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# Ag<sub>3</sub>PO<sub>4</sub>@holmium phosphate core@shell composites with enhanced photocatalytic activity

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In this study, Ag<sub>3</sub>PO<sub>4</sub>@holmium phosphate (HP) composite photocatalysts were first prepared by silver-ammonia-solution-assisted solution co-deposition. During co-deposition, Ag<sub>3</sub>PO<sub>4</sub> particles were encapsulated by a flocculent amorphous substance layer of HP, affording a Ag<sub>3</sub>PO<sub>4</sub>@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 Ag<sub>3</sub>PO<sub>4</sub>. In addition, the photocatalytic mechanism of Ag<sub>3</sub>PO<sub>4</sub>@HP was discussed.

## 1. Introduction

Semiconductor photocatalysts have attracted considerable attention as they demonstrate the potential of addressing energy and environmental issues,<sup>1–4</sup> including photochemical water splitting,<sup>5</sup> organic pollutant degradation,<sup>6</sup> and CO<sub>2</sub> photocatalytic reduction.<sup>7</sup> In 2010, Ye reported a novel semiconductor photocatalyst Ag<sub>3</sub>PO<sub>4</sub>, which exhibited strong photooxidative activities for O<sub>2</sub> evolution from water splitting in the presence of a sacrificial reagent AgNO<sub>3</sub>, and a high degradation rate for organic dyes under visible-light irradiation.<sup>8</sup> The photocatalytic activity of Ag<sub>3</sub>PO<sub>4</sub> is superior to those of previously reported visible-light photocatalysts, *e.g.*, BiVO<sub>4</sub> (ref. 8) and N-doped TiO<sub>2</sub>.<sup>9,10</sup> Hence, it has been widely investigated.<sup>11–16</sup>

According to previously reported studies, the heterojunction structure between Ag<sub>3</sub>PO<sub>4</sub> 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 Ag<sub>3</sub>PO<sub>4</sub>-based composite photocatalysts have been developed, *e.g.*, AgX/Ag<sub>3</sub>PO<sub>4</sub> (X = Cl, Br, and I),<sup>17–19</sup> Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>,<sup>20,21</sup> Ag<sub>3</sub>PO<sub>4</sub>/CeO<sub>2</sub>,<sup>22,23</sup> Ag<sub>3</sub>PO<sub>4</sub>/WS<sub>2</sub>,<sup>24</sup> Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>,<sup>25</sup> Ag<sub>3</sub>PO<sub>4</sub>/BiPO<sub>4</sub>,<sup>26–28</sup> Ag<sub>3</sub>PO<sub>4</sub>/BiOBr,<sup>29</sup> and Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>.<sup>30–32</sup>

In this study, Ag<sub>3</sub>PO<sub>4</sub> and Ag<sub>3</sub>PO<sub>4</sub>@HP photocatalysts were prepared by silver-ammonia-solution-assisted solution co-deposition. The core-shell structure and photocatalytic properties of Ag<sub>3</sub>PO<sub>4</sub>@HP were investigated in detail.

## 2. Experimental

### 2.1 Preparation

**2.1.1 Preparation of Ag<sub>3</sub>PO<sub>4</sub>.** First, AgNO<sub>3</sub> and KH<sub>2</sub>PO<sub>4</sub> were separately dissolved in distilled water. Second, a NH<sub>3</sub>·H<sub>2</sub>O solution was slowly added to the AgNO<sub>3</sub> solution under constant magnetic stirring, affording a silver ammonia solution, until the brown precipitate disappeared. Then, a KH<sub>2</sub>PO<sub>4</sub> solution with a Ag(NH<sub>3</sub>)<sub>2</sub>NO<sub>3</sub> : KH<sub>2</sub>PO<sub>4</sub> 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 °C for 30 min, affording Ag<sub>3</sub>PO<sub>4</sub>.

**2.1.2 Preparation of Ag<sub>3</sub>PO<sub>4</sub>@HP.** First, Ho<sub>2</sub>O<sub>3</sub> was dissolved in nitric acid, affording a Ho(NO<sub>3</sub>)<sub>3</sub> solution. Second, the Ho(NO<sub>3</sub>)<sub>3</sub> solution was mixed with the silver ammonia solution in a molar ratio of Ho/Ag/PO<sub>4</sub><sup>3-</sup> at  $x/3-x/1$  ( $x = 0.01, 0.05, 0.1,$  and  $0.5$ ). The next steps were the same as those for the preparation of Ag<sub>3</sub>PO<sub>4</sub>. The prepared Ag<sub>3</sub>PO<sub>4</sub>@HP samples were denoted as 1-Ag<sub>3</sub>PO<sub>4</sub>@HP, 2-Ag<sub>3</sub>PO<sub>4</sub>@HP, 3-Ag<sub>3</sub>PO<sub>4</sub>@HP, and 4-Ag<sub>3</sub>PO<sub>4</sub>@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<sup>-1</sup>, 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

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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,  $\eta = C/C_0$ , where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of the reaction solution before illumination,  $C$  is the concentration of the reaction solution ( $\text{mg L}^{-1}$ ) 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  $\text{CuK}\alpha$  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 afterglow curves were recorded on a Hitachi F-7000 fluorescence spectrophotometer (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  $\text{BaSO}_4$  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  $\text{Ag}_3\text{PO}_4$ @HP and  $\text{Ag}_3\text{PO}_4$ . All of the diffraction peaks for as-prepared  $\text{Ag}_3\text{PO}_4$  were indexed to the cubic phase of  $\text{Ag}_3\text{PO}_4$  (JCPDS card 06-0505, Fig. 1). The XRD pattern of PH did not exhibit strong diffraction peaks, indicative of poor crystallinity. At low  $\text{Ho}^{3+}$  concentrations ( $x \leq 0.1$ ), nearly no impurity peaks were observed for  $\text{Ag}_3\text{PO}_4$ @HP, and no

obvious shift in the diffraction peaks was observed compared to those observed for pure  $\text{Ag}_3\text{PO}_4$ . The values of the lattice parameter  $a$  were 6.0190, 6.0154, 6.0194, and 6.0190 for the samples 1- $\text{Ag}_3\text{PO}_4$ @HP to 4- $\text{Ag}_3\text{PO}_4$ @HP, respectively, indicating that low  $\text{Ho}^{3+}$  concentrations almost do not affect the crystal lattice parameters of  $\text{Ag}_3\text{PO}_4$ . However, with the increase in the Ho/Ag molar ratio to 0.5/2.5, the strength of diffraction peaks significantly decreased, suggesting that  $\text{Ho}^{3+}$  does not enter the crystal lattice of  $\text{Ag}_3\text{PO}_4$ , but forms a new compound phase HP.

