

## Supporting Information

### Phase evolution of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanoparticles from in situ formed binary sulphides under solvothermal conditions

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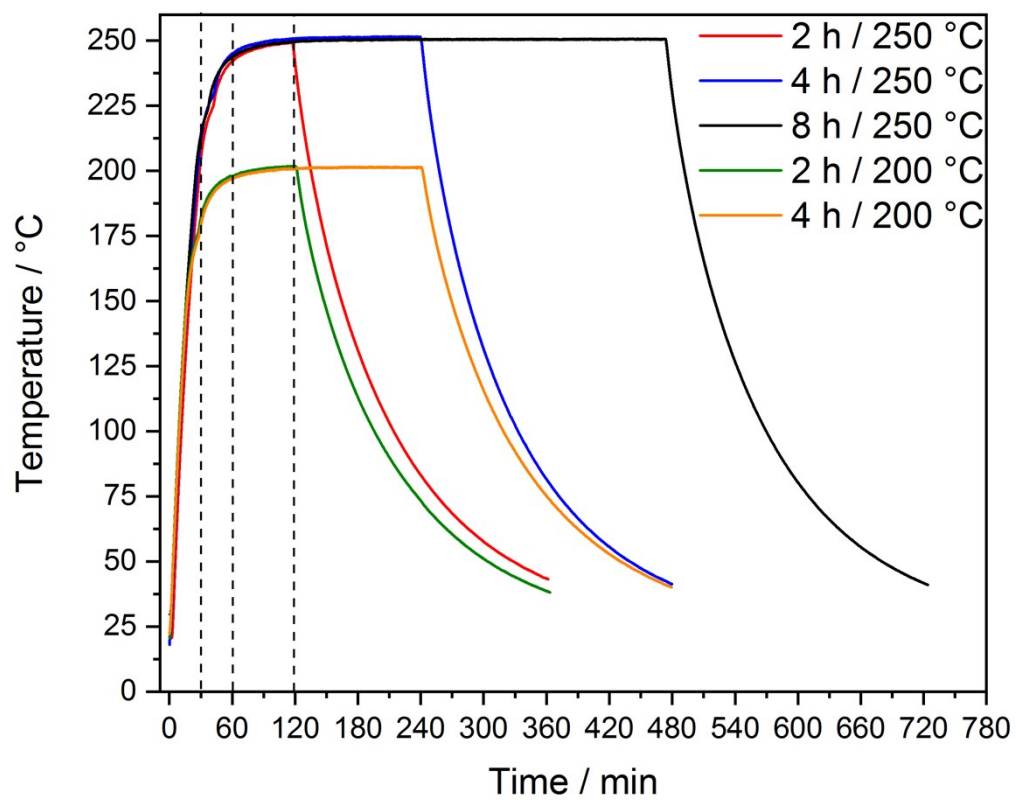
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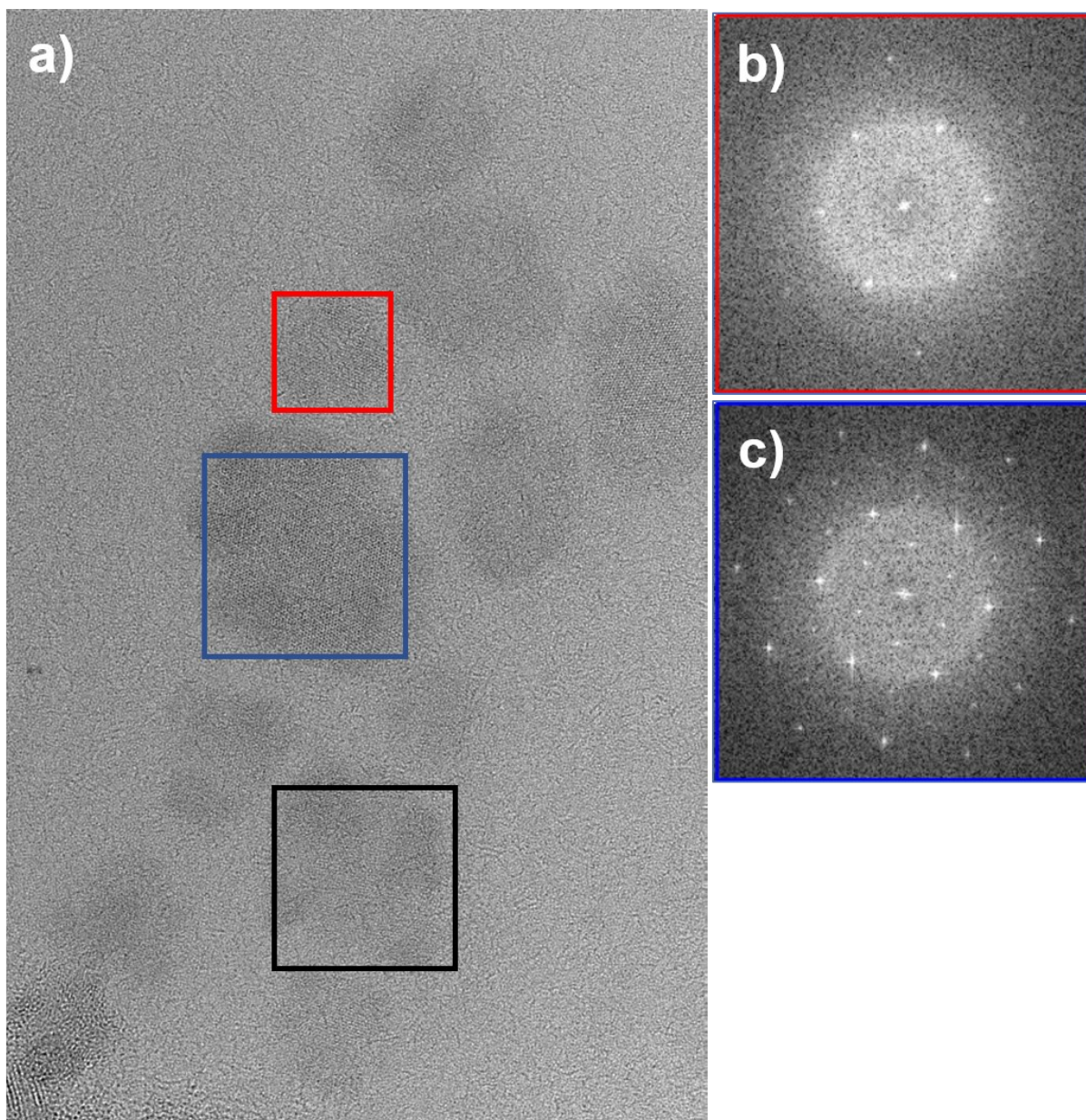
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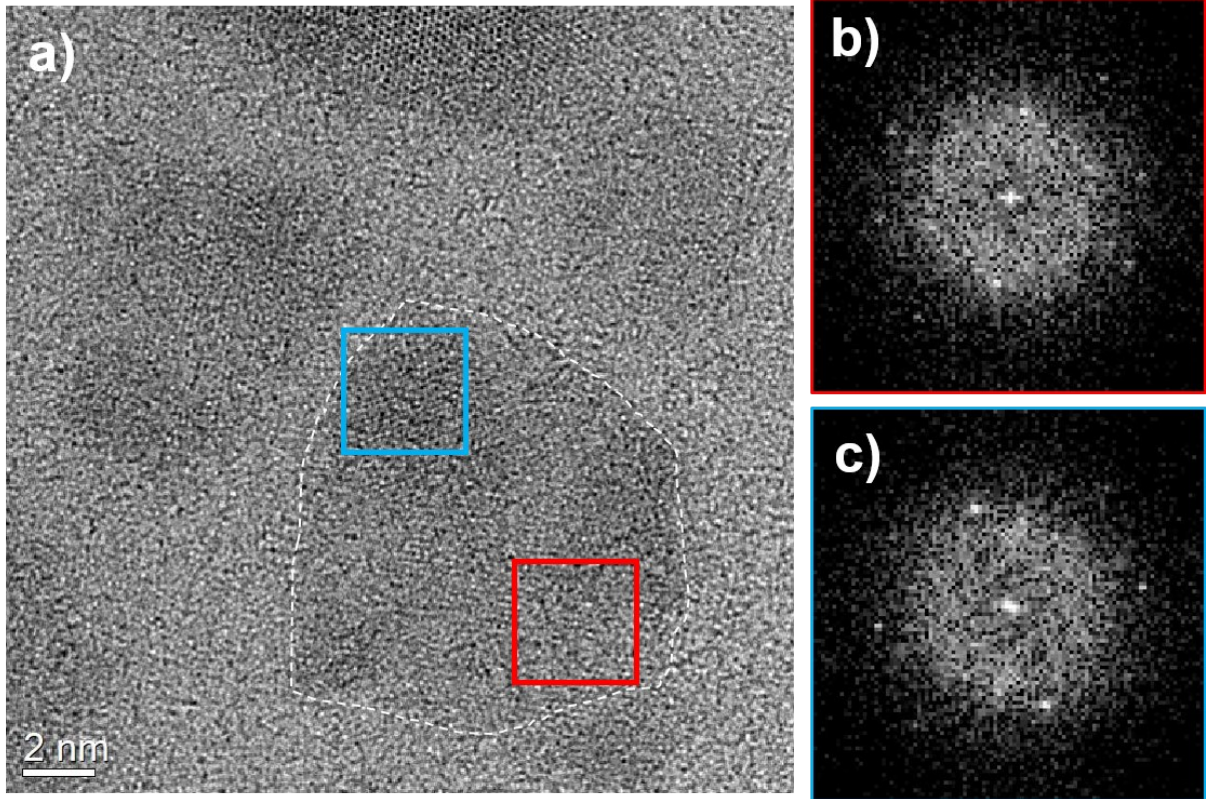
