

**An innovative glycine complexing approach to silver  
phosphate myriapods with improved photocatalytic activity**

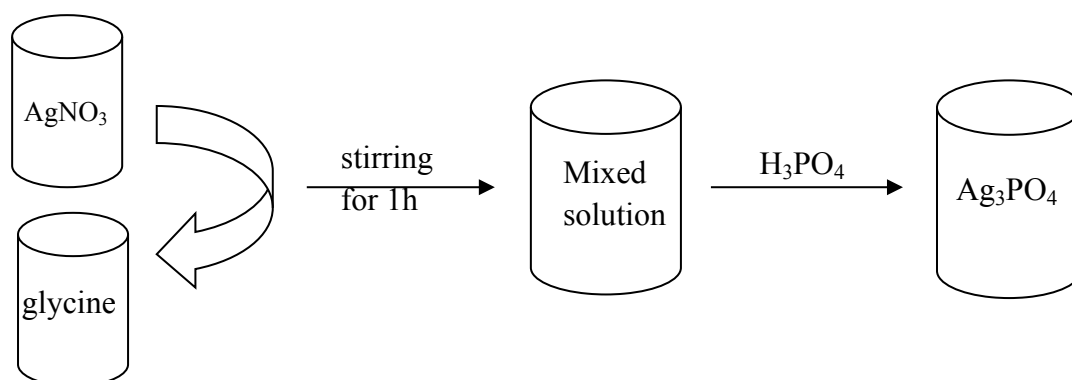
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## 1. Experimental Section

**1.1 Chemicals:** All chemicals used were analytic grade reagents without further purification; glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), silver nitrate ( $\text{AgNO}_3$ ), 85% phosphoric acid (85%  $\text{H}_3\text{PO}_4$ ), were purchased from Shanghai Reagents Company (Shanghai, China).

**1.2 Synthesis of etched and hollow  $\text{Ag}_3\text{PO}_4$  dendrites:** In a typical synthesis, 0.075~0.6006g glycine (1mmol~8mmol) and 0.3398g (2mmol)  $\text{Ag}_3\text{NO}_4$  was dissolved into 10 mL deionized water, severally. Then,  $\text{Ag}_3\text{NO}_4$  solution was poured into glycine solution under stirring for 1h. Finally, 28 $\mu\text{L}$  of 85 wt.%  $\text{H}_3\text{PO}_4$  was added drop wise to the solution above. Upon  $\text{H}_3\text{PO}_4$  was introduced into the system, did the color of the reaction mixture change from hyaline colorless to bright yellow. The whole process was carried out at room temperature (20 °C) under stirring. After stirring for 40 min, the yellow precipitation was collected, washed with deionized water for several times, and dried at room temperature. Schematic S1 shows the preparation process for etched and hollow  $\text{Ag}_3\text{PO}_4$  dendrites.



**Scheme S1.** Schematic illustration of the preparation process

**1.3 Synthesis of solid  $\text{Ag}_3\text{PO}_4$  tetrapods:** Solid sample is synthesized as our previously reported.<sup>1</sup> In a typical procedure, 3 mmol of 85%  $\text{H}_3\text{PO}_4$  was dissolved in 80 mL of deionized water and 2.5 mmol of  $\text{AgNO}_3$  was added under stirring. Then, 37.5 mmol of urea were put into the above solution. The resulting precursor was transferred into a Teflon-lined stainless steel autoclave and maintained at 80°C for 24h. After cooling to room temperature, the yellow precipitation was collected and washed with deionized water several times, and dried overnight at 60°C.

**1.4 Synthesis of Irregular  $\text{Ag}_3\text{PO}_4$ :** The irregular  $\text{Ag}_3\text{PO}_4$  particles were synthesized as previously reported.<sup>1</sup> Typically, appropriate amounts of raw powders of  $\text{Na}_2\text{HPO}_4$  and  $\text{AgNO}_3$  were thoroughly ground until the initial white changed to yellow.

