Supporting Information for

Facile synthesis of porous Ag₃PO₄ photocatalysts with high self-stability and activity

Hongchao Yu, a,b,c Zhengbo Jiao, a Bingjun Jin, a Chenchen Feng, c Gongxuan Lu,* a and Yingpu Bi* a

a State Key Laboratory for Oxo Synthesis & Selective Oxidation, and National Engineering Research Center for Fine Petrochemical Intermediates, Lanzhou Institute of Chemical Physics, CAS, Lanzhou 730000, China.
b University of Chinese Academy of Sciences, Beijing 100049, China.
c Lanzhou University, Lanzhou 730000, China.

Email: yingpubi@licp.cas.cn

Experimental Section

1. Materials
   All chemicals were of analytical grade and used as received without further purification. And all chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Deionized water with a resistivity of 18.25 MΩ.cm was used in all reactions.

2. Preparation of Ag₃PO₄ microrods
   The hollow porous Ag₃PO₄ microrods were fabricated by anion exchange route using Ag₂WO₄ as raw material. Ag₂WO₄ microrods were firstly achieved by a simple precipitation reaction between Ag⁺ and WO₄²⁻ ions in distilled water. In a typical synthesis, AgNO₃ (0.05g) was dissolved in 200 mL aqueous solution, Na₂WO₄ aqueous solution (0.01 M) was added to the above solution, and Ag₂WO₄ white precipitation would be formed. The obtained Ag₂WO₄ samples for morphology analysis and subsequently preparation were washed with distilled water and dried under atmosphere. In a typical anion exchange synthesis procedure, the obtained microrods were distributed evenly in the water under vigorous magnetic stirring, then, Na₂HPO₄ aqueous solution (0.05 M) was added with drop by drop to form yellow suspension. The whole anion exchange process will be finished in 10 min. Then, the Ag₃PO₄ hollow porous microrods obtained were collected by centrifugation and washing with deionized water.

3. Photodegradation Tests
   Rhodamine B (RhB) and methyl orange (MO) were employed as representative pollutants to
test the photocatalytic properties of the hollow porous $\text{Ag}_3\text{PO}_4$ microrods. Experimental details were as follows: a 100 mL RhB and MO solution with an initial concentration of 8 mg/L in the presence of the catalyst (0.2 g) was mixed. Before light irradiating, the suspension was magnetically stirred in the dark for 20 min to ensure the adsorption-desorption equilibrium. Then, the reaction system was irradiated with a 300 W Xe arc lamp equipped with an ultraviolet cutoff filter to provide visible light with $\lambda \geq 420$ nm. The concentration change of RhB and MO remaining in the solution was monitored by a UV-vis spectrometer at 554 nm and 464 nm, respectively. Before the spectroscopy measurement, this photocatalyst was removed from the photocatalytic reaction systems by a dialyzer (Millipore, Millex-LH 0.45 $\mu$m).

4. Photoelectrochemical measurements

The photoelectric conversion properties were investigated in a conventional three-electrode cell by using computer-controlled electrochemical workstation (CHI 650A). Firstly, 50 mg catalysts was suspended in 2 mL nafion aqueous solution (1 wt %), the mixtures were ultrasonically scattered for 10 min to form homogeneous solution. Then, 0.1 mL solution was dropped on the Fluorine doped tin oxide (FTO) glass (0.5×4 cm). After evaporation of the water in air, the catalyst was attached on the FTO glass surface. A Pt wire, saturated calomel electrode (SCE), and 0.1 M sodium sulfate were used as the working electrode, the counter-electrode, the reference electrode, and the electrolyte, respectively. The current-time (i-t) curves were collected at 1 V vs SCE. The light source was a 300W Xe lamp, and a cutoff filter of 420 nm was employed for the visible-light irradiation.

5. Characterizations

The morphologies of the samples were carried out on a field-emission scanning electron microscope (FE-SEM, JSM-6701F, JEOL) operated at an accelerating voltage of 5 kV. X-ray diffraction (XRD) measurements were performed on X’ pert PRO diffractometer using Cu K$\alpha$ radiation (40 kV). The XRD patterns were recorded from 10° to 90° with a scanning rate of 0.067°/s. X-ray photoelectron spectroscopy (XPS) was observed by an ESCALAB 250 Xi XPS system of Thermo Fisher Scientific, England and excited by monochromatic Al K$\alpha$ radiation (1486.6 eV) as the excitation source to analyze samples’ elemental composition. UV-vis absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer by using BaSO4 as the reference at room temperature.
Additional Figures and Discussions

**Fig. S1** (A, B, C) SEM images of Ag\(_2\)WO\(_4\) microrods with different magnifications; (D) XRD pattern of the Ag\(_2\)WO\(_4\) microrods.
**Fig. S2** SEM images of the hollow porous Ag₃PO₄ microrods with different magnifications.

**Fig. S3** XPS spectra of the banded Ag₃PO₄ product: (A) Ag 3d region; (B) P 2p region; (C) O 1s region.

**Fig. S4** EDS spectra of the as-synthesized Ag₃PO₄ microrods.