

Electronic Supplementary Information

One-pot Synthesis of Large-scaled Janus Ag-Ag₂S Nanoparticles and Their Photocatalytic Properties

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Synthesis of Ag-DEDTC precursor

(All of the chemical are bought from Sinopharm Chemical Reagent Co. China, and are analytical pure and used as received without further purification). Ag-DEDTC precursor was prepared by reacting AgNO₃ with sodium diethyldithiocarbamate. A solution of SDEDTC (10 mmol) in 5 mL of distilled water was added into another solution containing AgNO₃ (10 mmol) and distilled water (10 mL) under magnetic stirring, forming a pale yellow turbid solution. Then, the pale yellow turbid solution was kept for 1h of stirring. Lastly, the pale yellow Ag-DEDTC precursor was obtained by a filtration and dried at room temperature under vacuum before use.

Synthesis of Ag-Ag₂S JNPs

Various nanoparticles were prepared by a modified thermal decomposition process¹. In a typical synthesis, 15 mL OM was slowly heated to 120-180 °C under vacuum

with magnetic stirring for 30 min to remove residual water and oxygen in which the flask was purged periodically with dry nitrogen gas. Then another 5 mL of OM containing 1 mmol Ag-DEDTC was injected into the above hot OM, and the resulted solution became black immediately. After keeping the temperature for 30 min, the result solution was cooled to 60 °C naturally. The addition of ethanol (30 mL) to the reaction mixture afforded a black product by centrifuging, and the precipitations were then washed twice with ethanol, and further purified by dispersing in a small amount (~ 5 mL) of chloroform and then precipitated with excess ethanol. The as-prepared Ag-Ag₂S JNPs were easily dispersed in various nonapolar organic solvents such as hexane, toluene, and chloroform.

Synthesis of Ag₂S NPs

For comparison of the photocatalytic behavior, Ag₂S NPs were prepared by a modified room-temperature approach that involved the transfer of Ag(I) ions from water to n-hexane using a method mediated by ethanol and OM and reaction with elemental sulfur in toluene². Typically, 6 mL of 1 mM AgNO₃ aqueous solution was mixed with 6 mL of ethanol containing 240 µL of OM. After 3 min. stirring, 6 mL of n-hexane was added and stirred for 1 more min. Phase transfer of Ag ions from water to n-hexane would then occur quickly and completely. The Ag ions in toluene were separated from the aqueous phase, and then 6 mL of n-hexane containing 0.5 mL of OM and 3 mmol of sulfur was dropped. After being stirred for 30 min at room temperature, 30 mL of ethanol was added to the reaction mixture to afford black products by centrifuging, and the precipitations were then washed twice with ethanol.

Preparation of two composites of Ag-Ag₂S JNPs coupled P25 TiO₂ and Ag₂S NPs coupled P25 TiO₂

The Ag-Ag₂S JNPs coupled P25 TiO₂ composites and Ag₂S coupled P25 TiO₂ composites were both prepared by a modified method using the bifunctional linker molecule (thioglycolic acid)³. For one solution, 1 mL of thioglycolic acid is added dropwise to a 10 mL of tetrahydrofuran/ethanol (volume ratio of 1:1) solution containing 0.1 g Ag-Ag₂S JNPs or 0.1 g Ag₂S NPs. For another solution, 1 g of P25 TiO₂ colloids was dispersed in 10 mL ethanol by ultrasound. The two solutions were then mixed in a volume ratio of 1:1, allowing the P25 TiO₂ to bind to Ag-Ag₂S JNPs or Ag₂S NPs through the linker molecules (thioglycolic acid). The resulting solution is stirred for 2 h before being employed for later photodegradation reactions.

Characterization

Sizes and morphologies of the Ag-Ag₂S JNPs were examined using a JEOL JEM-2010F high-resolution transmission electron microscope (HRTEM) at 200 kV. The elemental composition and distribution of the Ag-Ag₂S JNPs were analyzed and demonstrated using a TEM coupled with energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) measurements were performed with a Bruker D4 X-ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm). UV-visible absorption spectra were measured using a Shimadzu UV-2550 ultraviolet-visible-near-infrared spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded using an IRPRESTIGE-21 spectrometer (Shimadzu) using the KBr pressed pellets

Photodegradation reactions

The photoactivity of the as-prepared Ag-Ag₂S JNPs coupled P25 TiO₂ composites was tested by the degradation of methyl orange (MO) under visible light irradiation. In a typical experiment, 40 mg photocatalyst and 40 mL aqueous solution of MO (10 mol/l) were added into a 100 mL flask, and then the mixed solution was oscillated in darkness overnight. After reaching adsorption equilibrium, the photocatalytic reaction was initiated by irradiating the solution system with a 500W Xe lamp. At a given time interval, 4mL aliquots were collected, centrifuged, and then filtered to remove the catalyst particles for analysis. The filtrates were finally analyzed by a UV-vis spectrophotometer (UV-2550). To eliminate the effect due to heating from irradiation, the beaker was wrapped in a sponge soaked with an ice–water mixture. Ag₂S NPs coupled P25 TiO₂ composites were also tested for a comparison of the photocatalytic behavior using the same procedure.

