

Electronic Supplementary Information

Formation of MS-Ag and MS (M=Pb, Cd, Zn) nanotubes via microwave-assisted cation exchange and their enhanced photocatalytic activities

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Experimental details

Materials Synthesis. All reagents were of analytical grade, purchased from Shanghai Chemical Reagent Factory, and used as received without further purification. Porous Ag₂S-Ag HSNTs were prepared according to our previous work. Briefly, ~50 mg of Ag₂CO₃ NRs and 6.8 mg (~4.5 mM) of thioacetamide (TAA) were added into a round-bottom flask and dispersed in 20 mL of ethanol with the assistance of ultrasonication for 10 min. Then, the above mixture was placed in a microwave refluxing system and irradiated at 400 W for 15 min. The final products were collected by centrifugation and washed with ethanol and deionized (DI) water three times before drying at 60 °C for 6 h.

Synthesis of porous PbS-Ag HSNTs. In a typical synthesis, 1 g of PVP (MW~ 58K), 38 mg (~ 0.1 mmol) of lead acetate ($\text{Pb}(\text{COOH})_2 \cdot 3\text{H}_2\text{O}$) and 42 mg of the as-obtained Ag_2S -Ag were added into 10 mL of methanol with the assistance of ultrasonication to form a mixture. Then, 200 μL of tributylphosphine (TBP) in 5 mL of methanol was dropwise added into the mixture under vigorous stirring. Finally, the above mixture was placed in a microwave refluxing system irradiated at 400 W for 20 min to obtain the porous PbS-Ag HSNTs. The as-prepared products were collected by centrifugation, and then washed with ethanol and DI water three times before drying in a vacuum at 60 °C for 6 h. Similarly, PbS nanotubes could be obtained when Ag_2S was used as starting material, while other conditions were unchanged.

Synthesis of other porous HSNTs (CdS-Ag, ZnS-Ag) and nanotubes (PbS, CdS). They were all prepared with a similar method as preparation of porous PbS-Ag HSNTs and PbS nanotubes.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were recorded by using $\text{Cu K}\alpha_1$ irradiation on a Philips PW3040/60 X-ray diffractometer with a scanning rate of 0.06 deg s^{-1} . Scanning electron microscopy (SEM) analysis was performed with a Hitachi S-4800 scanning electron micro-analyzer using an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted at 200 kV with a JEM-2100F field emission TEM. Samples for TEM measurements were prepared for TEM by dispersing the products in ethanol and placing several drops of the suspension on holey carbon films supported by copper grids. PL spectra were recorded on an Edinburgh FLSP920 fluorescence spectrometer and the absorption spectra were measured using a PerkinElmer Lambda 900 UV-vis spectrophotometer at room temperature.

Photocatalytic test. The photocatalytic activities of PbS-Ag HSNTs and PbS nanotubes were evaluated by photocatalytic degradation of Congo red (CR) and reduction of Cr^{VI} under visible-light irradiation of a 500 W Xe lamp with a 420 nm cutoff filter. The reaction cell was placed in a sealed black box with a window on the top, and the cutoff filter was placed to provide visible-light

irradiation. In a typical process, 5 mg of photocatalyst was added into 20 mL of 10 mg L⁻¹ CR solution, and 8 mg of photocatalyst was added into 20 mL of Cr^{VI} solution (20 mg L⁻¹ based on Cr in a dilute K₂Cr₂O₇ solution). After the photocatalyst was dispersed in the solution with an ultrasonic bath for 5 min, the solution was stirred for 2 h for CR solution and 1 h for Cr^{VI} solution in the dark to reach adsorption equilibrium and then exposed to visible-light irradiation. The photocatalysts were removed by centrifugation at given time intervals, and the CR concentration was measured colorimetrically at 496 nm using the UV-vis spectroscopy. The Cr^{VI} reduction was determined at 540 nm using the diphenylcarbazide (DPC) method. The ·OH radical reaction was conducted following a similar method reported previously.¹⁻³ Briefly, 3 mg of the different samples was suspended in 10 mL of aqueous solution containing 10 mM of NaOH and 5 mM of terephthalic acid (TA). Before exposing to visible-light, the suspension was stirred in the dark for 10 min. After irradiated for 10 min, the solutions were centrifuged for fluorescence spectroscopy measurements. A fluorescence spectrophotometer was used to measure the fluorescence signal of the 2-hydroxy-terephthalic acid (TAOH) generated. The excitation light wavelength used in recording fluorescence spectra was 320 nm.

