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## Interesting $\text{Ag}_3\text{PO}_4$ concave rhombic dodecahedra: the same face with different morphologies and photocatalytic properties

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Herein, a novel and interesting  $\text{Ag}_3\text{PO}_4$  crystal with concave rhombic dodecahedra morphology ( $\text{Ag}_3\text{PO}_4$  CRD) *via* facile wet chemical method is presented. Compared to  $\text{Ag}_3\text{PO}_4$  with rhombic dodecahedra structure ( $\text{Ag}_3\text{PO}_4$  RD), the  $\text{Ag}_3\text{PO}_4$  CRD was also enclosed by  $\{110\}$  facets but with different geometrical shapes, formed through carving out four parallelepipeds at special junctions. The photocatalytic activity of  $\text{Ag}_3\text{PO}_4$  CRD dramatically decreased, this was attributed to the concave nature inducing easier recombination of photogenerated holes and electrons and the reaction with organic molecules being more difficult due to space limitation and the shadow effect. The results indicated that the geometrical distribution of crystal facets could play an important role in determining photocatalytic properties.

## Introduction

Photocatalysts have received great attention as environmentally friendly and efficient materials in the field of environmental protection.<sup>1–5</sup> Developing visible-light-driven photocatalysts has become a very active topic, such as chalcogenides, silver halide, and so on.<sup>6–9</sup> With a band gap of 2.36 eV,  $\text{Ag}_3\text{PO}_4$  shows excellent, high photocatalytic activity in the degradation of organic dyes under visible light irradiation.<sup>10</sup> Morphology control of  $\text{Ag}_3\text{PO}_4$  has been considered to be one of the most promising methods to improve its photocatalytic activity.<sup>11–14</sup> Accordingly, it is of great value to further investigate  $\text{Ag}_3\text{PO}_4$  crystals with new morphologies and structures.

Recently, some morphologies of  $\text{Ag}_3\text{PO}_4$  have been reported. Ye *et al.* fabricated  $\text{Ag}_3\text{PO}_4$  rhombic dodecahedrons (RD) with only  $\{110\}$  facets exposed, which exhibited much higher photocatalytic activities than cubes bound by  $\{100\}$  facets for the degradation of organic contaminants.<sup>10</sup> Zheng *et al.* reported the tetrahedral  $\text{Ag}_3\text{PO}_4$  microcrystals with exposed  $\{111\}$  facets showed the highest photocatalytic activity in visible light irradiation among the  $\{111\}$ ,  $\{110\}$  and  $\{100\}$  facets.<sup>11</sup> It was elucidated that the excellent performance of tetrahedral  $\text{Ag}_3\text{PO}_4$  crystals composed of  $\{111\}$  facets, was attributed to a high surface energy, leading to high charge carrier mobility and active surface reaction sites. More

importantly, the reported  $\text{Ag}_3\text{PO}_4$  crystals with various morphologies were obtained by adjusting internal experimental conditions such as raw materials, solvents, pH values, and additives,<sup>15–19</sup> which also could result in the difference of photocatalytic activity. Thus, it is valuable and necessary to investigate the  $\text{Ag}_3\text{PO}_4$  crystals with various morphologies obtained by almost the same condition.

In our work,  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD were obtained *via* a facile wet chemical method only by tuning the concentration of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  (keep pH ≈ 7). With the same exposed  $\{110\}$  facets but different geometrical shapes, some outside faces of  $\text{Ag}_3\text{PO}_4$  CRD were replaced by the corresponding inner faces at four special junctions. Thus, the relationships between morphologies and photocatalytic activities can be singly investigated in this situation.

## Experimental

### Sample preparation

**Synthesis of  $\text{Ag}_3\text{PO}_4$  RD.** 106 mg silver nitrate was dissolved in 800 mL distilled water, and 0.86 mL ammonia solution (14 M) was added. After stirring for 30 min, concentrated phosphoric acid was slowly dropped into the above solution until pH ≈ 7 and the yellow precipitate was observed. Finally, the obtained yellow precipitate was washed with water several times and dried overnight.

**Synthesis of  $\text{Ag}_3\text{PO}_4$  CRD.** In the above process, 106 mg silver nitrate was dissolved in 800 mL distilled water, and 3.1 mL ammonia solution (14 M) was added. After stirring for 30 min, concentrated phosphoric acid was slowly dropped into the above solution until pH ≈ 7 and the yellow precipitate was observed. Finally, the obtained yellow precipitate was washed with water several times and dried overnight.

