**Ag₃PO₄@holmium phosphate core@shell composites with enhanced photocatalytic activity**

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In this study, Ag₃PO₄@holmium phosphate (HP) composite photocatalysts were first prepared by silver-ammonia-solution-assisted solution co-deposition. During co-deposition, Ag₃PO₄ particles were encapsulated by a flocculent amorphous substance layer of HP, affording a Ag₃PO₄@HP core–shell heterojunction structure with a Ho/Ag molar ratio of 0.05/2.95. The core–shell structure significantly improved the photocatalytic activity of Ag₃PO₄. In addition, the photocatalytic mechanism of Ag₃PO₄@HP was discussed.

### 1. Introduction

Semiconductor photocatalysts have attracted considerable attention as they demonstrate the potential of addressing energy and environmental issues, including photochemical water splitting, organic pollutant degradation, and CO₂ photocatalytic reduction. In 2010, Ye reported a novel semiconductor photocatalyst Ag₃PO₄, which exhibited strong photo-oxidative activities for O₂ evolution from water splitting in the presence of a sacrificial reagent AgNO₃, and a high degradation rate for organic dyes under visible-light irradiation. The photocatalytic activity of Ag₃PO₄ is superior to those of previously reported visible-light photocatalysts, e.g., BiVO₄ (ref. 8) and N-doped TiO₂. Hence, it has been widely investigated.

According to previously reported studies, the heterojunction structure between Ag₃PO₄ and other semiconductor materials may modulate the band gap, improve dispersion stability, and enhance the separation efficiency of photoelectron–hole pairs, leading to the enhanced photocatalytic activity of the composite catalyst. Several Ag₃PO₄-based composite photocatalysts have been developed, e.g., AgₓAg₃PO₄ (X = Cl, Br, and I), Ag₃PO₄/TiO₂, Ag₃PO₄/CeO₂, Ag₃PO₄/WS₂, Bi₂O₃/Ag₃PO₄, Ag₃PO₄/BiPO₃, Ag₃PO₄/BiOBr, and Ag₃PO₄/g-C₃N₄.

In this study, Ag₃PO₄ and Ag₃PO₄@HP photocatalysts were prepared by silver-ammonia-solution-assisted solution co-deposition. The core–shell structure and photocatalytic properties of Ag₃PO₄@HP were investigated in detail.

### 2. Experimental

#### 2.1 Preparation

**2.1.1 Preparation of Ag₃PO₄.** First, AgNO₃ and KHP were separately dissolved in distilled water. Second, a NH₃·H₂O solution was slowly added to the AgNO₃ solution under constant magnetic stirring, affording a silver ammonia solution, until the brown precipitate disappeared. Then, a KH₂PO₄ solution with a Ag(NH₃)₂NO₃ : KH₂PO₄ molar ratio of 1 : 3 was added into the silver ammonia solution under intense stirring for 5 min before standing for 10 min, and the precipitates were collected by centrifugation. The obtained precipitate was washed three times with absolute ethanol and distilled water, followed by drying at 80 ℃ for 30 min, affording Ag₃PO₄.

**2.1.2 Preparation of Ag₃PO₄@HP.** First, Ho₂O₃ was dissolved in nitric acid, affording a Ho(NO₃)₃ solution. Second, the Ho(NO₃)₃ solution was mixed with the silver ammonia solution in a molar ratio of Ho/Ag/PO₄ of 1 : 3 : 1 (x = 0.01, 0.05, 0.1, and 0.5). The next steps were the same as those for the preparation of Ag₃PO₄. The prepared Ag₃PO₄@HP samples were denoted as 1-Ag₃PO₄@HP, 2-Ag₃PO₄@HP, 3-Ag₃PO₄@HP, and 4-Ag₃PO₄@HP, corresponding to x values of 0.01, 0.05, 0.1, and 0.5, respectively.

