Electronic supplementary information

Morphology-controlled synthesis of Ag_3PO_4 microcrystals for high performance photocatalysis

Yang-Sen Xu, Wei-De Zhang*

School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, People's Republic of China

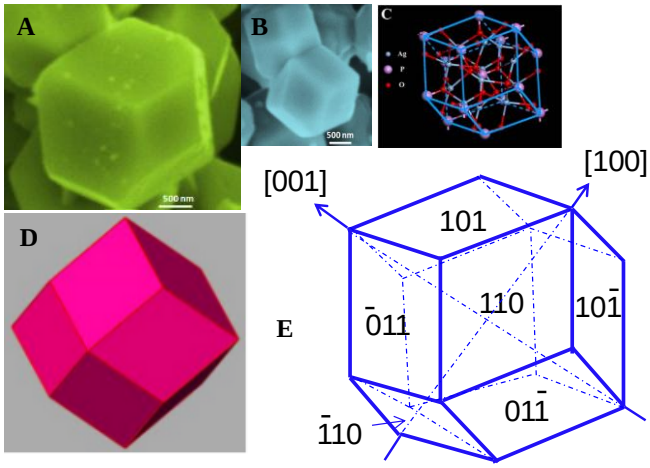

Fig. S1 (A, B) the obtained Ag_3PO_4 rhombic dodecahedron; (C) index of a rhombododecahedral crystal model;[1] (D) a structure model of rhombic dodecahedron; (E) crystal model of Ag_3PO_4 rhombic dodecahedron (which is cleaved from a 2×2×2 super cell)[2].

* Corresponding author. Tel and Fax: 86-20-8711 4099, E-mail address: zhangwd@scut.edu.cn (W. D. Zhang).

Experimental section

Materials

$AgNO_3$, Na_2HPO_4, $NH_3 \cdot H_2O$ (mass fraction 2%), glycine, triethanolamine, ethylenediamine, sodium oxalate, sodium citrate, EDTA-Na, EtOH and NaAc were purchased from local chemical agents and were of reagent grade without further purification.

Synthesis of Ag_3PO_4 sub-micrometer crystals

In this study, silver-based complexes were used as the Ag^+ source for the preparation of Ag_3PO_4. Briefly, $AgNO_3$ (60 mg) was dissolved in 30 mL deionized water, different ligands (as shown in Fig. S2) were added to form a transparent solution under stirring. The Ag_3PO_4 crystals were prepared using a facile ion exchange reaction by directly mixing the above solutions containing various complexes with Na_2HPO_4 (0.10 M) by dropwise addition followed by vigorous stirring. After continuous stirring the mixture or maintaining in a certain temperature for 1-10 h, the slightly yellow precipitate was collected, washed with deionized water thoroughly, and dried in air. In particular, a similar process was employed for the synthesis of Ag_3PO_4 hollow structures by using the sodium oxalate as ligand which can firstly form the octahedral $Ag_2C_2O_4$ microcrystals as precursors. The obtained $Ag_2C_2O_4$ crystals were subsequently used as templates for the fabrication of the corresponding silver hollow structures. In a typical synthesis procedure, the obtained Ag_3PO_4 precursor crystals were dispersed in water and then 0.10 M Na_2HPO_4 was

added at room temperature. After aging the mixture at 60-90 °C for 1-10 h in the solution, the resulted precipitate was collected by centrifugation at 4000 rpm and washed with water repeatedly and dried at 70 °C for 12 h.

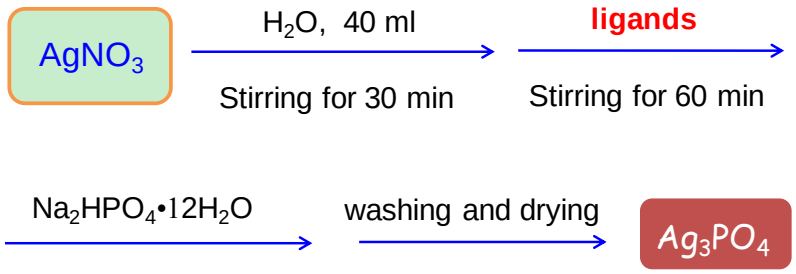

Fig. S2 Schematic illustration of the growth process of the Ag_3PO_4 crystals with different morphologies by varying the ligands.

Characterization

The crystal structures and phase compositions of the prepared samples were determined by powder X-ray diffractometer (X'Pert PRO MPD). The particle size and surface morphology of the samples were observed by a scanning electron microscope (SEM, LEO). The UV-vis diffuse reflectance spectra (DRS) were recorded on a UV-vis spectrometer (Hitachi U-3010) by using $BaSO_4$ as a reference.

