

Supporting Information

Spontaneous Heteroattachment of Single Component Colloidal Precursors for the Synthesis of Asymmetric Au-Ag₂X (X = S, Se) Heterodimers

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Supporting Experiments

Synthesis of 11 nm and 25 nm Au NPs

1.7 g (6.4 mmol, 2.9 ml) of oleylamine was added into 49 ml of toluene and the whole mixture was heated to boil, followed by a rapid injection of 50 mg (0.15 mmol) of tetrachloroauric acid in 1.0 g (3.7 mmol, 1.2 ml) of oleylamine and 1.0 ml of toluene. The reaction mixture was heated under reflux for 16 mins for 11nm Au NPs, and 2h for 25 nm Au NPs. The color change from yellow to red was started to be observed from 5 mins. Afterwards, the reaction mixture was cooled down to room temperature and washed three times with EtOH by centrifugation. The final product was dispersed in 1mL toluene.

Supporting Figures

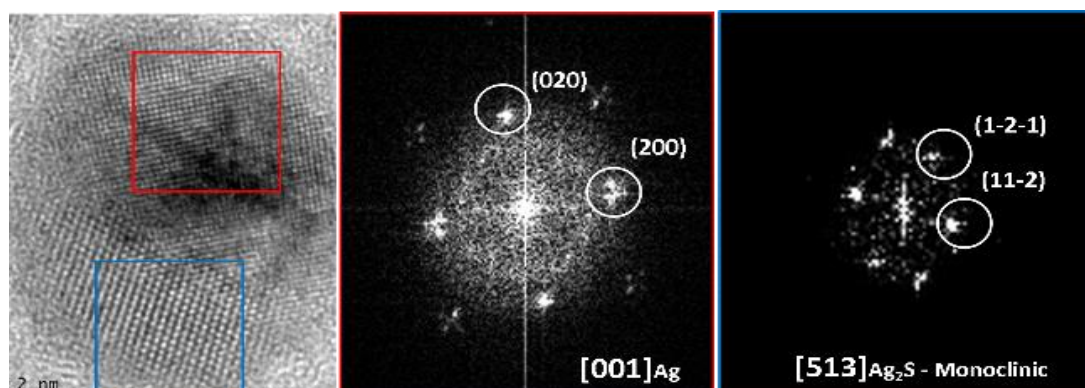


Figure S1. HRTEM image from a dark-contrasted *acanthite* and corresponding indexed FFT.

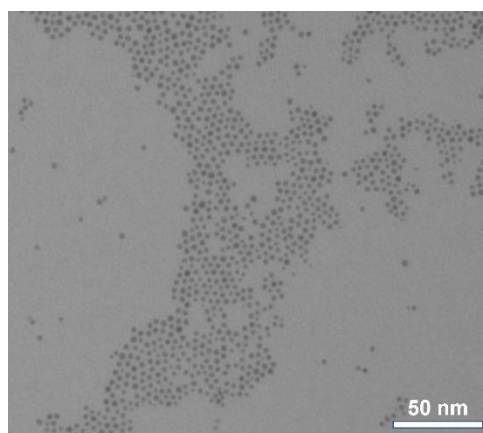


Figure S2. TEM image of Au NPs.

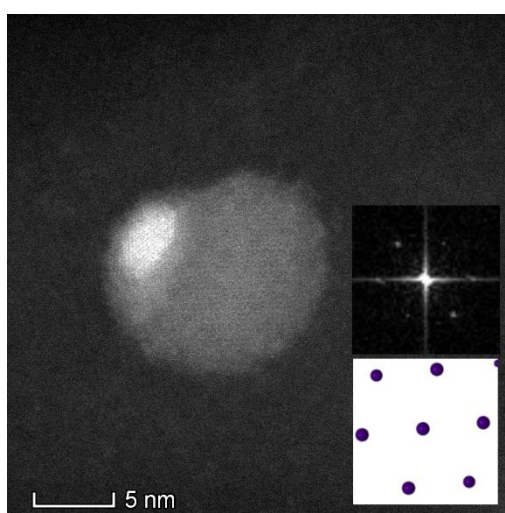


Figure S3: HR-STEM image of a Au-Ag₂Se particle with a FFT of the Au bright part that could be indexed as [101] oriented gold (see theoretical diffraction below the FFT).