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## Sample characterization

X-ray diffraction (XRD) experiments were carried out with a D/max-2400 diffractometer (Rigaku, Japan) using Cu-K $\alpha$  radiation. The morphologies were examined by scanning electron microscopy (SEM, Hitachi S-4800). Diffuse reflectance ultraviolet-visible (UV-Vis) absorption spectra were measured by a PerkinElmer Lambda 950 spectrometer in the region of 200–700 nm, while BaSO<sub>4</sub> was used as a reference. Electrochemical and photoelectrochemical measurements were performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte solution in a three-electrode quartz cell, platinum wire and Ag/AgCl electrode were served as the counter electrode and reference electrode respectively. The measurements were performed on a CHI-660C electrochemical workstation. Specific surface areas were computed from the isotherms by applying the Brunauer–Emmett–Teller (BET) method using a Micromeritics ASAP 2000 system.

## Evaluation of photocatalytic activity

The photocatalytic activity of samples was measured by the decomposition of Rhodamine B (RhB) solution in a reactor at room temperature. In a typical process for degradation, 200 mg of photocatalyst was suspended in the RhB solution (10 mg L<sup>-1</sup>, 80 mL). Before irradiation, the suspensions were stirred for 30 min in the dark to ensure the establishment of adsorption–desorption equilibrium. A 350 W Xenon lamp equipped with an ultraviolet cutoff filter ( $\lambda \geq 420$  nm) was employed for the visible light irradiation source which was positioned 20 cm away from the reactor to trigger the photocatalytic reaction. A certain volume of suspension was withdrawn at selected times for analysis. After recovering the photocatalyst by centrifugation, the concentration of dye solution was analyzed by measuring the light absorption of the clear solution at 554 nm ( $\lambda_{\text{max}}$  for RhB solution) using a spectrophotometer (WFJ-7200, Unico, USA). The percentage of degradation was calculated by  $C/C_0$ . Here,  $C$  is the concentration of remaining dye solution at each irradiated time interval, while  $C_0$  is the initial concentration.

## Results and discussion

XRD patterns of Ag<sub>3</sub>PO<sub>4</sub> CRD and Ag<sub>3</sub>PO<sub>4</sub> RD shown in Fig. 1 indicate that all peaks of the Ag<sub>3</sub>PO<sub>4</sub> can be indexed very well

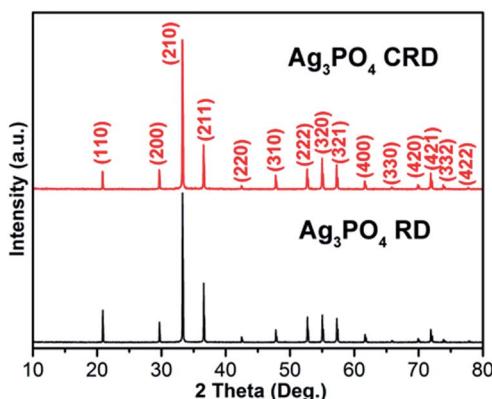


Fig. 1 XRD patterns of Ag<sub>3</sub>PO<sub>4</sub> CRD and Ag<sub>3</sub>PO<sub>4</sub> RD.

Table 1 Intensity ratios of XRD peaks (110)/(222) and (211)/(222) of Ag<sub>3</sub>PO<sub>4</sub> CRD and Ag<sub>3</sub>PO<sub>4</sub> RD

Intensity ratio	Ag <sub>3</sub> PO <sub>4</sub> RD	Ag <sub>3</sub> PO <sub>4</sub> CRD
(110)/(222)	1.5	1.1
(211)/(222)	2.9	2.5

with JCPDS No. 06-0505, and no peaks of other impurities can be detected. Compared with Ag<sub>3</sub>PO<sub>4</sub> RD, the relative intensity of the (110) peak decreases as shown in Table 1, which could be attributed to the change of the geometrical shape of two kinds of Ag<sub>3</sub>PO<sub>4</sub>.<sup>20</sup>

