Electronic Supplementary Material (ESI) for CrystEngComm.

A comprehensive study on the mechanism behind formation and depletion of Cu_2ZnSnS_4 (CZTS) phases

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Supporting information

Temperature profiles

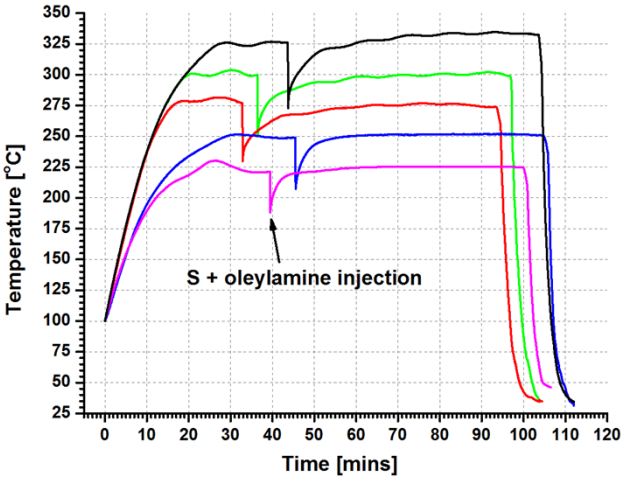

Fig. S1. As recorded temperature vs. time profile inside the reaction mixture for the five reactions carried out at 225 °C, 250 °C, 275 °C, 300 °C and 330 °C

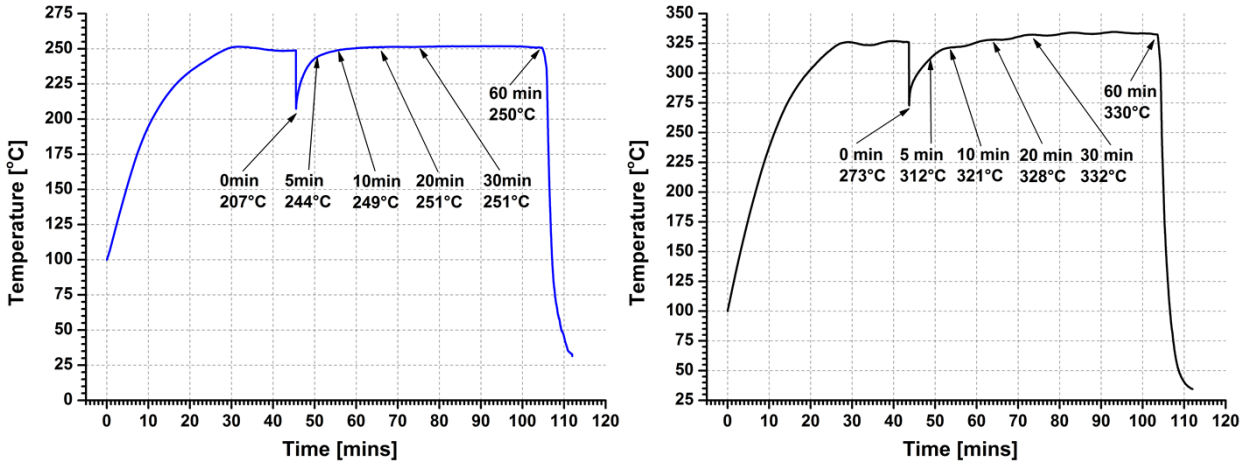

Fig. S2. Temperature vs. time profiles for reactions carried out at 250°C [left] and 330°C [right], showing time and temperature when samples were taken out of the reaction mixture to carry out a kinetic study

Instrumental details and sample preparation protocol:

Heating mantles:

For temperatures 225 °C and 250 °C, a standard heating plate from Heidolph (US) was used coupled with standard metallic heating mantles. For higher temperatures i.e. 275 °C, 300 °C and 330 °C, a specially designed heating mantle with a temperature regulator from Horst (Germany) was used.