**1.5 N-doped  $\text{TiO}_2$  (NTs):** Nitrogen doping was conducted as described previously.<sup>2</sup> Typically, 0.5 g of Degauss P25  $\text{TiO}_2$  powders was suspended in ethanol (5 mL). Then, urea (1 g) was dissolved in 2.5 mL ethanol and 0.5 mL  $\text{H}_2\text{O}$  was added into the suspension above. The mixture was stirred and heated to completely evaporate the solvent, followed by calcination in air at 400 °C for 4 h.

## 2. Photocatalytic degradation reactions

Photocatalytic activities of the samples were evaluated by photocatalytic decomposition of rhodamine B (RhB). Typically, 0.1 g of powders were put into a solution of RhB (200 mL, 50 mg/L), which was irradiated with a 300W Xe arc lamp equipped with an ultraviolet cut off filter to provide visible light ( $\lambda \geq 420$  nm).

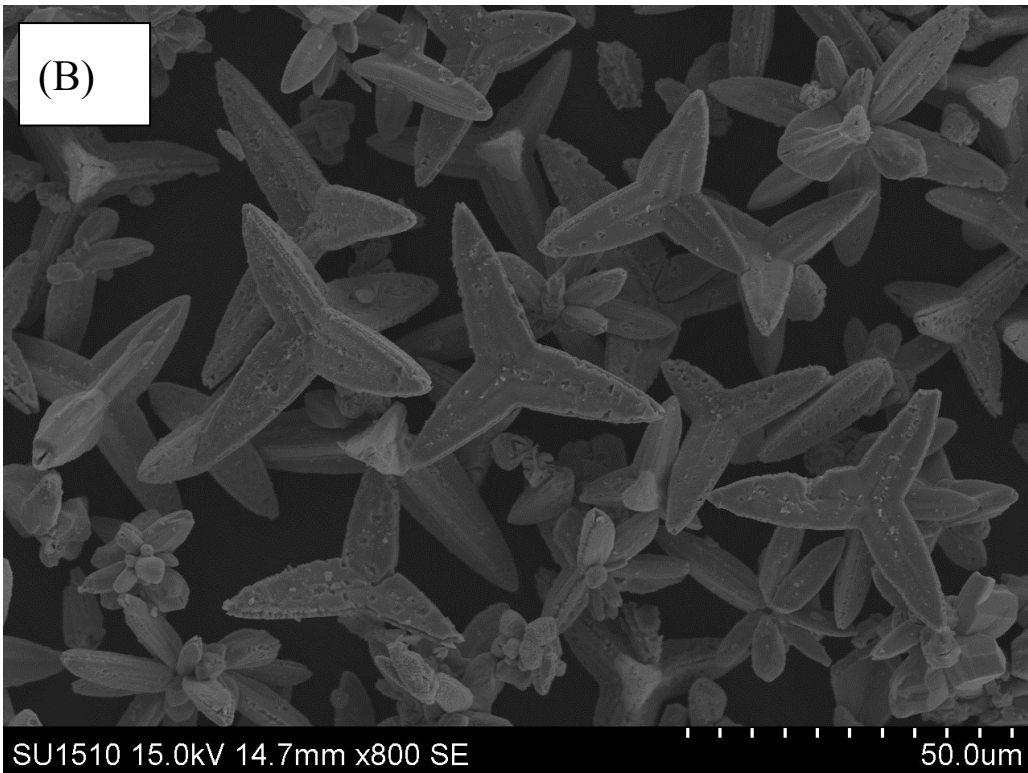
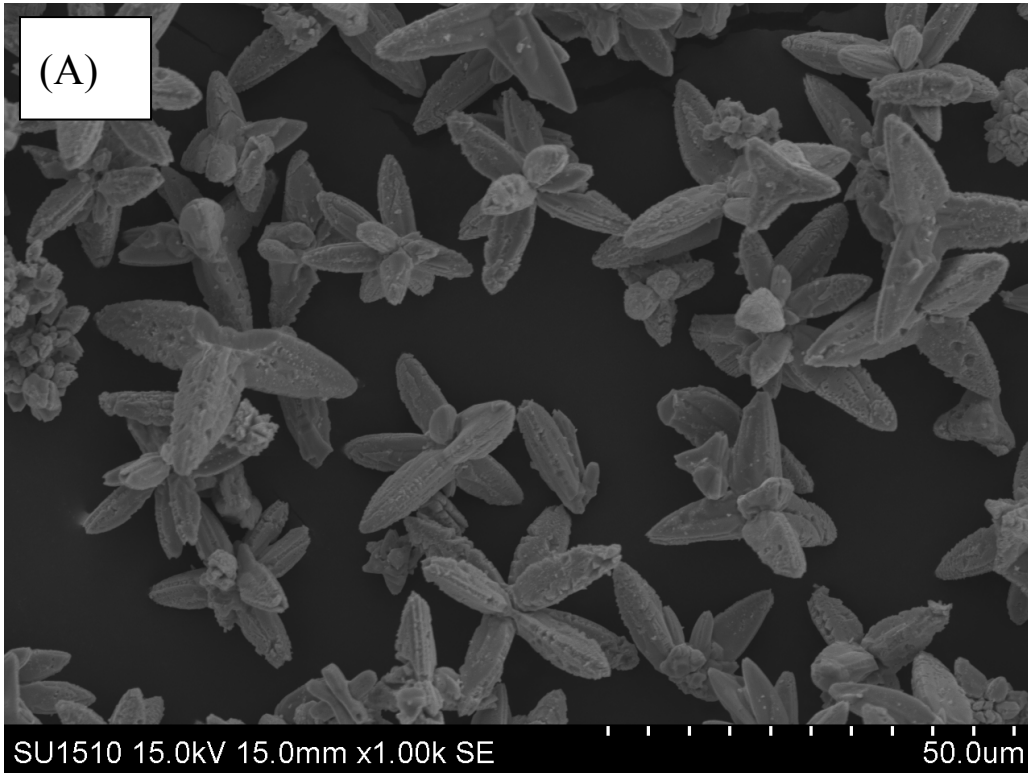
The cycle experiments are carried out under the same conditions as above.

