Supporting Information

Colloidal synthesis and photocatalytic properties of orthorhombic AgGaS₂ nanocrystals

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Experimental Details

(99.9995%), gallium(III) chloride (99.999%), sodium Materials. Silver(I) nitrate diethyldithiocarbamate trihydrate (98%), diethylammonium diethyldithiocarbamate (98%), dodecanethiol (DDT, >98%), hexadecanethiol (HDT, 97%), oleylamine (OM, 70%), hexadecylamine (HDA, 95%), trioctylamine (TOA, ≥98%), oleic acid (OA, 90%), trioctylphosphine (TOP, 90%) and Rhodamine B (RhB) were purchased from commercial sources and used without further purification.

Synthesis of metal dithiocarbamates. Silver(I) diethyldithiocarbamate, Ag(S₂CNEt₂), was synthesized based on a previously published method.¹ AgNO₃ (20 mmol) and Na(S₂CNEt₂).3H₂O (20 mmol) were separately dissolved in H₂O. The two aqueous solutions were mixed and the resulting mixture was kept stirring for 2 h. The yellow-tan precipitate was isolated through filtration, washed with H_2O and air-dried at 55–60 °C. Gallium(III) diethyldithiocarbamate, Ga(S₂CNEt₂)₃, was prepared as follows. In an Ar-filled glovebox, GaCl₃ (4 mmol) was carefully dissolved in 10 mL ethanol. The resulting colorless solution was then slowly added with magnetic stirring to a 30-mL ethanol solution of NH₂Et₂(S₂CNEt₂) (12 mmol). The mixture was taken out of the glovebox and kept stirring for 30 min. The white precipitate was isolated through filtration, washed with ethanol and air-dried at 60 °C.

Synthesis of orthorhombic AgGaS₂ (AGS) nanocrystals. In a typical synthesis, DDT (10 mL) was added to a 50-mL three-neck flask containing 0.1 mmol each of the metal dithiocarbamate precursors (i.e., Ag(S₂CNEt₂) and Ga(S₂CNEt₂)₃). The mixture was degassed at 80-100 °C for 20 min and the clear vellowish solution that formed was heated under Ar to 280 °C with magnetic stirring. A gradual change in the color of the solution from yellowish to dark brown was observed as the temperature is increased. The dark brown mixture was kept at 280 °C for 2 h, during which the color of the mixture gradually turned yellow-orange. The resulting mixture was then cooled to 40 °C with the aid of a H₂O bath. Ethanol was added to precipitate the nanocrystals, and this was followed by centrifugation. The yellow solid obtained was washed thoroughly with hexane and methanol.

Effect of varying the coordinating solvent. The effect of different coordinating solvents was investigated by replacing DDT in the synthetic procedure described above. HDT, OM, HDA, TOA. OA and TOP were used in place of DDT. The results are summarized in Table S1.

Characterization. Transmission electron microscopy (TEM) images were primarily taken using a Philips EM300 electron microscope operated at an accelerating voltage of 300 kV. Additional imaging was performed using a JEOL 2100 electron microscope (accelerating voltage: 200 kV), which is equipped with an energy-dispersive X-ray (EDX) detector that was used for elemental analysis. In preparing the specimens, a drop of nanocrystals dispersed in hexane was placed on the surface of a lacey formvar/carbon 300-mesh Cu grid or onto formvar/carbon 200-mesh Ni grid. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Thermo Fisher Scientific Thetaprobe XPS spectrometer with an Al K α monochromatic X-ray source at 15 kV and 100 W. X-ray diffraction (XRD) patterns were collected on a Bruker GADDS D8 Discover diffractometer using Cu K α radiation (1.5418 Å). Room-temperature absorption spectra were recorded using a Shimadzu UV-3150 UV-Vis-NIR spectrophotometer. The nanocrystal samples were dispersed in CHCl₃ and loaded into a quartz cuvette.