Transmission electron microscopy (TEM) and **high-resolution TEM** (HRTEM):

The electron microscope was operated at 300 kV acceleration using LaB6 filament. TEM images were recorded with a FastScan type F214 charge coupled device (CCD) camera in the bright field mode from TVIPS (Tietz Video and Image Processing Systems), having an image size of 2048 x 2048 pixels. Particle size distribution (PSD) was calculated by estimating manually (using ImageJ) the area of single nanoparticle (for ~200 nanoparticles) in each sample, which allows to calculate the diameter (x_a), that is equivalent diameter of sphere with the same projection area (in a fixed position)

Raman spectroscopy:

The spectra were recorded using Synapse CCD detector (1024 x 256 pixels) with Edge filter with an instrumental error of 2 pixels using 600 l/mm grating. The green and red lasers were operated at 0.9% and 1% of full power which corresponds to an average power on the sample surface of less than $0.3\,mW$ and $0.2\,mW$, respectively. The irradiation time was chosen as 90 sec. Such low laser power was used to avoid any thermal changes in the samples. All spectra presented were smoothened using 3pt FFT filter and straight line background subtracted using Origin.

Rietveld refinement:

An example of a Rietveld refinement performed on 250 °C reaction product

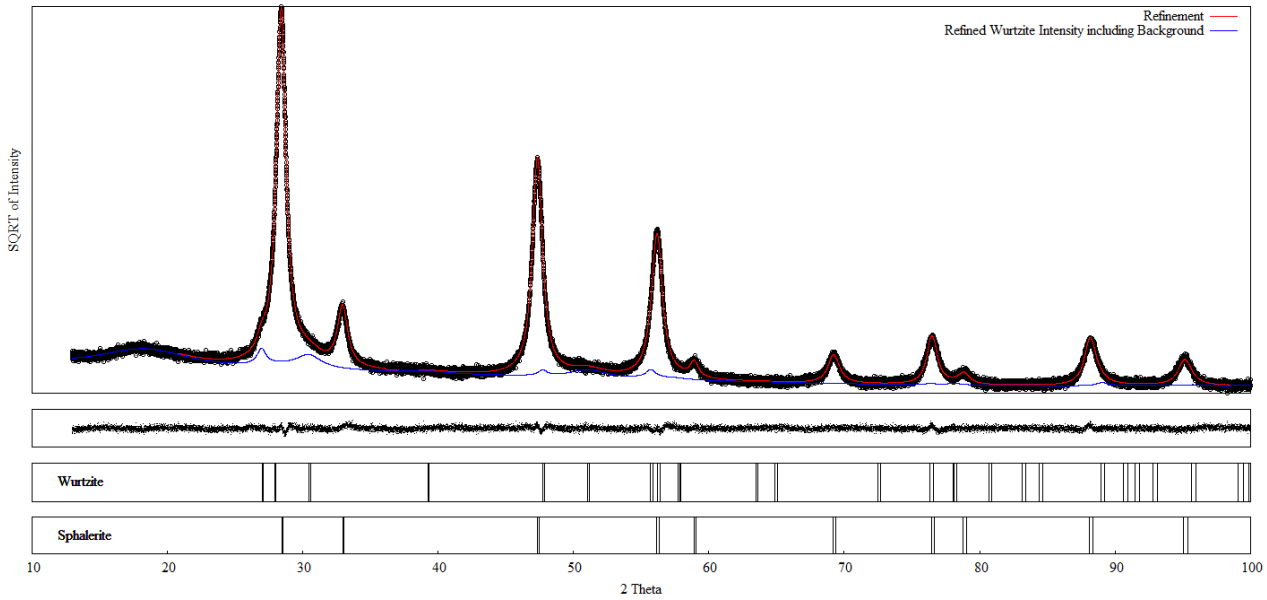

Fig S3. Shown is the data together with the two phase fit and the difference plot between measurement and fit.

To visualize the contribution of the Wurtzite type Kesterite to the diffractogram, this contribution is plotted separately under the measured data. The Wurtzite type reflections are strongly anisotropically broadened, leading to an almost invisible 002 type reflection.