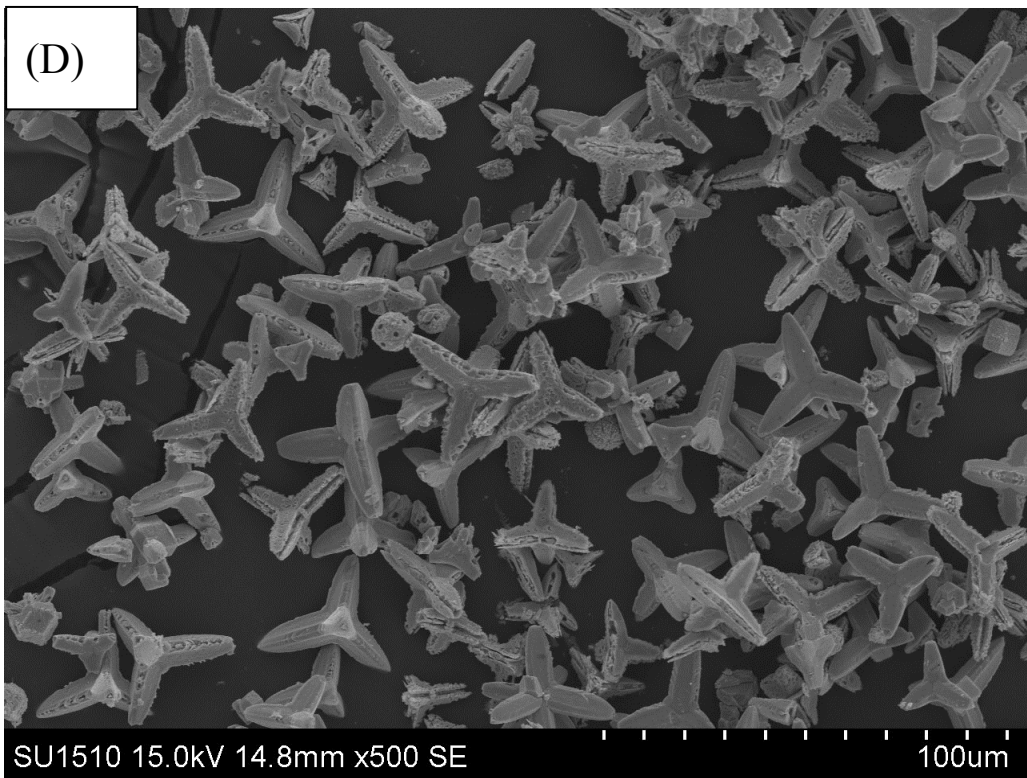
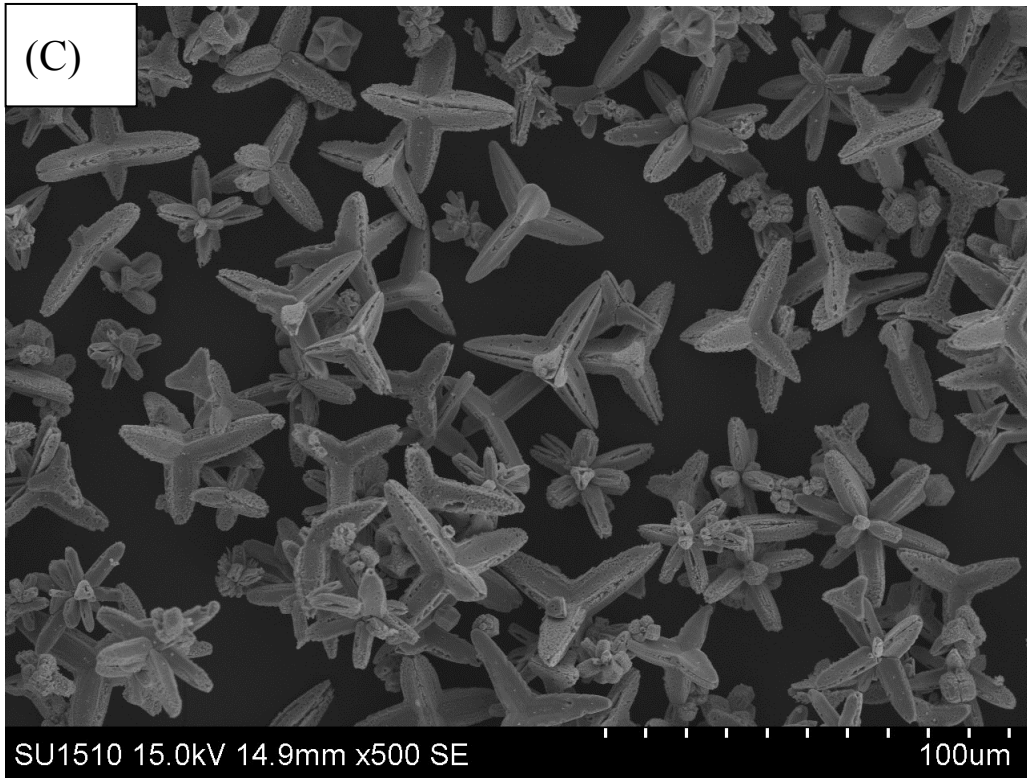
## 3. Characterization

