

## Supporting Information for

# Facile synthesis of novel $\text{Ag}_3\text{PO}_4$ tetrapods and the {110} facets-dominated photocatalytic activity

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## Experimental Section

**Chemicals:** All chemicals used were analytical grade reagents without further purification; silver nitrate ( $\text{AgNO}_3$ ), 85% phosphoric acid (85%  $\text{H}_3\text{PO}_4$ ), urea ( $\text{CO}(\text{NH}_2)_2$ ), titanium dioxide ( $\text{TiO}_2$ ) were purchased from Shanghai Reagents Company (Shanghai, China).

**Synthesis of  $\text{Ag}_3\text{PO}_4$  tetrapods:** 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 above solution. The resulting precursor was transferred into a Teflon-lined stainless steel autoclave and maintained at 80 °C for 24 h. After cooling to room temperature, the yellow precipitation was collected and washed with deionized water several times, and dried overnight at 60 °C.

**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. The SEM images and XRD pattern of irregular  $\text{Ag}_3\text{PO}_4$  were showed in Fig. S1B.

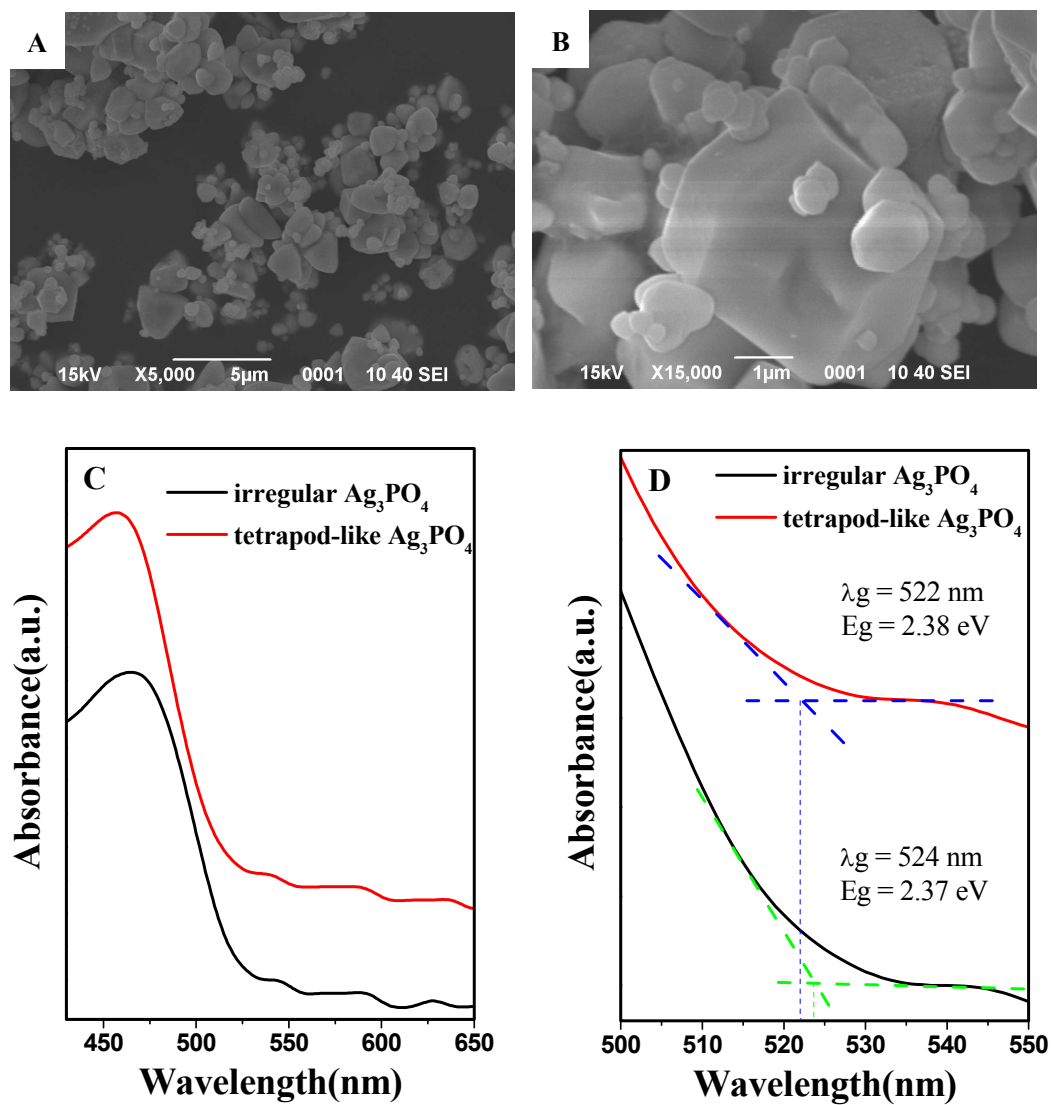
**Synthesis of N-TiO<sub>2</sub>:** Nitrogen doping was conducted as described previously.<sup>2</sup> P25 (0.5 g) was suspended in ethanol (5 mL). Then, urea (1 g) was dissolved in 2.5 mL ethanol and 0.5 mL H<sub>2</sub>O was added into the suspension. The mixture was stirred and heated to completely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