Fig. 2 shows the FE-SEM images of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4$ @HP. Without the introduction of  $\text{Ho}^{3+}$ , globular  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$  particles, with sizes increasing to 300–400 nm (Fig. 2b).  $\text{Ag}_3\text{PO}_4$  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. 4c and d). The crystalline-phase structure of the  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$  particle surface was surrounded by HP, making the shape of the  $\text{Ag}_3\text{PO}_4$  particles irregular. Moreover, with the increase in the Ho/Ag molar ratio to 0.5/2.5,  $\text{Ag}_3\text{PO}_4$  particles were fully encapsulated in the massive HP, and the size of the  $\text{Ag}_3\text{PO}_4$  particles decreased to 100–200 nm.

EDX elemental mapping images were also recorded for further confirming the 2- $\text{Ag}_3\text{PO}_4$ @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  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$  and 2- $\text{Ag}_3\text{PO}_4$ @HP samples. The size of the predominantly globular  $\text{Ag}_3\text{PO}_4$  particles was  $\sim 200$ – $300$  nm, and  $\text{Ag}_3\text{PO}_4$  particles exhibited a smooth surface with few edges and corners, but there was serious aggregation (Fig. 4a). As shown in Fig. 4b,  $\text{Ag}_3\text{PO}_4$  particles presented a cubic shape with a mean size of  $\sim 350$  nm. The sharp edges and corners of the  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$  particles, improving the dispersion of  $\text{Ag}_3\text{PO}_4$  particles and permitting the unrestricted growth of  $\text{Ag}_3\text{PO}_4$  particles into cubes. This result is consistent with FE-SEM results. The specific surface areas of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4$ @HP were estimated as  $3 \text{ m}^2 \text{ g}^{-1}$  and  $11 \text{ m}^2 \text{ g}^{-1}$ , respectively. The higher specific surface area of  $\text{Ag}_3\text{PO}_4$ @HP is related to the amorphous structure of HP and the improved dispersion of  $\text{Ag}_3\text{PO}_4$ .

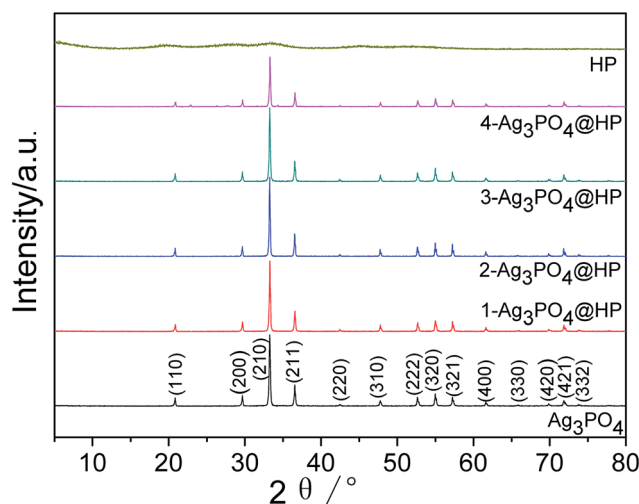


Fig. 1 XRD patterns of  $\text{Ag}_3\text{PO}_4$ , HP and  $\text{Ag}_3\text{PO}_4$ @HP with the mole ratio of Ho/Ag at 0.01 : 2.99, 0.05 : 2.95, 0.1 : 2.9, 0.5 : 2.5.



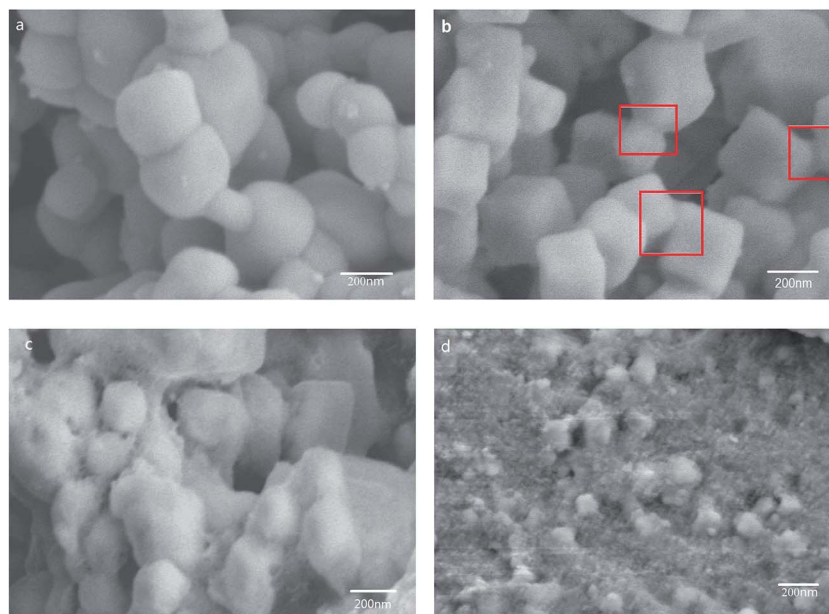


Fig. 2 FE-SEM images of  $\text{Ag}_3\text{PO}_4$  (a) and  $\text{Ag}_3\text{PO}_4@\text{HP}$  with the mole ratio of  $\text{Ho}/\text{Ag}$  at 0.05 : 2.95 (b), 0.1 : 2.9 (c), 0.5 : 2.5 (d).

