Supplementary Material (ESI) for Chemical Communications

Supporting Information

The Stoichiometry of Single Nanoparticles of Copper Zinc Tin Selenide

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1. Materials and Methods

All chemicals were purchased from Sigma Aldrich in the purest form available and used for the syntheses without further purification.

Copper-I-acetate (122.6 mg, 1.0 mmol), zinc-II-iodide (159.6 mg, 0.5 mmol), and tin-IV-acetate (177.4 mg, 0.5 mmol) were dispersed in 10 mL oleylamine. The suspension was heated for 30 min to 170 °C to get a clear solution. Then the solution was cooled down to room temperature. Meanwhile a solution of 157.9 mg selenium (2.0 mmol) in 5 mL oleylamine was prepared, which was added at once to the cold solution containing the metal salts. Finally the reaction solution was heated to 230 °C for 90 minutes.

Purification of the prepared particles from the reaction solution was done by pouring the solution in cold methanol to precipitate the black $Cu_2ZnSnSe_4$-nanoparticles. After centrifugation, the nanoparticles were dispersed in methanol and separated from the solution by centrifugation a second time. The residual was dried at 60 °C overnight giving a slightly oily black product.

A suspension of $Cu_2ZnSnSe_4$ nanoparticles in $CHCl_3$ was filtered with a 1.2 µm-filter to hold back large agglomerates. For TEM sample preparation a drop of the suspension was placed on a holey carbon film on a nickel grid and the solvent evaporated. SEM samples were prepared by placing the nanoparticles on a polished Al-sample holder.

TEM investigations were conducted on a Tecnai F 20 microscope (FEI Company, 200 kV, Schottky emitter), a Gatan GIF Quantum energy filter system, an UltraScanCCD camera and a Model 806 HAADF STEM Detector. EDX spectra were acquired with EDAX Sapphire Si(Li) detector and evaluated using the thinfilm technique. The Cu K, Zn K, Sn L and Se K lines were used for quantification.

Scanning electron microscopy images were recorded at 10 kV with a Zeiss Ultra 55 using an In-Lens and AsB-Backscatter detector. SEM-EDX measurements were done using a EDAX Phoenix detector at 20 kV. The Cu K, Zn K, Sn L and Se K lines were used for quantification.

Powder-X-ray diffraction (XRD) measurements were performed on a Siemens D-5005 powder-diffractometer (theta-theta geometry, Cu-Kα-radiation).

The sample was placed on a silicium substrate and applied to a scan rate of 0.036 ° s^{-1} to record the patterns in the 2θ range between 20 and 80°.

The diameters of the crystallites were estimated according to the broadening of the diffraction peaks using the Scherrer relationship (equation 1):

$$D_{XRD} \approx \frac{K * \lambda}{\Delta(2\theta) * \cos\theta} \qquad (1)$$

with Δ(2θ) is the full width at half maximum (FWHM) of the peak in radians, θ is half of the scattering angle 2θ, λ the wavelength of the X-rays, and K is the shape factor (K = 0.9 for spherical particles).

2. TEM Bright Field and electron diffraction

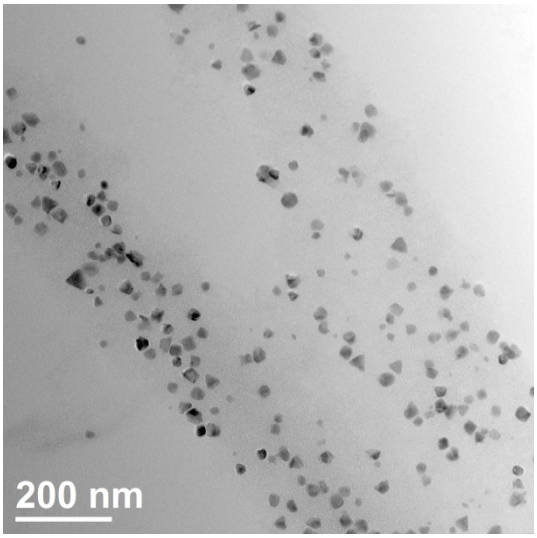
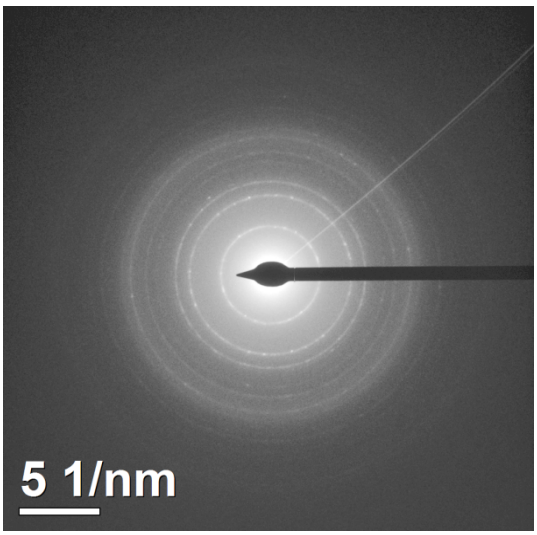


Figure S1. TEM-BF images of $Cu_2ZnSnSe_4$ nanoparticles.