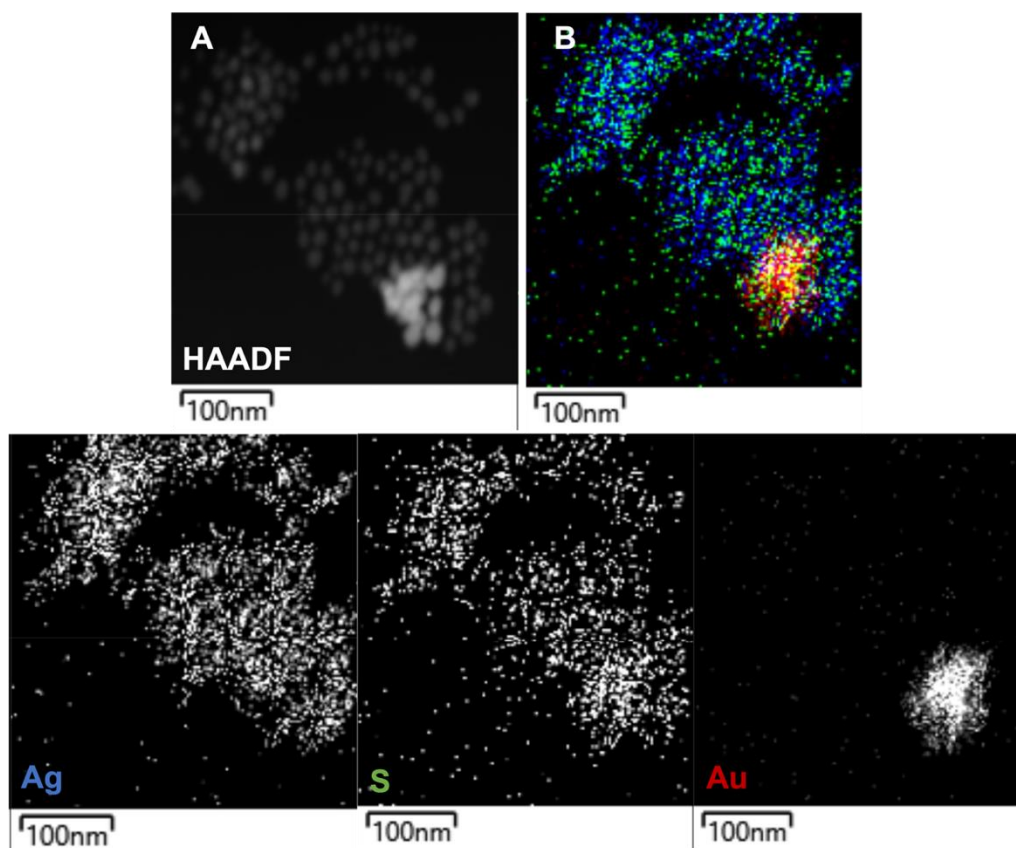


Figure S4: (A) HAADF image after reaction of Ag_2S NPs with 25 nm Au NPs, (B) Elemental mappings extracted from XEDS spectra.

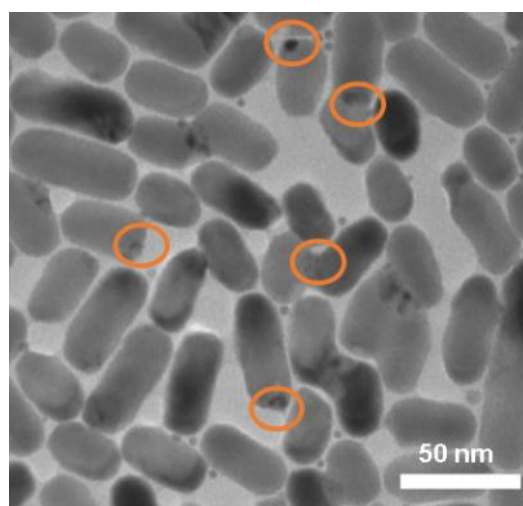


Figure S5: TEM image after reaction of Ag_2S NRs with 3.5 nm Au NPs.