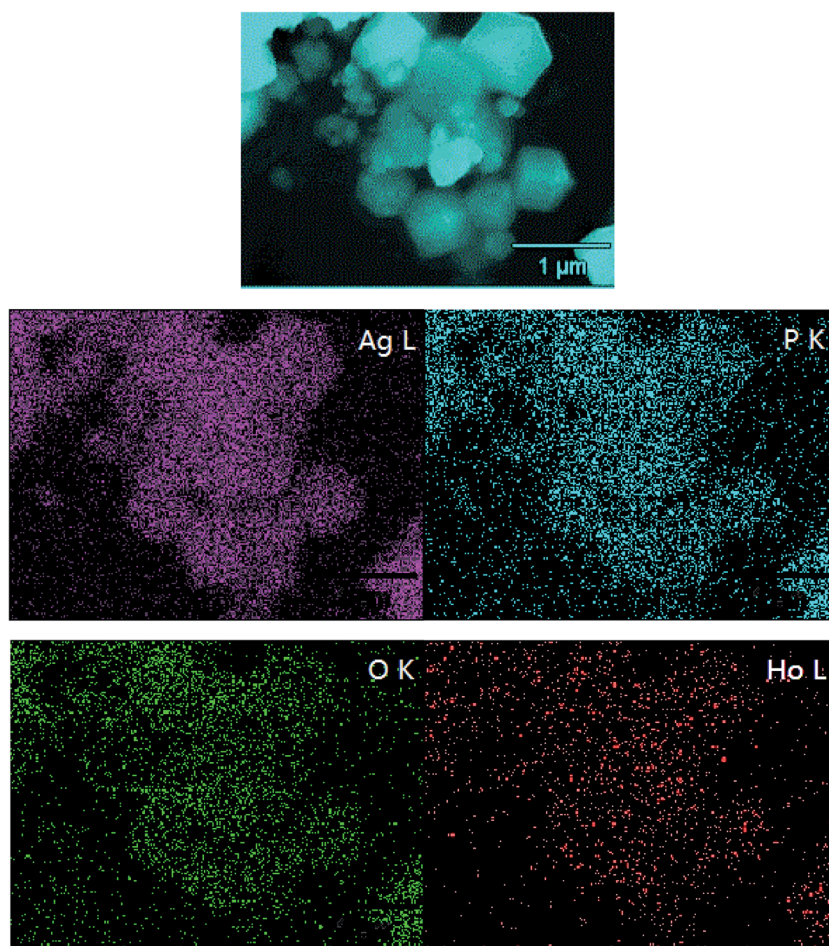
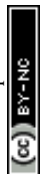


Fig. 3 EDX elemental mapping images of  $2\text{-Ag}_3\text{PO}_4@\text{HP}$  with the mole ratio of  $\text{Ho}/\text{Ag}$  at 0.05 : 2.95.



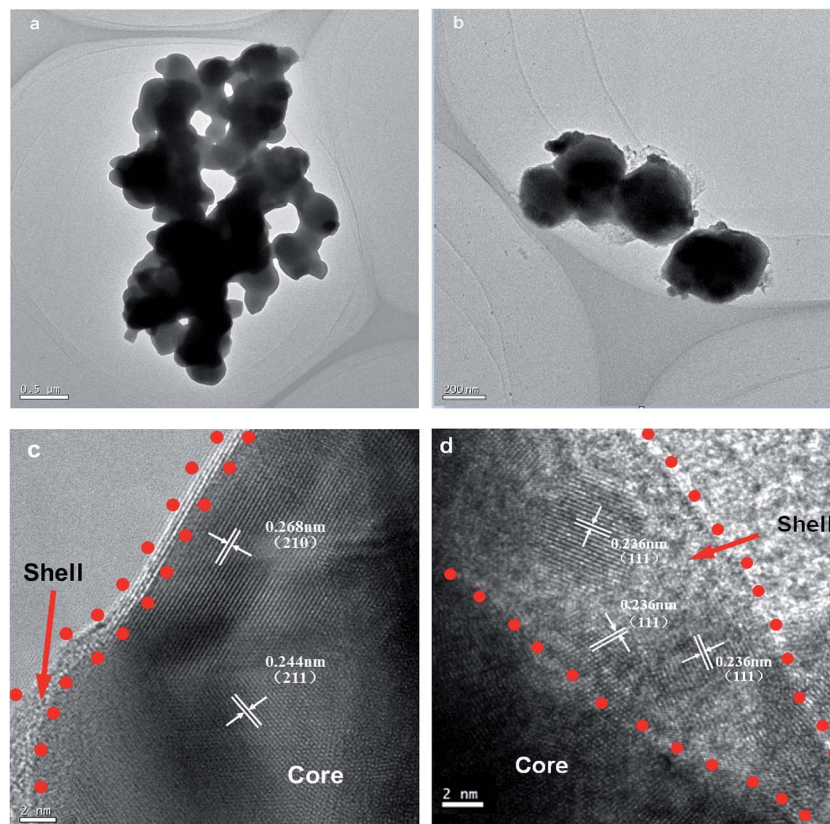


Fig. 4 TEM images of  $\text{Ag}_3\text{PO}_4$  (a) and  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  (b) and HRTEM of  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  (c, d) with the mole ratio of  $\text{Ho}/\text{Ag}$  at 0.05 : 2.95.

In the HRTEM image shown in Fig. 4a, c and d crystalline lattice structure for  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  was clearly observed. As shown in Fig. 4c and d,  $\text{Ag}_3\text{PO}_4$  particles were further confirmed to be encapsulated by an HP layer, affording the  $\text{Ag}_3\text{PO}_4\text{@HP}$  core-shell composite. The shell layer of the HP amorphous material was distinctly different from the  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$ , 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  $\text{Ag}^0$ .  $\text{Ag}^0$  is possibly produced by the reduction of  $\text{Ag}^+$ , owing to daylight illumination during preparation.<sup>21</sup> The reaction can be proposed as shown in eqn (1):