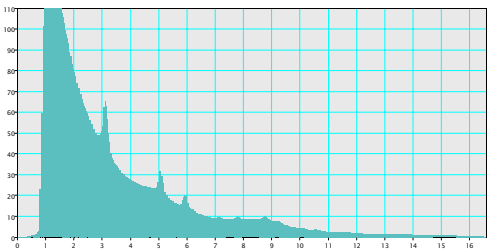


Figure S2. SAED image of $Cu_2ZnSnSe_4$ nanoparticles and corresponding radial intensity profile. d-values from SAED are in good accordance with JCPDS 52-868

Quantitative chemical analysis of nanoparticles

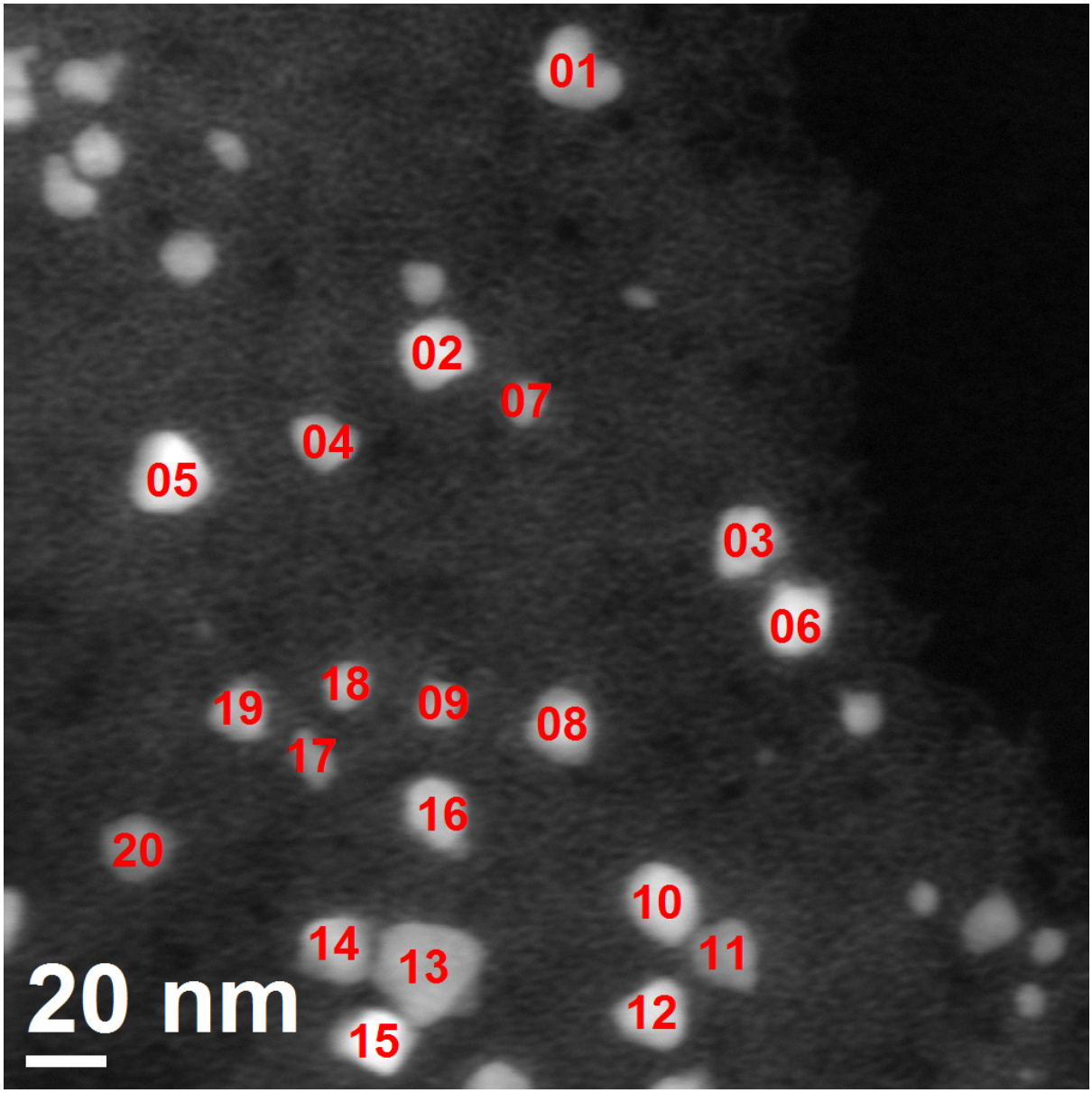
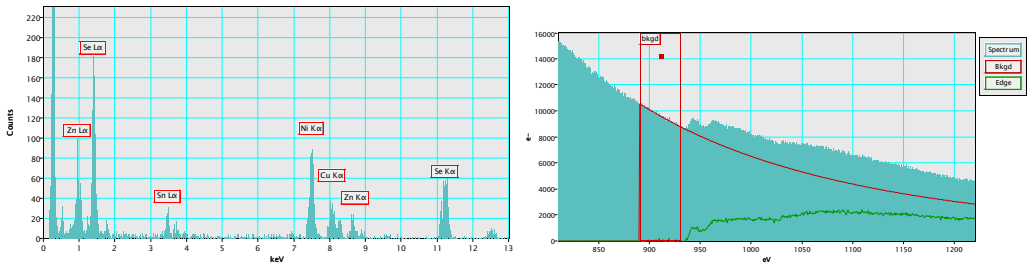


Figure S3. HAADF-STEM image of used for measurement of 20 individual nanoparticles.

