

Supporting Information

Novel visible light responsive Ag@(Ag₂S/Ag₃PO₄) photocatalysts: synergistic effect between Ag and Ag₂S for their enhanced photocatalytic activity

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Chemicals and reagents

AgNO_3 , $\text{NH}_3\cdot\text{H}_2\text{O}$, NaH_2PO_4 , Na_2S , rhodamine B (RhB) were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group.

Preparation of Ag_3PO_4

In a typical synthesis, 1.826 g of AgNO_3 was dissolved in 50 mL of deionized water at room temperature in order to obtain a homogeneous solution. Then, 275 mL of $\text{NH}_3\cdot\text{H}_2\text{O}$ aqueous solution (0.10 mol/L) and 180 mL of NaH_2PO_4 aqueous solution (0.15 mol/L) were added successively to the solution. The resulting mixture was stirred at room temperature for 4 h in the dark. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h in a oven, then calcined at different temperature for 6 h. The finally obtained product was labeled as “ $AP-T$ ”, where “ T ” denotes degree centigrade of the calcination temperature. It is worth mentioning that $AP-25$ refers to the Ag_3PO_4 sample synthesized at room temperature without further calcination treatment.

Preparation of $\text{Ag}_2\text{S}/\text{Ag}_3\text{PO}_4$ composites

The obtained Ag_3PO_4 (0.304 g) was ultrasonically scattered in 15 mL of deionized water for 1h. Then, 1.3 mL of aqueous solution (0.10 mol/L) of Na_2S was added. The resulting mixture was stirred at room temperature for 24 h in the dark. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h in a oven, then calcined at different temperature for 6 h. The finally obtained product was labeled as “ $AS/AP-T$ ”, where “ T ” denotes degree centigrade of the calcination temperature. $AS/AP-25$ refers to the $\text{Ag}_2\text{S}/\text{Ag}_3\text{PO}_4$ sample synthesized at room temperature without further calcination treatment.

Preparation of Ag_2S

A desired amount of AgNO_3 aqueous solution was dropwise added to Na_2S aqueous solution. The

resulting mixture was stirred at room temperature for 30 min. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h in a oven, then calcined at different temperature for 6 h. The finally obtained Ag_2S sample was labeled as “ $AS-T$ ”, where “ T ” denotes degree centigrade of the calcination temperature. $AS-25$ refers to the Ag_3PO_4 sample synthesized at room temperature without further calcination treatment.

Preparation of $\text{Ag}/\text{Ag}_3\text{PO}_4$ composite

$\text{Ag}/\text{Ag}_3\text{PO}_4$ composite was obtained according to the previously reported light-induced method (*Catal. Commun.*, 2012, **17**, 200). The obtained Ag_3PO_4 was dispersed into a aqueous solution of RhB and irradiated with a 500W Xe arc lamp (Perfectlight Co., PLS-SXE300, a cutoff filter of 420 nm) for 5 h. Then the product was collected and dried at 70 °C for 8 h in the dark.

Preparation of $\text{AgX}/\text{Ag}_3\text{PO}_4$ (X = Cl, Br and I) composites

$\text{AgX}/\text{Ag}_3\text{PO}_4$ (X = Cl, Br and I) composite were obtained according to the previously reported process (*Phys. Chem. Chem. Phys.*, 2011, **13**, 10071). The obtained Ag_3PO_4 (0.304 g) was ultrasonically scattered for 1h in 10 mL of deionized water. Then, 1.3 mL of aqueous solution (0.10 mol/L) of KX (X = Cl, Br and I) was added. The resulting mixture was stirred at room temperature in the dark for 6 h. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h in a oven.