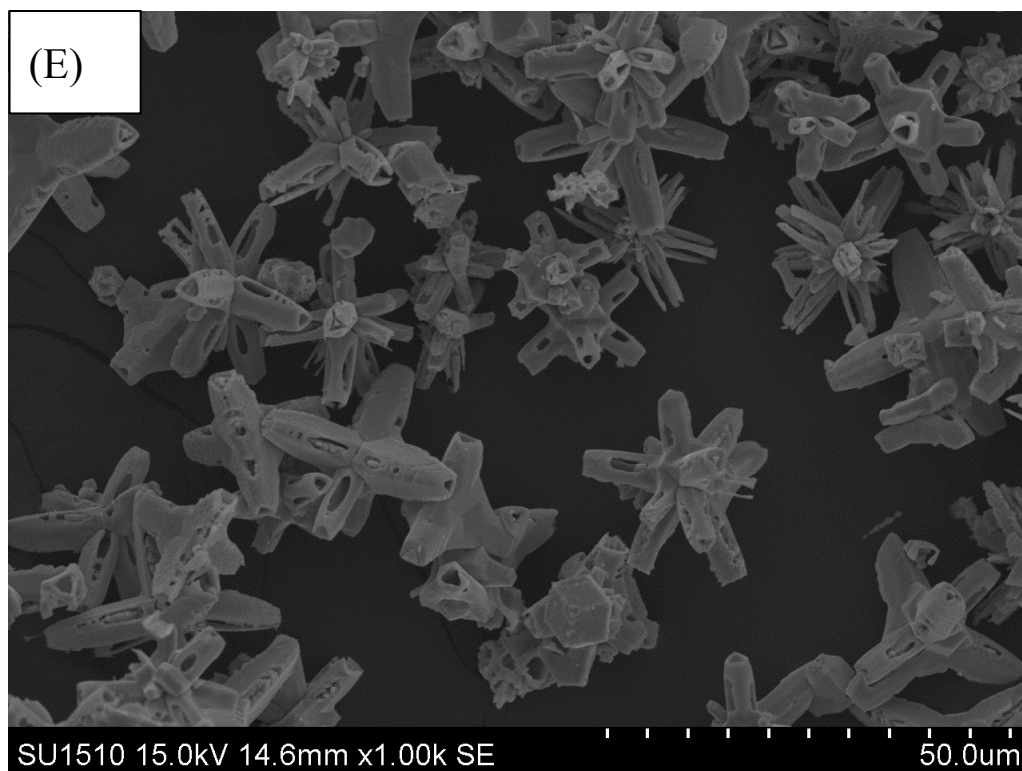
Scanning electron microscope (SEM) images of the samples were obtained on a Hitachi SU-1510 operated at 120 kV. The samples were coated with 5-nm-thick gold layer before observation. The phase compositions of the samples were determined by X-ray diffractometer (Rigaku D/max-2550VB) using graphite monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm), operating at 40 kV and 50mA. The XRD patterns were scanned in the range of 20-80° ( $2\theta$ ) at a scanning rate of 5 °min<sup>-1</sup>. Nitrogen adsorption-desorption isotherms were collected at 77 K using the NOVOE 4000 adsorption apparatus.

