

Raman and X-ray Photoelectron Spectroscopic Study of Aqueous Thiol-Capped Ag-Zn-Sn-S Nanocrystals

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Details of the synthesis of AZTS NCs with varied composition.

Ag_xCu_{1-x}ZnSnS₄ (ACZTS) NC series

General protocol: 3 mL H₂O + 0.3 mL 0.5 M SnCl₂ in 4 M NaOH + 0.1 mL 5 M NH₄OH + 3.0 mL 1.0 M MAA + 0.15 mL 1.0 M Zn(NO₃)₂ + 3.0 mL (a mixture of different amounts of 0.1 M AgNO₃ + 0.1 M Cu(NO₃)₂) + 0.5 mL 1.0 M Na₂S. Heating: 5 min.

Note: all solutions are prepared in DI water.

The following nominal compositions were prepared: Ag₃₀Cu₀Zn₁₅Sn₁₅S₅₀, Ag₂₅Cu₅Zn₁₅Sn₁₅S₅₀, Ag₂₀Cu₁₀Zn₁₅Sn₁₅S₅₀, Ag₁₅Cu₁₅Zn₁₅Sn₁₅S₅₀, Ag₁₀Cu₂₀Zn₁₅Sn₁₅S₅₀, Ag₅Cu₂₅Zn₁₅Sn₁₅S₅₀, Ag₀Cu₃₀Zn₁₅Sn₁₅S₅₀.

The as-prepared colloids were purified by adding 2.5 mL 2-propanol to 5.0 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

Variation of silver content - Ag_xZnSnS₄ NCs.

General protocol: (6-X) mL H₂O + 0.3 mL 0.5 M SnCl₂ in 4 M NaOH + 0.1 mL 5 M NH₄OH + 3.0 mL 1.0 M MAA + 0.15 mL 1.0 M Zn(NO₃)₂ + X mL 0.1 M AgNO₃ + 0.4 mL 1.0 M Na₂S. *Note:* all solutions are prepared in DI water. Heating: 7 min.

The following nominal compositions were prepared:

Ag₀Zn₁₅Sn₁₅S₄₀ (X = 0)

Ag₅Zn₁₅Sn₁₅S₄₀ (X = 0.5 mL)

Ag₁₀Zn₁₅Sn₁₅S₄₀ (X = 1.0 mL)

Ag₁₅Zn₁₅Sn₁₅S₄₀ (X = 1.5 mL)

Ag₂₀Zn₁₅Sn₁₅S₄₀ (X = 2.0 mL)

Ag₂₅Zn₁₅Sn₁₅S₄₀ (X = 2.5 mL)

Ag₃₀Zn₁₅Sn₁₅S₄₀ (X = 3.0 mL)

The as-prepared colloids were purified by adding 5 mL 2-propanol to 10 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

Variation of zinc content - $\text{Ag}_2\text{Zn}_x\text{SnS}_4$ NCs.

General protocol: 3 mL H_2O + 0.3 mL 0.5 M SnCl_2 in 4 M NaOH + 0.1 mL 5 M NH_4OH + 3.0 mL 1.0 M MAA + X mL 1.0 M $\text{Zn}(\text{NO}_3)_2$ + 3.0 mL 0.1 M AgNO_3 + 0.4 mL 1.0 M Na_2S . *Note:* all solutions are prepared in DI water. Heating: 10 min.

The following nominal compositions were prepared:

$\text{Ag}_{30}\text{Zn}_0\text{Sn}_{15}\text{S}_{40}$ (X = 0)

$\text{Ag}_{30}\text{Zn}_5\text{Sn}_{15}\text{S}_{40}$ (X = 0.5 mL)

$\text{Ag}_{30}\text{Zn}_{10}\text{Sn}_{15}\text{S}_{40}$ (X = 1.0 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{40}$ (X = 1.5 mL)

$\text{Ag}_{30}\text{Zn}_{20}\text{Sn}_{15}\text{S}_{40}$ (X = 2.0 mL)

$\text{Ag}_{30}\text{Zn}_{25}\text{Sn}_{15}\text{S}_{40}$ (X = 2.5 mL)

$\text{Ag}_{30}\text{Zn}_{30}\text{Sn}_{15}\text{S}_{40}$ (X = 3.0 mL)

The as-prepared colloids were purified by adding 5 mL 2-propanol to 10 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

Variation of tin content - $\text{Ag}_2\text{ZnSn}_x\text{S}_4$ NCs.