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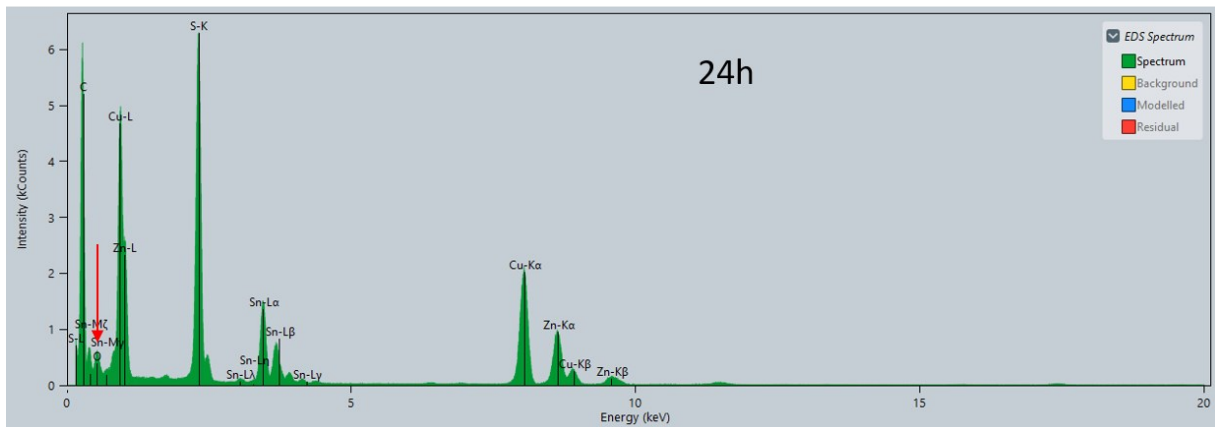
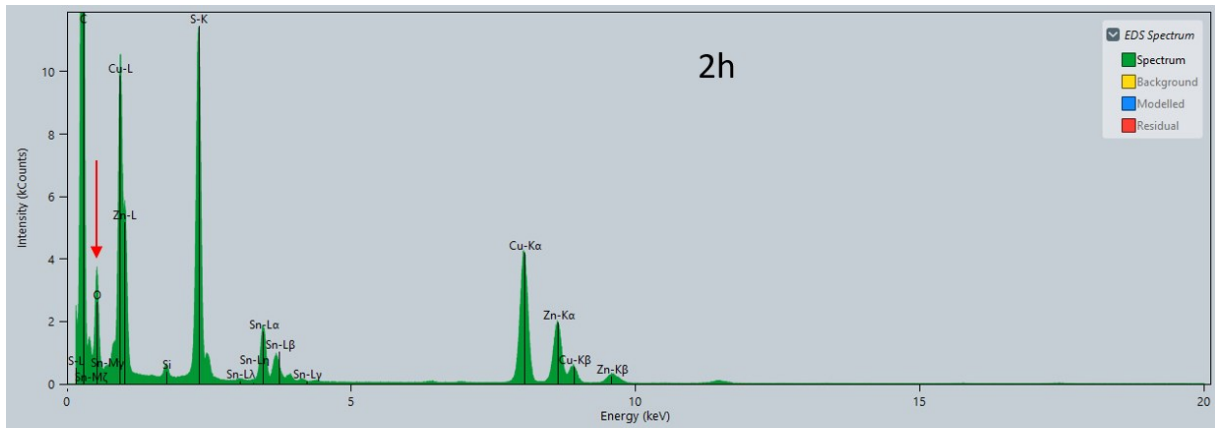
**Fig. S1.** Heating profiles at 200 °C and 250 °C for various time lengths.