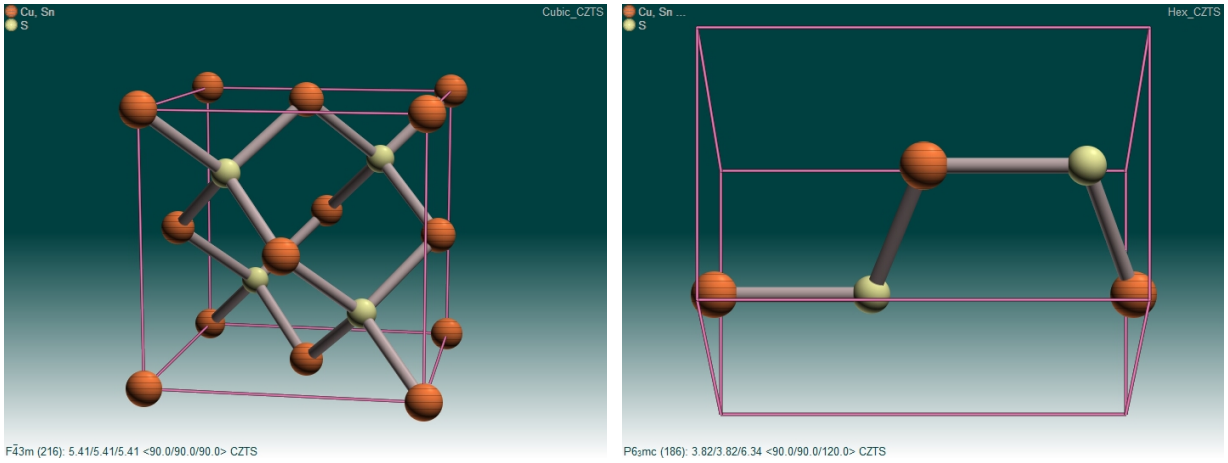

Fig. S4. Proposed crystal structures for cubic [left] and wurtzite [right] CZTS.

Table S1. Lattice parameters of cubic and wurtzite CZTS as obtained from Rietveld refinements.

Reaction Temperature	**Phases**	**Lattice Parameters**
225° C	Cubic CZTS	a = 5.4239(1) Å
	Wurtzite CZTS	a = 3.816(2) Å c = 6.359(2) Å
250° C	Cubic CZTS	a = 5.4276(1) Å
	Wurtzite CZTS	a = 3.814(2) Å c = 6.389(2) Å
275 °C	Cubic CZTS	a = 5.4309(1) Å
	Wurtzite CZTS	a = 3.821(2) Å c = 6.461(2) Å

Kinetics study:

Reaction at 330 °C:

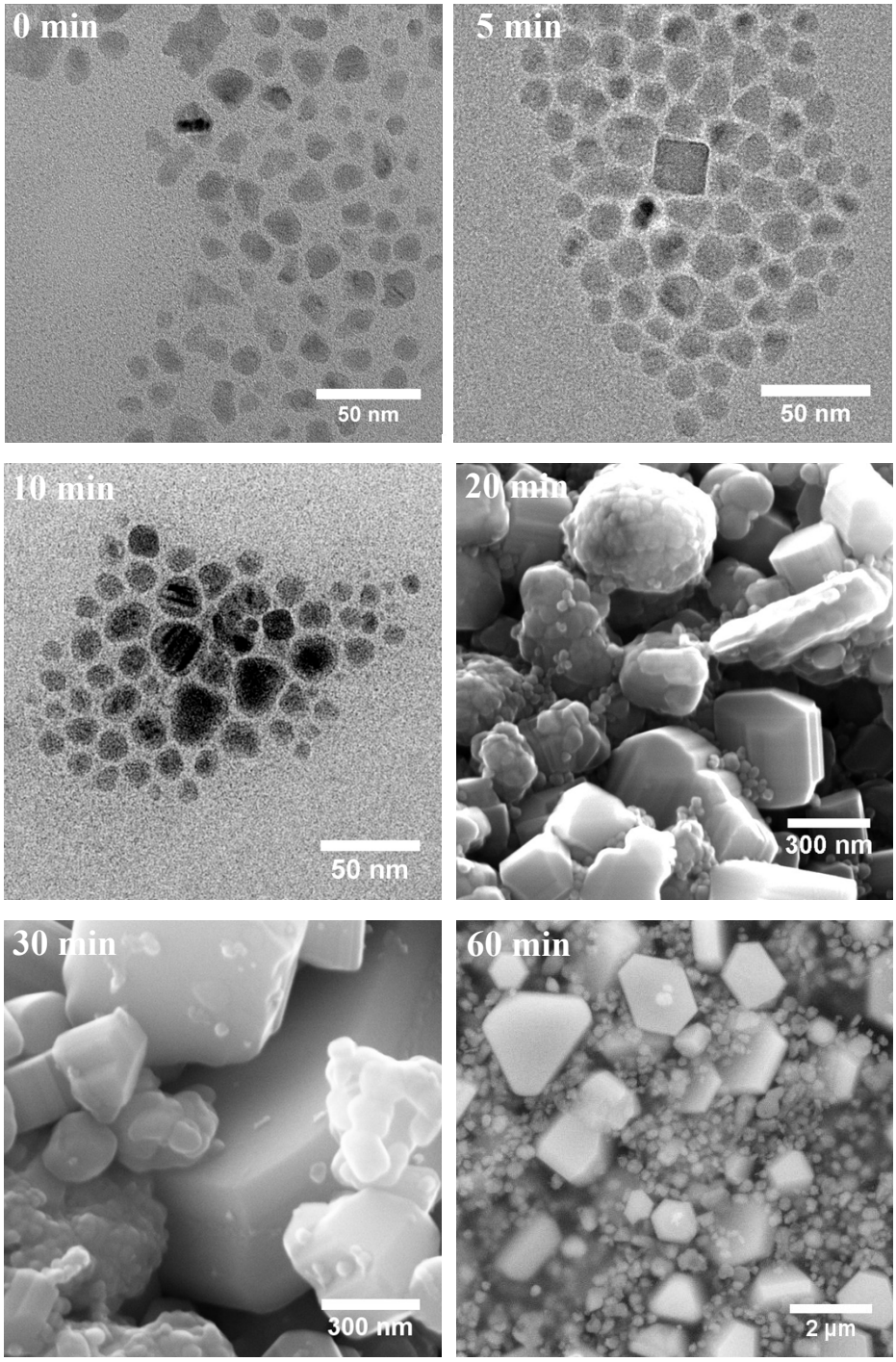

Fig S4. HRTEM and SEM images of samples taken out at 0 min, 5 min, 10 min and 20 min, 30 min, 60 min after injection from reaction at 330 °C, respectively.

Reaction at 250 °C:

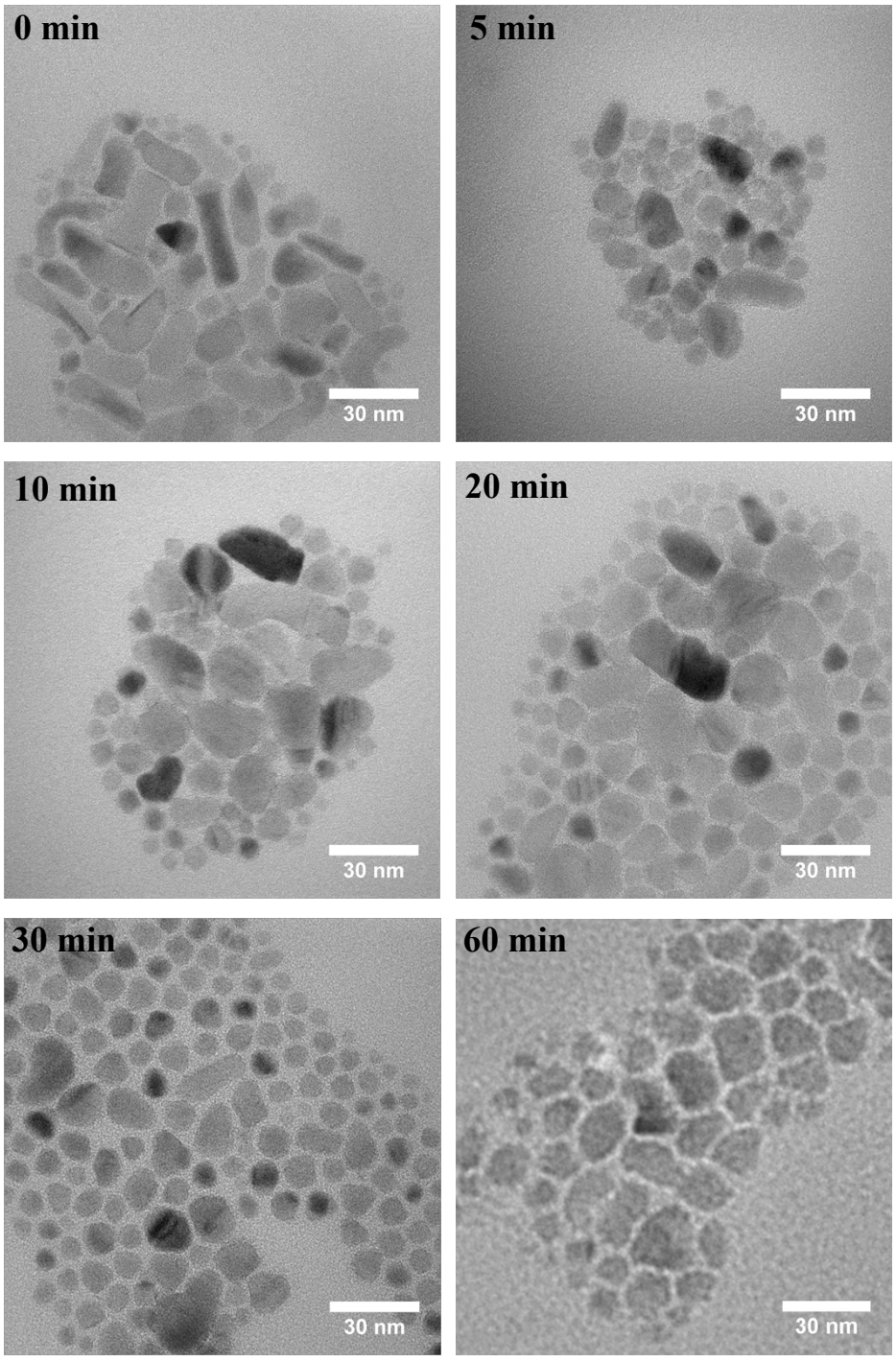

Fig S5. HRTEM images of samples taken out at 0 min, 5 min, 10 min and 20 min, 30 min, 60 min after injection from reaction at 250 °C, respectively.

ICP-OES Analysis:

Further the supernatant obtained after the first centrifugation was analysed using ICP-OES. This supernatant consists mainly of dissolved elements along with some small particles which were not separated. For this purpose only the supernatants from synthesis carried out at 250 °C and 300 °C were compared (table S2). This choice was made because in this temperature regime the most significant differences occurred.

Table S2. A comparison of elemental ratios of supernatants obtained from synthesis at 250 °C and 300 °C.

	S:(Cu+Zn+Sn)	**Sn:Cu**	**Zn:Cu**
250 °C	1.0	0.6	1.3
300 °C	0.4	13.2	43.0

If compared with ideal CZTS (fig. 5a), for reaction at 250 °C the supernatant is only slightly rich in Zn content which is quite in agreement to the solid composition which is slightly Zn poor. The supernatant from the reaction product at 300 °C appears to have much higher amounts of Zn, Sn and S in contrast to the solid product which was found poor in Zn, Sn and S contents.

The two techniques (ICP-OES and EDX) vary significantly in terms of accuracy and precision of amount of elements detected. Therefore for sake of comparison between ICP and EDX, the composition of solid part (as synthesised particles) was also analysed by ICP only for synthesis at 250 °C (table S3).

Table S3. A comparison of composition of solid particles (sediment) obtained from ICP-OES and EDX analysis for synthesis at 250 °C.