General protocol: 3 mL H_2O + X mL 0.5 M SnCl_2 in 4 M NaOH + 0.1 mL 5 M NH_4OH + 3.0 mL 1.0 M MAA + 0.15 mL 1.0 M $\text{Zn}(\text{NO}_3)_2$ + 3.0 mL 0.1 M AgNO_3 + 0.4 mL 1.0 M Na_2S . *Note:* all solutions are prepared in DI water. Heating: 7 min.

The following nominal compositions were prepared:

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_0\text{S}_{40}$ (X = 0.25 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{2.5}\text{S}_{40}$ (X = 0.25 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{5.0}\text{S}_{40}$ (X = 0.35 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{7.5}\text{S}_{40}$ (X = 0.40 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{10}\text{S}_{40}$ (X = 0.45 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{12.5}\text{S}_{40}$ (X = 0.50 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{40}$ (X = 1.00 mL)

The as-prepared colloids were purified by adding 2.5 mL 2-propanol to 5.0 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

Variation of sulfur content - $\text{Ag}_2\text{ZnSnS}_x$ NCs.

General protocol: 3 mL H_2O + 0.3 mL 0.5 M SnCl_2 in 4 M NaOH + 0.1 mL 5 M NH_4OH + 3.0 mL 1.0 M MAA + 0.15 mL 1.0 M $\text{Zn}(\text{NO}_3)_2$ + 3.0 mL 0.1 M AgNO_3 + X mL 1.0 M Na_2S . *Note:* all solutions are prepared in DI water. Heating: 5 min.

The following nominal compositions were prepared:

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{25}$ (X = 0.25 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{30}$ (X = 0.25 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{35}$ (X = 0.35 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{40}$ (X = 0.40 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{45}$ (X = 0.45 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{50}$ (X = 0.50 mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{100}$ (X = 1.00 mL)

The as-prepared colloids were purified by adding 2.5 mL 2-propanol to 5.0 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

Variation of both silver and zinc content - $\text{Ag}_x\text{Zn}_y\text{SnS}_4$ NCs.

General protocol: 3 mL H_2O + 0.3 mL 0.5 M SnSO_4 in 4 M NaOH + 0.1 mL 5 M NH_4OH + 3.0 mL 1.0 M MAA + X mL 1.0 M $\text{Zn}(\text{NO}_3)_2$ + 2X mL 0.1 M AgNO_3 + 0.4 mL 1.0 M Na_2S . *Note:* all solutions are prepared in DI water. Heating: 10 min.

The following nominal compositions were prepared:

$\text{Ag}_0\text{Zn}_{10}\text{Sn}_{15}\text{S}_{40}$ ($X = 0$)

$\text{Ag}_5\text{Zn}_{12.5}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.025$ mL)

$\text{Ag}_{10}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.050$ mL)

$\text{Ag}_{15}\text{Zn}_{17.5}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.075$ mL)

$\text{Ag}_{20}\text{Zn}_{20}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.100$ mL)

$\text{Ag}_{25}\text{Zn}_{12.5}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.125$ mL)

$\text{Ag}_{30}\text{Zn}_{15}\text{Sn}_{15}\text{S}_{40}$ ($X = 0.150$ mL)

The as-prepared colloids were purified by adding 2.5 mL 2-propanol to 5.0 mL colloidal solution followed by the centrifugation (5 min at 5000 rpm). The precipitate was separated, dissolved in a minimal amount of DI water and then diluted with more DI water to 1.0 mL.