Characterization

Scanning electron microscopy (SEM) experiment was undertaken on a FEI Quanta 200 microscope at an accelerating voltage of 20 kV. An energy-dispersive (ED) detector was equipped with this scanning electron microscope and operated 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 θ /min = 4 $^\circ$ /min. The accelerating voltage and applied current were 40 kV and 100 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Multilab 2000 X instrument with Al K α X-ray monochromatized source ($h\nu$ = 1486.6 eV) in vacuum of 2×10^{-8} Pa. The binding energies were obtained from the XPS analysis were corrected by referencing that of C1s to 284.60. High resolution transmission electron microscopy (HRTEM) was obtained with a JEM-2100F electron microscope operating with acceleration voltage of 200 kV. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a Shimadzu UV-2550 ultraviolet-visible spectrophotometer with BaSO $_4$ as the reference.

Photocatalytic activity measurement

The photocatalytic activity was evaluated by degradation of RhB in aqueous solution under visible light irradiation from a 500 W Xe arc lamp (Perfectlight Co., PLS-SXE300) equipped with one ultraviolet cutoff filter ($\lambda \geq 420$ nm). In all photocatalytic experiments, 0.20 g of photocatalysts were dispersed in 100 mL of 8.0 mg/L RhB solution. 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 solution. During the photocatalytic degradation progress, 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 variations of the absorption band maximum (553 nm) of RhB in UV-vis spectra by using a PerkinElmer Lambda 35 spectrophotometer.

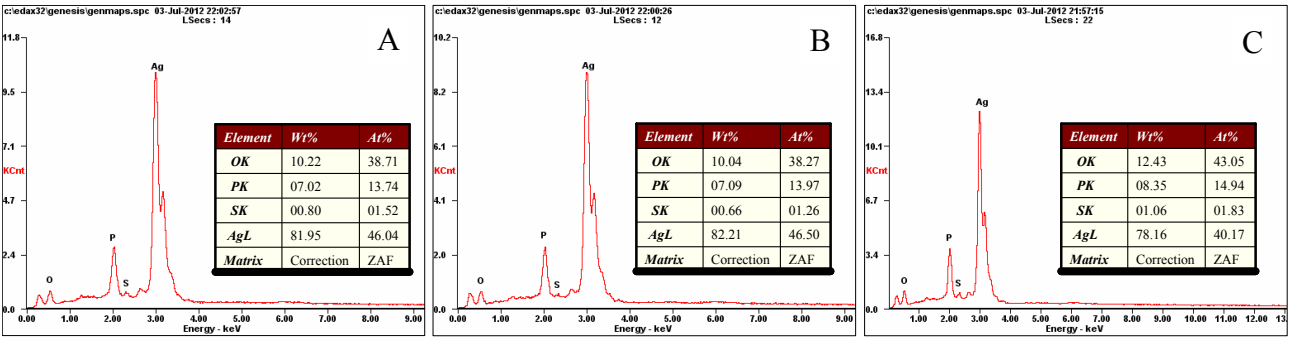


Fig. S1: EDS patterns of *AS/AP-25* (A), *AS/AP-250* (B) and *AS/AP-350* (C).