	ICP	**EDX**
S:(Cu+Zn+Sn)	1.16	1.15
Sn:Cu	0.51	0.60
Zn:Cu	0.39	0.42

It can be observed that the average compositions obtained from both the techniques matches closely.

Particle size distributions:

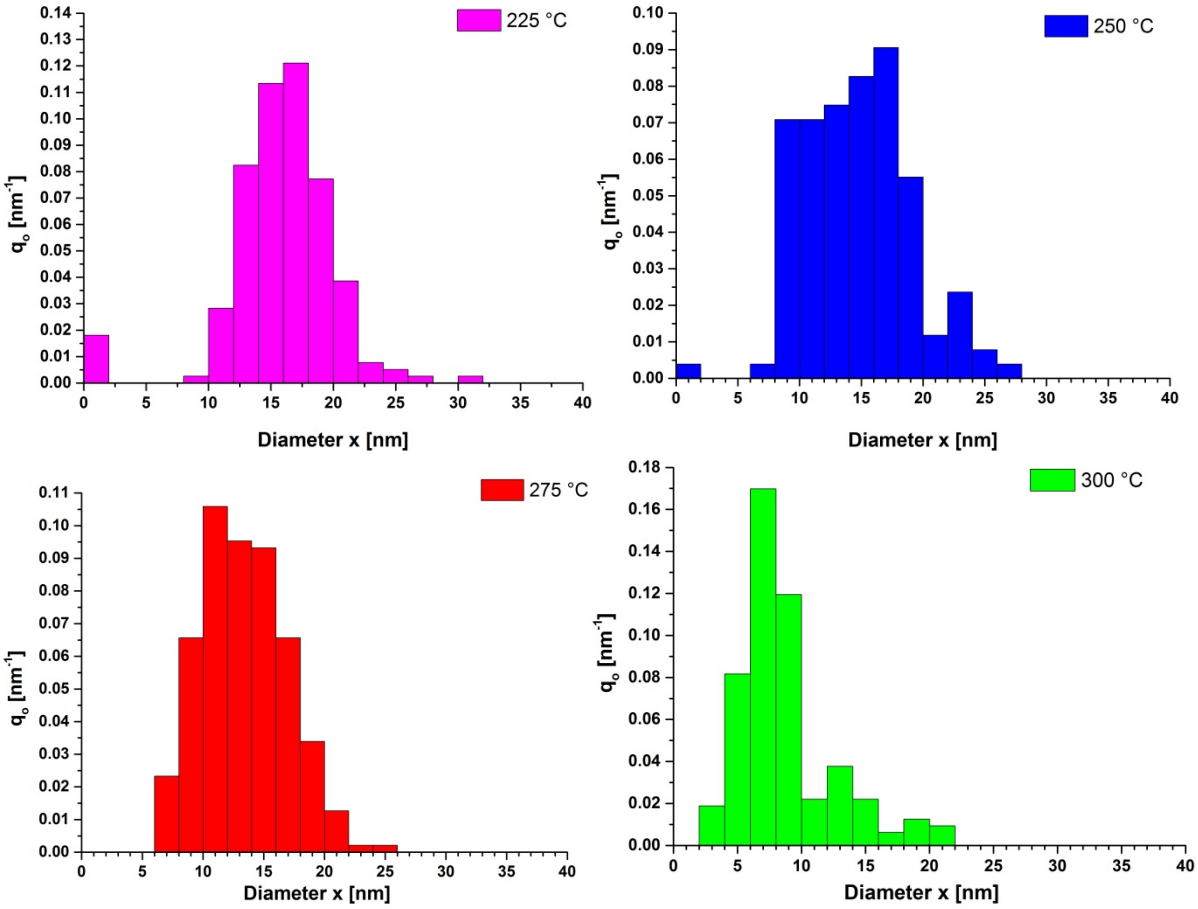

Fig. S6. Number weighted density distributions of the particles synthesised at different temperatures

SEM images:

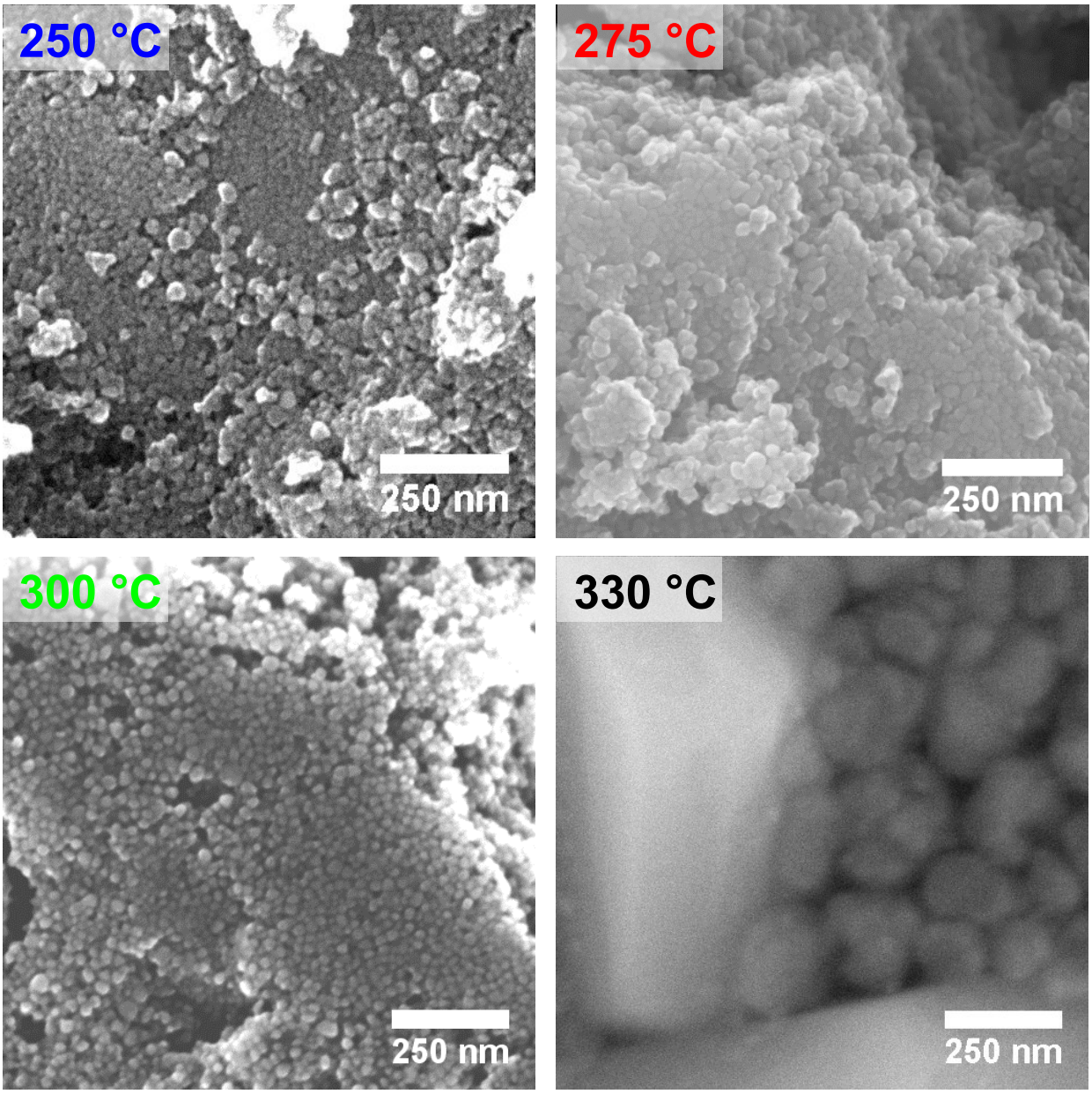

Fig. S7. Some of the low magnification SEM images of the samples synthesised at different temperatures after 1hr of reaction time, showing particles of different shapes and sizes.

In combination with fig. S5 (60 min), it must be noted that relatively faceted and disc like hexagons can only be observed at 330 °C.