#### 2.2 Photocatalytic activity experiments

Photocatalytic activity experiments were carried out in a photo-reactor at room temperature. BL-GHX-V Xe lamp with a 500 W electric power was used as the light source to simulate sunlight. The reaction solution included 30 mL of a rhodamine B, dahlia B, or methylthionine chloride solution, with an initial concentration of 5 mg L⁻¹, along with 0.05 g of the photocatalyst, respectively. First, the suspensions were stirred in the dark for 30 min to attain the adsorption–desorption equilibrium. After irradiation was started, the reaction solution was removed and immediately filtered after every 15 min. The reaction solution...
concentration was measured by UV-Vis spectroscopy to evaluate the residual efficiency of the reaction solution. The residual efficiency can be calculated by the following equation, \( \eta = C_0/C \), where \( C_0 \) (mg L\(^{-1}\)) is the initial concentration of the reaction solution before illumination, \( C \) is the concentration of the reaction solution (mg L\(^{-1}\)) after a certain illumination time (min), which is proportional to the absorbance.

### 2.3 Characterization

X-ray diffraction (XRD) patterns were recorded on a XRD instrument (BDX3200) with CuK\(_\alpha\) radiation. The morphology images and energy-dispersive X-ray (EDX) spectra of the samples were obtained by field-emission scanning electron microscopy (FE-SEM, S-4800). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a TEM (FEI F30) instrument. Binding energy (BE) was analyzed on a Perkin-Elmer PHI-1600 X-ray photoelectron spectroscopy (XPS) system, which was calibrated using adventitious carbon (C 1s) as the reference peak. Photoluminescence (PL) and autofluorescence spectra (UV-Vis DRS) were obtained on a UV-Vis spectrometer (Puxi, Japan) equipped with a 450 W Xe lamp as the excitation light source. UV-Vis diffuse reflectance spectra (UV-Vis DRS) were obtained on a UV-Vis spectrometer (Puxi, UV1901), with an integral sphere, using BaSO\(_4\) as the reference in the measurement range from 220 nm to 800 nm.

### 3. Results and discussion

#### 3.1 Structural characterization

Fig. 1 shows the XRD patterns of Ag\(_3\)PO\(_4\)@HP and Ag\(_3\)PO\(_4\). All of the diffraction peaks for as-prepared Ag\(_3\)PO\(_4\) were indexed to the cubic phase of Ag\(_3\)PO\(_4\) (JCPDS card 06-0505, Fig. 1). The XRD pattern of PH did not exhibit strong diffraction peaks, indicative of poor crystallinity. At low Ho\(^{3+}\) concentrations (\( x \leq 0.1 \)), nearly no impurity peaks were observed for Ag\(_3\)PO\(_4\)@HP, and no obvious shift in the diffraction peaks was observed compared to those observed for pure Ag\(_3\)PO\(_4\). The values of the lattice parameter a were 6.0190, 6.0154, 6.0194, and 6.0190 for the samples 1-Ag\(_3\)PO\(_4\)@HP to 4-Ag\(_3\)PO\(_4\)@HP, respectively, indicating that low Ho\(^{3+}\) concentrations almost do not affect the crystal lattice parameters of Ag\(_3\)PO\(_4\). However, with the increase in the Ho/Ag molar ratio to 0.5/2.5, the strength of diffraction peaks significantly decreased, suggesting that Ho\(^{3+}\) does not enter the crystal lattice of Ag\(_3\)PO\(_4\), but forms a new compound phase HP.

Fig. 2 shows the FE-SEM images of Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)@HP. Without the introduction of Ho\(^{3+}\), globular Ag\(_3\)PO\(_4\) particles were primarily observed with sizes ranging from 200 to 300 nm (Fig. 2a). However, at a Ho/Ag molar ratio of 0.05/2.95, regular cubes were observed for Ag\(_3\)PO\(_4\) particles, with sizes increasing to 300–400 nm (Fig. 2b). Ag\(_3\)PO\(_4\) particles were coated by a thin layer of a flocculent amorphous substance HP, which was clearly observed at the junction of two neighboring particles; this observation was further confirmed from the TEM and HRTEM results (Fig. 2c and d). The crystalline-phase structure of the Ag\(_3\)PO\(_4\) particles was distinctly improved, growing under the action of a thin layer of HP. As shown in Fig. 2c, with the increase in the Ho/Ag molar ratio to 0.1/2.9, the amount of flocculent amorphous substance HP rapidly increased. In Fig. 2c, the Ag\(_3\)PO\(_4\) particle surface was surrounded by HP, making the shape of the Ag\(_3\)PO\(_4\) particles irregular. Moreover, with the increase in the Ho/Ag molar ratio to 0.5/2.5, Ag\(_3\)PO\(_4\) particles were fully encapsulated in the massive HP, and the size of the Ag\(_3\)PO\(_4\) particles decreased to 100–200 nm.

