Supporting Information

Percentage of conversion

The percentage of conversion from CZTS to CZTSe is calculated from the areas under the XRD peaks of the (112)-reflections, and compared to the EDX data in Table S.1. The amount of conversion is larger from the XRD data, where 100% conversion is assumed for the film formed using the particles obtained after 60 min of reaction and that the amount of mixed-phase sulfide/selenide material is negligible.

Table S.1. Percentage of conversion from CZTS to CZTSe calculated from XRD and EDX measurements: From the area under the (112)-reflection in the XRD pattern in Fig. 2 (where the peak area for 60 min is set equal to 100%), and extracted from a fit to the EDX curve in Fig. 3(b).

	Percentage of conversion (%)	
Reaction time (min)	**XRD**	**EDX**
5	33.1	12.5
10	46.6	28.4
30	84.5	64.5
60	100	81.6

Particle size

The particle size as a function of time was determined from the TEM images in Fig. 5, and is displayed in Fig. S.1. A polydisperse particle size distribution is observed, and both the average size of large particles, small particles, and all particles are plotted.

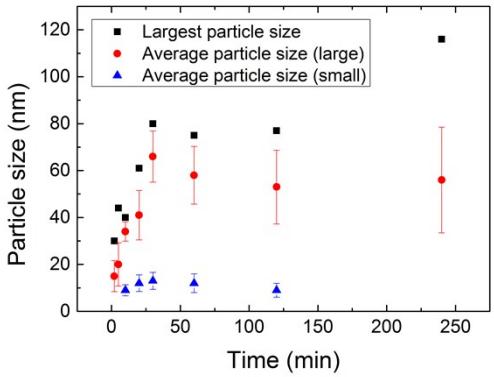
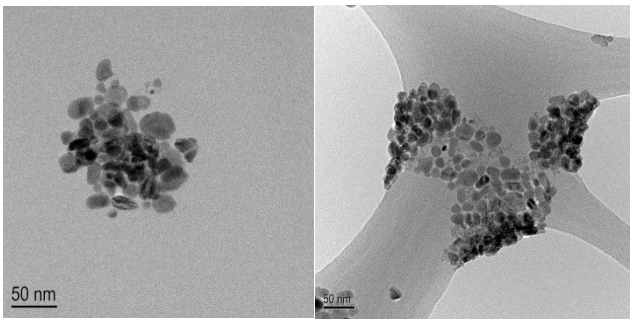


Figure S.1. Average particle size measured from TEM images synthesized at 250°C with 1.33 M Se. A bimodal distribution of particle sizes is seen for most cases.

Influence of surfactant

A TEM image of the nanoparticles obtained just before Se-injection is shown in Figs. S.2(a), *i.e.* after reaction at 220°C for 20 min. Fig. S.2(b) shows these CZTS NPs after only TOP injection. The NPs in Fig. S.2(a) were precipitated by centrifugation and re-dispersed in hexadecane, followed by injection of TOP without Se and heated at 250°C for 30 min and the NPs are showed in Fig. S.2(b).

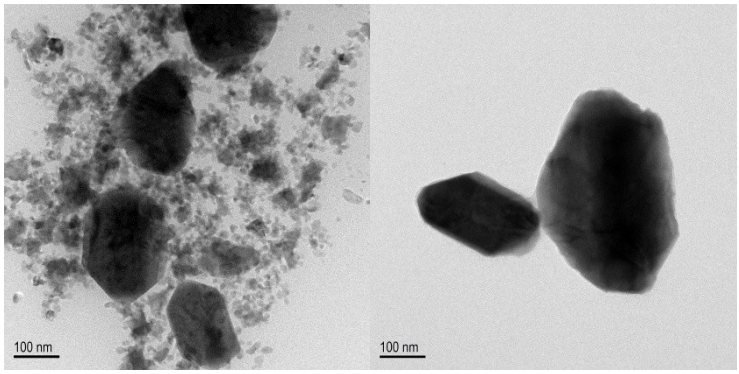


(a) (b)

Figure S.2. TEM images of CZTS NPs after (a) 20 min reaction at 220°C, and (b) after 50 min reaction with TOP injection. This is the result of a reference experiment to see if TOP alone would initiate grain growth of the CZTS NPs. In the case of (b), the reaction was stopped after 20 min and started again with injection of TOP (without Se) for 30 min.

Larger particles

We have also studied particle growth at 230°C and 0.66 M Se (Fig. S.3(a)) and at 260°C and 1 M Se (Fig. S.3(b)). The distinct faceted shapes of the Se-rich particles imply a highly crystalline material, and after 1 h reaction at 260°C and 1 M Se the largest particle size was approaching 0.5 µm in diameter.



(a) (b)

Figure S.3. TEM image of CZTSe particles grown for (a) 2 hr after Se-injection, at 230°C and 0.66 M Se, and (b) 1 hr after Se-injection, at 260°C and 1 M Se. These reaction conditions result in very large particles, approaching 500 nm.

Elemental map

The STEM-EDX elemental map in Fig. S.4 shows the NPs after Se-injection, and it supports the XRD results. The large particles are Se-rich, and the S-signal can come either from small S-rich NPs aggregating on the surface of the large particles, or from a small amount of S inside the Se-rich particles, as the XRD and Raman analysis also suggest. No sign of a core/shell-structure is observed.

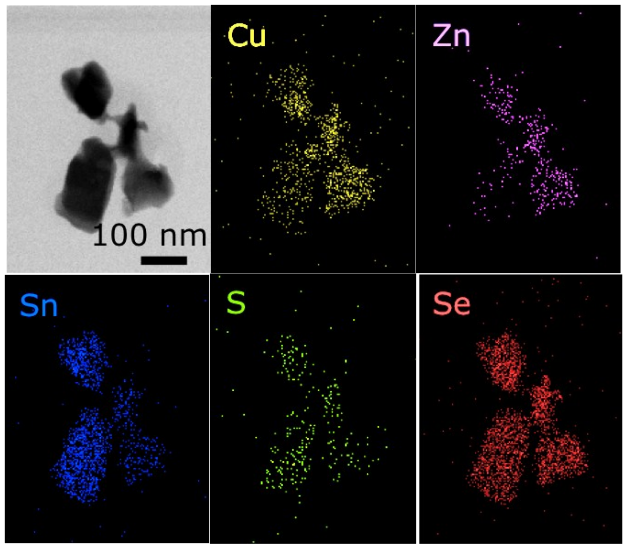


Figure S.4. STEM-EDX elemental map of NPs heated at 260°C for 30 min after Se-injection.