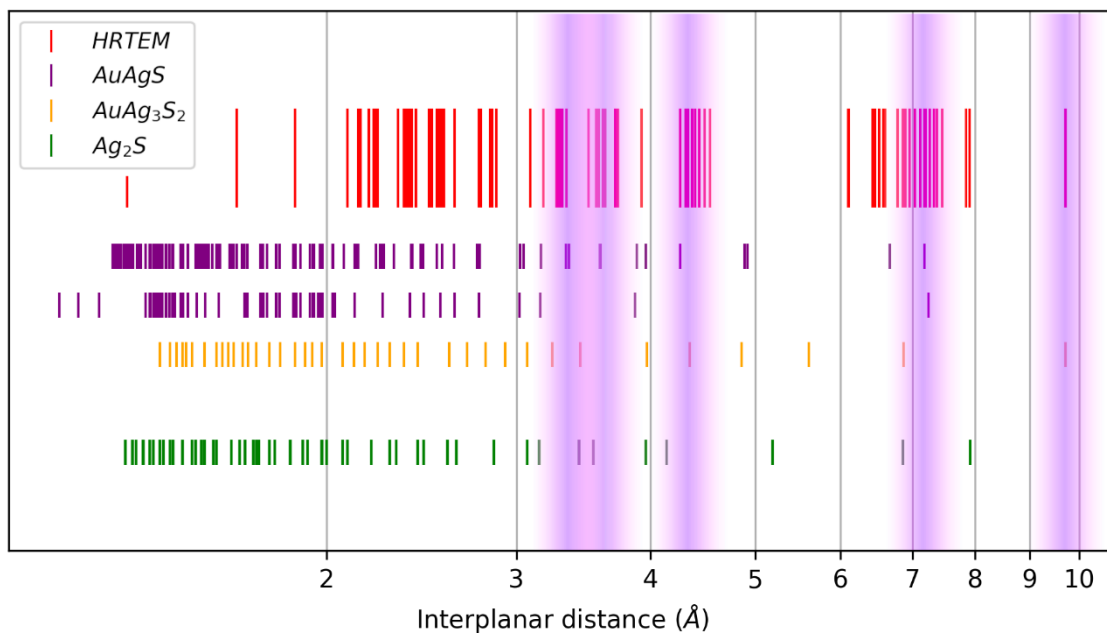


Figure S6: The measured interplanar distances in 14 HRTEM images of Au-Ag-S samples (in red) in comparison with the interplanar distances from reference patterns (AuAgS in purple, Ag₂S in green, and AuAg₃S₂ in yellow) in logarithmic scale. The shaded areas in the graph show interplanar distances that can unequivocally be attributed to one of the ternary compounds. Y axis is arbitrary to separate the different samples and references.

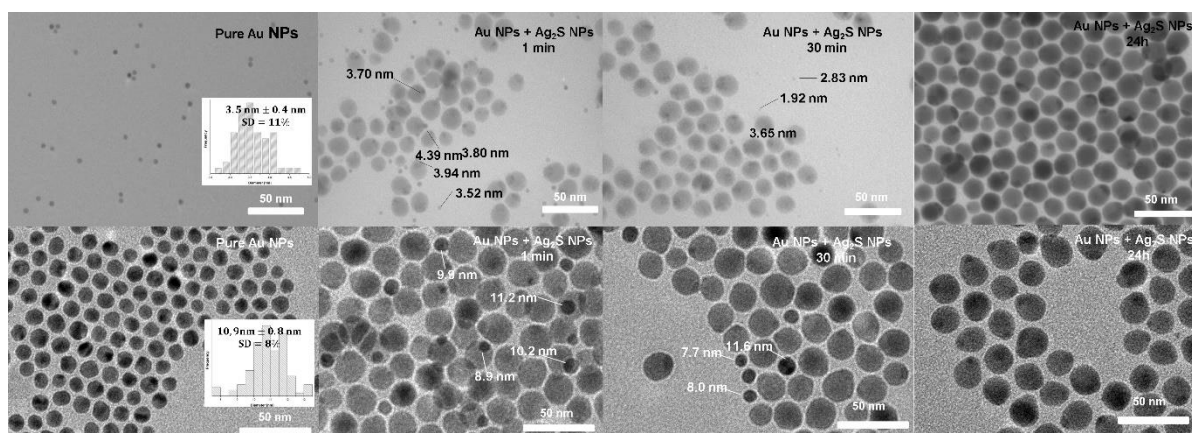


Figure S7: TEM images of added Au-precursors and aliquots at specific time along the reaction of mixing Ag₂S NPs with 2 different sized Au NPs: top: 3.5 nm Au NPs, bottom: 11 nm Au NPs.