EDX elemental mapping images were also recorded for further confirming the 2-Ag\(_3\)PO\(_4\)@HP composite structure. The elemental mapping images of silver, phosphorus, and oxygen exhibited similar shape as well as location (Fig. 3), confirming the existence of Ag\(_3\)PO\(_4\) in the composite. The mapping of Ho revealed that Ho is well distributed in the sample, indicative of the presence of holmium. Furthermore, the mapping density of Ag on the surface was clearly greater than that of the other elements, which is possible for providing more photoelectrons for photocatalysis.

Fig. 4 shows the TEM and HRTEM images of the Ag\(_3\)PO\(_4\) and 2-Ag\(_3\)PO\(_4\)@HP samples. The size of the predominantly globular Ag\(_3\)PO\(_4\) particles was ~200–300 nm, and Ag\(_3\)PO\(_4\) particles exhibited a smooth surface with few edges and corners, but there was serious aggregation (Fig. 4a). As shown in Fig. 4b, Ag\(_3\)PO\(_4\) particles presented a cubic shape with a mean size of ~350 nm. The sharp edges and corners of the Ag\(_3\)PO\(_4\) particles significantly increased. It is because that a small amount of the HP flocculent amorphous substance was generated on the surface or in the vicinity of the Ag\(_3\)PO\(_4\) particles, improving the dispersion of Ag\(_3\)PO\(_4\) particles and permitting the unrestricted growth of Ag\(_3\)PO\(_4\) particles into cubes. This result is consistent with FE-SEM results. The specific surface areas of Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)@HP were estimated as 3 m\(^2\) g\(^{-1}\) and 11 m\(^2\) g\(^{-1}\), respectively. The higher specific surface area of Ag\(_3\)PO\(_4\)@HP is related to the amorphous structure of HP and the improved dispersion of Ag\(_3\)PO\(_4\).
Fig. 2  FE-SEM images of Ag$_3$PO$_4$ (a) and Ag$_3$PO$_4$@HP with the mole ratio of Ho/Ag at 0.05 : 2.95 (b), 0.1 : 2.9 (c), 0.5 : 2.5 (d).

Fig. 3  EDX elemental mapping images of 2-Ag$_3$PO$_4$@HP with the mole ratio of Ho/Ag at 0.05 : 2.95.
In the HRTEM image shown in Fig. 4a, c and d crystalline lattice structure for 2-Ag₃PO₄@HP was clearly observed. As shown in Fig. 4c and d, Ag₃PO₄ particles were further confirmed to be encapsulated by an HP layer, affording the Ag₃PO₄@HP core–shell composite. The shell layer of the HP amorphous material was distinctly different from the Ag₃PO₄ core, and the thickness of the shell layer was approximately 2–10 nm. Lattice spacings of 0.27 and 0.24 nm were observed, corresponding to the (210) and (211) planes of Ag₃PO₄, respectively. Interestingly, as shown in Fig. 4d, some small particles with sizes of 4–5 nm were crystallized in the thicker HP shell. The lattice spacing of these small particles was 0.236 nm, corresponding to the (111) planes of Ag⁰. Ag⁰ is possibly produced by the reduction of Ag⁺, owing to daylight illumination during preparation.\(^{21}\) The reaction can be proposed as shown in eqn (1):

\[
2\text{AgNO}_3 = 2\text{Ag} + 2\text{NO}_2 \uparrow + \text{O}_2 \uparrow \quad (1)
\]