For each nanoparticle shown in Figure S3 an EDX and electron energy loss (EEL) spectrum was recorded by placing the probe on the particle. EDX spectra were used for quantification (see Table 2). EEL spectra were recorded with a dispersion of 0.2 eV in the region from 810 to 1220 eV, which features the Cu-L edge (930 eV) and the Zn-L edge (1020 eV). Background subtraction using power law yields overlaid the signal for both edges, which complicates the extraction of the Zn edge; however the edges can be used for qualitative confirmation of the results from TEM-EDX.

Nanoparticle 01



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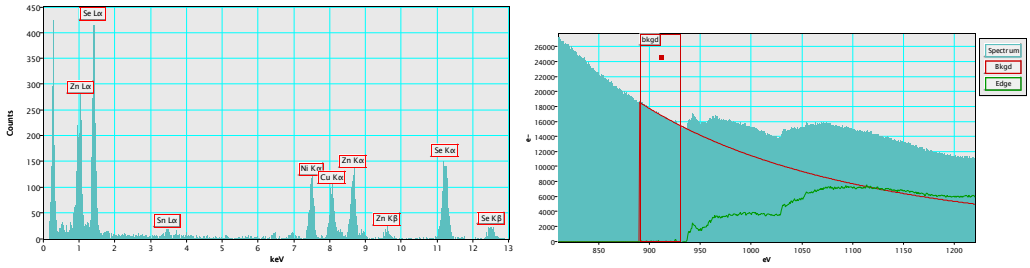

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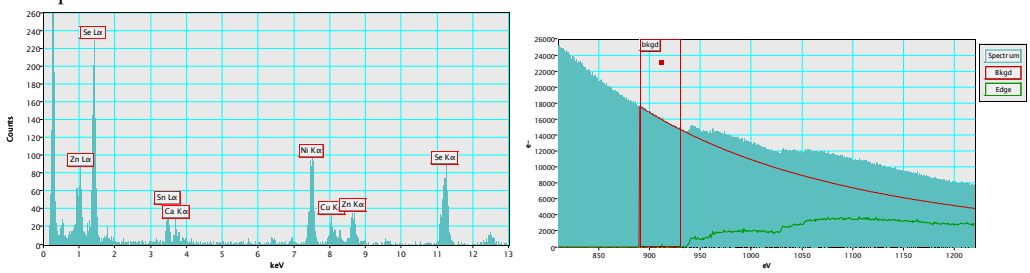

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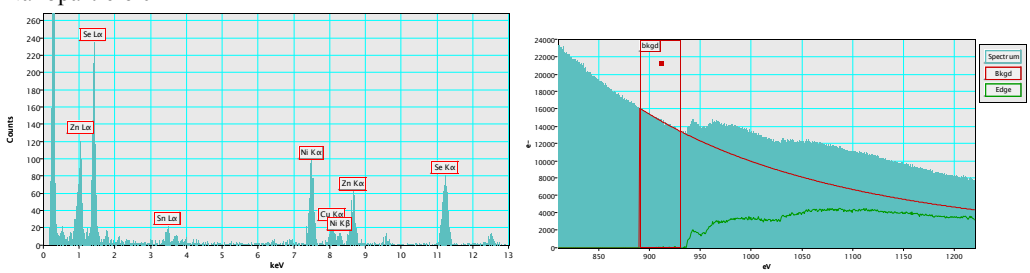

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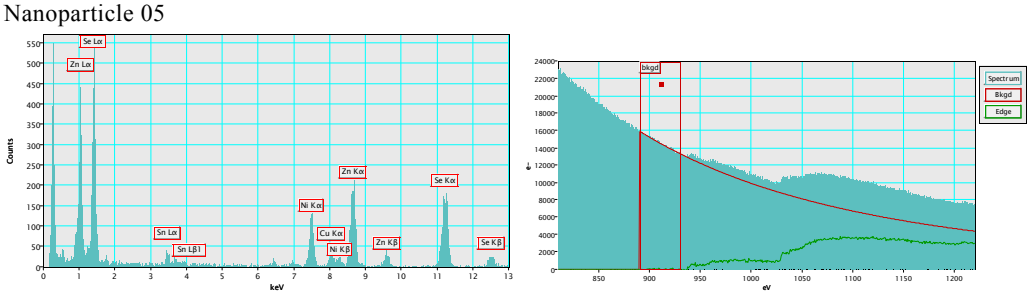

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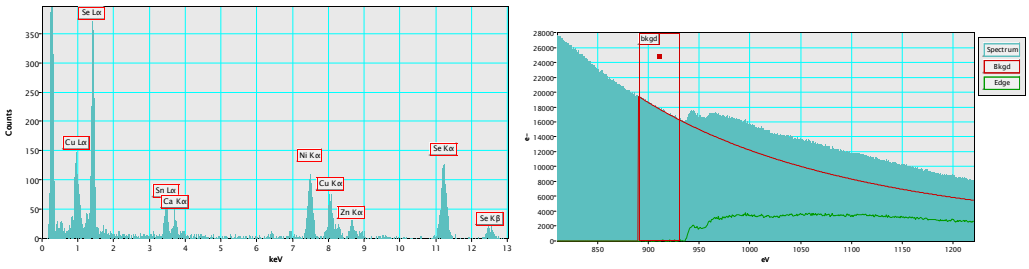

