

Electronic Supplementary Material for:

***In situ* monitoring amorphous calcium phosphate formation by dynamic light scattering and laser diffraction**

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Fig. S1 Particle height analysis of AFM 2D height for the particles formed in precipitation systems without stirring

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Fig. S2 AFM 3D topographic view of aggregated nanoparticles obtained in precipitation System A with stirring

Fig. S3 Particle height analysis of AFM 2D height for the particles formed in precipitation systems with stirring

Table S2 Particle height analysis of AFM 2D height for the particles formed in precipitation systems with stirring

Fig. S4 TEM micrographs and the corresponding particles length distributions

Fig S5 Distribution of particles' sizes obtained in time-averaged experiment and representative distributions obtained in time-resolved experiment at corresponding reaction times.

Fig S6 Changes of vol. % of particles formed in systems A and B, measured by DLS in time resolved experiment at the same time scale.

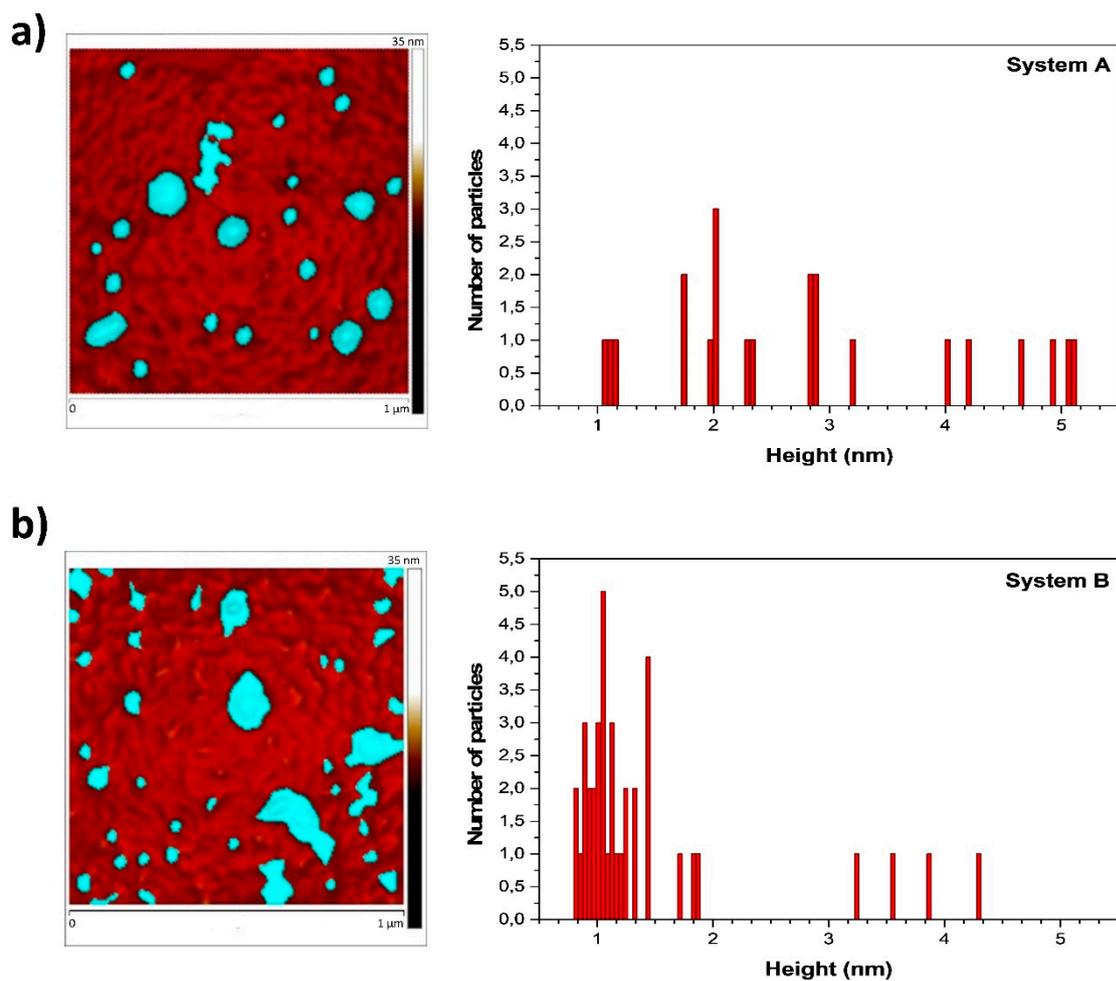


Figure S1. Topographic height images (left) and particle height histograms (right) obtained by analysis of AFM 2D height data of particles formed in precipitation systems at conditions corresponding to DLS measurements, i.e without stirring after 30 min ageing time: a) system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$), b) system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$), $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$.