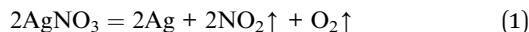


Fig. 5a shows the full-scan XPS spectra of  $\text{Ag}_3\text{PO}_4$  and  $2\text{-Ag}_3\text{PO}_4\text{@HP}$ : all elements ( $\text{Ag}$ (b),  $\text{O}$ (c),  $\text{P}$ (d), and  $\text{Ho}$ (e)) were observed in  $2\text{-Ag}_3\text{PO}_4\text{@HP}$ , among which  $\text{Ho}$  was only observed in  $\text{Ag}_3\text{PO}_4\text{@HP}$ . Fig. 5b shows the  $\text{Ag}$  3d spectra of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4\text{@HP}$  samples: Two characteristic BE peaks were observed at 367.7/373.9 eV and 367.6/373.8 eV, attributed to  $\text{Ag}$  3d<sub>5/2</sub> and  $\text{Ag}$  3d<sub>3/2</sub> bands, respectively. After the peak fitting of  $\text{O}$  1s, two sets of binding energy at 530.6/532.7 eV and 530.4/532.5 eV, corresponding to  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4\text{@HP}$

samples, respectively (Fig. 5c). Two peaks corresponded to the crystal lattice oxygen and surface hydroxyl groups, respectively. The  $\text{P}$  2p peaks of  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  and  $\text{Ag}_3\text{PO}_4$  were observed at 133.2 and 132.8 eV, respectively (Fig. 5d); both peaks were assigned to the sample lattice  $\text{P}^{5+}$ . Compared with that corresponding to  $\text{Ag}_3\text{PO}_4$ , the  $\text{P}$  2p peak of  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  slightly shifted to higher BE, indicating that  $\text{P}$  2p on the  $\text{Ag}_3\text{PO}_4$  surface undergoes a different chemical reaction from the inside, which is the formation of the HP shell. A BE peak was observed at 163.1 eV in the XPS spectrum for  $\text{Ho}$  (Fig. 5e), corresponding to  $\text{Ho}$  4d<sub>5/2</sub>. This result further indicated the presence of  $\text{Ho}$  as  $\text{Ho}^{3+}$  in the composite.

Fig. 6 shows the UV-Vis DRS spectra of  $\text{Ag}_3\text{PO}_4$  and  $2\text{-Ag}_3\text{-PO}_4\text{@HP}$ . Absorption edges of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4\text{@HP}$  were observed in the visible region (Fig. 6a), and considerable absorption was observed in the visible spectrum in the range of ~200–530 nm.  $\text{HoPO}_4$  exhibited strong absorption in the UV region (<350 nm). In addition, some sharp absorption peaks were observed in the visible range of HP, related to the characteristic absorption of  $\text{Ho}^{3+}$ . Absorption peaks were observed at 421 nm, 447 nm, 457 nm, 477 nm, 540 nm, and 642 nm, corresponding to the energy-level transitions of  $\text{Ho}^{3+}$ ,  ${}^5\text{G}_5 \rightarrow {}^5\text{I}_8$ ,  ${}^5\text{G}_0({}^5\text{F}_1) \rightarrow {}^5\text{I}_8$ ,  ${}^5\text{G}_6 \rightarrow {}^5\text{I}_8$ ,  ${}^5\text{F}_3 \rightarrow {}^5\text{I}_8$ ,  ${}^5\text{S}_2({}^5\text{F}_4) \rightarrow {}^5\text{I}_8$ , and  ${}^5\text{F}_5 \rightarrow {}^5\text{I}_8$ , respectively. The direct band gaps of  $\text{Ag}_3\text{PO}_4$  and HP were obtained from the plot of  $(\alpha h\nu)^2$  versus  $h\nu$ , which were 2.42 eV and 3.50 eV, respectively (Fig. 6b).



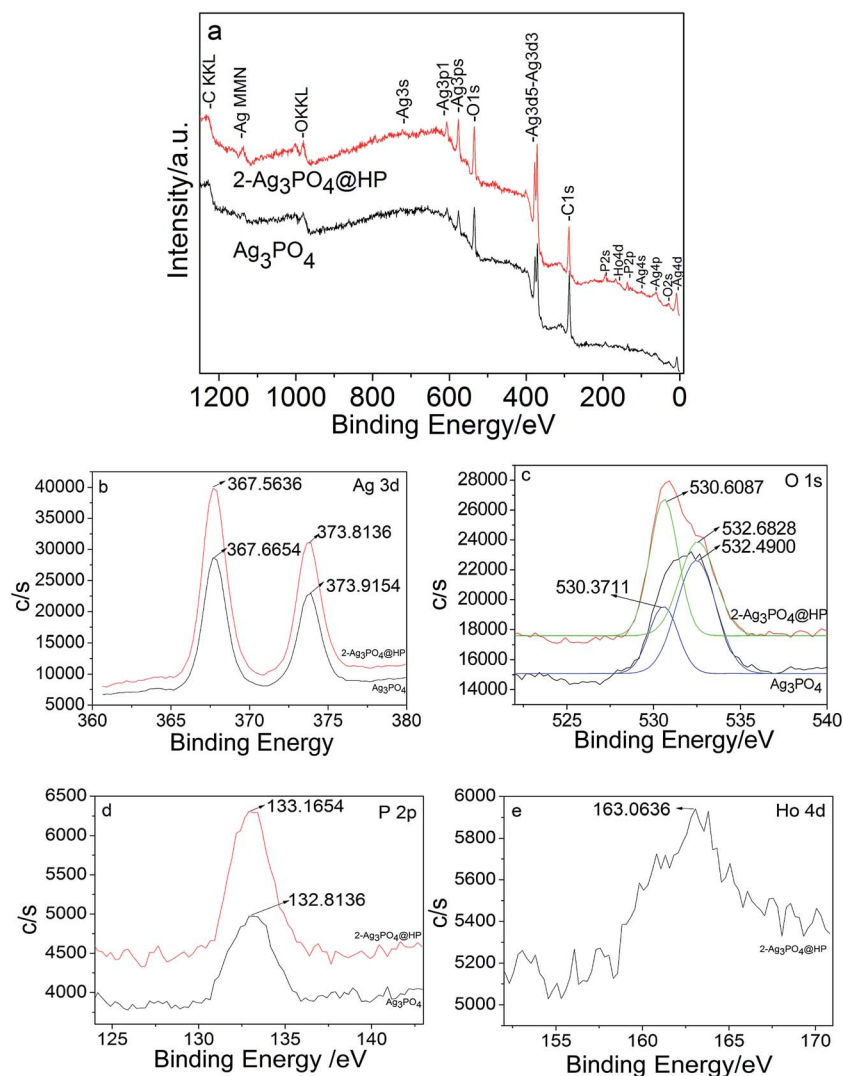


Fig. 5 The XPS results images of  $\text{Ag}_3\text{PO}_4$  and  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  with the mole ratio of  $\text{Ho}/\text{Ag}$  at 0.05 : 2.95.