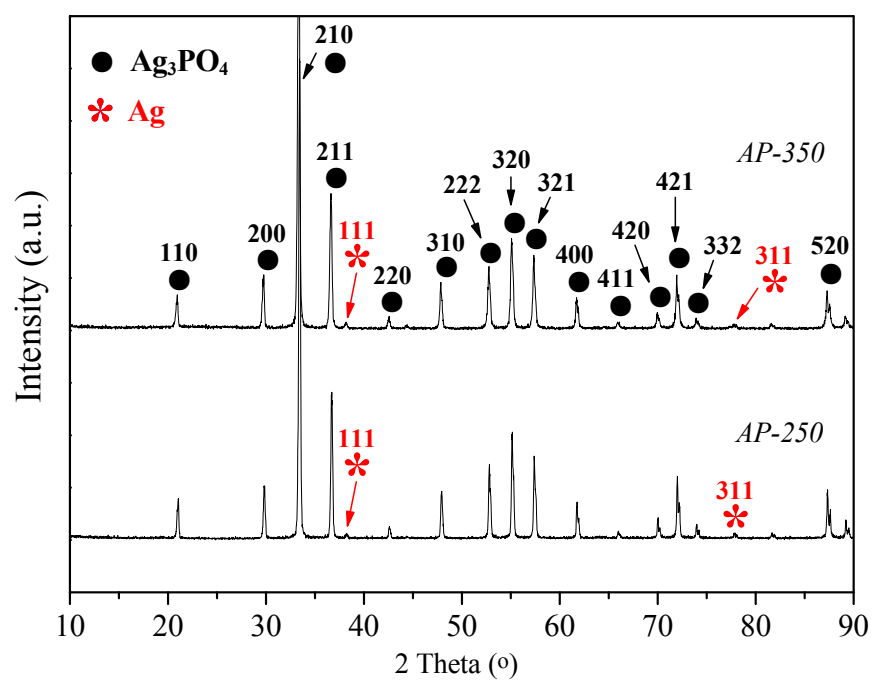


Fig. S2: Magnified figure for the XRD patterns of *AP-250* and *AP-350*.

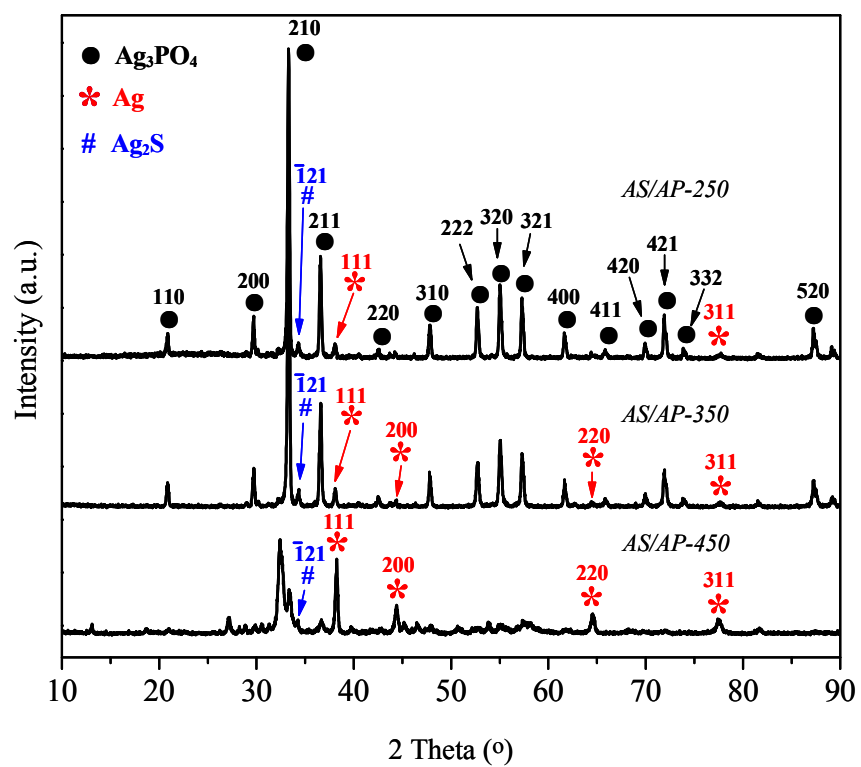


Fig. S3: XRD pattern of *AS/AP-450* and magnified figure for the XRD patterns of *AS/AP-250*, *AS/AP-350*.