**Photocatalytic reactions:** Photocatalytic activities of the samples were evaluated by the photocatalytic decomposition of rhodamine B (RhB). Typically, 0.1 g of powders were put into a solution of RhB dye (100 ml, 8 mg/L), which was irradiated with a 300W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with  $\lambda \geq 420$  nm.

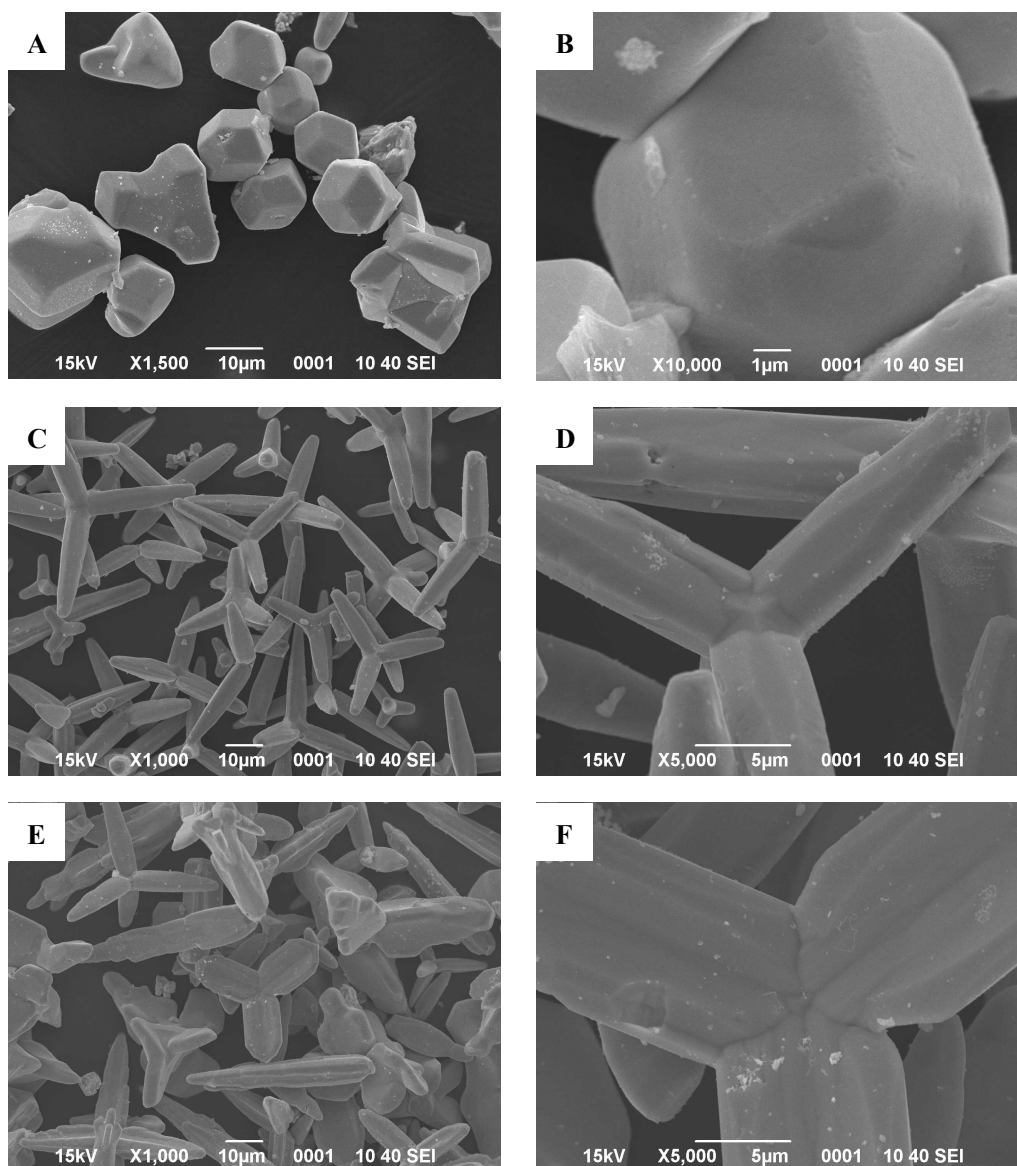
**Characterizations:** Scanning electron microscope (SEM) images of the samples were obtained on a Hitachi SU-1510 operated at 120kV. The samples were coated with 5-nm-thick gold layer before observation. The phase compositions of the samples were determined by X-ray diffractometer (Rigaku D/max-2550VB): using graphite monochromatized 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.