Table S1. Particle dimensions obtained from AFM height data analysis of the particles formed in precipitation systems at conditions corresponding to DLS measurements, i.e without stirring after 30 min ageing time: system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$), system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$), $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$.

| System A | | | | |
|-------------------------|----------|---------|-----------|----------|
| Parameter | Mean | Minimum | Maximum | Sigma |
| Total Count | 22.000 | 22.000 | 22.000 | 0.000 |
| Height (nm) | 2.821 | 1.065 | 5.107 | 1.27 |
| Area (nm ²) | 3634.983 | 759.549 | 12098.524 | 3265.344 |
| Diameter (nm) | 62.363 | 31.098 | 124.114 | 27.185 |
| System B | | | | |
| Parameter | Mean | Minimum | Maximum | Sigma |
| Total Count | 39.000 | 39.000 | 39.000 | 0.000 |
| Height (nm) | 1.419 | 0.815 | 4.296 | 0.833 |
| Area (nm ²) | 3253.122 | 678.168 | 22325.30 | 4558.415 |
| Diameter (nm) | 55.595 | 29.385 | 168.599 | 32.422 |

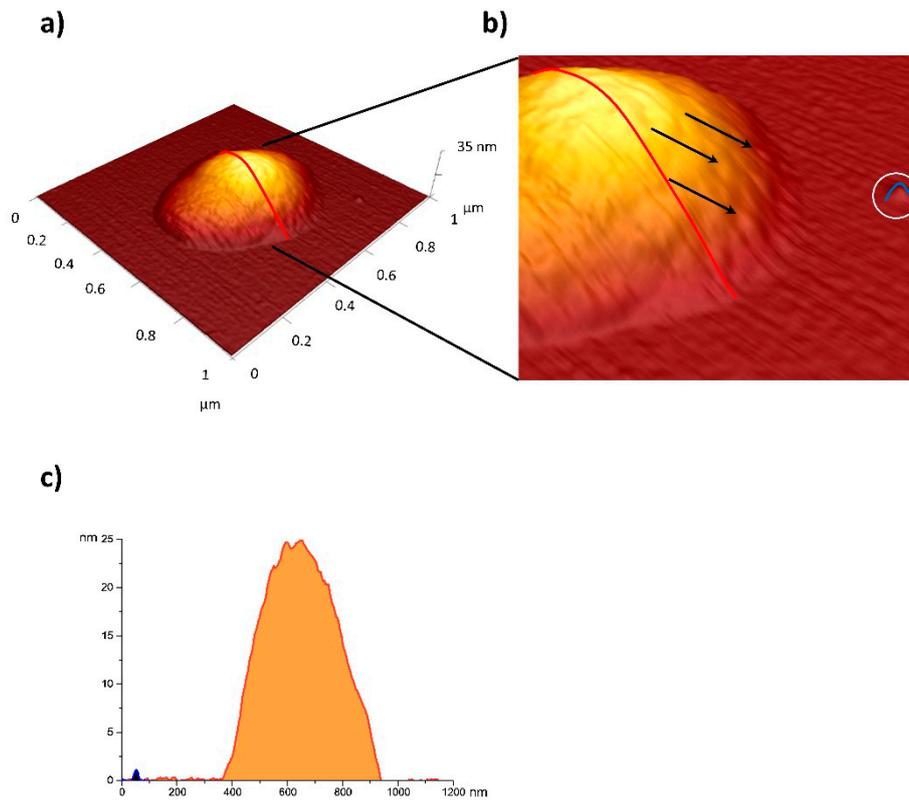


Figure S2. a) AFM 3D topographic view of representative aggregated nanoparticle obtained from precipitation system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$) at conditions corresponding to LD measurements, i.e with mechanical stirring and b) enlargement of aggregates with indicated individual nanoparticles, still observable on the surface of the aggregate (black arrows) and mica (white circle), c) profile sections cross highlighted lines with corresponding colour (red or blue line) on 3D topographic image b.