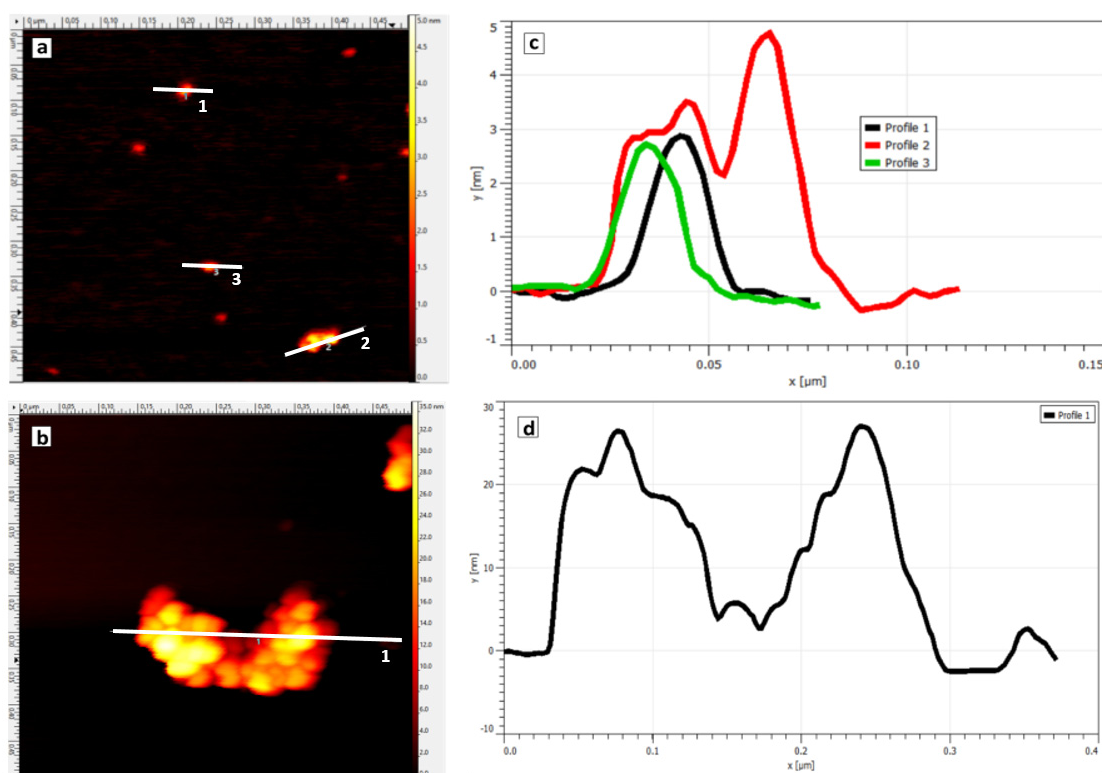


Figure S1. AFM images (a,b) and profiles (c,d) of separate AZTS NCs (a,c) and a NC aggregate (b,d).