Fig. 5a shows the full-scan XPS spectra of Ag₃PO₄ and 2-Ag₃PO₄@HP: all elements (Ag(b), O(c), P(d), and Ho(e)) were observed in 2-Ag₃PO₄@HP, among which Ho was only observed in Ag₃PO₄@HP. Fig. 5b shows the Ag 3d spectra of Ag₃PO₄ and Ag₃PO₄@HP samples: Two characteristic BE peaks were observed at 367.7/373.9 eV and 367.6/373.8 eV, attributed to Ag 3d₅/₂ and Ag 3d₅/₂ bands, respectively. After the peak fitting of O 1s, two sets of binding energy at 530.6/532.7 eV and 530.4/532.5 eV, corresponding to Ag₃PO₄ and Ag₃PO₄@HP

Fig. 4  TEM images of Ag₃PO₄ (a) and 2-Ag₃PO₄@HP (b) and HRTEM of 2-Ag₃PO₄@HP (c, d) with the mole ratio of Ho/Ag at 0.05 : 2.95.
3.2 Photocatalytic activity

Fig. 7(a–c) show the photocatalytic degradation of rhodamine B, dahlia B, and methylthionine chloride using Ag₃PO₄, HP, and Ag₃PO₄@HP under sunlight irradiation, respectively. Ag₃PO₄ and Ag₃PO₄@HP samples almost degraded the three dyes within 45 min with different degradation rates, but HP marginally affected the degradation of all dyes. From the comparison of the photocatalytic experimental results, at a Ho : Ag molar ratio of less than 0.1 : 2.9, the photocatalytic activity of Ag₃PO₄@HP was typically greater than that of pure Ag₃PO₄. After irradiation for 30 min, 2-Ag₃PO₄@HP exhibited...
the best degradation rates of 96.70%, 93.05%, and 93.98% for rhodamine B, dahlia B, and methylthionine, respectively, while the corresponding degradation rates for Ag₃PO₄ were 74.66%, 69.11%, and 77.58%, calculated from the data shown in Fig. 7(a–c). Generally, the photocatalytic activity of Ag₃PO₄ follows the first-order kinetics. According to the first-order kinetics (\(\ln(C_0/C) = kt\)), the reaction rate constant \(k\) can be calculated (Fig. 7d). The \(k\) values for rhodamine B, dahlia B, and methylthionine chloride using 2-Ag₃PO₄@HP were 0.1251 min⁻¹, 0.1088 min⁻¹, and 0.10317 min⁻¹. These values were 3.1, 2.8, and 2.4 times greater than that of pure Ag₃PO₄, respectively.

Fig. 7e shows the visible-light photocatalytic activities of Ag₃PO₄ and Ag₃PO₄@HP for the degradation of rhodamine B using a Xe lamp with a 420 nm cutoff filter. After irradiation for 30 min, the degradation rates of rhodamine B for Ag₃PO₄, 1-Ag₃PO₄@HP, ~4-Ag₃PO₄@HP, and HP were 56.30%, 72.50%, 84.97%, 81.99%, 37.62%, and 6.07%, respectively. 2-Ag₃PO₄@HP still exhibited better visible-light photocatalytic activity compared to the other tested photocatalysts.

In addition, the cycling stability of photocatalysts is an important property for practical applications. Hence, the stability of 2-Ag₃PO₄@HP was examined in terms of the recycling degradation of a rhodamine B solution under sunlight irradiation. As shown in Fig. 8a, after five recycling runs, 2-Ag₃PO₄@HP completely degraded the reaction solution with a concentration of 5 mg L⁻¹ in 60 min, suggesting a high recycling stability for 2-Ag₃PO₄@HP. To evaluate the structural stability, the crystalline structures of Ag₃PO₄ and Ag₃PO₄@HP before and after recycling experiments were examined (Fig. 8b). No diffraction peaks corresponding to metallic Ag were observed in the unused photocatalyst samples. However, metallic Ag was observed in the HRTEM images of unused 2-Ag₃PO₄@HP (Fig. 4d), possibly because of the low amount of the metallic Ag, resulting in the absence of the XRD diffraction peaks of Ag. After five recycling runs, diffraction peaks corresponding to metallic Ag were clearly observed in the XRD pattern of pure Ag₃PO₄ at \(2\theta = 38.115^\circ\) and 44.299°, indicating that Ag₃PO₄ is partially reduced into metallic Ag particles during
photocatalytic degradation. Compared to the XRD pattern of pure Ag₃PO₄, smaller diffraction peaks corresponding to metallic Ag were observed in the XRD pattern of 2-Ag₃PO₄@HP after five recycling runs, indicating that the HP shell enhances the stability of Ag₃PO₄.