Fig. 2 shows the SEM images of Ag<sub>3</sub>PO<sub>4</sub> CRD and Ag<sub>3</sub>PO<sub>4</sub> RD. Compared with Ag<sub>3</sub>PO<sub>4</sub> RD, there are four pits at the special corners on Ag<sub>3</sub>PO<sub>4</sub> CRD. Fig. 3(a1–a3) presents the geometrical shapes of the Ag<sub>3</sub>PO<sub>4</sub> RD from different view. It can be seen that the Ag<sub>3</sub>PO<sub>4</sub> RD consists of 12 rhombus facets and 14 junctions. Fig. 3(b1–b3) and (c1–c3) present the diamond visualization of Ag<sub>3</sub>PO<sub>4</sub> RD and Ag<sub>3</sub>PO<sub>4</sub> CRD from different view, respectively, and the atoms of Ag and O were hided and only P displayed in order to identify easily. Compared with Ag<sub>3</sub>PO<sub>4</sub> RD, every three face at special corners on Ag<sub>3</sub>PO<sub>4</sub> CRD, such as the blue site pointed in Fig. 3(a1–a3), were carving out a parallelepiped. Then, four concaves with four new inner junctions were formed and corresponding four initial outside junctions disappear, as shown in Fig. 3(c1–c3). Thus, the spacial facets of Ag<sub>3</sub>PO<sub>4</sub> RD were replaced by the new inner facets in Ag<sub>3</sub>PO<sub>4</sub> CRD with the same area and the same {110} facet, which is firstly reported.

Before testing the photocatalytic activity for RhB solution, the UV-Vis absorption spectra of Ag<sub>3</sub>PO<sub>4</sub> CRD and Ag<sub>3</sub>PO<sub>4</sub> RD were measured. As shown in Fig. 4, there is a slight difference between the samples. Ag<sub>3</sub>PO<sub>4</sub> RD is able to absorb light up to approximately 535 nm, while Ag<sub>3</sub>PO<sub>4</sub> CRD has an absorption edge around 520 nm. Since the size of the crystals is very similar (2  $\mu$ m) and there are no signs of foreign elemental doping in the sample, it is thought that the absorption edge shift is likely to be due to the morphology transformation, which may result in the XRD peaks ratios change.<sup>10,21</sup> According to the previous report,<sup>11</sup> the band gaps of the Ag<sub>3</sub>PO<sub>4</sub> {111}, {110} and {100} surfaces were calculated to be 2.736 eV, 2.613 eV and 2.032 eV, respectively.

This indicates that Ag<sub>3</sub>PO<sub>4</sub> CRD with lower intensity ratios of XRD peaks (110)/(222) can be attributed to the morphology transformation, thus possesses larger band gap value, which is consisted with the blue shift of absorption edge.

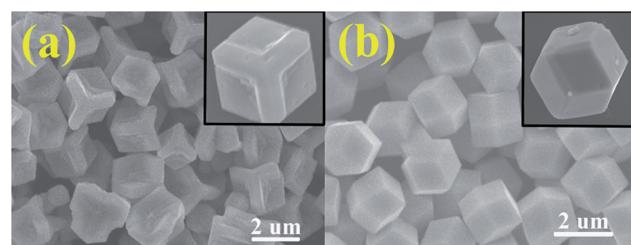


Fig. 2 SEM images of (a) Ag<sub>3</sub>PO<sub>4</sub> CRD and (b) Ag<sub>3</sub>PO<sub>4</sub> RD.



Using the BET method, it is turned out to be that the  $\text{Ag}_3\text{PO}_4$  RD has a specific surface of  $1.6 \text{ m}^2 \text{ g}^{-1}$  and the  $\text{Ag}_3\text{PO}_4$  CRD is  $5.91 \text{ m}^2 \text{ g}^{-1}$ , respectively. According to the different morphologies of  $\text{Ag}_3\text{PO}_4$  RD and  $\text{Ag}_3\text{PO}_4$  CRD, it can be seen that every three face at special corners on  $\text{Ag}_3\text{PO}_4$  CRD was carved out a parallelepiped, then every  $\text{Ag}_3\text{PO}_4$  CRD crystal is more lighter than  $\text{Ag}_3\text{PO}_4$  RD. So the numbers of  $\text{Ag}_3\text{PO}_4$  CRD crystals are more than that of  $\text{Ag}_3\text{PO}_4$  RD in the same unit mass and the surface area of  $\text{Ag}_3\text{PO}_4$  RD was somewhat smaller than that of  $\text{Ag}_3\text{PO}_4$  CRD, which also demonstrated that the improved catalytic activity of  $\text{Ag}_3\text{PO}_4$  RD was not caused by the specific surface area to a certain extent.