Measurement of photocatalytic activity

Photocatalytic activity of the samples was evaluated by photodegradation of RhB under visible light. A 300 W tungsten halide lamp (Foshan Electric Light Ltd., Foshan,

China) combined with a 420 nm cut-off filter provides visible light irradiation. In a typical photocatalytic experiment, 0.05 g photocatalyst was dispersed in 50 mL RhB solution (5.0 mg L^{-1}). Prior to light illumination, the suspension was magnetically stirred in dark for 30 min to ensure the adsorption/desorption equilibrium. Then, the solution was exposed to visible light irradiation under magnetic stirring. At given time intervals, 1 mL of the sample was withdrawn after periodical intervals of irradiation, which was centrifuged at 12000 rpm for 6 min, and then analyzed by a Hitachi U-3310 UV-vis spectrophotometer.

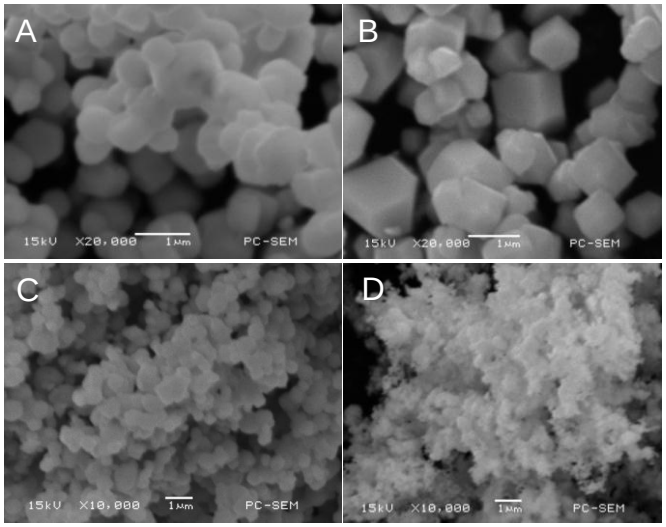

Fig. S3 SEM images of the as-synthesized Ag_3PO_4 crystals with different morphologies using different ligands, (A) glycine, (B) ammonia, (C) sodium tartrate, and (D) sodium citrate.

Table S1 Formation constants for silver complexes with various ligands

ligand	log K_1	log K_2
Ammonia	3.24	7.05
Glycine	3.41	6.89
Triethanolamine	2.30	3.64
1,10-Phenanthroline	5.02	12.07
Oxalate	2.41	-
Citric acid	7.1	-
EDTA	7.32	-

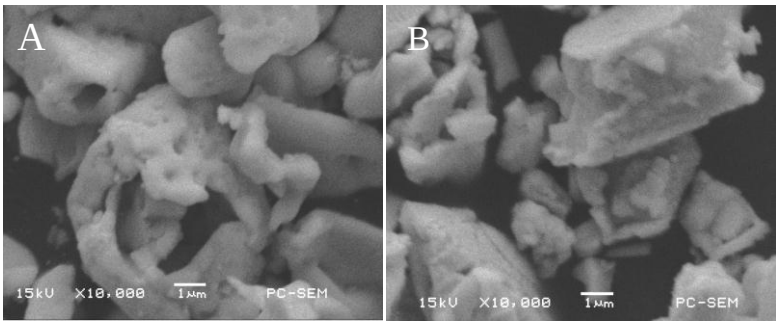

Fig. S4 SEM images of the as-synthesized truncated tetragonal bipyramids Ag_3PO_4 microboxes obtained at 70 °C.

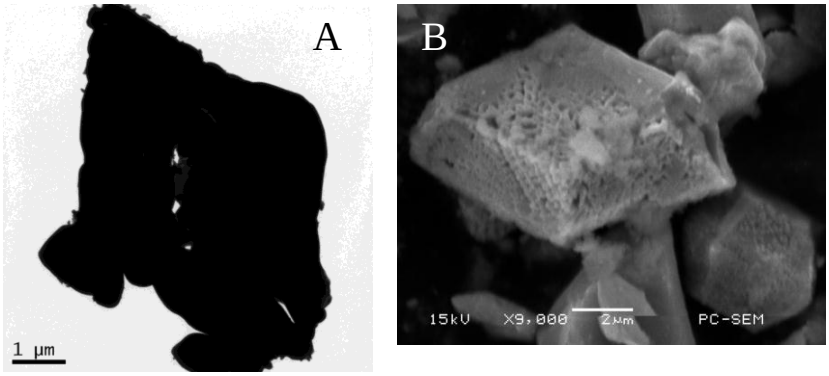

Fig. S5 (A) TEM image of the as-synthesized truncated tetragonal bipyramids Ag_3PO_4 microboxes obtained at 80 °C, (B) SEM images of the truncated tetragonal bipyramids Ag_3PO_4 microboxes obtained at 90 °C.