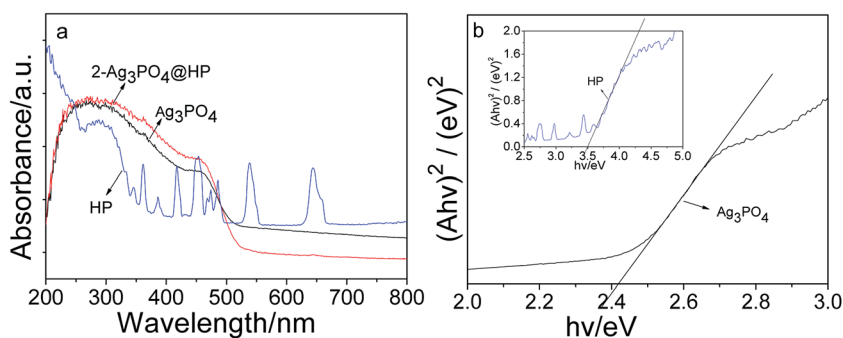


Fig. 6 UV-Vis diffuse reflection spectrum of  $\text{Ag}_3\text{PO}_4$ , HP and  $2\text{-Ag}_3\text{PO}_4\text{@HP}$ .

### 3.2 Photocatalytic activity

Fig. 7(a–c) show the photocatalytic degradation of rhodamine B, dahlia B, and methylthionine chloride using  $\text{Ag}_3\text{PO}_4$ , HP, and  $\text{Ag}_3\text{PO}_4\text{@HP}$  under sunlight irradiation, respectively.  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4\text{@HP}$  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  $\text{Ho} : \text{Ag}$  molar ratio of less than 0.1 : 2.9, the photocatalytic activity of  $\text{Ag}_3\text{PO}_4\text{@HP}$  was typically greater than that of pure  $\text{Ag}_3\text{PO}_4$ . After irradiation for 30 min,  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  exhibited



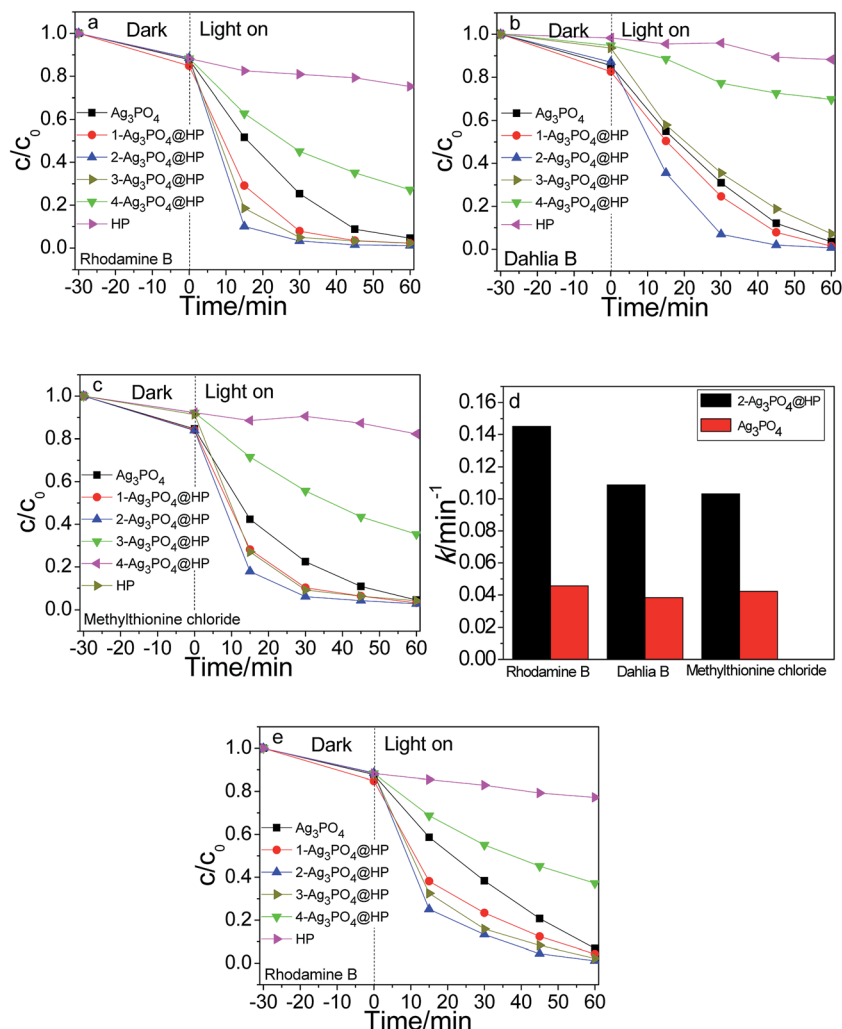


Fig. 7 The photocatalytic degradation results of  $Ag_3PO_4$ , HP and  $Ag_3PO_4@HP$ . The degradation results of rhodamine B (a), dahlia B (b), and methylthionine chloride (c); the values of the reaction rate constant  $k$  (d) of the photocatalytic degradation; the visible-light photocatalytic activities (e) in the degradation of rhodamine B, using a Xe-lamp with a 420 nm cutoff filter.

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  $Ag_3PO_4$  were 74.66%, 69.11%, and 77.58%, calculated from the data shown in Fig. 7(a–c). Generally, the photocatalytic activity of  $Ag_3PO_4$  fits 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- $Ag_3PO_4@HP$  were  $0.1251 \text{ min}^{-1}$ ,  $0.1088 \text{ min}^{-1}$ , and  $0.10317 \text{ min}^{-1}$ . These values were 3.1, 2.8, and 2.4 times greater than that of pure  $Ag_3PO_4$ , respectively.

