

Supporting Information for:

A novel AgIO₄ semiconductor with ultrahigh activity in photodegradation of organic dyes: insights into the photosensitization mechanism

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Chemicals and reagents

KIO₄ was purchased from Beijing Chemical Works of China. AgNO₃, rhodamine B (RhB) and other reagents were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group.

Preparation of AgIO₄

In a typical synthesis of AgIO₄, 0.3864 g of KIO₄ was dissolved in deionized water at room temperature. Then, the KIO₄ solution and 13 mL of a AgNO₃ aqueous solution (0.10 mol L⁻¹) were added dropwise at the same time to a beaker containing 20 mL of nitric acid (0.20 mol L⁻¹) under stirring within 1h. The product AgIO₄ was obtained after filtration, washing with dilute nitric acid (0.03 mol L⁻¹) for several times, and drying at room temperature.

Preparation of Ag₃PO₄

Ag₃PO₄ was prepared according to the reported process.¹ In a typical synthesis, 1.826 g of AgNO₃ was dissolved in 50 mL of deionized water at room temperature to obtain a homogeneous solution. Then, 275 mL of a NH₃•H₂O aqueous solution (0.10 mol L⁻¹) and 180 mL of a NaH₂PO₄ aqueous solution (0.15 mol L⁻¹) were added successively to the solution. The resulting mixture was stirred at room temperature for 2 h in the dark. The product Ag₃PO₄ was obtained after filtration, washing with deionized water for several times, and drying at 60 °C for 5 h.

Preparation of Ag₃AsO₄

Ag₃AsO₄ was obtained according to the reported process.² In a typical synthesis, 0.4 mL of a

Na_2HAsO_3 aqueous solution (2.6 mol L^{-1}) was mixed with 0.2 mL of H_2O_2 (30 wt%), 10 mL of a $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution (0.1 mol L^{-1}) and 20 mL of deionized water in turn to give a homogeneous solution. Another solution was obtained by mixing 37 mL of a AgNO_3 aqueous solution (0.1 mol L^{-1}) with 35 mL of deionized water. Then, the two solutions were dropwise added at the same time to a beaker under stirring within 1h. The product Ag_3AsO_4 was obtained after filtration, washing with deionized water for several times, and drying at 60°C for 5 h.

Photodegradation activity test

The photodegradation activity was evaluated by degradation of RhB under visible-light irradiation from a 500 W Xe arc lamp (PLS-SXE300, Perfectlight Co., China) equipped with ultraviolet cutoff ($\lambda \geq 420 \text{ nm}$) or band pass (420, 470, 495 or 550 nm) filters. In all photodegradation experiments, 75 mg of photocatalysts were dispersed in 100 mL of RhB aqueous solution (12 mg L^{-1}). Prior to irradiation, the solutions suspended with photocatalysts were stirred for 60 min in the dark to ensure the establishment of adsorption-desorption equilibrium between the photocatalysts and RhB. During the photodegradation progresses, 2.5 mL of solution was collected at intervals of irradiation by pipette and subsequently centrifuged to remove the photocatalysts. Then the filtrates were analyzed by recording the intensity variation at absorption wavelength of RhB (553 nm) in UV-vis spectra using a spectrophotometer (Lambda 35, PerkinElmer Co., America).

Estimation on band gap of AgIO_4

The band gap of a crystalline semiconductor can be calculated by the following equation using the optical absorption data near the band edge:³ $\alpha h\nu = A(h\nu - E_g)^n$, where α , ν , A and E_g are absorption

coefficient, light frequency, proportionality constant and band gap, respectively. In this formula, n decides the characteristics of the transition in a semiconductor, i.e., direct transition ($n = 0.5$) or indirect transition ($n = 2$). The values of n and E_g were determined by the following steps: Firstly, plotted $\ln(ah\nu)$ versus $\ln(h\nu - E_g)$ using an approximate value of E_g , and then estimated the value of n with the slope of the straightest line near the band edge. The value of n for AgIO_4 was thus estimated to be near 2.0. Then, plotted $(ah\nu)^2$ versus $h\nu$ and evaluated the band gap E_g by extrapolating the straight line to the axis intercept. Following this method, the value of E_g for AgIO_4 was estimated to be 2.65 eV.

References

- 1 J. Tang, W. Gong, T. Cai, T. Xie, C. Deng, Z. Peng and Q. Deng, *RSC Adv.*, 2013, **3**, 2543.
- 2 J. Tang, Y. Liu, H. Li, Z. Tan and D. Li, *Chem. Commun.*, 2013, **49**, 5498.
- 3 (a) M. A. Butler, *J. Appl. Phys.*, 1977, **48**, 1914; (b) J. Luan, S. Wang, K. Ma, Y. Li and B. Pan, *J. Phys. Chem. C*, 2010, **114**, 9398.