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(2) Y. Liu, Y. Hu, M. J. Zhou, H. S. Qian, X. Hu, *Appl. Catal. B-Environ.* **2012**, *125*, 425.

(3) W. L. Yang, Y. Liu, Y. Hu, M. J. Zhou, H. S. Qian, *J. Mater. Chem.* **2012**, *22*, 13895.

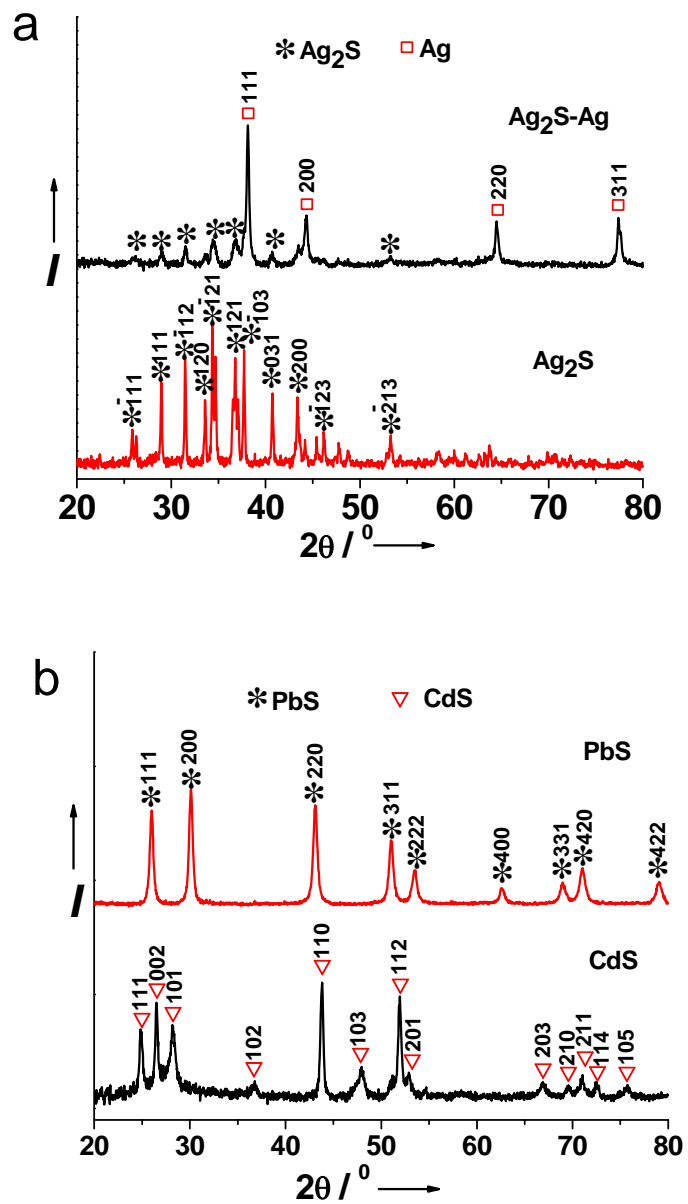


Fig. S1 XRD pattern of (a) Ag₂S-Ag HSNTs and Ag₂S NTs, and (b) MS nanotubes (M=Pb, Cd).

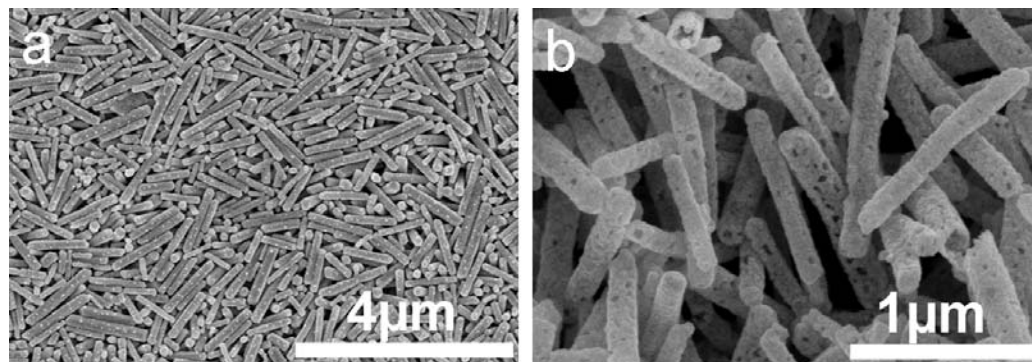


Fig. S2 SEM images of (a) Ag₂CO₃ nanorods, and (b) Ag₂S-Ag HSNTs.