On the basis of previous reports, the separation efficiency of electrons and holes played an important role and the photoelectrochemical parameters could be used to investigate the excitation and transfer of photo-generated charge carriers in the photocatalytic process.<sup>22,23</sup> To better confirm the reason why the same face with different morphology and photocatalytic properties of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD, the photocurrent

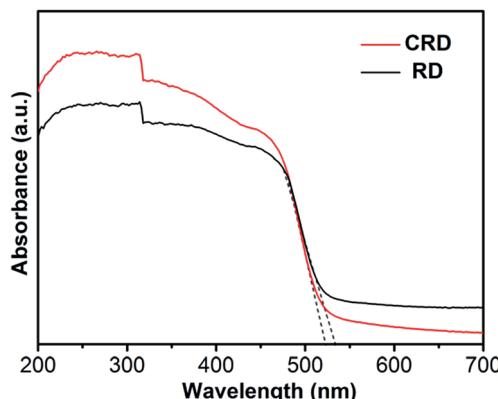


Fig. 4 UV-Vis absorption spectra of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD.

responses in an electrolyte under visible light and EIS (Nyquist plot) using a three-electrode system in  $0.5 \text{ M Na}_2\text{SO}_4$  solution were performed, which may indirectly correlate with the

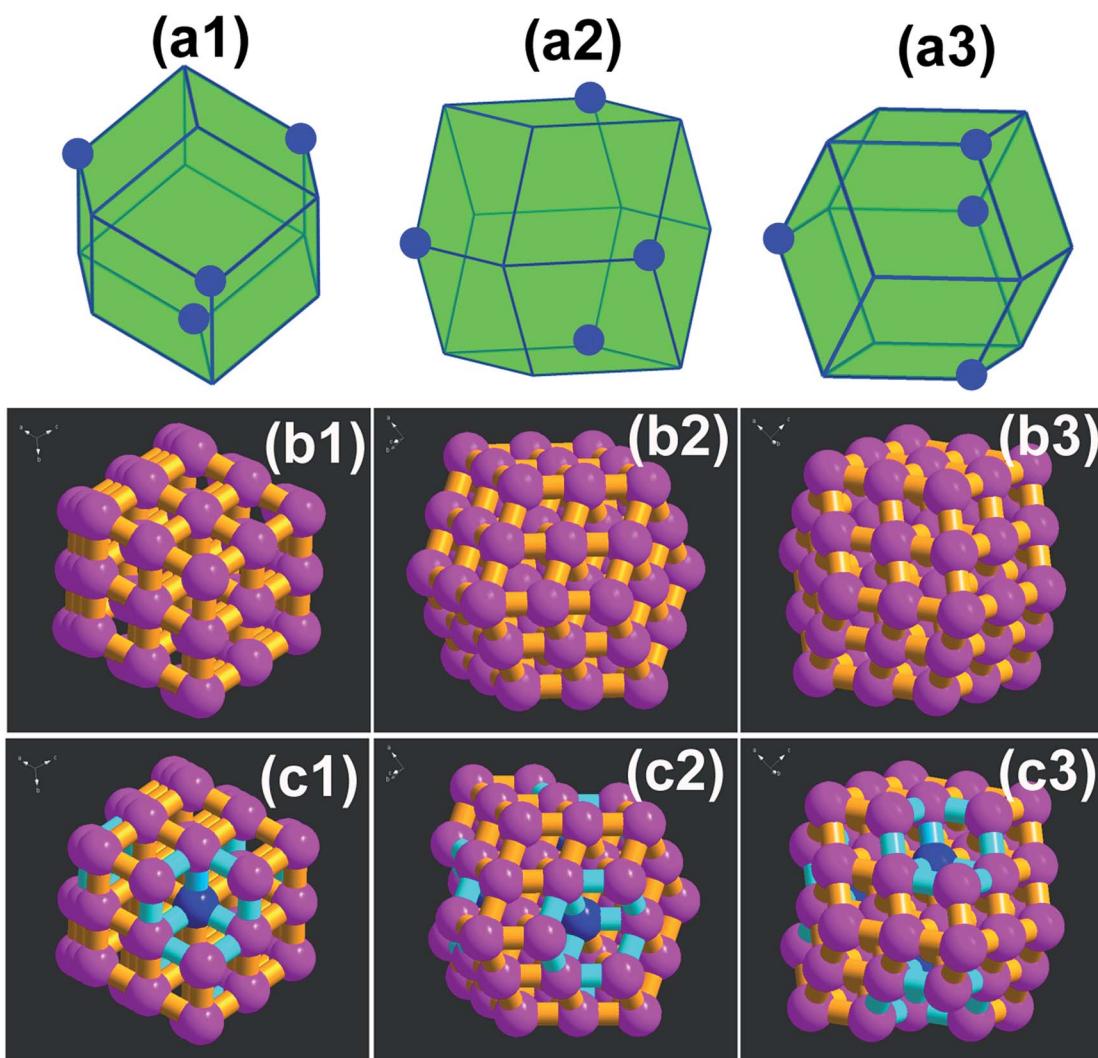


Fig. 3 (a1–a3) Geometrical shapes of the  $\text{Ag}_3\text{PO}_4$  RD from different view; diamond visualization of (b1–b3)  $\text{Ag}_3\text{PO}_4$  RD and (c1–c3)  $\text{Ag}_3\text{PO}_4$  CRD from different view.



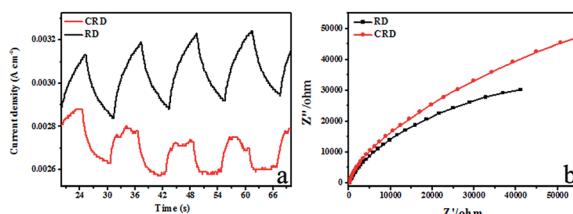


Fig. 5 Transient photocurrent of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD under visible light irradiation (a) and electrochemical impedance spectra (Nyquist plot) of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD (b).

generation and transfer to the photoinduced charge carriers in the photocatalytic process of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD. The current abruptly increased and decreased when the light source was switched on and off. Remarkably, the  $\text{Ag}_3\text{PO}_4$  RD exhibited an obviously enhanced photocurrent response compared with  $\text{Ag}_3\text{PO}_4$  CRD as shown in Fig. 5a, which implied that less efficient separation of the photogenerated electron–hole pairs and slow transfer of photoinduced charge carriers occurred in the  $\text{Ag}_3\text{PO}_4$  CRD. Moreover, the EIS measurements were used to study the charge transfer and recombination process.