Fig. 7e shows the visible-light photocatalytic activities of  $Ag_3PO_4$  and  $Ag_3PO_4@HP$  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  $Ag_3PO_4$ , 1- $Ag_3PO_4@HP$ , 2- $Ag_3PO_4@HP$ , 3- $Ag_3PO_4@HP$ , 4- $Ag_3PO_4@HP$ , and HP were 56.30%, 72.50%, 84.97%, 81.99%, 37.62%, and 6.07%, respectively. 2- $Ag_3PO_4@HP$  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- $Ag_3PO_4@HP$  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- $Ag_3PO_4@HP$  completely degraded the reaction solution with a concentration of  $5 \text{ mg L}^{-1}$  in 60 min, suggesting a high recycling stability for 2- $Ag_3PO_4@HP$ . To evaluate the structural stability, the crystalline structures of  $Ag_3PO_4$  and  $Ag_3PO_4@HP$  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- $Ag_3PO_4@HP$  (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  $Ag_3PO_4$  at  $2\theta = 38.115^\circ$  and  $44.299^\circ$ , indicating that  $Ag_3PO_4$  is partially reduced into metallic Ag particles during



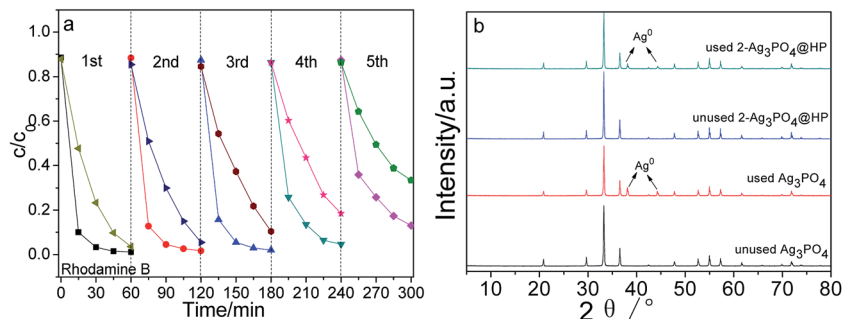


Fig. 8 Recycling runs of  $\text{Ag}_3\text{PO}_4$  and  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  samples in the degradation of rhodamine B.

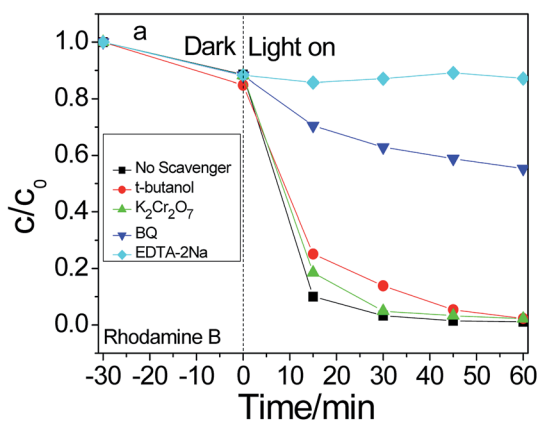


Fig. 9 Photodegradation efficiency of rhodamine B with  $2\text{-Ag}_3\text{-PO}_4\text{@HP}$  as photocatalyst under different scavengers.

photocatalytic degradation. Compared to the XRD pattern of pure  $\text{Ag}_3\text{PO}_4$ , smaller diffraction peaks corresponding to metallic Ag were observed in the XRD pattern of  $2\text{-Ag}_3\text{PO}_4\text{@HP}$  after five recycling runs, indicating that the HP shell enhances the stability of  $\text{Ag}_3\text{PO}_4$ .

### 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  $\text{Ag}_3\text{PO}_4\text{@HP}$  systems, *t*-butanol, benzoquinone (BQ), EDTA-2Na, and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) were separately added to the RhB solutions as the scavengers ([scavenger] = 0.3 mmol  $\text{L}^{-1}$ ) for hydroxyl radicals ( $\cdot\text{OH}^-$ ), superoxide radicals ( $\cdot\text{O}_2$ ), holes ( $\text{h}^+$ ), and electrons ( $\text{e}^-$ ), respectively (Fig. 9).  $\text{K}_2\text{Cr}_2\text{O}_7$  negligibly affected the photodegradation rates of RhB. The results indicated that  $\text{e}^-$  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  $\text{h}^+$  and  $\cdot\text{O}_2$  possibly play a crucial role during the photocatalytic degradation of RhB. The contribution of the reactive species for photocatalytic degradation follows the order of  $\text{h}^+ > \cdot\text{O}_2 > \cdot\text{OH}^- > \text{e}^-$ .

Considering the energy-band structure theory, a previous study,<sup>33</sup> and structural and performance characteristics, a possible energy-band structure model was proposed for improving the photocatalytic activity and stability of the  $\text{Ag}_3\text{-PO}_4\text{@HP}$  heterostructures, as shown in Fig. 10. The valence-band (VB) and conduction-band (CB) potentials of  $\text{Ag}_3\text{PO}_4$  can be calculated by the following empirical formula (as shown in eqn (2) and (3), respectively), where  $X$  is the Mulliken electronegativity ( $X_{\text{HP}} \cong 6.3205$  eV),  $E_e$  is the energy of free electrons on the hydrogen scale ( $E_e \cong 4.5$  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.