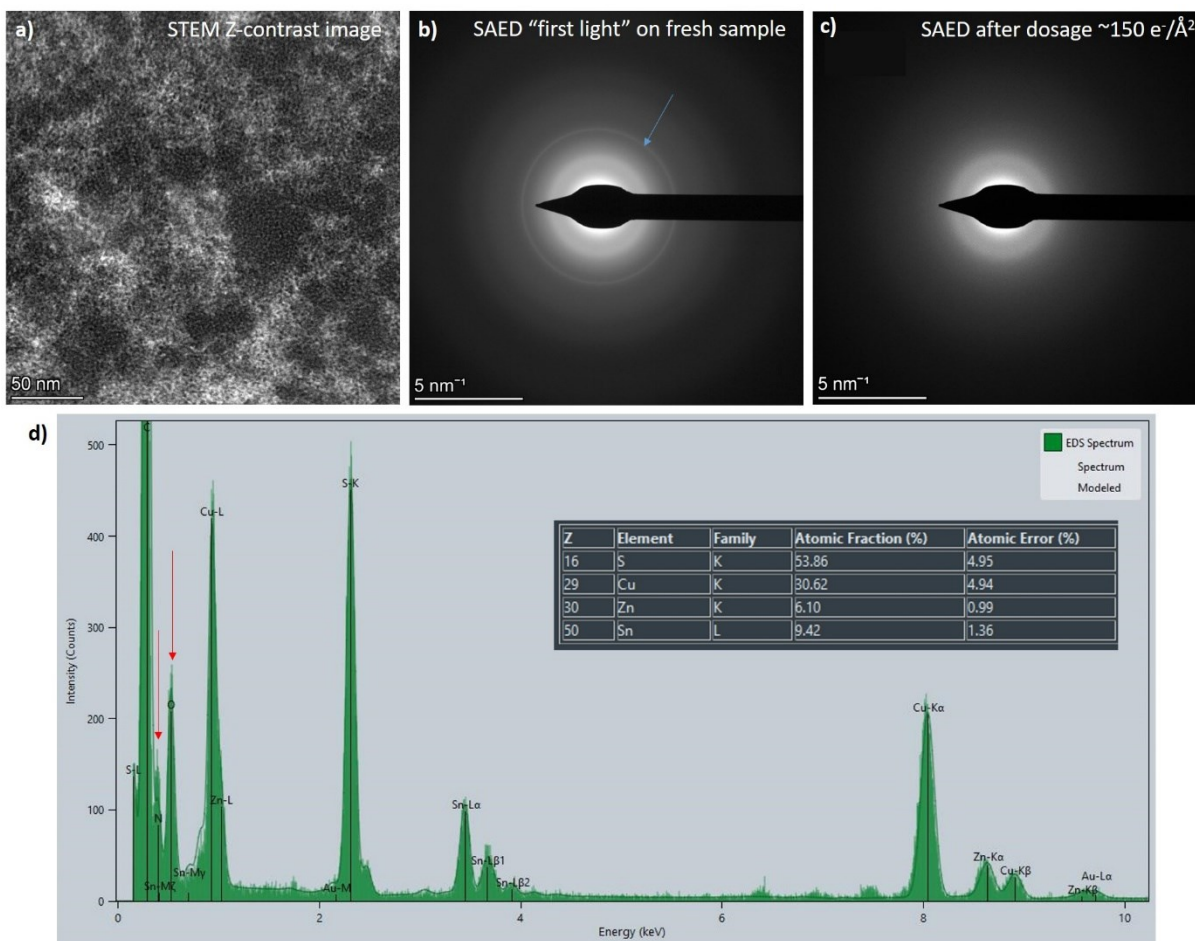
**Fig. S2.** HRTEM images and corresponding FT of particles synthesized at 250 °C for 2 h. The particle included in the black box is enlarged and analysed in Fig. S3.



**Fig. S3:** The different lattice pattern and orientation across the same big particle indicate that the large particle might be assembled by smaller ones.



**Fig. S4.** Representative raw EDX signal from (top) 2h and (bottom) 24h sample.



**Fig. S5.** TEM analysis of initial (0 h) sample. STEM Z-contrast image (a) reveal tiny particle embryos. Only one ring at  $3.6 \text{ nm}^{-1}$  is visible in selected area electron diffraction of fresh sample region (b), and it vanishes soon under a moderate dosage of  $\sim 150 \text{ e}^{-}/\text{\AA}^2\text{s}$  (c), which makes high resolution imaging not possible (HRTEM typically requires  $10^3 \text{ e}^{-}/\text{\AA}^2\text{s}$  on our microscope). (d) EDX signal from an area of  $\sim 500 \text{ nm}$  with dispersed particles.