### 3.3 Possible photocatalytic mechanism

To examine the reactive species, scavenging experiments were carried out to elucidate the possible pathway or mechanism for photocatalytic degradation. To probe different reactive species during the photocatalysis of Ag₃PO₄@HP systems, t-butanol, benzoquinone (BQ), EDTA-2Na, and potassium dichromate (K₂Cr₂O₇) were separately added to the RhB solutions as the scavengers ([scavenger] = 0.3 mmol L⁻¹) for hydroxyl radicals (·OH⁻), superoxide radicals (·O₂⁻), holes (h⁺), and electrons (e⁻), respectively (Fig. 9). K₂Cr₂O₇ negligibly affected the photodegradation rates of RhB. The results indicated that e⁻ do not appear to be the main reactive species during photocatalysis. The addition of EDTA-2Na and BQ caused the rapid termination of photocatalysis, indicating that the photogenerated h⁺ and ·O₂⁻ possibly play a crucial role during the photocatalytic degradation of RhB. The contribution of the reactive species for photocatalytic degradation follows the order of h⁺ > ·O₂⁻ > ·OH⁻ > e⁻.

Considering the energy-band structure theory, a previous study,³³ and structural and performance characteristics, a possible energy-band structure model was proposed for improving the photocatalytic activity and stability of the Ag₃PO₄@HP heterostructures, as shown in Fig. 10. The valence-band (VB) and conduction-band (CB) potentials of Ag₃PO₄ can be calculated by the following empirical formula (as shown in eqn (2) and (3), respectively), where $X$ is the Mulliken electronegativity ($X_{HP} = 6.3205$ eV), $E_e$ is the energy of free electrons on the hydrogen scale ($E_e = 4.5$ eV), and $E_g$ is the bandgap ($E_g = 3.5$ eV). Therefore, the VB and CB potentials of HP were calculated as $3.44$ eV and $-0.06$ eV, respectively.

$$E_{VB} = X - E_e + 0.5E_g$$  \tag{2}$$

$$E_{CB} = E_{VB} - E_g$$  \tag{3}$$

Under Xe lamp irradiation, both Ag₃PO₄ and HP were excited, and the photogenerated electrons and holes were simultaneously created. The CB potential ($0.45$ eV) of Ag₃PO₄ was lower than that of HP ($-0.06$ eV), and the VB potential ($2.89$ eV) was greater than that of HP ($3.44$ eV). Thus, the photogenerated electrons and holes spontaneously shift from HP to Ag₃PO₄. Simultaneously, the photogenerated electrons rapidly migrate from the CB of Ag₃PO₄ to the Ag nanoparticles via the Schottky barrier. Ag nanoparticles on the Ag₃PO₄ surface acted as a sink for electrons, these electrons reacted with the adsorbed O₂ to generate the active ion species (·O₂⁻). This process
promoted the separation of the photogenerated electron–hole pairs. However, the holes [h+] in the VB of Ag3PO4 were directly transferred to the organic dye surface for further reaction. Thus, this photocatalytic system, consisting of LnPO4, Ag nanoparticles, and Ag3PO4, may be more effective for the degradation of organic pollutants.

In addition, the higher specific surface area of Ag3PO4@HP was crucial for enhancing the photocatalytic activity of Ag3PO4, related to the more efficient adsorption of the dye molecules. Therefore, the high photocatalytic activity of Ag3PO4@HP is believed to be related to the combination of two effects.

4. Conclusions

In this study, Ag3PO4@Ag3PO4@HP composite photocatalysts were prepared by silver-ammonia-solution-assisted solution co-deposition. The core–shell structure of the Ag3PO4@HP composite significantly improved the photocatalytic activity of Ag3PO4.

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