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

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

Under Xe lamp irradiation, both  $\text{Ag}_3\text{PO}_4$  and HP were excited, and the photogenerated electrons and holes were simultaneously created. The CB potential (0.45 eV) of  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_3\text{PO}_4$ . Simultaneously, the photogenerated electrons rapidly migrate from the CB of  $\text{Ag}_3\text{PO}_4$  to the Ag nanoparticles *via* the Schottky barrier. Ag nanoparticles on the  $\text{Ag}_3\text{PO}_4$  surface acted as a sink for electrons, these electrons reacted with the adsorbed  $\text{O}_2$  to generate the active ion species ( $\cdot\text{O}_2^-$ ). This process

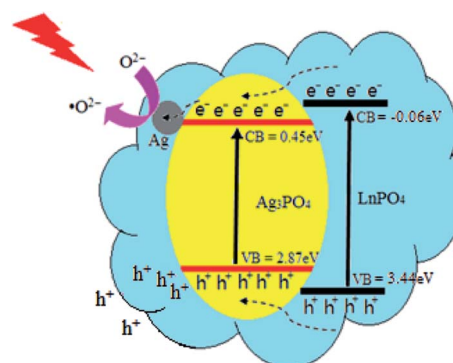


Fig. 10 The photocatalytic mechanism model of  $\text{Ag}_3\text{PO}_4\text{@HP}$ .



promoted the separation of the photogenerated electron-hole pairs. However, the holes ( $h^+$ ) in the VB of  $Ag_3PO_4$  were directly transferred to the organic dye surface for further reaction. Thus, this photocatalytic system, consisting of  $LnPO_4$ , Ag nanoparticles, and  $Ag_3PO_4$ , may be more effective for the degradation of organic pollutants.

In addition, the higher specific surface area of  $Ag_3PO_4@HP$  was crucial for enhancing the photocatalytic activity of  $Ag_3PO_4$ , related to the more efficient adsorption of the dye molecules. Therefore, the high photocatalytic activity of  $Ag_3PO_4@HP$  is believed to be related to the combination of two effects.

## 4. Conclusions

In this study,  $Ag_3PO_4@Ag_3PO_4@HP$  composite photocatalysts were prepared by silver-ammonia-solution-assisted solution co-deposition. The core-shell structure of the  $Ag_3PO_4@HP$  composite significantly improved the photocatalytic activity of  $Ag_3PO_4$ .

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## References

- 1 A. Fujishima and K. Honda, Electrochemical photocatalysis of water at semiconductor electrode, *Nature*, 1972, **238**, 53–58.
- 2 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science*, 2001, **293**, 269–271.
- 3 M. Z. Ge, C. Y. Cao, J. Y. Huang, S. H. Li, Z. Chen, K. Q. Zhang, S. S. Aldeyab and Y. K. Lai, A review of one-dimensional  $TiO_2$  nanostructured materials for environmental and energy applications, *J. Mater. Chem. A*, 2016, **4**, 6772–6801.
- 4 S. Obregón and G. Colón, On the origin of the photocatalytic activity improvement of  $BiVO_4$  through rare earth tridoping, *Appl. Catal., A*, 2015, **501**, 56–62.
- 5 X. F. Zhang, B. Y. Zhang, K. Cao, J. Brillet, J. Y. Chen, M. K. Wang and Y. Shen, Perovskite Solar Cell- $TiO_2@BiVO_4$  Photoelectrochemical System for Direct Solar Water Splitting, *J. Mater. Chem. A*, 2015, **3**, 21630–21636.
- 6 T. A. Kandiel, A. Y. Ahmed and D. Bahnemann,  $TiO_2(B)/anatase$  heterostructure nanofibers decorated with anatase nanoparticles as efficient photocatalysts for methanol oxidation, *J. Mol. Catal. A: Chem.*, 2016, **425**, 55–60.
- 7 H. K. Jin, G. Magesh, H. J. Kang, M. Banu, H. K. Ju, J. Lee and J. S. Lee, Carbonate-coordinated cobalt co-catalyzed  $BiVO_4/WO_3$  composite photoanode tailored for  $CO_2$  reduction to fuels, *Nano Energy*, 2015, **15**, 153–163.
- 8 Z. G. Yi, J. H. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuartwilliams, H. Yang, J. Cao, W. Luo and Z. Li, An orthophosphate semiconductor with photooxidation properties under visible-light irradiation, *Nat. Mater.*, 2010, **9**, 559–564.
- 9 Y. Bi, H. Hu, Z. Jiao, H. Yu, G. Lu and J. Ye, Two-dimensional dendritic  $Ag_3PO_4$  nanostructures and their photocatalytic properties, *PCCP*, 2012, **14**, 14486–14488.
- 10 Y. Bi, H. Hu, S. Ouyang, G. Lu, J. Cao and J. Ye, Photocatalytic and photoelectric properties of cubic  $Ag_3PO_4$  sub-microcrystals with sharp corners and edges, *Cheminform*, 2012, **43**, 3748–3750.
- 11 W. Y. Lin, S. J. Zhang, D. Y. Wang, C. X. Zhang and D. L. Sun, Ultrasound-assisted synthesis of high-efficiency  $Ag_3PO_4/CeO_2$  heterojunction photocatalyst, *Ceram. Int.*, 2015, **41**, 8956–8963.
- 12 C. Wang, J. X. Zhu, X. Y. Wu, H. Xu, Y. H. Song, J. Yan, Y. X. Song, H. Y. Ji, K. Wang and H. M. Li, Photocatalytic degradation of bisphenol A and dye by graphene-oxide/ $Ag_3PO_4$  composite under visible light irradiation, *Ceram. Int.*, 2014, **40**, 8061–8070.
- 13 U. Sulaeman, F. Febiyanto, S. Yin and T. Sato, The highly active saddle-like  $Ag_3PO_4$  photocatalyst under visible light irradiation, *Catal. Commun.*, 2016, **85**, 22–25.
- 14 Q. Wu, P. F. Wang, F. T. Niu, C. P. Huang, Y. Li and W. F. Yao, A novel molecular sieve supporting material for enhancing activity and stability of  $Ag_3PO_4$  photocatalyst, *Appl. Surf. Sci.*, 2016, **378**, 552–563.
- 15 S. S. Patil, D. R. Patil, S. K. Apte, M. V. Kulkarni, J. D. Ambekar, C. J. Park, S. W. Gosavi, S. S. Kolekar and B. B. Kale, Confinement of  $Ag_3PO_4$  nanoparticles supported by surface plasmon resonance of Ag in glass: efficient nanoscale photocatalyst for solar  $H_2$  production from waste  $H_2S$ , *Appl. Catal., B*, 2016, **190**, 75–84.
- 16 Q. H. Xiang, L. Di, T. T. Shen and L. Fan, Graphene-modified nanosized  $Ag_3PO_4$  photocatalysts for enhanced visible-light photocatalytic activity and stability, *Appl. Catal., B*, 2015, **162**, 196–203.
- 17 P. Amornpitoksuk and S. Suwanboon, Photocatalytic decolorization of methylene blue dye by  $Ag_3PO_4-AgX$  ( $X = Cl^-, Br^-$  and  $I^-$ ) under visible light, *Adv. Powder Technol.*, 2014, **25**, 1026–1030.
- 18 J. Cao, B. Luo, H. Lin, B. Xu and S. Chen, Visible light photocatalytic activity enhancement and mechanism of  $AgBr/Ag_3PO_4$  hybrids for degradation of methyl orange, *J. Hazard. Mater.*, 2012, **217–218**, 107–115.
- 19 H. Katsumata, T. Hayashi, M. Taniguchi, T. Suzuki and S. Kaneco,  $AgI/Ag_3PO_4$  hybrids with highly efficient visible-light driven photocatalytic activity, *Mater. Res. Bull.*, 2015, **63**, 116–122.
- 20 W. F. Yao, B. Zhang, C. P. Huang, C. Ma, X. L. Song and Q. J. Xu, Synthesis and characterization of high efficiency and stable  $Ag_3PO_4/TiO_2$  visible light photocatalyst for the degradation of methylene blue and rhodamine B solutions, *J. Mater. Chem.*, 2012, **22**, 4050–4055.
- 21 C. N. Tang, E. Z. Liu, J. Fan, X. Y. Hu, L. M. Kang and J. Wan, Heterostructured  $Ag_3PO_4/TiO_2$  nano-sheet film with high efficiency for photodegradation of methylene blue, *Ceram. Int.*, 2014, **40**, 15447–15453.