Characterization

Analysis of element content was performed on Agilent ICP-MS7500CE spectrometer, the sample was dissolved in concentrated nitric acid for analysis. Scanning electron microscopy (SEM) experiment was undertaken on a FEI Quanta 200 microscope at an accelerating voltage of 20 kV. X-ray diffraction (XRD) patterns were recorded on a D/MAX-2500/PC powder diffractometer under Cu-K_α radiation at a scanning rate of $2\theta/\text{min} = 4^\circ/\text{min}$. The accelerating voltage and applied current

were 40 kV and 250 mA, respectively. Ultraviolet-visible diffuse reflectance spectra were recorded on a Shimadzu UV-2550 ultraviolet-visible spectrophotometer with BaSO₄ as the reference.

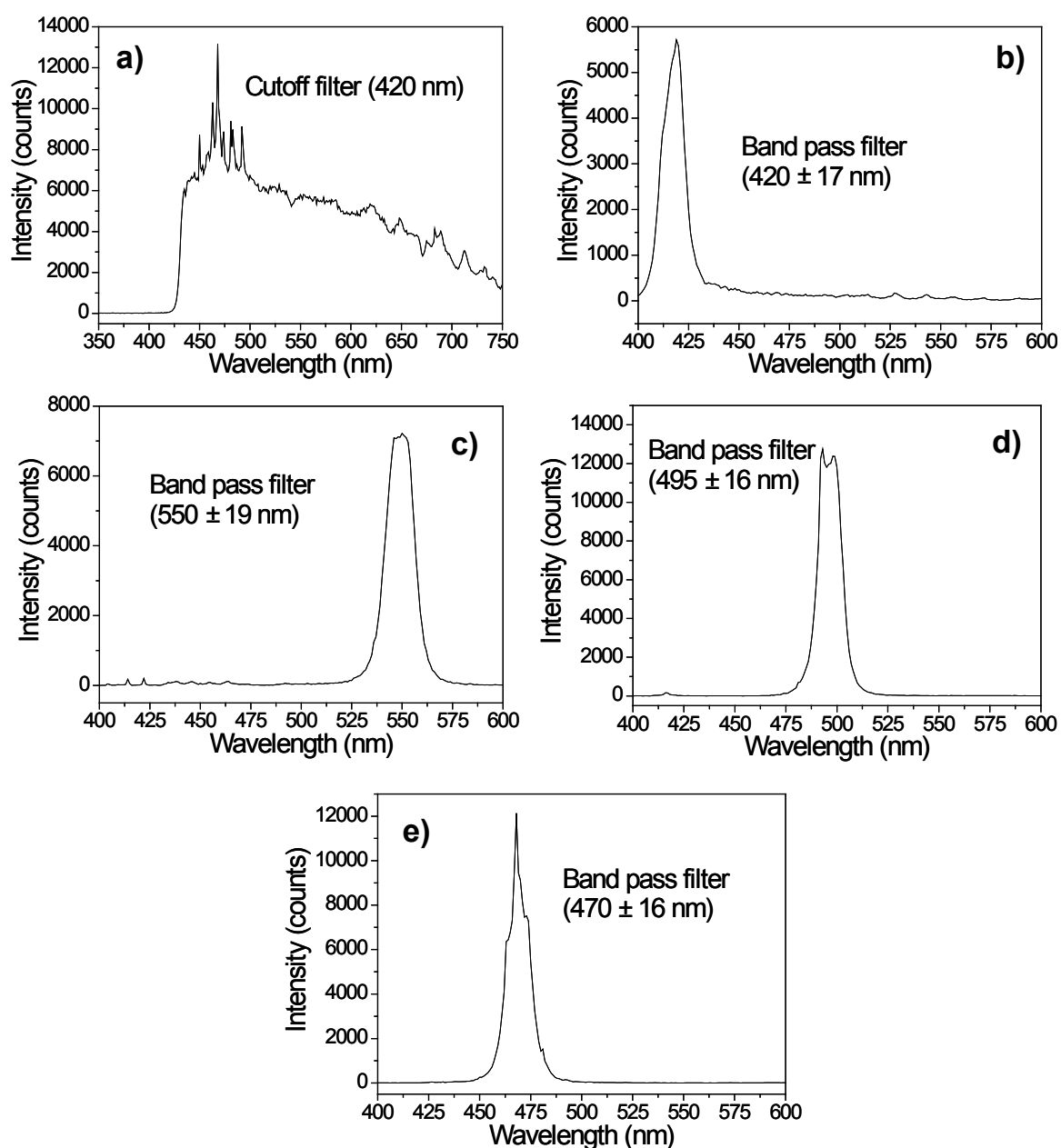


Fig. S1 The intensity and wavelength distribution of the irradiation light employed in the RhB degradation experiments. Integral area proportional to irradiation intensity was measured under the actual experimental conditions. (a) $\sim 1.60 \times 10^6$. (b) $\sim 9.72 \times 10^4$. (c) $\sim 1.36 \times 10^5$. (d) $\sim 1.88 \times 10^5$. (e) $\sim 1.42 \times 10^5$.