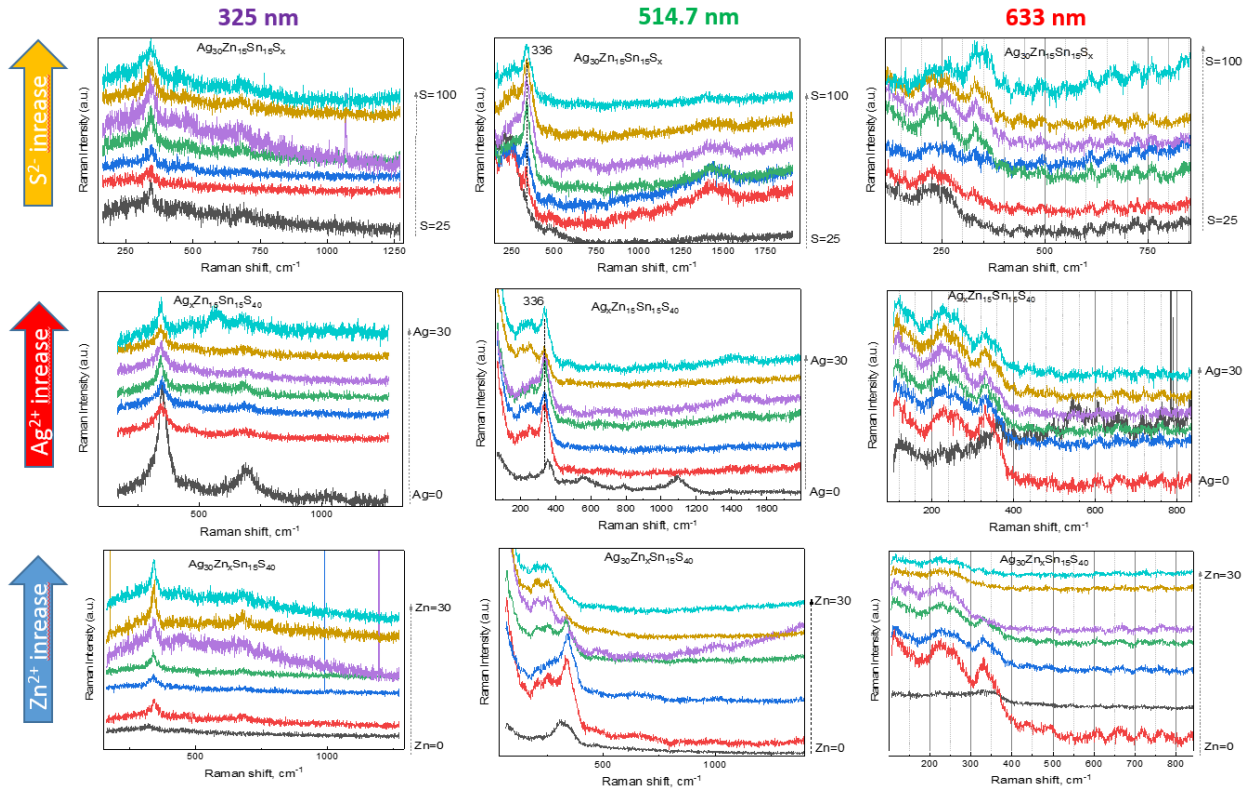


Figure S2. A comparative plot of normalized Raman spectra of S-, Ag, and Zn-series of Ag-Zn-Sn-S NCs at λ_{exc} =325 nm, 514.7 nm (b), and 633 nm (c).