- 22 Z. M. Yang, G. F. Huang, W. Q. Huang, J. M. Wei, X. G. Yan, Y. Y. Liu, C. Jiao, Z. Wan and A. Pan, Novel  $\text{Ag}_3\text{PO}_4/\text{CeO}_2$  composite with high efficiency and stability for photocatalytic applications, *J. Mater. Chem. A*, 2014, **2**, 1750–1756.
- 23 W. Y. Lin, S. J. Zhang, D. Y. Wang, C. X. Zhang and D. L. Sun, Ultrasound-assisted synthesis of high-efficiency  $\text{Ag}_3\text{PO}_4/\text{CeO}_2$  heterojunction photocatalyst, *Ceram. Int.*, 2015, **41**, 8956–8963.
- 24 H. J. Yu, Y. Yu, J. H. Liu, P. Y. Ma, Y. C. Wang, F. Zhang and Z. Y. Fu, Space-confined growth of  $\text{Ag}_3\text{PO}_4$  nanoparticles within  $\text{WS}_2$  sheets:  $\text{Ag}_3\text{PO}_4/\text{WS}_2$  composites as visible-light-driven photocatalysts for decomposing dyes, *J. Mater. Chem. A*, 2015, **3**, 19439–19444.
- 25 F. Ding, S. Z. Zhang, X. G. Luo and X. Y. Lin, Fabrication of  $\text{Ag}_3\text{PO}_4/\alpha\text{-Bi}_2\text{O}_3$  composites with enhanced photocatalytic properties under visible light, *RSC Adv.*, 2015, **5**, 96685–96694.
- 26 N. Mohaghegh, M. Tasviri, E. Rahimi and M. Gholami, A novel p–n junction  $\text{Ag}_3\text{PO}_4/\text{BiPO}_4$ -based stabilized Pickering emulsion for highly efficient photocatalysis, *RSC Adv.*, 2015, 12944–12955 in press.
- 27 Y. G. Lv, K. Huang, W. Zhang, B. Yang, F. L. Chi, S. L. Ran and X. G. Liu, One step synthesis of  $\text{Ag}/\text{Ag}_3\text{PO}_4/\text{BiPO}_4$  double-heterostructured nanocomposites with enhanced visible-light photocatalytic activity and stability, *Ceram. Int.*, 2014, **40**, 8087–8092.
- 28 S. Y. Wu, H. Zheng, Y. Y. Wu, W. Lin, T. Z. Xu and M. Guan, Hydrothermal synthesis and visible light photocatalytic activity enhancement of  $\text{BiPO}_4/\text{Ag}_3\text{PO}_4$  composites for degradation of typical dyes, *Ceram. Int.*, 2014, **40**, 14613–14620.
- 29 O. Mehraj, N. A. Mir, B. M. Pirzada and S. Sabir, Fabrication of novel  $\text{Ag}_3\text{PO}_4/\text{BiOBr}$  heterojunction with high stability and enhanced visible-light-driven photocatalytic activity, *Appl. Surf. Sci.*, 2015, **332**, 419–429.
- 30 S. Kumar, T. Surendar, A. Baruah and V. Shanker, Synthesis of a novel and stable g- $\text{C}_3\text{N}_4$ - $\text{Ag}_3\text{PO}_4$  hybrid nanocomposite photocatalyst and study of the photocatalytic activity under visible light irradiation, *J. Mater. Chem. A*, 2013, **1**, 5333–5340.
- 31 J. F. Zhang, J. L. Lv, K. Dai, Q. Liu, C. H. Liang and G. P. Zhu, Facile and green synthesis of novel porous g- $\text{C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  composite with enhanced visible light photocatalysis, *Ceram. Int.*, 2016, **43**, 1522–1529.
- 32 L. Li, Y. H. Qi, J. R. Lu, S. L. Lin, W. J. An, Y. H. Liang and W. Q. Cui, A stable  $\text{Ag}_3\text{PO}_4@$ g- $\text{C}_3\text{N}_4$  hybrid core@shell composite with enhanced visible light photocatalytic degradation, *Appl. Catal., B*, 2015, **183**, 133–141.
- 33 T. Y. Huang, Y. J. Chen, C. Y. Lai, *et al.* Synthesis, characterization, enhanced sunlight photocatalytic properties, and stability of  $\text{Ag}/\text{Ag}_3\text{PO}_4$  nanostructure-sensitized  $\text{BiPO}_4$  [J], *RSC Adv.*, 2015, **5**, 43854–43862.