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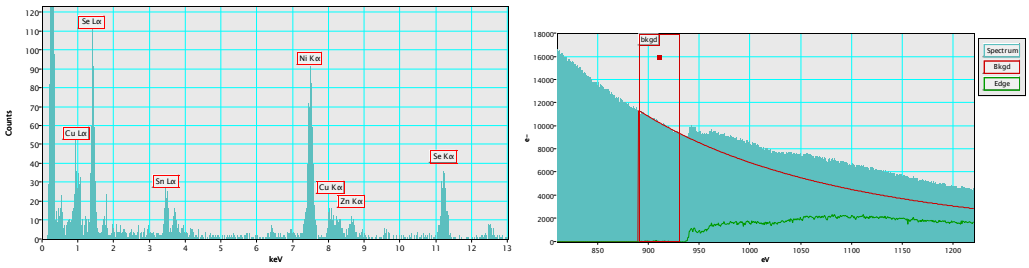

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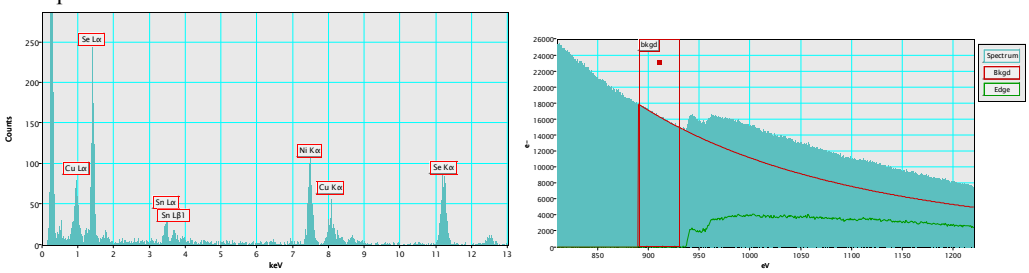

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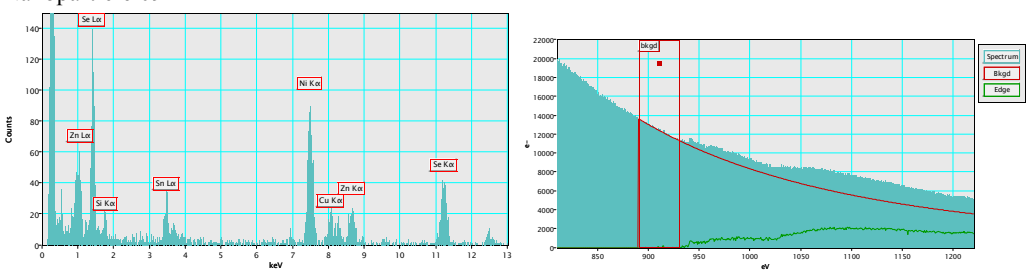

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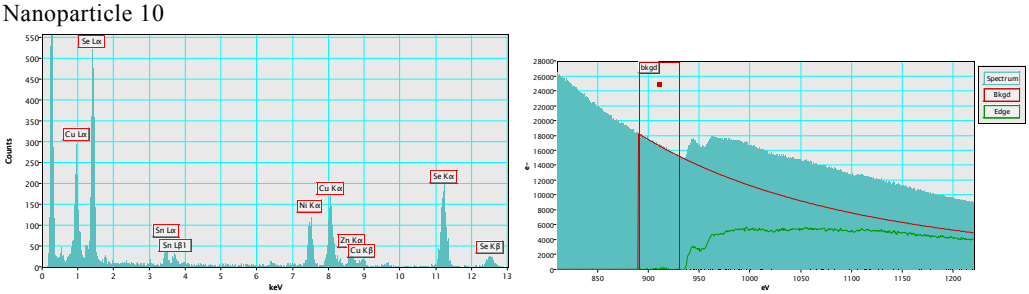

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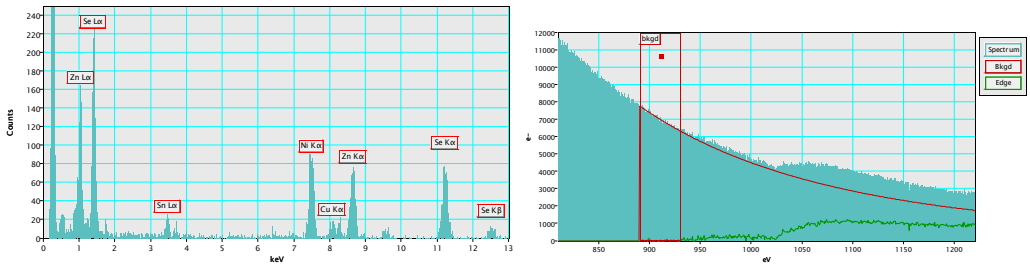