## References

- (1) J. Wang, F. Teng, M. Chen, J. Xu, Y. Song and X. Zhou, *CrystEngComm.*, 2013, **15**, 39.
- (2) Mitoraj, D. and Kisch, H., *Angew. Chem., Int. Ed.*, 2008, **47**, 9975.



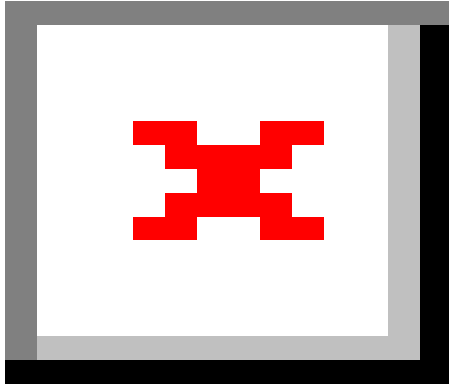




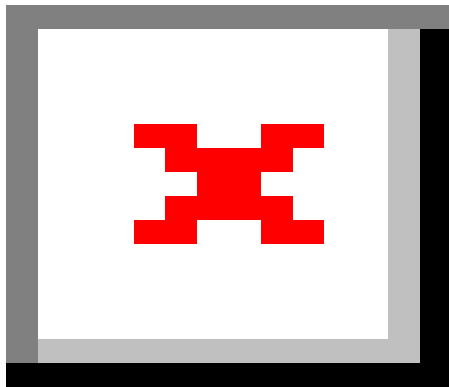
**Fig. S1** Low-magnification SEM images of  $\text{Ag}_3\text{PO}_4$  crystals synthesized at different molar ratios of glycine to  $\text{AgNO}_3$ : (A) 0.5:1; (B) 1:1; (C) 2:1; (D) 3:1; (E) 4:1. Reaction temperature: 20 °C; Stirring time upon adding phosphate acid: 40 min.

When the reaction time and temperature are different, the morphology of  $\text{Ag}_3\text{PO}_4$  changes from eroded myriapods to hollow dendrites.

