Supporting Information

A novel Ag₃AsO₄ visible-light-responsive photocatalyst: facile synthesis and exceptional photocatalytic performance

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Chemicals and reagents

AgNO$_3$, NH$_3$•H$_2$O, H$_2$O$_2$, Na$_2$HAsO$_3$, NaH$_2$PO$_4$, KI, rhodamine B (RhB) and methyl orange (MO) were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group.

Preparation of Ag$_3$PO$_4$

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 NH$_3$•H$_2$O aqueous solution (0.10 mol/L) and 180 mL of NaH$_2$PO$_4$ aqueous solution (0.15 mol/L) were added successively to the solution. The resulting mixture was stirred at room temperature for 2 h in the dark. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h.

Preparation of AgI

In a typical synthesis, 22 mL of AgNO$_3$ aqueous solution (0.1 mol/L) and 25 mL of KI aqueous solution (0.1 mol/L) were dropwise added at the same time in 30 mL of deionized water under stirring during 2 h. The resulting product was washed with deionized water for several times, dried at 60 °C for 5 h.

Characterization

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$_\alpha$ radiation at a scanning rate of 2θ/min = 4°/min. The accelerating voltage and applied current were 40 kV and 100 mA, respectively.

Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on a Shimadzu UV-2550 ultraviolet-visible spectrophotometer with BaSO$_4$ as the reference.
The photoluminescence (PL) spectra were measured on a F-4500 fluorescence spectrometer at room temperature under 325 nm excitation.

N₂ sorption experiments were performed at -196 °C on a NOVA-2100e apparatus. Brunauer-Emmett-Teller (BET) specific surface area was calculated using the adsorption data in the relative pressure range of $P/P_0 = 0.05–0.25$.

**Photocatalytic activity test**

The photocatalytic activity was evaluated in degradation of RhB or MO under visible light irradiation from a 500 W Xe arc lamp (PLS-SXE300, Perfectlight Co.) equipped with one ultraviolet cutoff filter ($\lambda \geq 420$ nm). In all photocatalytic experiments, 75 mg of photocatalysts were dispersed in 100 mL of 12.0 mg/L RhB aqueous solution, or in 100 mL of 17.6 mg/L MO aqueous 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 or MO. During the photocatalytic degradation 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) or MO (489 nm) in UV-vis spectra using a PerkinElmer Lambda 35 spectrophotometer.

**Calculation on VB and CB edge potentials of Ag₃AsO₄**

The VB and CB potentials of Ag₃AsO₄ at the point of zero charge can be calculated by the formulas (*J. Electrochem. Soc.*, 1978, 125, 228; *Appl. Surf. Sci.*, 2011, 257, 8732):

$$E_{VB} = X - E_e + 0.5E_g,$$

$$E_{CB} = E_{VB} - E_g,$$

in which $E_{VB}$ or $E_{CB}$ are the VB or CB edge potentials of Ag₃AsO₄, respectively, $X$ is the absolute electronegativity of Ag₃AsO₄ and it is defined as the geometric mean of the absolute electronegativity of its constituent atoms, which was thus estimated to be 5.92 eV, $E_g$
is the energy of free electrons on the hydrogen scale (ca. 4.5 eV), and $E_g$ is the band gap of Ag$_3$AsO$_4$, i.e., 1.60 eV. Based on the above equations, $E_{VB}$ and $E_{CB}$ of Ag$_3$AsO$_4$ were calculated to be 2.22 eV and 0.62 eV, respectively.
Fig. S1: XRD patterns of Ag$_3$PO$_4$ and AgI.

All diffraction peaks in XRD patterns of Ag$_3$PO$_4$ and AgI can be indexed to the body-centered cubic structure of Ag$_3$PO$_4$ (JCPDS No. 06-0505) and the hexagonal β-AgI (JCPDS No. 09-0374), respectively.
Fig. S2: UV-Vis DRS of Ag₃PO₄ and AgI.
Fig. S3: Photocatalytic activity of Ag$_3$AsO$_4$, Ag$_3$PO$_4$ and AgI in degradation of MO under visible light irradiation ($\lambda \geq 420$ nm) at room temperature, where $C$ is the concentration of the MO solution at a certain reaction time, $C_0$ is the origin concentration of MO before photocatalyst was added.
**Fig. S4:** Comparison among PL spectra of the fresh and the used Ag₃AsO₄ photocatalysts.