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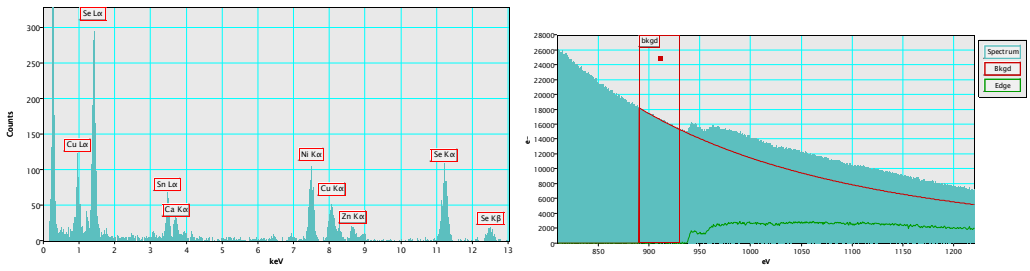

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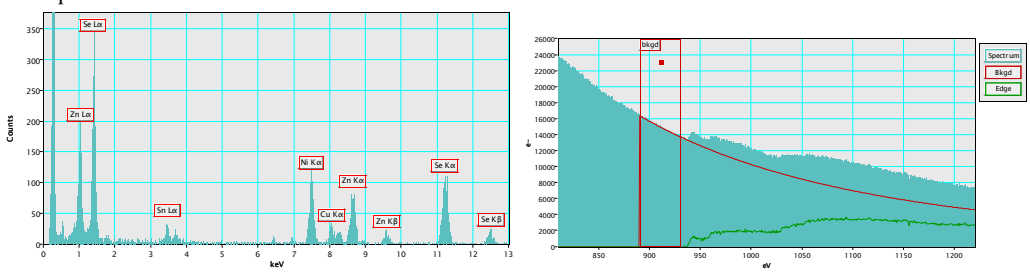

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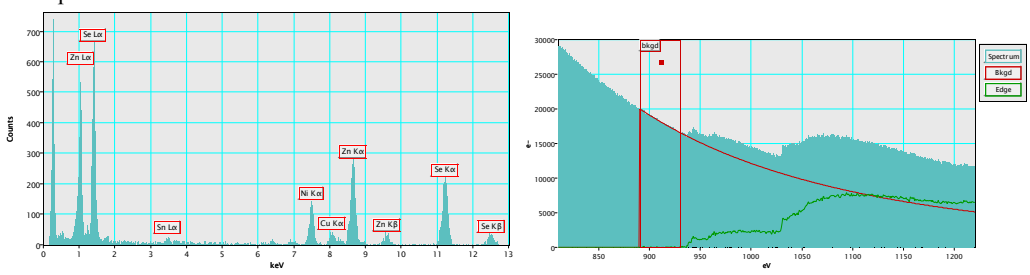

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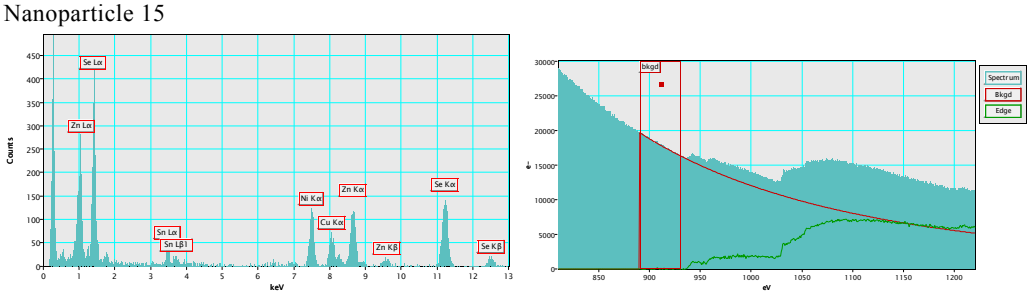

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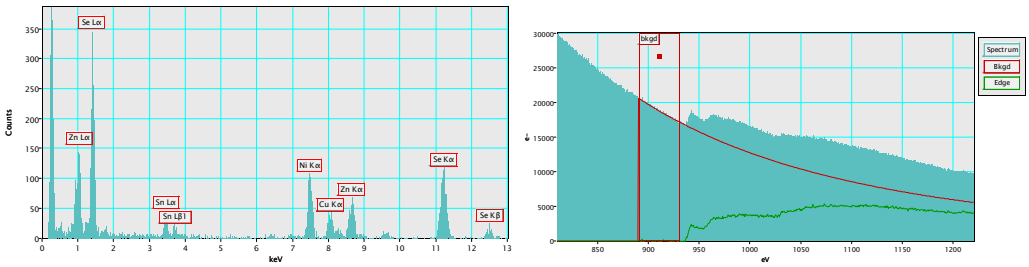

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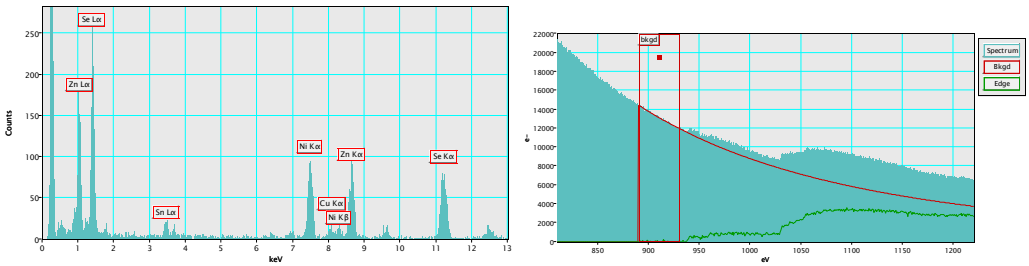

