Supporting Information

Synthesis and Characterization of Single-crystalline Bi$_{19}$Cl$_3$S$_{27}$ Nanorods

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2. Experimental

2.1. Preparation of single-crystalline Bi$_{19}$Cl$_3$S$_{27}$ nanorods

All of the chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), analytical grade, and used as received without any further treatment.

In this experiment, 5mmol BiCl$_3$, 4.6mmol thiourea and 60 mL ethanol was mixed under vigorous stirring for 1 h at room temperature in air. The primrose yellow suspension was converted into primrose yellow transparent solution gradually. Then the mixed solution was transferred into a 100 mL Teflon-lined stain-less steel autoclave. The sealed autoclave was heated at 180 °C for 72 h in an oven, and then naturally cooled to ambient temperature. The resulting precipitates were washed with deionized water and ethanol thoroughly to remove residual ions and dried at 60 °C for 12 h for further characterization.

2.2. Characterization

The crystalline structure of the catalysts was characterized by powder X-ray diffraction (XRD) (Bruker D8 Advance; Cu Kα = 1.5404 Å). The XRD pattern was recorded within 20 range from 10° to 55° at a scanning rate of 0.05°/s. The morphologies and particle sizes of the samples were observed by SU8000 field-emission scanning electron microscope (FESEM, Hitachi, Japan) at an accelerating voltage of 15 kV. Energy dispersive spectrum analysis (EDS) system was connected to the SEM. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using Al Kα radiation as the excitation source under vacuum at 2×10$^{-6}$ Pa. All the binding energy (BE) values were calibrated by the C 1s peak at 284.6 eV of the surface adventitious carbon. Transmission electron micrograph (TEM)
using a Tecnai G20 (FEI Co., Holland) microscope operated at accelerating voltage of 200 kV. The sample was prepared by dispersing the powder in ethanol and dropping a drop of very dilute suspension onto a carbon film-coated copper grid. UV-vis diffused spectrum (DRS) was measured using the diffuse reflectance method with a Shimadzu UV-2550 spectrophotometer using an integrating sphere accessory. BaSO₄ was used as a reference materials in UV-vis diffuse experiments. The Photoluminescence (PL) measurements were carried out at room temperature in a Hitachi F-7000 with a 150 W Xe lamp, the samples were excited at 345nm. Active trapping experiments were conducted by dissolving 0.05 mmol sacrificial agents, including benzoquinone (BQ), isopropanol (IPA), EDTA, to capture •O₂⁻ radical, •OH radical and photo-induced holes, respectively. In addition, electron paramagnetic resonance (EPR) spectra were recorded at room temperature or 77K by using JES FA-200 spectrometer (JEOL, Japan) equipped with 350 W Xe lamp and a 420 nm ultraviolet cutoff filter. And 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a spin trap, the etramethyl piperidine nitrogen oxides (TEMPO) to capture holes (h+).

2.3. Photocatalytic activities

The photocatalytic performance of the nanomaterials was evaluated by the degradation of RhB and reduction of Cr(VI) solution (20 mg·L⁻¹ based on Cr in a dilute K₂Cr₂O₇ solution) under visible-light irradiation of a 350 W Xe lamp with a 420 nm cutoff filter. The reaction unit was placed in a black box with a window on the top, and the cutoff filter was placed to provide visible-light irradiation. In each experiment, 50 mg of as-prepared samples was added into 50mL of RhB solution and Cr(VI) solution (20 mg·L⁻¹ based on Cr in a dilute K₂Cr₂O₇ solution). The suspensions were magnetically stirred for 3 h in the dark to ensure the establishment of an adsorption/desorption equilibrium between the organics and the catalysts, and then the suspensions were vertically irradiated by the visible-light. At given irradiation time intervals, 3 mL solution was sampled, centrifuged, and then filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. The concentration of RhB solution and Cr(VI) solution was analyzed by the UV-Vis spectrometer measurement (UV-2550, Shimadzu) respectively.
Fig. S1 XRD patterns of Bi$_{19}$Cl$_3$S$_{27}$ at different reaction time (a) 45 min, (b) 1 h, (c) 3 h, (d) 12 h, (e) 48 h, (f) 72 h.

Fig. S2 XPS spectra of the as-prepared samples (a) survey, (b) Bi 4f, (c) Cl 2p, (d) S 2s.
Fig. S3 SEM images of Bi$_{19}$Cl$_3$S$_{27}$ nanorods.

Fig. S4 EDS elemental mappings of Bi$_{19}$Cl$_3$S$_{27}$ nanorods (a) SEM, (b) Bi, (c) Cl, (d) S.
Fig. S5 Transformed Kubelka-Munk function versus light energy of Bi$_{19}$Cl$_3$S$_{27}$ and UV-Vis diffuse reflectance spectra (DRS) of Bi$_{19}$Cl$_3$S$_{27}$ (the inset).

Fig. S6 UPS spectrum of Bi$_{19}$Cl$_3$S$_{27}$. 
Fig. S7 XRD patterns of the sample before usage and after 4 cycling runs.

Fig. S8 $C_t/C_0$ versus time curves of Cr$^{VI}$ solution under visible light irradiation.
Fig. S9 Schematic diagram of the Bi$_{19}$Cl$_{57}$. 

Fig. S10 The active species trapping experiments.
Fig. S11 ESR spectra of (a) DMPO−•O$_2$ and (b) DMPO−•OH in the photocatalysis.

Fig. S12 PL spectra changes observed during simulation sunlight illumination of Bi$_{19}$Cl$_7$S$_{27}$ (180°C, 72h) in coumarin solution (excitation at 345 nm).