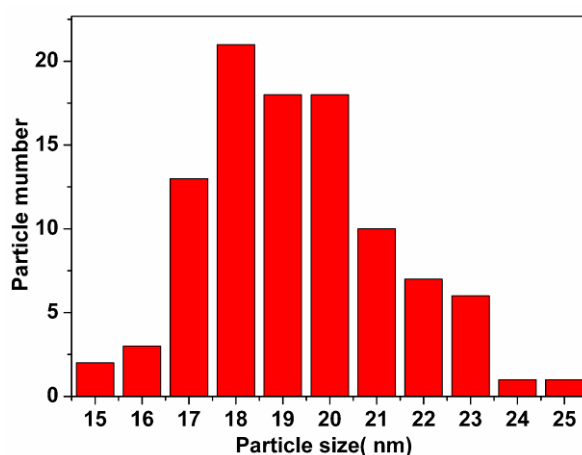


Figure S1 Histogram shows the particle size distribution of Ag-Ag₂S JNPs, which is obtained from the TEM image covering 100 particles, and reveals a narrow size distribution of ~ 15-25 nm of these JNPs.



Figure S2 A photograph of an eggplant that the as-prepared Janus Ag-Ag₂S nanoparticles appear as.

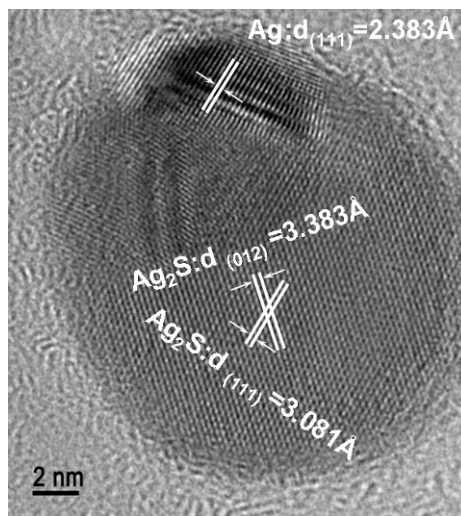


Figure S3 The high-resolution TEM image revealed that the lattice fringes' characteristic of the dark patch on the surface of a nanocomposite was different from that of the matrix. A resolved interplanar d -spacings of 0.238 nm on the dark patch matches well the (1, 1, 1) lattice separation of a face-centered cubic phase of Ag crystal, while d -spacings of \sim 0.338 nm and 0.308 nm on the matrix corresponds to the (0, 1, 2) and (1, 1, 1) plane separation of a monoclinic phase of Ag₂S crystal, respectively.

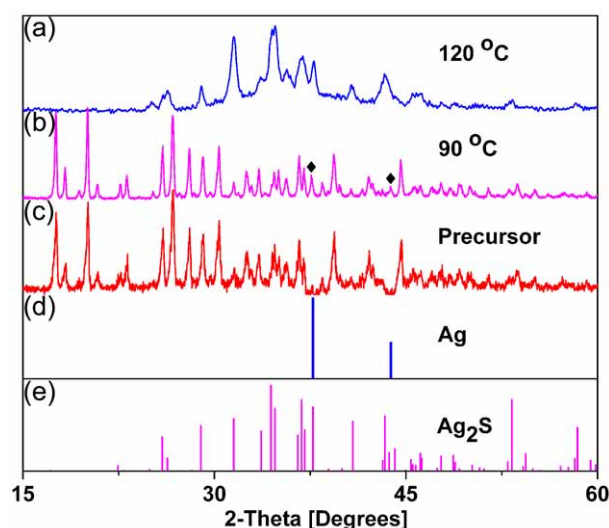


Figure S4 XRD patterns of the as-prepared products prepared at different temperature (a-b) and the precursor (c) and the standard (d) Ag (JCPDS card 65-8428, blue bar) and (e) Ag₂S powders (JCPDS card 65-2356, magenta bar). These results demonstrate that no Ag₂S but Ag NPs (marked with ♦) formed at the temperature lower than 90 °C.