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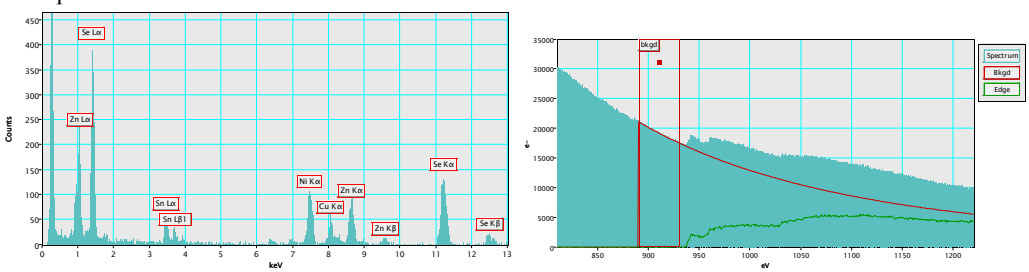

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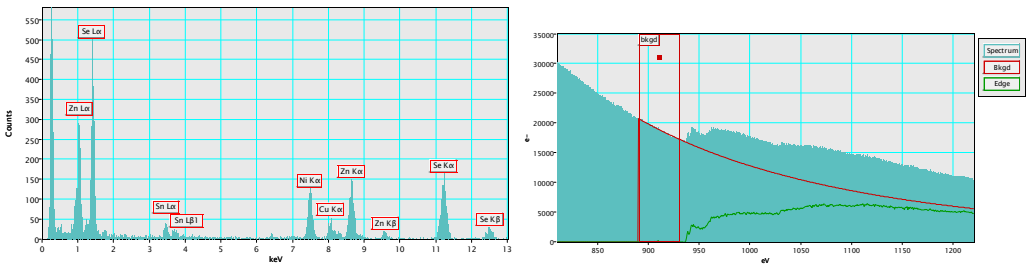

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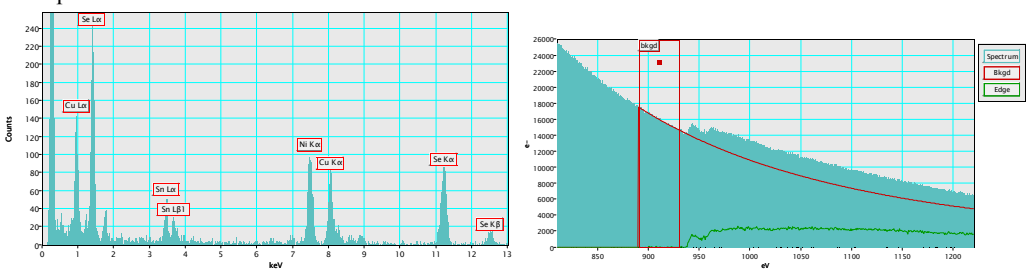

Figure S4. EDX and EEL spectra for 20 individual nanoparticles shown in Figure S3.

SEM-EDX 1

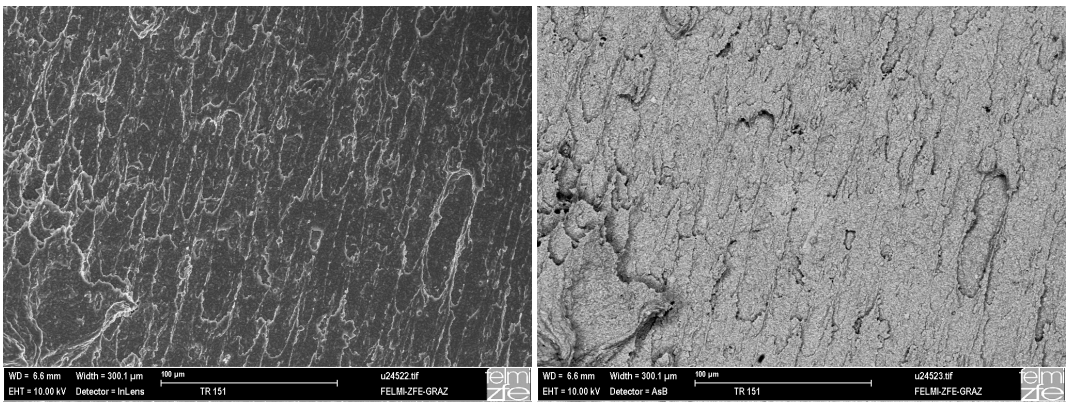

Figure S5. Secondary electron and Backscatter electron images for SEM-EDX measurement SEM 1 (Table 1).

