Electronic Supplementary Data

Experimental section

1. Sample preparation

In a typical preparation procedure, proper amounts of N,Ndimethylformamide (DMF) and deionized water (H₂O) were mixed together to form transparent solvent. The total volume of mixture solvent is kept constant to 20 mL. Then, 3 mmol of AgNO₃ was dissolved into the mixture solvent. Subsequently, H₃PO₄ (1 mL, 85%) was added dropwise into the above solution under static, magnetic force stirring, and ultrasonic conditions (ultrasonic reactor, KQ-100B, 40 kHz, 120 W/cm², Kunshan Co. China), respectively. After this process, the static, stirring, and ultrasonic conditions were maintained for a fixed time period. The schematic illustration of the growth process is shown in Scheme S1. The obtained precipitation was separated by centrifuge and followed by washing with ethanol and deionized water for 3 times, respectively, to remove the DMF and other residues. The product was then dried in a vacuum oven at 80 °C. For comparison purpose, irregular spherical Ag₃PO₄ particles were synthesized by a reported method.¹



Scheme S1. Schematic illustration of the growth process of the Ag₃PO₄ crystals with various morphologies.

2. Characterization

X-ray diffraction (XRD) experiments were carried out with a D/max-2400 diffractometer (Rigaku, Japan) using Cu-Ka radiation. The morphologies of the samples were examined by scanning electron microscopy (SEM, Hitachi S-4800). An energy-dispersive spectra (EDS) detector was equipped with this field-emission SEM and operated at an accelerating voltage of 15 kV. Fourier transform infrared (FTIR) spectra of the samples were recorded between 400 and 4000 cm⁻¹ on a Nicolet NEXUS 670 FTIR spectrometer. A FEI Tecnai G2 F30 transmission electron microscope, equipped with a Gatan imaging filter (GIF) system, was used for transmission electron microscopy (TEM) work. Ultraviolet-visible diffuse reflectance (UV-vis DRS) absorption spectra were measured using a Perkin Elmer 950 spectrometer, while BaSO₄ was used as a reference. Specific surface areas were computed from the isotherms by applying the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2000 system.

3. Evaluation of photocatalytic activity

The photocatalytic activity of samples was measured by the decomposition of methylene blue (MB) and rhodamine B (RhB) in a reactor at room temperature. In a typical process for degradation of a dye, 50 mg of photocatalyst was suspended in the dye solution (10 mg/L, 60 mL). Before irradiation, the suspensions were stirred in the dark for 50 min to ensure the

establishment of adsorption–desorption equilibrium. A 350 W Xe lamp with a cutoff filter of 420 nm was employed for the visiblelight irradiation source and 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 664 nm (λ_{max} for MB solution) or 555 nm (λ_{max} for RhB solution) using a Perkin Elmer 950 spectrometer. The percentage of degradation was calculated by C/C₀. Here, C is the concentration of remaining dye solution at each irradiated time interval, while C₀ is the initial concentration.

Supplementary figures:



Fig. S1 SEM images of Ag_3PO_4 products prepared with different static times: (a) 2 h, (b) 8 h, and (c) 12 h.



Fig. S2 SEM images of Ag_3PO_4 products prepared with different ultrasonic times: (a) 0.5 h, (b) 1 h, and (c) 3 h.



Fig. S3 TEM images of Ag_3PO_4 nanorods obtained at ultrasonic condition with 2 h (a) and 3 h (b).



Fig. S4 SEM images of Ag_3PO_4 products prepared with different times under magnetic force stirring condition: (a) 0 h, (b) 2 h, (c) 8 h, and (d) 24 h.



Fig. S5 SEM images of Ag_3PO_4 product prepared at ultrasonic condition for 2 h in the mixture solvent of 10 mL ethanol and 10 mL H₂O.



Fig. S6 SEM images of Ag_3PO_4 products prepared with different DMF/H₂O ratios under ultrasonic condition: (a) 20 mL DMF, (b) 15 mL DMF : 5 mL H₂O, (c-d) 5 mL DMF : 15 mL H₂O.



Fig. S7 SEM image of irregular spherical Ag_3PO_4 particles prepared by the reported method.



Fig. S8 EDS patterns of branched (a), tetrapod (b), nanorod-shaped (c), and triangular-prism-shaped (d) Ag_3PO_4 .



Fig. S9 The adsorption isotherms of MB (A) and RhB (B) in the presence of as-prepared samples under dark conditions.



Fig. S10 The color changes of the MB and RhB solutions separated from irregular spherical Ag₃PO₄ suspensions during illumination.



Fig. S11 UV–vis absorption spectra of MB and RhB solutions separated from irregular spherical Ag₃PO₄ (A) and branched Ag₃PO₄ (B) suspensions during illumination.

It is noted that the as-prepared irregular spherical Ag_3PO_4 required 30 minutes to degrade 78% of the MB solution, which is inconsistent with the reported results by Ye *et al.* ¹ They found that MB solution was decomposed completely within 10 min. The difference can be explained by the following factors:

(1) The photocatalytic measurement condition is different. In our work, the ratio of Ag_3PO_4 to MB solution is 0.83 mg/mL, which is 3 mg/mL for the reported value by Ye *et al.*¹ The high ratio of Ag_3PO_4 to MB solution is benefit for the rapid degradation of MB solution.

(2) The photocatalytic activity of the as-prepared samples was evaluated without adding any sacrificial reagent in our work. In contrast, Ye *et al.* used AgNO₃ as the sacrificial reagent to scavenge the photoexcited electrons for the photocatalytic experiments ¹.

(3) The visible-light irradiation source was positioned 20 cm away from the reactor in our work. The light intensity could be smaller than the reported value 1 .



Fig. S12 Plots of ln(C₀/C) versus irradiation time for MB (A) and RhB (B) degradation in the presence of branched (a), tetrapod (b), nanorod-shaped (c), triangular-prism-shaped (d), and irregular spherical (e) Ag₃PO₄ products.

The degradation of dyes can be ascribed to a pseudo-first order reaction with a Langmuir–Hinshelwood model when the initial concentration (C₀) of dye solution is small: ^{2, 3} $\ln(C_0/C) = kt$

where C_0 and C are the initial concentration and remaining concentration of MB solution, respectively, k is the reaction rate constant, and t is the irradiation time.

References

- Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo and Z. Li, *Nat. Mater.*, 2010, 9, 559-564.
- X. Wang, J. G. Li, H. Kamiyama, Y. Moriyoshi and T. Ishigaki, J. Phys. Chem. B, 2006, 110, 6804-6809.
- J. M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A. Gonzalez-Elipe and A. Fernandez, *Appl. Catal.*, *B*, 1997, 13, 219-228.