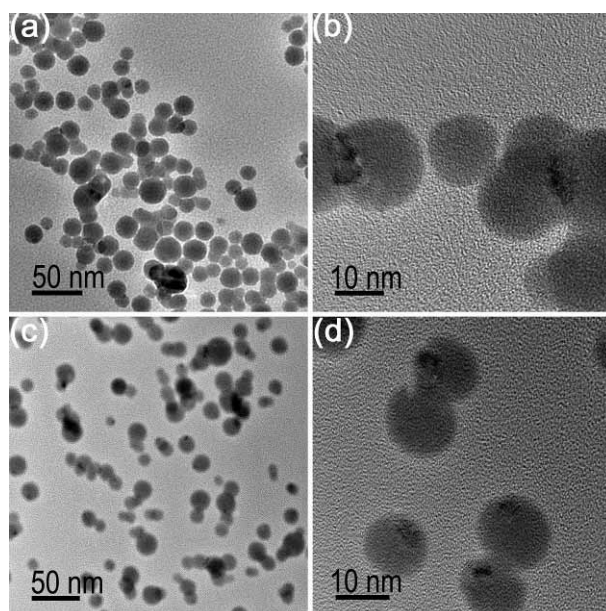


Figure S5 TEM and HRTEM images of the Ag-Ag₂S JNPs obtained via non-injection method. (a-b) The solution contained OM and Ag-DEDTC was slowly heated to 180 °C at a rate of 10 °C /min and kept at 180 °C for 30 min. (c-d) The solution contained OM and Ag-DEDTC was firstly kept at 90 °C for 30 min, and then further

heated up to 120 °C for another 30 min. Spherical particles with the diameter of 10-40 nm together with coupling and tripling of Ag-Ag₂S JNPs were observed using the non-injection method.

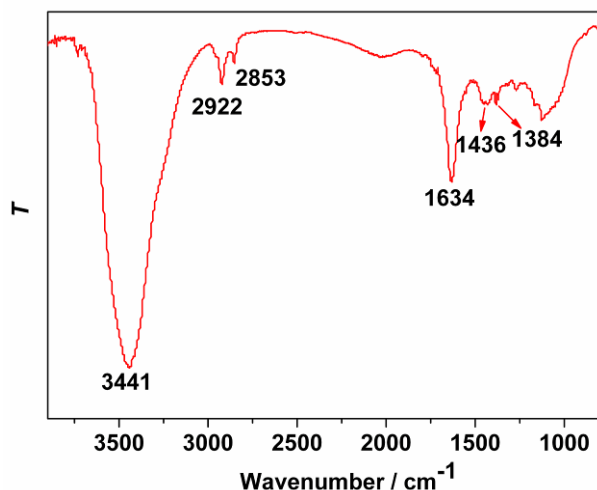


Figure S6 FTIR spectrum was recorded from the Ag-Ag₂S JNPs. The as-prepared Ag-Ag₂S JNPs exhibit a broad band at around 3441 cm⁻¹, corresponding to N-H stretching vibration of the NH₂ group⁴. The bands at 2925 and 2853 cm⁻¹ are respectively assigned to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of methylene (CH₂) units inside the OM. Two bands at 1634 and 1384 cm⁻¹ are assigned to N-H bending and C-N stretching modes, respectively. These results indicate the presence of the OM ligands on their surfaces of the Ag-Ag₂S JNPs^{5, 6}.

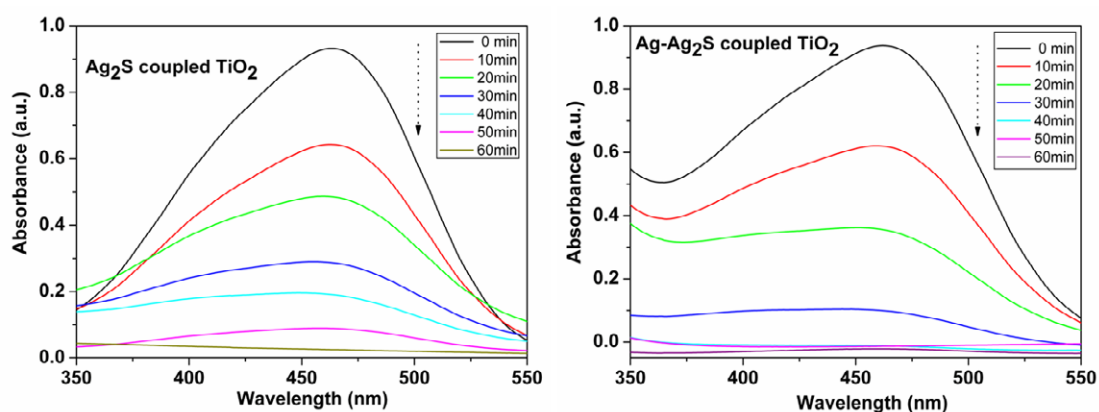


Figure S7 Absorption spectra of MO solution upon 500W Xe lamp irradiation in the presence of (a) Ag₂S NPs coupled P25 TiO₂ composites and (b) Ag-Ag₂S JNPs coupled P25 TiO₂ composites.

References

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