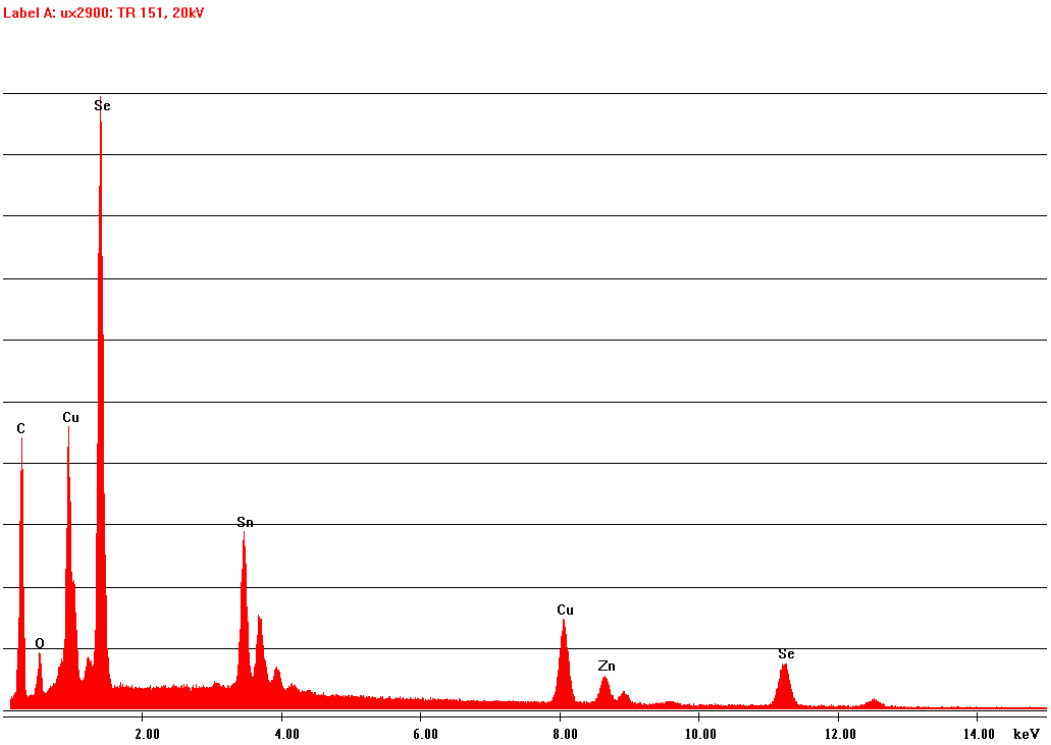

Figure S6. EDX spectrum for SEM 1 (Table 1).

SEM-EDX 2

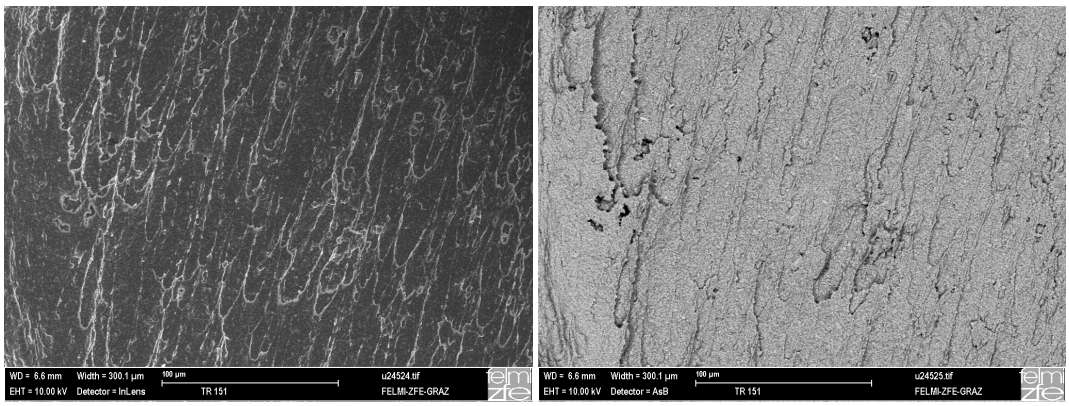

Figure S7. Secondary electron and Backscatter electron images for SEM-EDX measurement SEM 2 (Table 1).