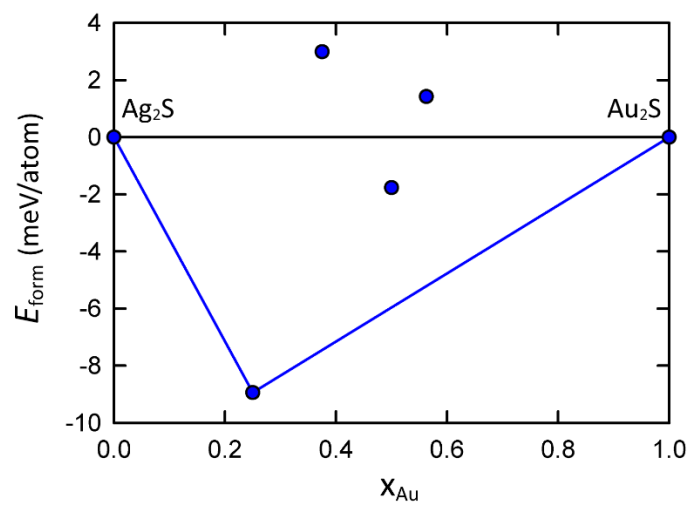


Figure S8. Relative stability of the $(Ag,Au)_2S$ phases evaluated with respect to Ag_2S and Au_2S , calculated using GGA-PBE using Eq. (2) in the main text. The numerical values are listed in Table S2. The blue line is the common tangent line connecting the energetically most favorable phases.

Supporting Tables

Table. S1: The TEM and corresponding XRD for the following samples.

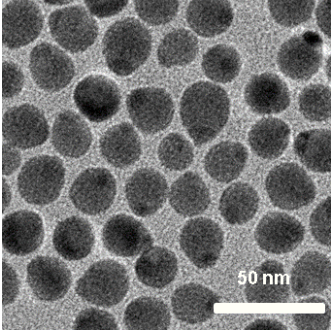
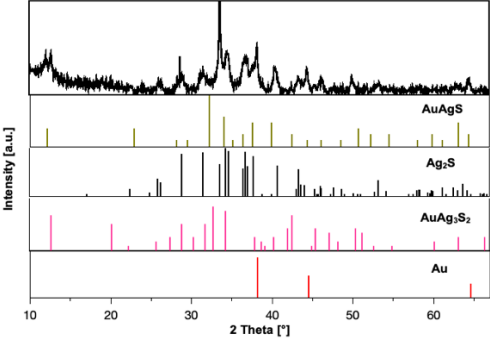
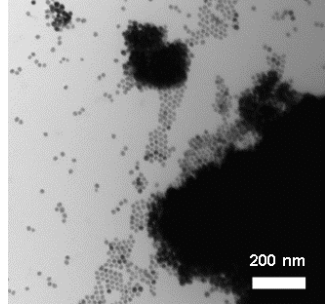
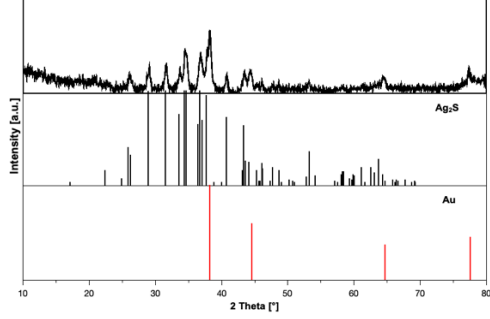
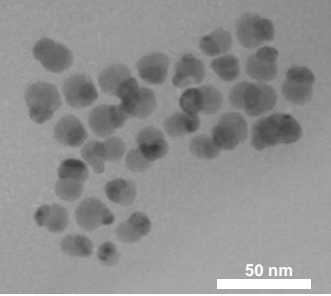
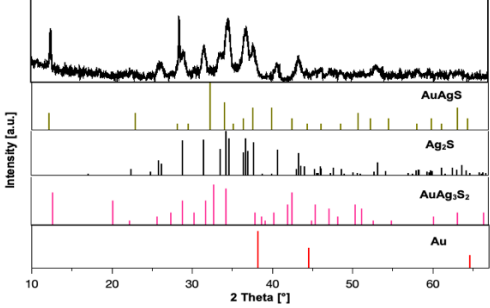
| TEM | XRD |
|--|--|
|  <p data-bbox="256 725 603 757">Ag₂S + 11nm Au (toluene)</p> |  |
|  <p data-bbox="256 1072 603 1104">Ag₂S + 25 nm Au (toluene)</p> |  |
|  <p data-bbox="256 1408 603 1440">Ag₂S + 3.5 nm Au (water)</p> |  |