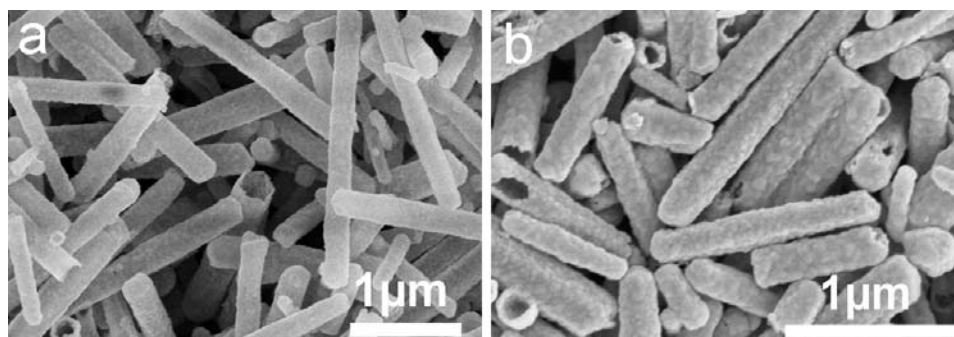


Fig. S3 SEM images of the as-obtained MS nanotubes via a rapid microwave-assisted cation-exchange reaction method: (a) PbS, and (b) CdS.

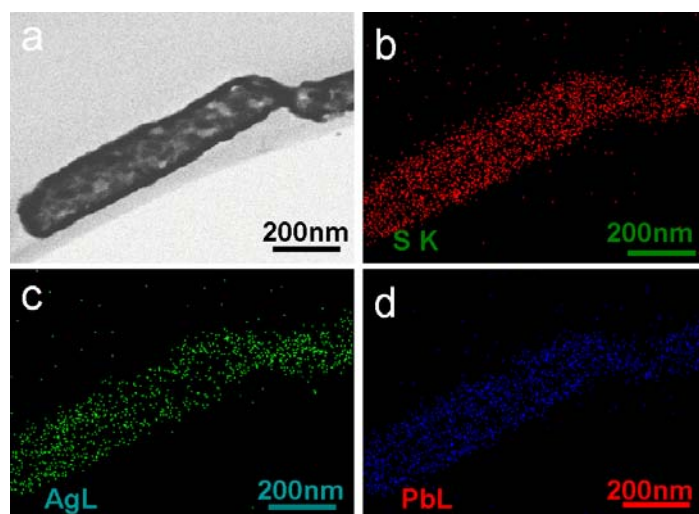


Fig. S4 (a) TEM image of one individual PbS-Ag HSNT, and the elemental mapping EDS images of S (b), Ag (c) and Pb (d).

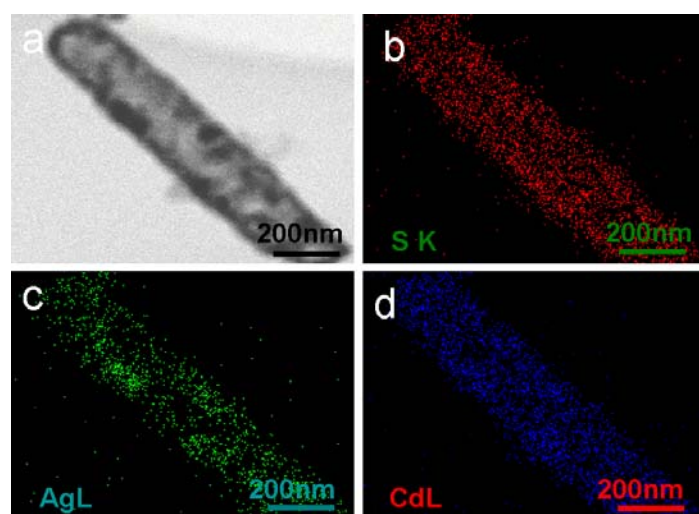


Fig. S5 (a) TEM image of one individual CdS-Ag HSNT, and the elemental mapping EDS images of S (b), Ag (c) and Cd (d).

