₀/ZnO composites were 54%, 66%, and 73%, respectively. However, when the Ag₃PW₁₂O₄₀ to ZnO ratio was increased to 40% and 50%, the degradation rate decreased to 70% and 65%, respectively. This indicates that when the Ag₃PW₁₂-O₄₀ content was increased from 10% to 50%, the photocatalytic activity of the nanoheterojunction first increased and then decreased gradually after reaching the highest point. This indicates that when present in the optimum amount, Ag₃PW₁₂-O₄₀ effectively inhibited the recombination of the photoexcited electrons and holes. However, excessive Ag₃PW₁₂O₄₀ facilitated the recombination of the photogenerated carriers, reducing the photocatalytic activity of the composite. Therefore, the optimum Ag₃PW₁₂O₄₀ content for achieving excellent photocatalytic activity was 30%. Thus, the experiments were carried out using the composite with $30\% \text{ Ag}_3\text{PW}_{12}\text{O}_{40}$.

The photocatalyst dosage and initial RhB concentration significantly affected the photocatalytic activity of the Ag₃- $PW_{12}O_{40}/ZnO$ nanoheterojunction. Experiments were conducted with different catalyst dosages and initial RhB concentrations, and the results are shown in Fig. 8b. When the photocatalyst amounts were 5, 10, 15, 20, and 25 mg, the final RhB degradation rates were 57%, 72%, 80%, 74%, and 70%, respectively. The RhB degradation rate increased gradually with an increase in the photocatalyst dosage up to 15 mg of the photocatalyst. This is probably because the photocatalyst amount was less than 15 mg. This also indicates that the photon could not be fully used because of the insufficient



Fig. 6 DRS profiles (a) and $h\nu$ -($\alpha h\nu$)² curves (b) of ZnO, Ag₃PW₁₂O₄₀, and Ag₃PW₁₂O₄₀/ZnO.

catalyst amount. With an increase in the input amount beyond 15 mg, the RhB photocatalytic degradation rate of the composite decreased gradually. This indicates that excessive catalyst shielded some of the photons, leading to a decrease in the utilization of photons, and hence the photocatalytic efficiency of the catalyst. The results showed that the optimum photocatalyst amount was 15 mg, which was used for further experiments.

As shown in Fig. 8c, the RhB photocatalytic degradation rates of 80%, 79%, 77%, 68%, and 65% were achieved for the initial RhB concentrations of 50, 60, 70, 80, and 90 mg/L, respectively. This indicates that the nanoheterojunction catalyst could effectively decompose the dye. However, excessively high dye concentrations affected the number of photons reaching the photocatalyst surface, thereby decreasing the dye degradation rate. Therefore, the optimum RhB concentration for achieving efficient dye degradation performance was 50 mg/L.

The adaptability of a photocatalyst to acids and alkalis is an important factor to be considered for its practical applications. In this study, the effect of the solution pH on the RhB degradation performance of the nanoheterojunction was investigated (Fig. 8d). The solution pH was adjusted to 3, 5, 7, 9, and 11. The RhB degradation rate of the nanoheterojunction



Fig. 7 N_2 adsorption–desorption isotherms and pore size distribution curves of ZnO, $Ag_3PW_{12}O_{40}$, and $Ag_3PW_{12}O_{40}/ZnO$.

was 65%, 72%, 78%, 81%, and 79% when the solution pH was 3, 5, 7, 9, and 11, respectively. This indicates that the asprepared $Ag_3PW_{12}O_{40}/ZnO$ composite photocatalyst had good adaptability to the variation in the pH of the photocatalytic system. The composite photocatalyst maintained good photocatalytic activity over the pH range of 3–11, and the photocatalytic efficiency was higher at pH = 9.

3.7.2. Degradation of RhB under optimum conditions

The photocatalytic degradation of RhB over the ZnO, Ag₃-PW₁₂O₄₀, and Ag₃PW₁₂O₄₀/ZnO composite photocatalysts was evaluated under the optimum conditions: Ag₃PW₁₂O₄₀ content = 30%, photocatalyst amount = 15 mg, initial dye concentration = 50 mg/L, and solution pH = 9, and the results are shown in Fig. 9. It can be observed from the figure that ZnO could degrade only approximately 15.1% of the dye within 60 min. Within the same time period, Ag₃PW₁₂O₄₀ degraded 74.1% of the dye. The physical mixture of ZnO and Ag₃PW₁₂O₄₀ could degrade 69.6% of the dye within 60 min. However, the Ag₃PW₁₂O₄₀/ZnO nanoheterojunction catalyst degraded 82.1% of the RhB dye within the same duration.

3.7.3. Recycling stability of the photocatalyst

Cycling stability is the prerequisite for realizing the practical applications of a photocatalyst. Therefore, the reusability of the $Ag_3PW_{12}O_{40}/ZnO$ heterojunction for the photodegradation of RhB was evaluated. Fig. 10 shows the photocatalytic degradation of RhB (50 mg/L) over the 30% $Ag_3PW_{12}O_{40}/ZnO$ catalyst under visible light irradiation. The RhB degradation rate of the nanoheterojunction in the first cycle was 82.5%, which reduced slightly to 80.5% in the second cycle. The degradation rates in the third and fourth cycles were 79.8% and 78.1%, respectively. These results indicate that the nanoheterojunction photocatalysts with high cycling stability. Therefore, heterojunction photocatalysts with high cycling stability can be practically utilized to eliminate organic dyes from sewage.