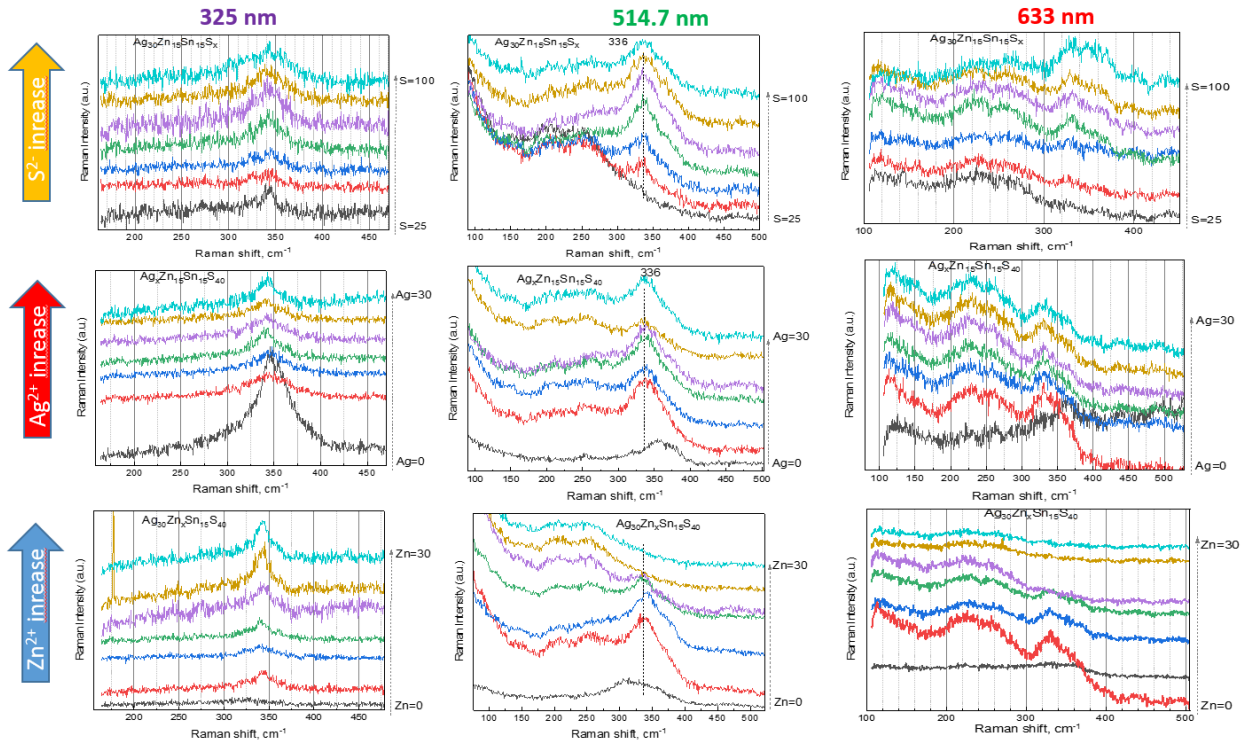


Figure S3. A comparative plot of as-measured Raman spectra of S-, Ag, and Zn-series of Ag-Zn-Sn-S NCs at λ_{exc} =325 nm, 514.7 nm (b), and 633 nm (c).

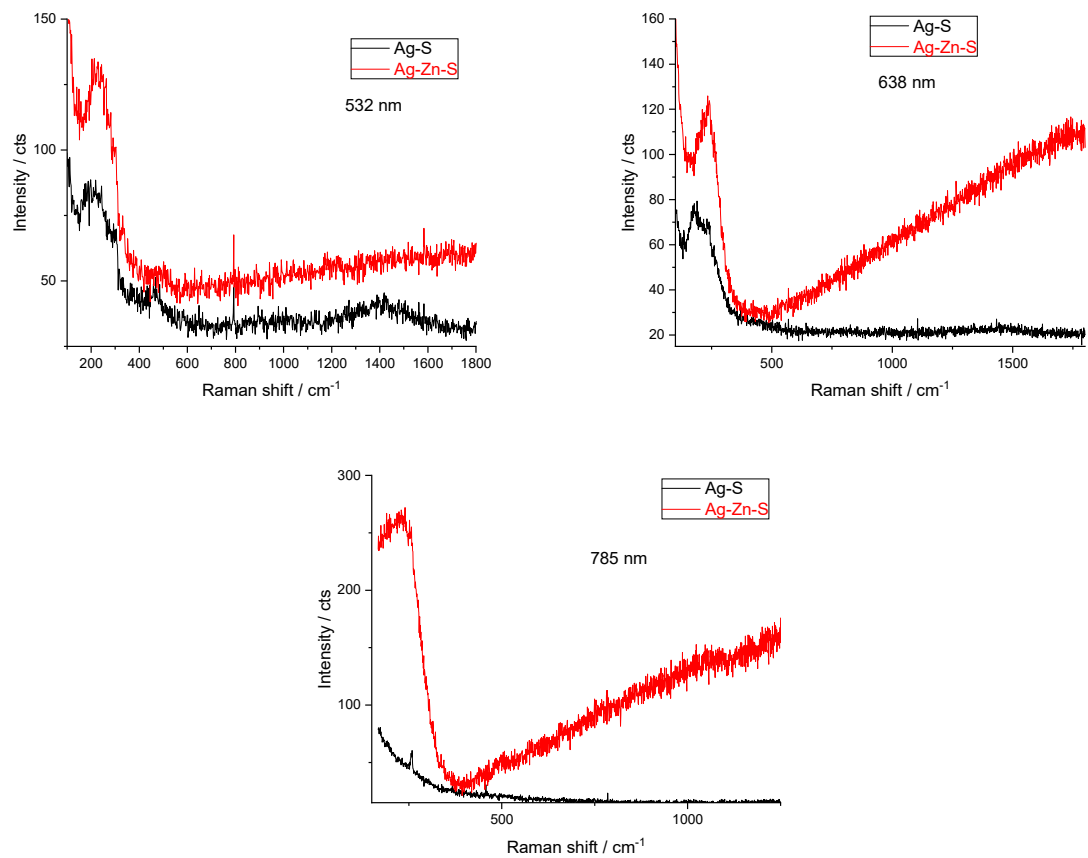


Figure S4. Raman spectra of Ag-S and Ag-Zn-S NCs at $\lambda_{\text{exc}}=532$ nm (a), 638 nm (b), and 785 nm (c).