Table. S2: Zeta-potential for the following samples

| Sample | Zeta-potential [mV] |
|--------------------------------|---------------------|
| Au-MUA in water | -62.1 |
| Ag ₂ S-MUA in water | -59.6 |

Table S3. Overview of M–S, M–Se, M, and M–M (M=Au,Ag) phases considered for the DFT calculations in this work, along with the used k -mesh and calculated lattice parameters as obtained after full relaxation with GGA-PBE.

| System | Compound | Atoms per unit cell | k -mesh | Lattice parameters |
|--------|---|---------------------|-----------|---|
| M–Se | Ag ₂ Se | 12 | 6×8×8 | $a=4.526 \text{ \AA}$, $b=7.080 \text{ \AA}$, $c=7.690 \text{ \AA}$ |
| | Ag ₃ AuSe ₂ | 48 | 4×4×4 | $a=10.109 \text{ \AA}$ |
| M–S | Ag ₂ S | 12 | 10×6×6 | $a=4.357 \text{ \AA}$, $b=7.924 \text{ \AA}$, $c=8.713 \text{ \AA}$, $\beta=116.2^\circ$ |
| | Ag ₃ AuS ₂ | 18 | 6×6×6 | $a=7.910 \text{ \AA}$, $c=8.738 \text{ \AA}$, $\gamma=120.0^\circ$ |
| | Ag ₃₀ Au ₁₈ S ₂₄ | 72 | 3×3×4 | $a=b=13.922 \text{ \AA}$, $c=9.011 \text{ \AA}$, $\alpha=90.1^\circ$, $\beta=89.9^\circ$, $\gamma=119.8^\circ$ |
| | AgAuS | 72 | 3×3×4 | $a=b=13.815 \text{ \AA}$, $c=9.215 \text{ \AA}$, $\alpha=90.1^\circ$, $\beta=89.9^\circ$, $\gamma=119.8^\circ$ |
| | Ag ₂₁ Au ₂₇ S ₂₄ | 72 | 3×3×4 | $a=b=13.918 \text{ \AA}$, $c=9.127 \text{ \AA}$, $\alpha=90.0^\circ$, $\beta=90.0^\circ$, $\gamma=120.0^\circ$ |
| | Au ₂ S | 6 | 8×8×8 | $a=5.324 \text{ \AA}$ |
| M | Ag | 4 | 28×28×28 | $a=4.162 \text{ \AA}$ |
| | Au | 4 | 28×28×28 | $a=4.156 \text{ \AA}$ |
| M–M | Ag ₃ Au ₁ | 4 | 28×28×28 | $a=4.144 \text{ \AA}$ |
| | Ag ₂ Au ₂ | 4 | 28×28×28 | $a=b=4.113 \text{ \AA}$, $c=4.208 \text{ \AA}$ |
| | Ag ₁ Au ₃ | 4 | 28×28×28 | $a=4.149 \text{ \AA}$ |

Table S4. Formation energies of the (Ag_{1-x}Au_x)₂S phases evaluated with respect to Ag₂S and Au₂S, calculated with GGA-PBE using Eq. (2) in the main text.

| Phase | Trivial name | x_{Au} | E_{form} (meV/atom) |
|---|-----------------|-----------------|---------------------------------|
| Ag ₂ S | | 0.00 | 0.0 |
| Ag ₃ AuS ₂ | uytenbogaardite | 0.25 | -8.9 |
| Ag ₃₀ Au ₁₈ S ₂₄ | petrovskaitite | 0.375 | 3.0 |
| AgAuS | petrovskaitite | 0.50 | -1.8 |
| Ag ₂₁ Au ₂₇ S ₂₄ | petrovskaitite | 0.563 | 1.4 |
| Au ₂ S | | 1.00 | 0.0 |