## Reference

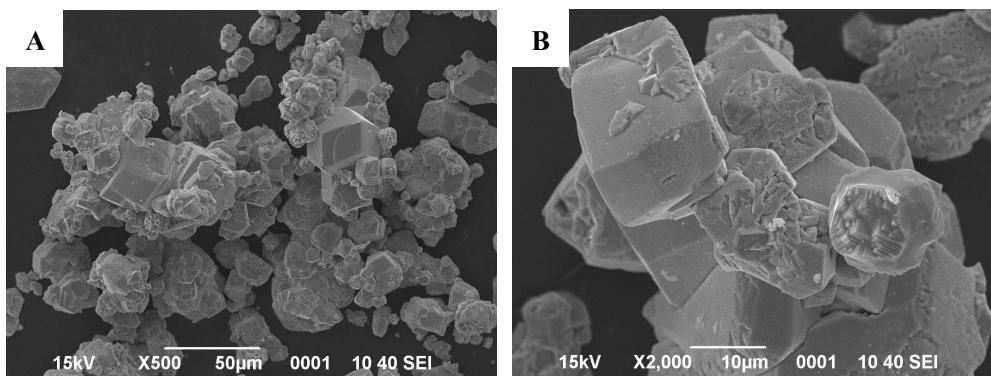
- (1) Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. S. Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu and R. L. Withers, *Nat. Mater.*, 2010, **9**, 559.
- (2) D. Mitoraj and H. Kisch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9975.



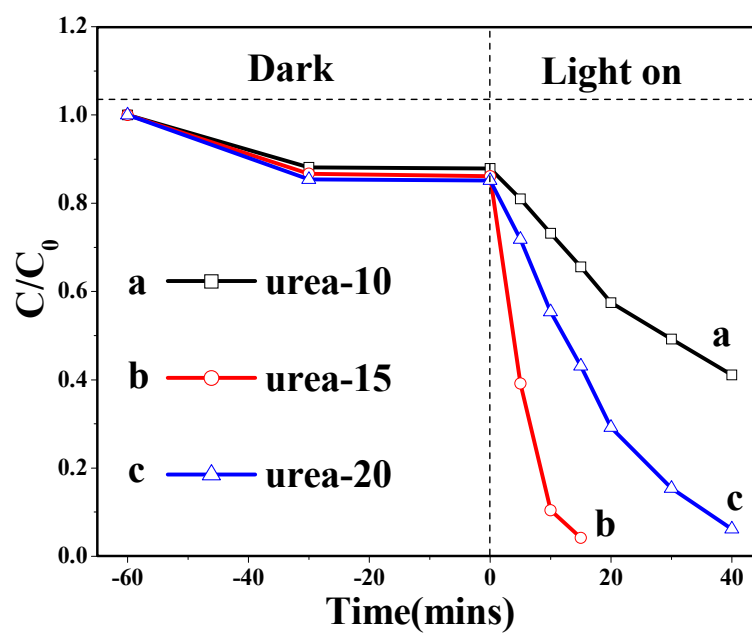
**Fig. S1** (A, B) SEM images of irregular  $\text{Ag}_3\text{PO}_4$ ; (C,D) UV-visible spectra of T- $\text{Ag}_3\text{PO}_4$  and irregular  $\text{Ag}_3\text{PO}_4$ .



**Fig. S2** SEM images of  $\text{Ag}_3\text{PO}_4$  microcrystals synthesized at different molar ratios of urea to  $\text{AgNO}_3$ : (A, B) 10; (C, D) 15; (E, F) 20.



**Fig. S3** SEM images of  $\text{Ag}_3\text{PO}_4$  microcrystals synthesized via an open refluxing system.



**Fig. S4** Photocatalytic activities of  $\text{Ag}_3\text{PO}_4$  synthesized at different molar ratios of urea to  $\text{AgNO}_3$ : (a) 10, (b) 15, (c) 20.

**Table S1** The textural properties of the polyhedrons and tetrapods.

Samples	Surface areas (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore Diameter (nm)
Polyhedrons	29.851	0.023	3.113
Tetrapods	37.952	0.030	3.112

Surface area, calculated by the Brunauer–Emmett–Teller method; Pore sizes, calculated by the Barret–Joyner–Halender method.