Supporting Information for

Facile synthesis of novel Ag₃PO₄ tetrapods and the \{110\} facets-dominated photocatalytic activity

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Experimental Section

Chemicals: All chemicals used were analytic grade reagents without further purification; silver nitrate (AgNO₃), 85% phosphoric acid (85% H₃PO₄), urea (CO(NH₂)₂), titanium dioxide (TiO₂) were purchased from Shanghai Reagents Company (Shanghai, China).

Synthesis of Ag₃PO₄ tetrapods: In a typical procedure, 3 mmol of 85% H₃PO₄ was dissolved in 80 mL of deionized water and 2.5 mmol of AgNO₃ 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 Ag₃PO₄: The irregular Ag₃PO₄ particles were synthesized as previously reported. Typically, appropriate amounts of raw powders of Na₂HPO₄ and AgNO₃ were thoroughly ground until the initial white changed to yellow. The SEM images and XRD pattern of irregular Ag₃PO₄ were showed in Fig. S1B.
**Synthesis of N-TiO$_2$:** Nitrogen doping was conducted as described previously.$^2$ 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$_2$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 Kα radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50mA. The XRD patterns were scanned in the range of 20-80° (2θ) at a scanning rate of 5°min$^{-1}$. Nitrogen adsorption-desorption isotherms were collected at 77 K using the NOVOE 4000 adsorption apparatus.

**Reference**


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

- **C**
  - irregular Ag$_3$PO$_4$
  - tetrapod-like Ag$_3$PO$_4$

- **D**
  - irregular Ag$_3$PO$_4$
  - tetrapod-like Ag$_3$PO$_4$

\[ \lambda_g = 522 \text{ nm} \]
\[ E_g = 2.38 \text{ eV} \]

\[ \lambda_g = 524 \text{ nm} \]
\[ E_g = 2.37 \text{ eV} \]
**Fig. S2** SEM images of Ag₃PO₄ microcrystals synthesized at different molar ratios of urea to AgNO₃: (A, B) 10; (C, D) 15; (E, F) 20.
**Fig. S3** SEM images of Ag$_3$PO$_4$ microcrystals synthesized via an open refluxing system.
Fig. S4 Photocatalytic activities of Ag₃PO₄ synthesized at different molar ratios of urea to AgNO₃: (a) 10, (b) 15, (c) 20.
Table S1 The textural properties of the polyhedrons and tetrapods.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface areas (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhedrons</td>
<td>29.851</td>
<td>0.023</td>
<td>3.113</td>
</tr>
<tr>
<td>Tetrapods</td>
<td>37.952</td>
<td>0.030</td>
<td>3.112</td>
</tr>
</tbody>
</table>

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