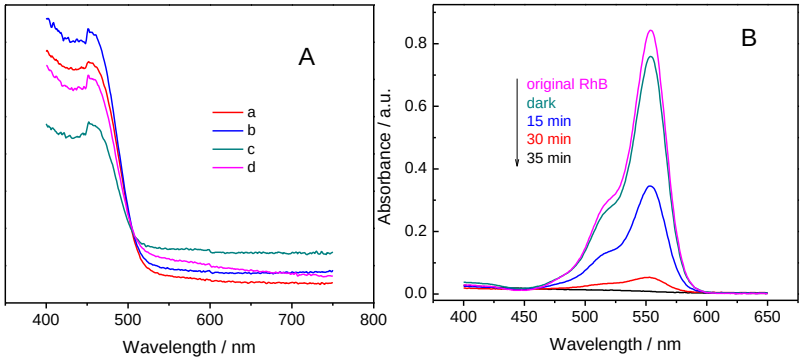

Fig. S6 (A) UV-vis diffuse reflectance spectra of the Ag_3PO_4 crystals with different morphologies and (B) photocatalytic activity towards degradation of RhB over sample c. (a) Octahedral Ag_3PO_4 microcrystals obtained at 60 °C, (b-d) truncated tetragonal bipyramid microboxes of Ag_3PO_4 at pH=9 at temperature of (b) 70 °C, (c) 80 °C and (d) 90 °C.

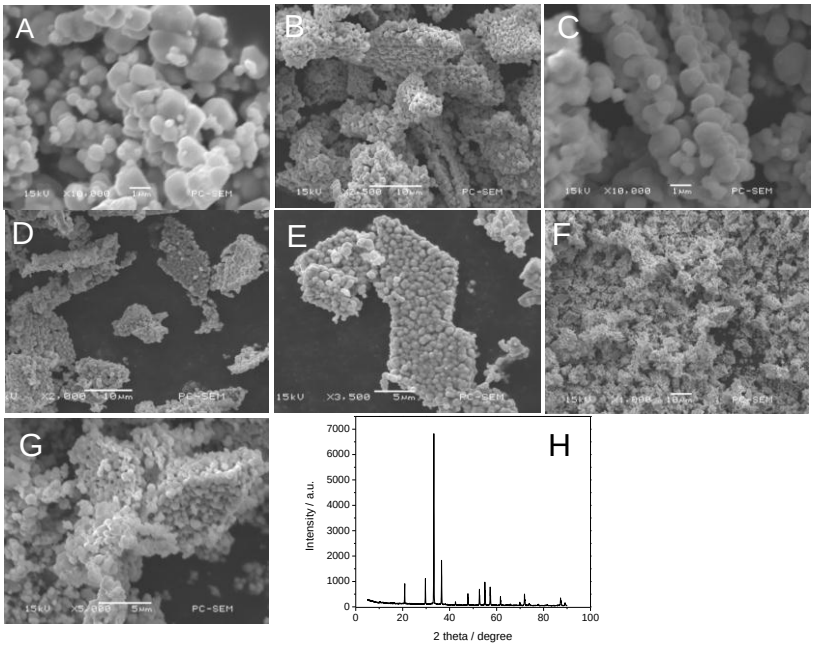

Fig. S7 SEM images of the Ag_3PO_4 crystals obtained as a function of aging time at 60 °C, (A) 0 h, (B, C) 3 h, (D, E) 6 h, (F, G) 8 h and XRD pattern of (B).

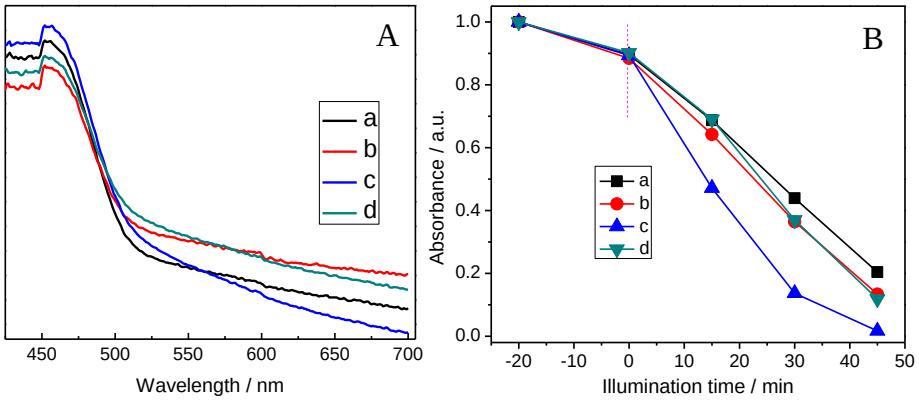

Fig. S8 (A) UV-vis diffuse reflectance spectra and (B) photocatalytic activity of the Ag_3PO_4 crystals obtained as a function of aging time at 60 °C, (a) 0 h, (b) 3 h, (c) 6 h, (d) 8 h.

References

1 Y. Bi, S. Ouyang, N. Umezawa, J. Cao and J. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 6490.

2 J. H. Yang, L. M. Qi, C. H. Lu, J. M. Ma and H. M. Cheng, *Angew. Chem. Int. Ed.*, 2005, **44**, 598.