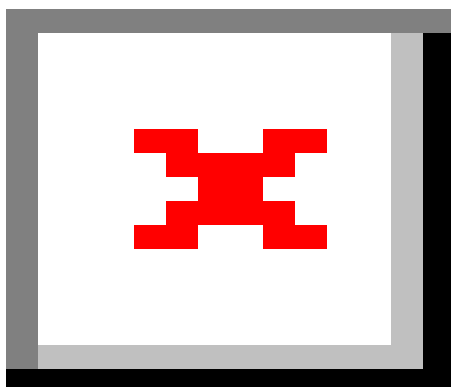
(A)



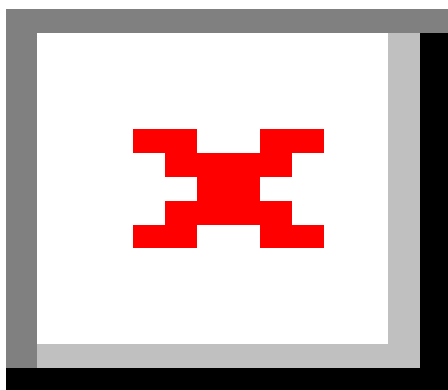
(B)



(C)



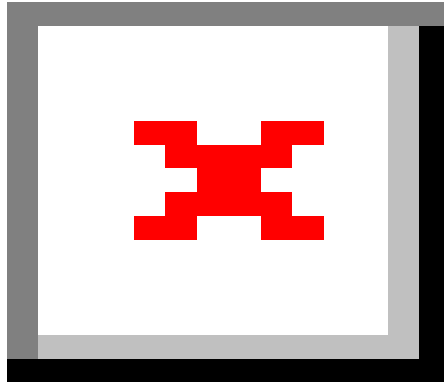
(D)



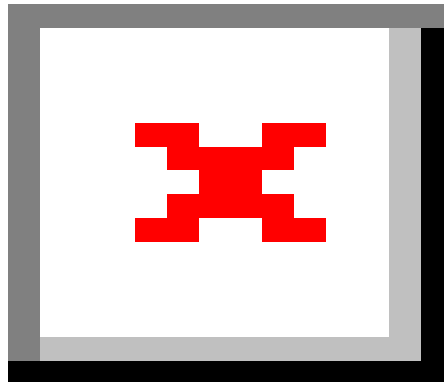
**Fig. S2** Low-magnification SEM images of Ag<sub>3</sub>PO<sub>4</sub> crystals synthesized at different stirring time upon adding phosphate acid: (A) 0 min; (B) 15min; (C) 30min; (D) 40min. Reaction temperature: 20 °C; glycine /Ag<sup>+</sup> =4:1 (molar ratio).



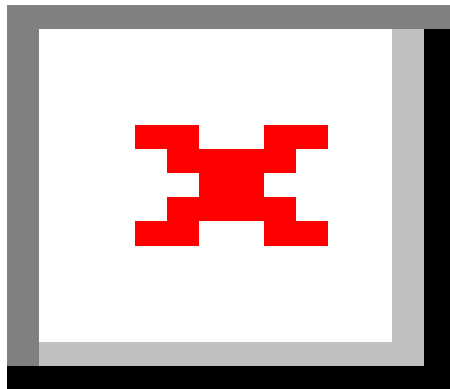
(A)



(B)

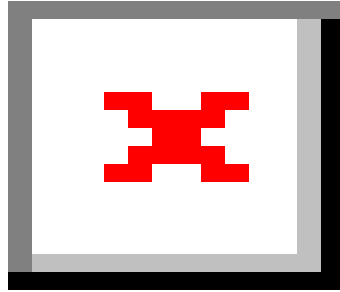


(C)

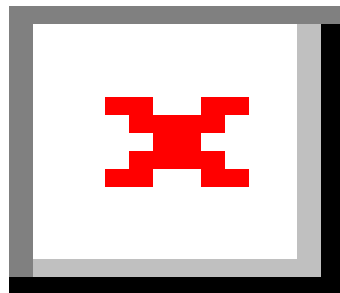


**Fig. S3** Low-magnification SEM images of  $\text{Ag}_3\text{PO}_4$  crystals synthesized at different temperature: (A) 30 °C; (B) 40°C; (C) 50 °C. glycine / $\text{Ag}^+$  =4:1 (molar ratio); Stirring time upon adding phosphate acid: 40 min.