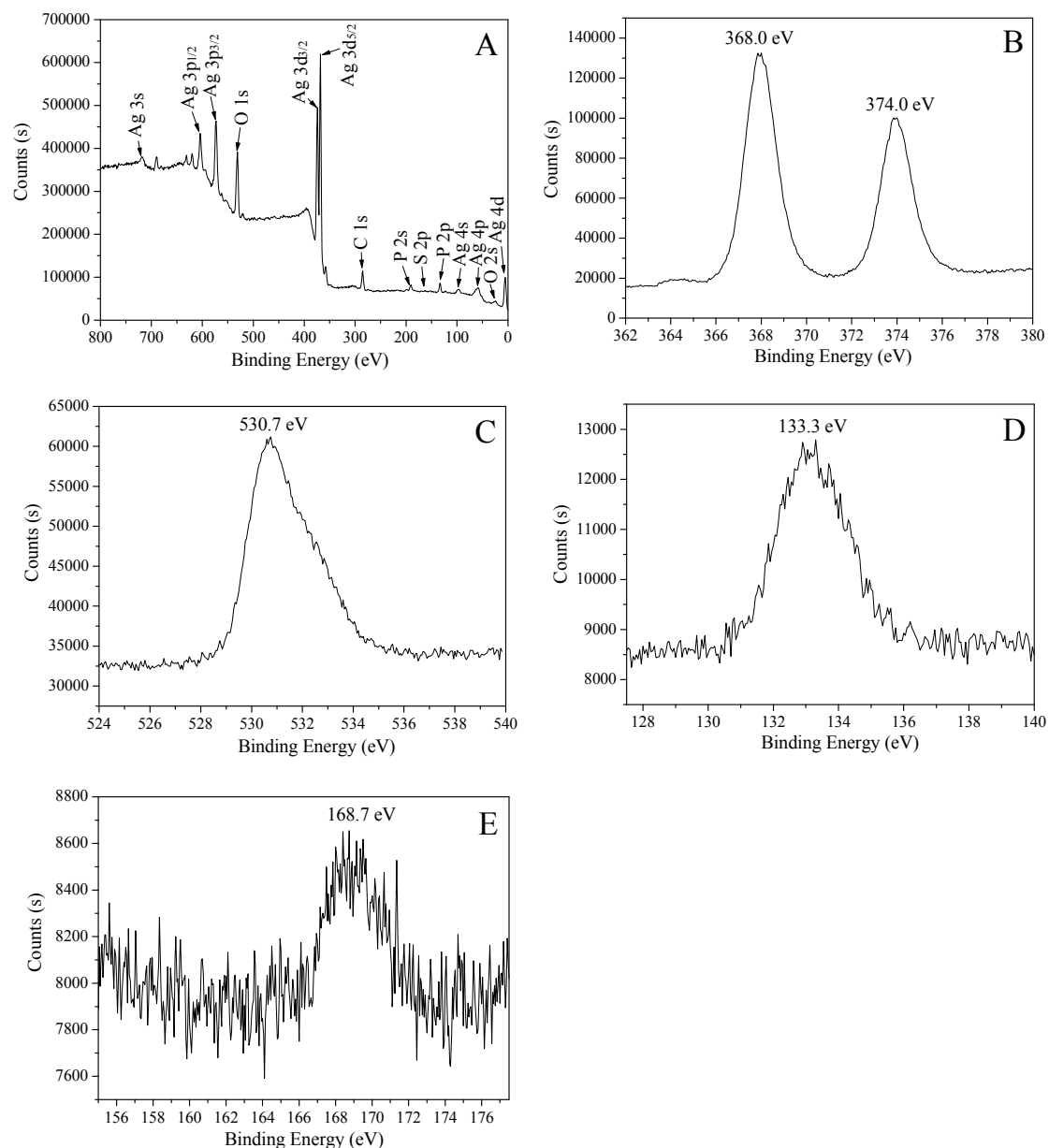


Fig. S4: XPS spectrum of *AS/AP-250* (A) and its high-resolution XPS spectra of Ag 3d (B), O 1s (C) ,
P 2p (D) and S 2p (E).