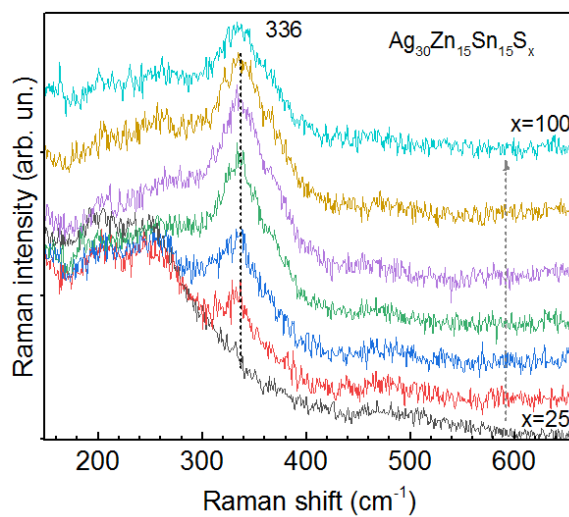


Figure S5. Raman spectra of Ag_2ZnSn_x NC series ($\lambda_{\text{exc}}=514.7$ nm).

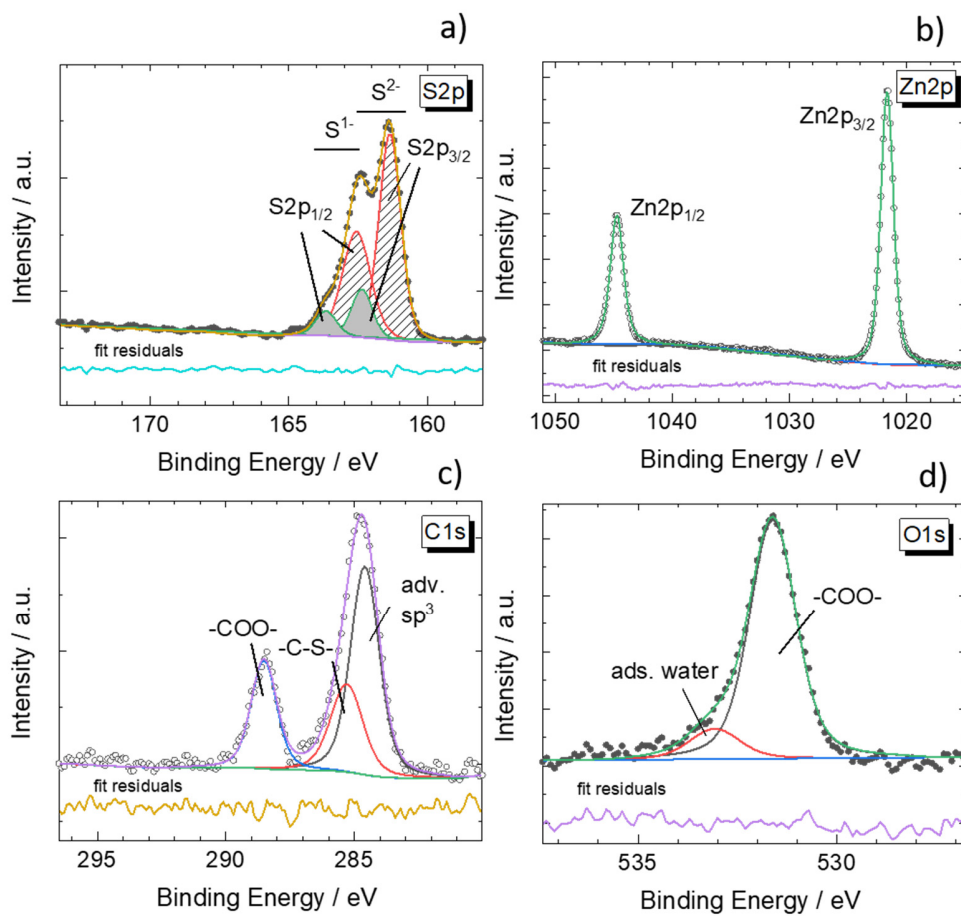


Figure S6. Representative high-resolution XPS spectra of $\text{Ag}_2\text{ZnSnS}_x$ NCs in the range of S2p (a), Zn2p (b), C1s (c), O1s (d) orbitals.