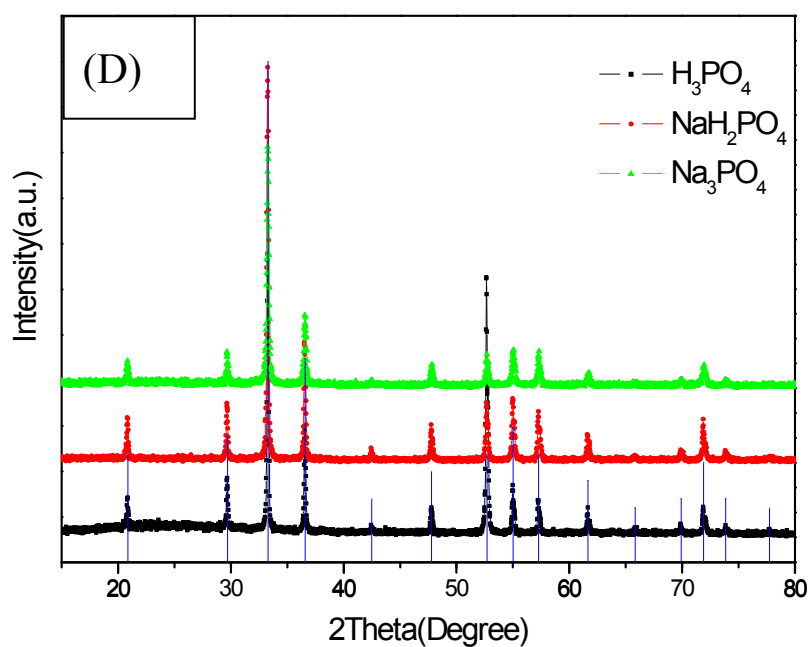
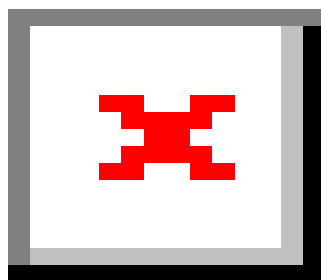
(A)



(B)



(C)



**Fig. S3** Low-magnification SEM images of  $\text{Ag}_3\text{PO}_4$  synthesized using 0.4092 mmol of different phosphorus sources and XRD patterns (D): (A) 85 wt.%  $\text{H}_3\text{PO}_4$ ; (B)  $\text{NaH}_2\text{PO}_4$ ; (C)  $\text{Na}_3\text{PO}_4$ . glycine / $\text{Ag}^+$  =4:1 (molar ratio); Stirring time upon adding of phosphate acid: 40 min.

Not only the amount of glycine added, reaction time and reaction temperature have affected the result, but also the pH values do. We control the pH values by changing phosphorus source only. 28  $\mu\text{L}$  of 85 wt.%  $\text{H}_3\text{PO}_4$  is equivalent to 0.4092 mmol. Thus, 0.4092 mmol (0.04909 g)  $\text{NaH}_2\text{PO}_4$  and (0.06708 g)  $\text{Na}_3\text{PO}_4$  were set to compare, aiming to keep the amount of  $\text{PO}_4^{3-}$  the same. The experiment process carried out exactly the same except phosphorus source changing. Fig. S3(B) is low-magnification SEM images using  $\text{NaH}_2\text{PO}_4$  source. The crystals of myriapods are small and cluster together. No hollow crystal is seen. Correspondingly, there is no specific morphology in Fig. S3(C) with  $\text{Na}_3\text{PO}_4$  source. Even so, the XRD patterns indicate all the samples are pure  $\text{Ag}_3\text{PO}_4$ . pH values of the three system is shown below in Table 1

**Table 1** pH values of the three system using  $\text{H}_3\text{PO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_3\text{PO}_4$

phosphorus source	pH
$\text{H}_3\text{PO}_4$	3.02
$\text{NaH}_2\text{PO}_4$	3.16
$\text{Na}_3\text{PO}_4$	4.85