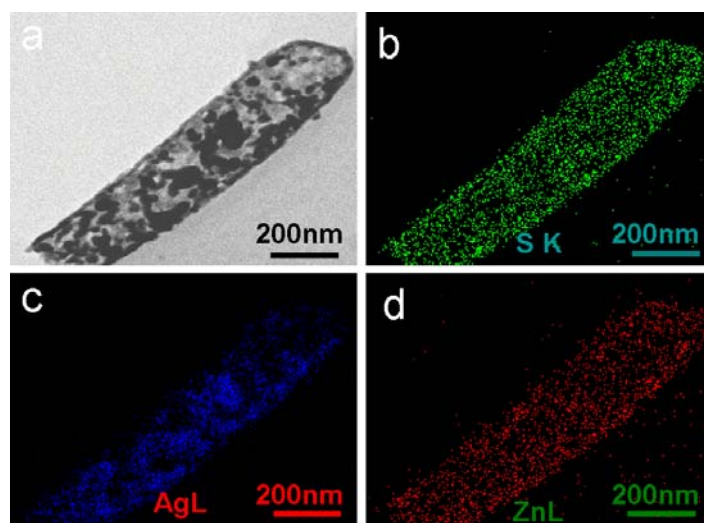


Fig. S6 TEM image of one individual ZnS-Ag HSNT, and the elemental mapping EDS images of S (b), Ag (c) and Zn (d).

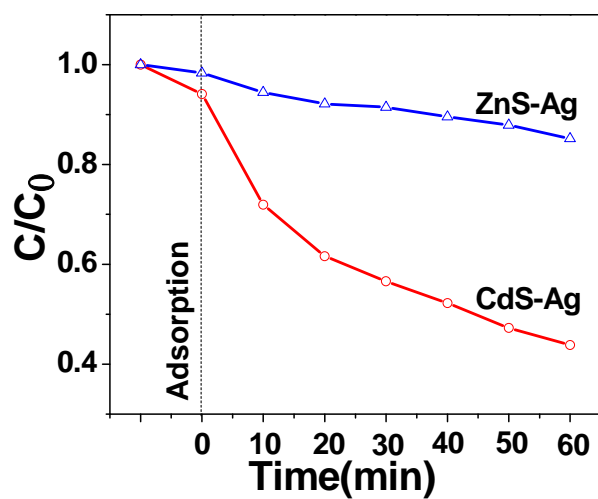


Fig. S7 Photocatalytic reduction of Cr(VI) using the as-obtained CdS-Ag and ZnS-Ag HSNTs as photocatalysts.

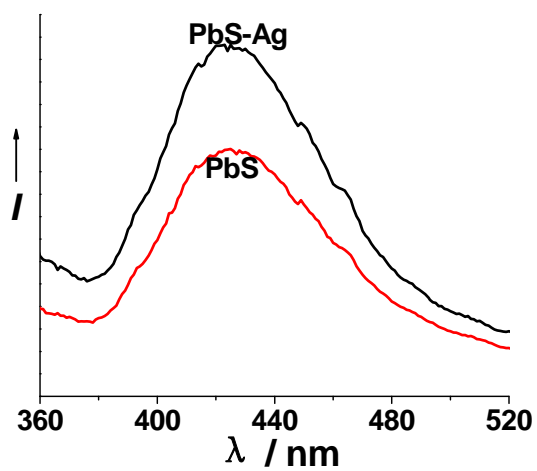


Fig. S8 Fluorescence spectra of TAOH formed by the reaction of TA with $\cdot\text{OH}$ radicals generated from different samples under visible-light irradiation for 10 min.

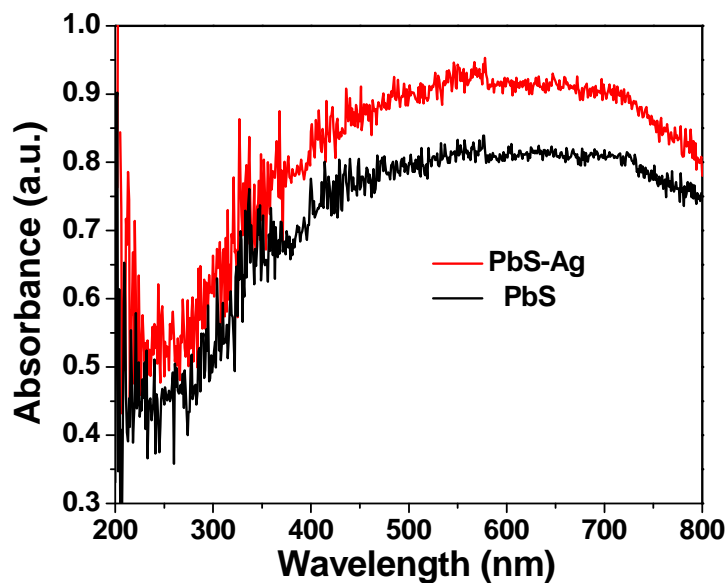


Fig. S9 UV-vis diffuse reflectance spectra of the as-prepared PbS-Ag HSNTs and PbS nanotubes.