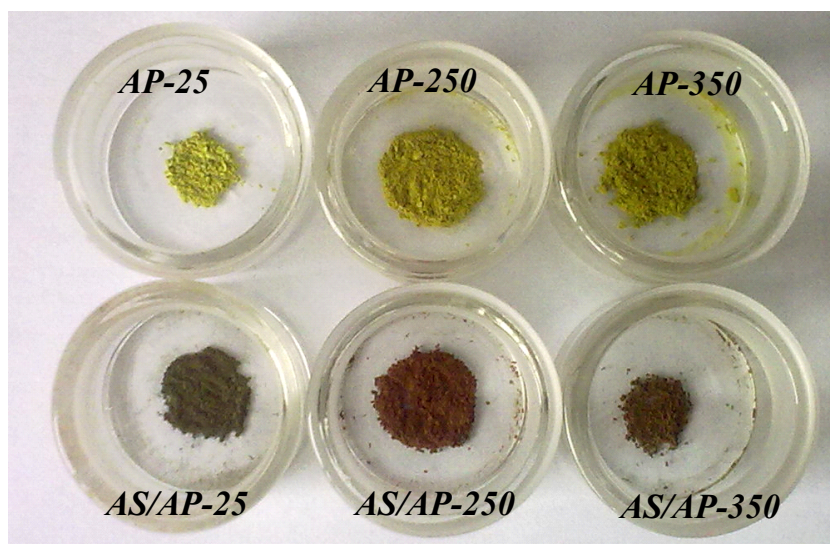


Fig. S5: Photos of Ag_3PO_4 and $\text{Ag}_2\text{S}/\text{Ag}_3\text{PO}_4$ composites.

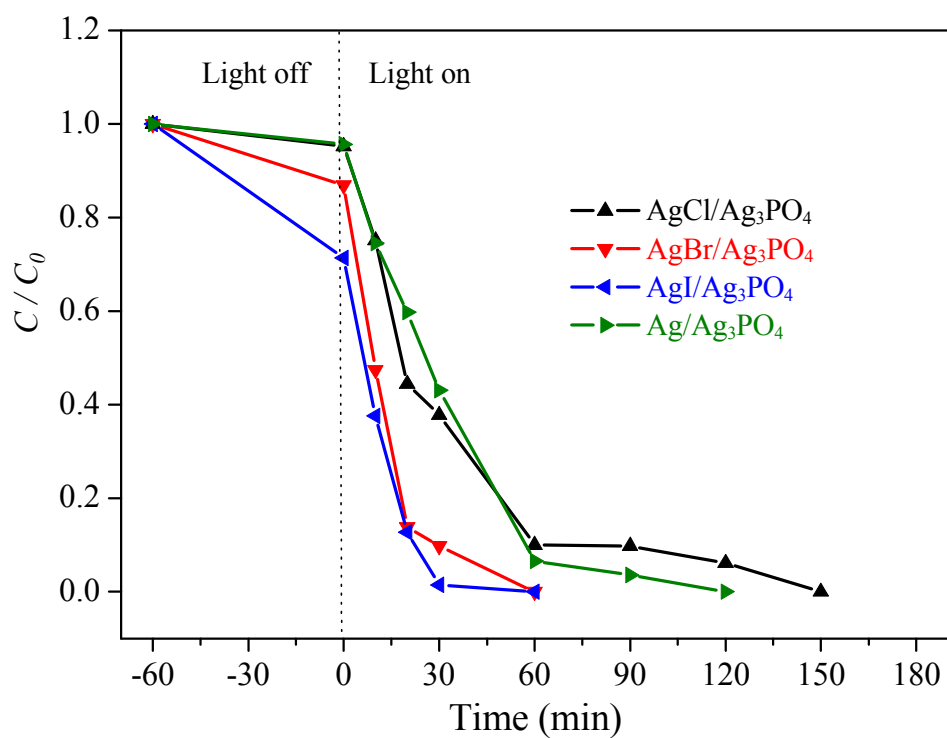


Fig. S6: Photocatalytic activities of the AgX/Ag₃PO₄ (X = Cl, Br and I) and Ag/Ag₃PO₄ photocatalysts in degradation of RhB under visible light irradiation ($\lambda \geq 420$ nm) at room temperature, where C is the concentration of the RhB solution at a certain reaction time, C_0 is the origin concentration of RhB before the photocatalyst was added.