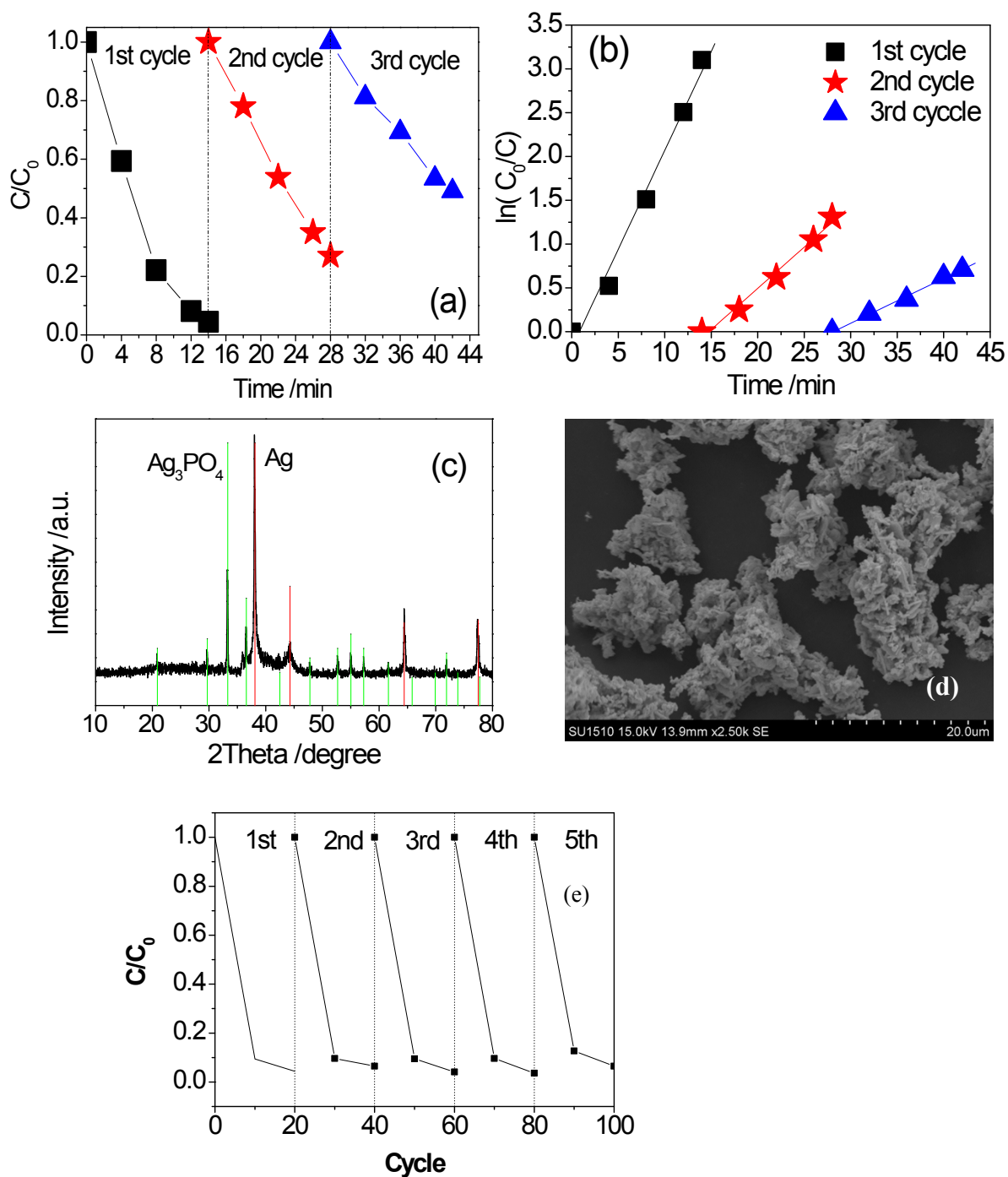


Fig. S4 Cycle curves (a,b), SEM (c) and XRD (d) of the etched  $\text{Ag}_3\text{PO}_4$  sample under visible light irradiation ( $\lambda > 420 \text{ nm}$ ): 200 mL  $50 \text{ mg mL}^{-1}$  RhB; 100 mg of the sample represented in Fig. 2D; (e) cycle curves of the un-etched  $\text{Ag}_3\text{PO}_4$  sample represented in solid.