Label A: ux2901: TR 151, 20kV

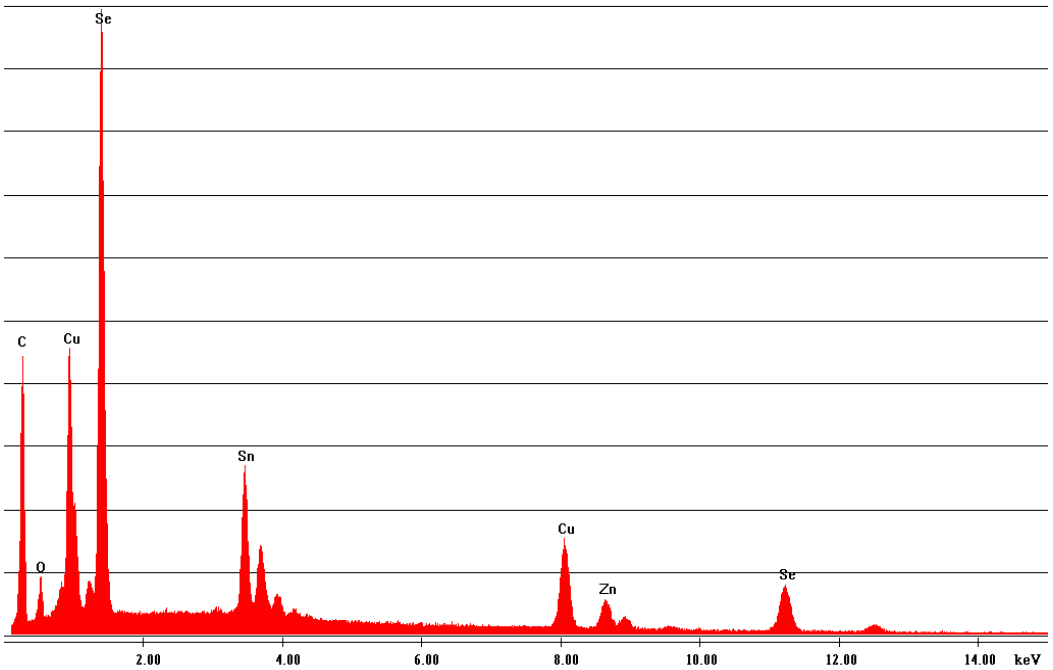

Figure S8. EDX spectrum for SEM 2 (Table 1).

SEM-EDX 3

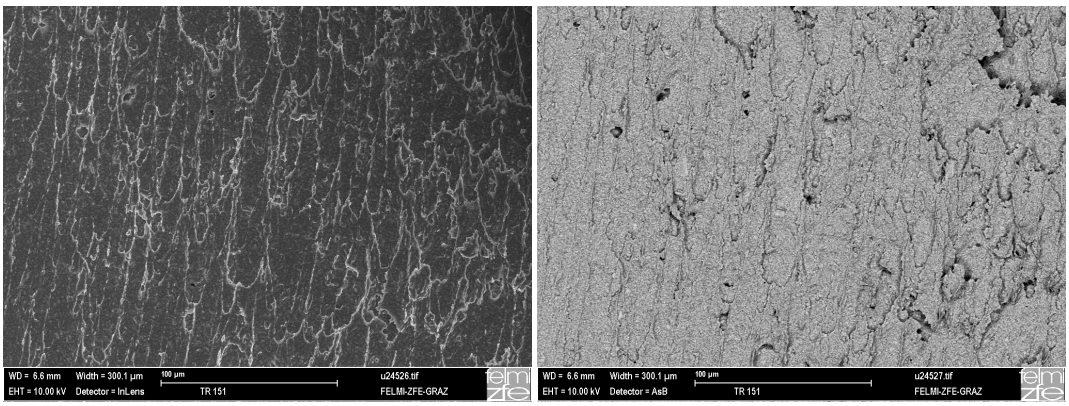

Figure S9. Secondary electron and Backscatter electron images for SEM-EDX measurement SEM 3 (Table 1).

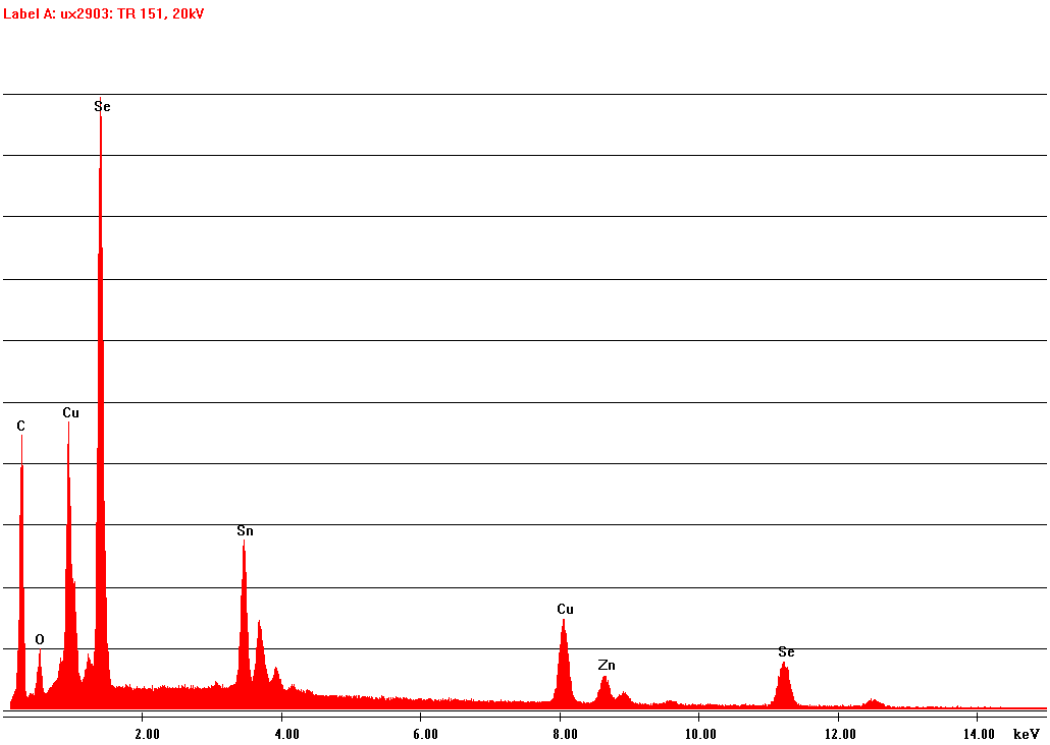

Figure S10. EDX spectrum for SEM 3 (Table 1).

Notes and references

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