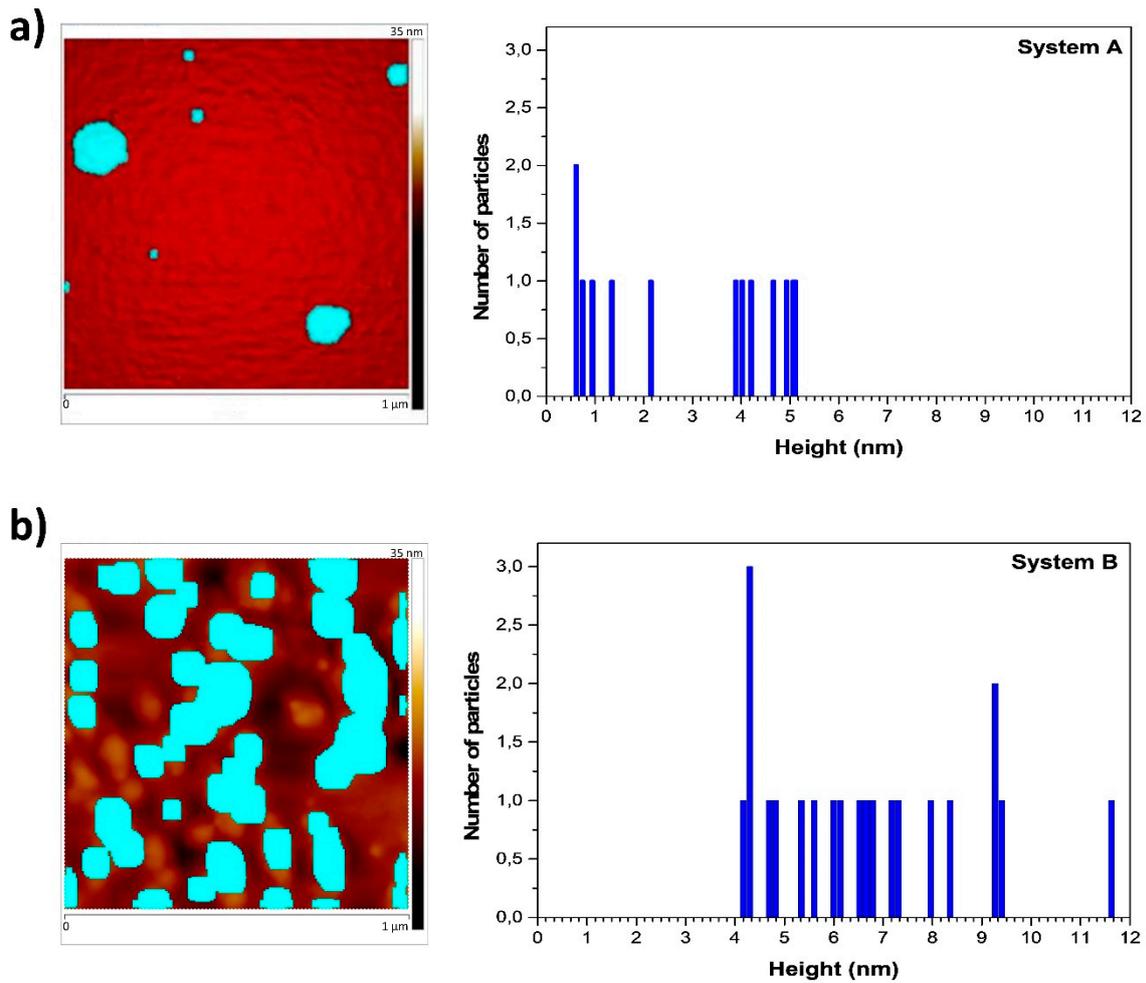


Figure S3. AFM topographic 2D view (left) and particle height histograms (right) obtained by analysis of AFM height data of particles formed in precipitation systems at conditions corresponding to LD measurements, i.e with mechanical stirring after 10 min ageing time: a) system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$), b) system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$), $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$.