Photocatalytic Evaluation. The photocatalytic activity of the orthorhombic AGS nanocrystals was evaluated for RhB degradation under visible light illumination. The nanocrystals (10 mg) were first suspended in 20 mL of deionized H₂O in a glass vial. An aqueous solution of RhB (300 µL, 1 mM) was then added to the suspension. Prior to irradiation, the resulting mixture was continuously stirred in the dark for 30-90 min to ensure the establishment of an adsorptiondesorption equilibrium. The mixture, which was constantly stirred, was illuminated with visible light using a 500-W Philips QVF135 Halolite lamp and a cutoff filter at a 15-cm distance. The cut-off filter was used to completely eliminate any radiation at wavelength below 430 nm. At a specified time interval, 1 mL of the irradiated mixture were taken out and centrifuged to remove the solid nanocrystal catalyst. The RhB dye concentration in the filtrate was monitored by measuring the absorbance of RhB at 553 nm. A decrease in intensity of the RhB absorption peak is indicative of the decrease in RhB concentration due to degradation. The degradation efficiency ($E_{\rm ff}$) was determined using the equation, $E_{\rm ff}$ (%) = (1 - C/C_0) × 100%, where C₀ and C are the absorbance of the dye solution at 553 nm before and after irradiation, respectively. For comparison purposes, RhB degradation was also monitored for a similar mixture that was kept stirring in the dark (i.e., without illumination). A blank experiment was also conducted in the absence of AGS nanocrystals under visible-light illumination.

Coordinating solvent	Product obtained based on XRD pattern [*]
A. Dodecanethiol (DDT)	orthorhombic AGS (Fig. 1a in main text)
B. Hexadecanethiol (HDT)	orthorhombic AGS (Fig. 1b in main text)
C. Oleylamine (OM)	orthorhombic AGS (Fig. 1c in main text)
D. Hexadecylamine (HDA)	orthorhombic AGS (Fig. 1d in main text)
E. Trioctylamine (TOA)	tetragonal AGS + Ag ₉ GaS ₆ (Fig. S4)
F. Oleic acid (OA)	$Ag + Ag_2S$ (Fig. S5a)
G. Trioctylphosphine (TOP)	Ag (Fig. S5b)

Table S1. Product obtained upon thermal decomposition of the metal dithiocarbamate precursors in different coordinating solvents.

*XRD patterns are shown in the Figures specified in the table.



Fig. S1. (a) Rietveld refinement of the diffraction data for orthorhombic $AgGaS_2$ (AGS) using the TOPAS software. Displayed are the observed (blue) and refined (red) patterns, the difference curve (grey), and the reflection positions of orthorhombic AGS (blue sticks at the bottom). (b) Crystal structure of orthorhombic AGS.



Fig. S2. Representative EDX spectrum of orthorhombic AGS nanocrystals. The Cu signals are attributed to the Cu TEM grid.



Fig. S3. High-resolution XPS analysis of orthorhombic AGS nanocrystals showing the Ag 3d (red), Ga 2p (green) and S 2p (blue) spectra.



Fig. S4. XRD pattern (top) and TEM image (bottom) of the product obtained when TOA was used as coordinating solvent. The blue pattern is from standard JCPDS file for tetragonal AGS (#27-0615). The red and green patterns are from the reported diffraction data for α -Ag₉GaS₆ (#32-1007) and β -Ag₉GaS₆ (#33-1178), respectively.² The weak peaks marked with pink asterisks are unidentified peaks.



Fig. S5. XRD pattern (left) and TEM image (right) of nanostructures produced when the coordinating solvent employed is: (a) OA and (b) TOP.



Fig. S6. (a) Room-temperature absorption spectra of orthorhombic AGS nanocrystals prepared using different coordinating solvents: DDT, HDT, OM and HDA. (b) Plots of $(\alpha h \nu)^2$ vs. photon energy (*hv*). An estimation of the band gap energy, E_g , is obtained by extrapolating the linear part of the plot. This is based on the Tauc equation: $(\alpha h \nu)^{1/n} = A(h\nu - E_g)$, where α is the absorption coefficient, *h* is the Planck's constant, ν is the frequency of vibration, *A* is a proportionality constant, E_g is the band gap energy, and $n = \frac{1}{2}$ for direct allowed transition.



Fig. S7. Temporal evolution of the absorption spectra of an aqueous RhB solution (a) in the presence of orthorhombic AGS nanocrystals without illumination (performed in the dark) and (b) in the absence of orthorhombic AGS nanocrystals with visible-light illumination.



Fig. S8. XRD pattern of orthorhombic AGS nanocrystals (a) before and (b) after the photocatalytic experiment.

References:

(1) T. X. Wang, H. Xiao and Y. C. Zhang, *Mater. Lett.*, 2008, **62**, 3736–3738.

(2) G. Brandt and V. Krämer, Mater. Res. Bull., 1976, 11, 1381–1388.