<sup>24,25</sup> As shown in Fig. 5b, the diameter of the arc radius on the EIS Nyquist plot of the  $\text{Ag}_3\text{PO}_4$  CRD was much larger than  $\text{Ag}_3\text{PO}_4$  RD, which indicated that the more effective separation of photogenerated electron–hole pairs and fast interface charge transfer occurred in the  $\text{Ag}_3\text{PO}_4$  RD.<sup>26</sup>

The Mott–Schottky plots under dark conditions were also investigated to compare the charge carrier density of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD, which were scanned using the voltage in the range of 0–1.5 eV and the frequency of 1000 Hz. The platinum wire and Ag/AgCl electrode were served as the counter electrode and reference electrode, respectively. The positive slope of the  $C^{-2} - E$  as shown in Fig. 6 indicated that the  $\text{Ag}_3\text{PO}_4$  RD and  $\text{Ag}_3\text{PO}_4$  CRD belonged to n-type semiconductors.<sup>27</sup> By plotting  $1/C^2$  versus  $E$ , the flat-band potential of the n-type semiconductor could be quantified from the slope, which was found to shift from 0.54 eV for the  $\text{Ag}_3\text{PO}_4$  CRD to 0.46 eV for the  $\text{Ag}_3\text{PO}_4$  RD, and the more negative potential shift demonstrated that the separation efficiency of charge carrier was improved in the  $\text{Ag}_3\text{PO}_4$  RD.<sup>28</sup>

Over all, easier generation, more efficient separation and enhanced transfer efficiency of photogenerated electron–hole

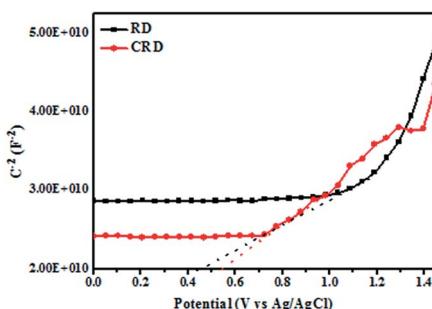


Fig. 6 Mott–Schottky plots of  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD.

pairs could be achieved in  $\text{Ag}_3\text{PO}_4$  RD than  $\text{Ag}_3\text{PO}_4$  CRD for degradation of RhB under visible light irradiation.