3.7.4. Photocatalytic degradation mechanism

To identify the reactive species that participated in the photocatalytic degradation of RhB over the nanoheterojunction,



Fig. 8 RhB photocatalytic degradation curves of the nanoheterojunction catalyst at (a) different $Ag_3PW_{12}O_{40}$ to ZnO mass ratios, (b) different photocatalyst amounts, (c) different initial dye concentrations, (d) different pH values.

scavenger analysis was conducted by adding three different scavengers, isopropyl alcohol (IPA, 2 mM), benzoquinone (BQ, 2 mM), and methanol (2 mM), to the reaction system. Among these scavengers, IPA was used to trap hydroxyl radicals, BQ was used as a scavenger for superoxide radicals, and methanol was used to quench holes (Alam, Shah et al., 2019; Lu, Xiao et al., 2020; Reddy, Reddy et al., 2020). As can be observed from Fig. 11, the RhB photocatalytic degradation rate of the composite decreased remarkably after the addition of the scavengers, IPA, BQ, and methanol, to the reaction



Fig. 9 Photocatalytic degradation of RhB over ZnO, Ag_3PW_{12} - O_{40} , ZnO and $Ag_3PW_{12}O_{40}$ mixture, and $Ag_3PW_{12}O_{40}$ /ZnO under the optimum conditions.



Fig. 10 Cycling stability of the $Ag_3PW_{12}O_{40}/ZnO$ photocatalyst for the degradation of RhB over four cycles under visible light irradiation.



Fig. 11 Effects of BQ, IPA, and methanol on the photocatalytic degradation of RhB by $Ag_3PW_{12}O_{40}/ZnO$.

system. The RhB degradation rates of the composite catalyst were very close when the three scavengers were added alone to the solution. This indicates that the hydroxyl radicals, superoxide radicals, and holes played important roles in the photocatalytic degradation of RhB, and these three radicals made similar contributions to the photocatalytic degradation process.

In semiconductors, the electrons in the valence band (VB) move to the conduction band (CB) under irradiation. The excited electrons de-excite and recombine with the holes in the VB to release photons of a certain wavelength. Therefore, the PL of a semiconductor represents the recombination of the photogenerated carriers. Therefore, PL spectroscopy was used to analyze the charge separation of the composite photocatalyst. Generally, the lower the PL emission intensity, the lower is the recombination rate of electron-hole pairs. Fig. 12 shows the PL spectra of ZnO and the Ag₃PW₁₂O₄₀/ZnO heterojunction under light irradiation. ZnO exhibited strong emission peaks at approximately 398 and 533 nm. Interestingly, the PL intensity of the Ag₃PW₁₂O₄₀/ZnO heterojunction decreased remarkably as compared to that of ZnO. This indicates that the heterojunction between ZnO and Ag₃PW₁₂O₄₀ significantly suppressed the recombination of the photogenerated electron-hole pairs. Therefore, as compared to ZnO, the Ag₃PW₁₂O₄₀/ZnO nanoheterojunction showed improved photocatalytic performance.

It is well-known that ZnO and $Ag_3PW_{12}O_{40}$ are n-type semiconductors. In this study, a heterojunction was formed by combining these two semiconductors. The electron rearrangement was complete because of the different Fermi energy levels of ZnO and $Ag_3PW_{12}O_{40}$. The electrons migrated from $Ag_3PW_{12}O_{40}$ to ZnO until the Fermi level reached equilibrium. This migration of electrons resulted in a decrease in the electronic density of $Ag_3PW_{12}O_{40}$ and an increase in that of ZnO. Consequently, a built-in electric field was generated owing to the potential difference between the $Ag_3PW_{12}O_{40} \rightarrow$ ZnO). The built-in electric field substantially accelerated the transfer and separation of the photogenerated carriers. Therefore, the $Ag_3PW_{12}O_{40}/ZnO$ nanoheterojunction synthesized in this study is a direct Z-scheme photocatalyst.



Fig. 12 PL spectra of ZnO and $Ag_3PW_{12}O_{40}/ZnO$.

In the Z-scheme heterojunction, the bandgaps of Ag_3PW_{12} -O₄₀ and ZnO were 3.12 and 3.15 eV, respectively. Both generated charge carriers under ultraviolet light excitation. The photoexcited electrons in the CB of ZnO recombined with the holes in the VB of $Ag_3PW_{12}O_{40}$ under the effect of the built-in electric field. As a result, highly reductive photogenerated electrons and highly oxidizing holes accumulated in the CB of $Ag_3PW_{12}O_{40}$ and the VB of ZnO, respectively. Some of the photogenerated electrons with strong reducibility were captured by O₂ in water to generate \dot{sO}_2^- . Holes were captured by the H₂O molecules to generate \dot{sOH} . Therefore, the Zscheme $Ag_3PW_{12}O_{40}/ZnO$ heterojunction showed high photogenerated charge carrier separation efficiency, and hence excellent photocatalytic performance.

4. Conclusions

A Ag₃PW₁₂O₄₀/ZnO nanoheterojunction was successfully constructed via a chemical process. The as-synthesized nanoheterojunction showed good crystallinity and dispersity and had a particle diameter of approximately 800 nm. The bandgap of the composite was approximately 2.92 eV, and its absorption threshold extended to the visible light region. The specific surface area of the composite was approximately 10.5 m².g⁻¹. Under the optimum reaction conditions, the $Ag_3PW_{12}O_{40}/$ ZnO nanoheterojunction photocatalyst degraded approximately 82.1% of RhB. Moreover, the novel $Ag_3PW_{12}O_{40}/$ ZnO nanoheterojunction also exhibited excellent recycling stability. Hydroxyl radicals, superoxide radials, and holes played an important role in the photocatalytic degradation of RhB. The excellent photocatalytic performance and efficient charge carrier separation of the heterojunction catalyst could be well explained by the Z-scheme mechanism. This work provides useful theoretical guidance and a strong experimental foundation for the application of Ag₃PW₁₂O₄₀/ZnO nanoheterojunctions in the treatment of environmental organic pollutants.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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