Fig. 7 shows the photocatalytic activity of the  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD for RhB degradation under visible light irradiation. It can be seen that about 63% of RhB solution was degraded in 140 min for  $\text{Ag}_3\text{PO}_4$  RD. However, only 24% of RhB was degraded for  $\text{Ag}_3\text{PO}_4$  CRD with the same visible light irradiation. The dramatically decrease of photocatalytic activity of  $\text{Ag}_3\text{PO}_4$  CRD is mainly attributed to the morphology change. With the concave geometrical shapes, the recombination of photogenerated holes and electrons become easier and the reaction with organic molecules could be harder due to the space limitation and shadow effect.

In this work, holes ( $\text{h}^+$ ), superoxide radicals ( $\text{O}_2^-$ ) or hydroxyl radicals ( $\text{OH}^\cdot$ ) might be active species in photocatalytic process. To further explore the major species, radical-trapping experiments with different scavengers were performed as shown in Fig. 8. In this way, 1 mM ethylenediamine tetraacetic acid disodium (EDTA-2Na, a scavenger of  $\text{h}^+$ ), 1 mM benzoquinone (BQ, a scavenger of  $\text{O}_2^-$ ), and 1 mM tertiary butanol (t-BuOH, a scavenger of  $\text{OH}^\cdot$ ) were adopted in the degradation of RhB (3.5 ppm, 80 mL), which indicated that  $\text{OH}^\cdot$  radicals were not the dominant active species compared to no scavenger. The degradation efficiency was almost decreased completely after addition of EDTA-2Na and was decreased remarkably when the BQ added, which suggest that the  $\text{h}^+$  was the main active specie

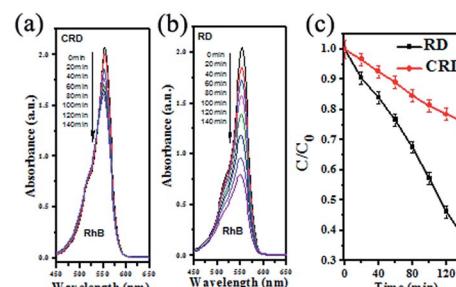


Fig. 7 Absorption of RhB aqueous solutions versus visible-light irradiation time in the presence of  $\text{Ag}_3\text{PO}_4$  CRD (a) and  $\text{Ag}_3\text{PO}_4$  RD (b); photocatalytic activity of the  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD for RhB degradation under visible light irradiation (c).

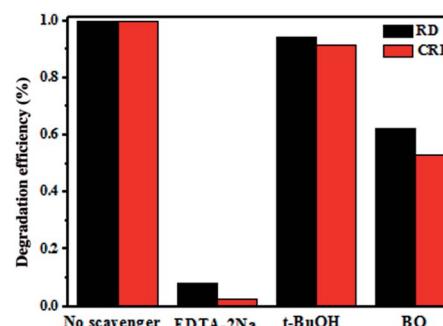


Fig. 8 Trapping experiment of active species during the photocatalytic degradation of RhB over  $\text{Ag}_3\text{PO}_4$  CRD and  $\text{Ag}_3\text{PO}_4$  RD under visible light irradiation.



and  $\cdot\text{O}^{2-}$  also played a certain role in the photocatalytic degradation of RhB solution.

## Conclusion

In this work, a novel and interesting  $\text{Ag}_3\text{PO}_4$  CRD was synthesized *via* a facile wet chemical method. Both enclosed by  $\{110\}$ , the  $\text{Ag}_3\text{PO}_4$  CRD showed different geometrical shape, lower intensity ratios of XRD peaks  $(110)/(222)$ , blue shift of absorption edge, less efficient separation and enhanced transfer efficiency of photogenerated electron–hole pairs compared with the  $\text{Ag}_3\text{PO}_4$  RD. It was found that the  $\text{Ag}_3\text{PO}_4$  CRD was formed through carving out four parallelepiped at special junctions. Furthermore, the photocatalytic activity of  $\text{Ag}_3\text{PO}_4$  CRD dramatically decreased compared with  $\text{Ag}_3\text{PO}_4$  RD, which was attributed to the concave nature-induced easier recombination of photogenerated holes and electrons and harder reaction with organic molecules with the space limitation and shadow effect. Apart from other reported vital factors, this work indicated that the geometrical distribution of crystal facets also plays an important role in photocatalytic property during the multielement determination.

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