Table S2. Particle dimensions obtained from AFM height data analysis of the particles formed in precipitation systems at conditions corresponding to LD measurements, i.e with mechanical stirring after 30 min ageing time: system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$), system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$), $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$.

| System A | | | | |
|-------------------------|-----------|----------|-----------|-----------|
| Parameter | Mean | Minimum | Maximum | Sigma |
| Total Count | 7.000 | 7.000 | 7.000 | 0.000 |
| Height (nm) | 1.466 | 0.608 | 3.883 | 1.113 |
| Area (nm ²) | 5116.054 | 518.799 | 18707.275 | 6546.123 |
| Diameter (nm) | 65.340 | 25.701 | 154.334 | 47.378 |
| System B | | | | |
| Parameter | Mean | Minimum | Maximum | Sigma |
| Total Count | 22.000 | 22.000 | 22.000 | 0.000 |
| Height (nm) | 7.077 | 4.167 | 15.811 | 2.737 |
| Area (nm ²) | 16726.100 | 1274.957 | 86317.273 | 19863.344 |
| Diameter (nm) | 127.941 | 40.291 | 331.516 | 70.195 |

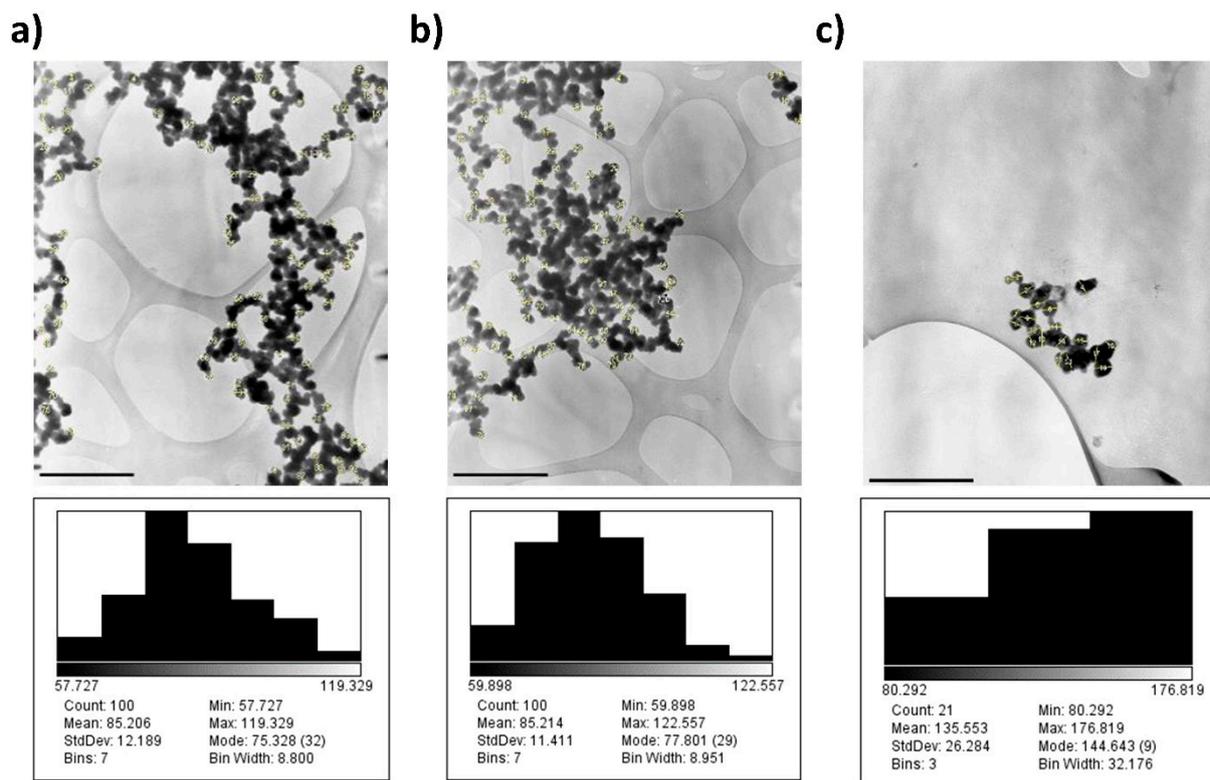


Figure S4. TEM micrographs and the corresponding particles length distributions measured using ImageJ software v.1.46r of the precipitate formed in system A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$) after a) 30 minutes without stirring and b) 10 minutes with mechanical stirring; c) in system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$) with mechanical stirring after 10 minutes aging time. $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$. TEM bar $1 \text{ }\mu\text{m}$.

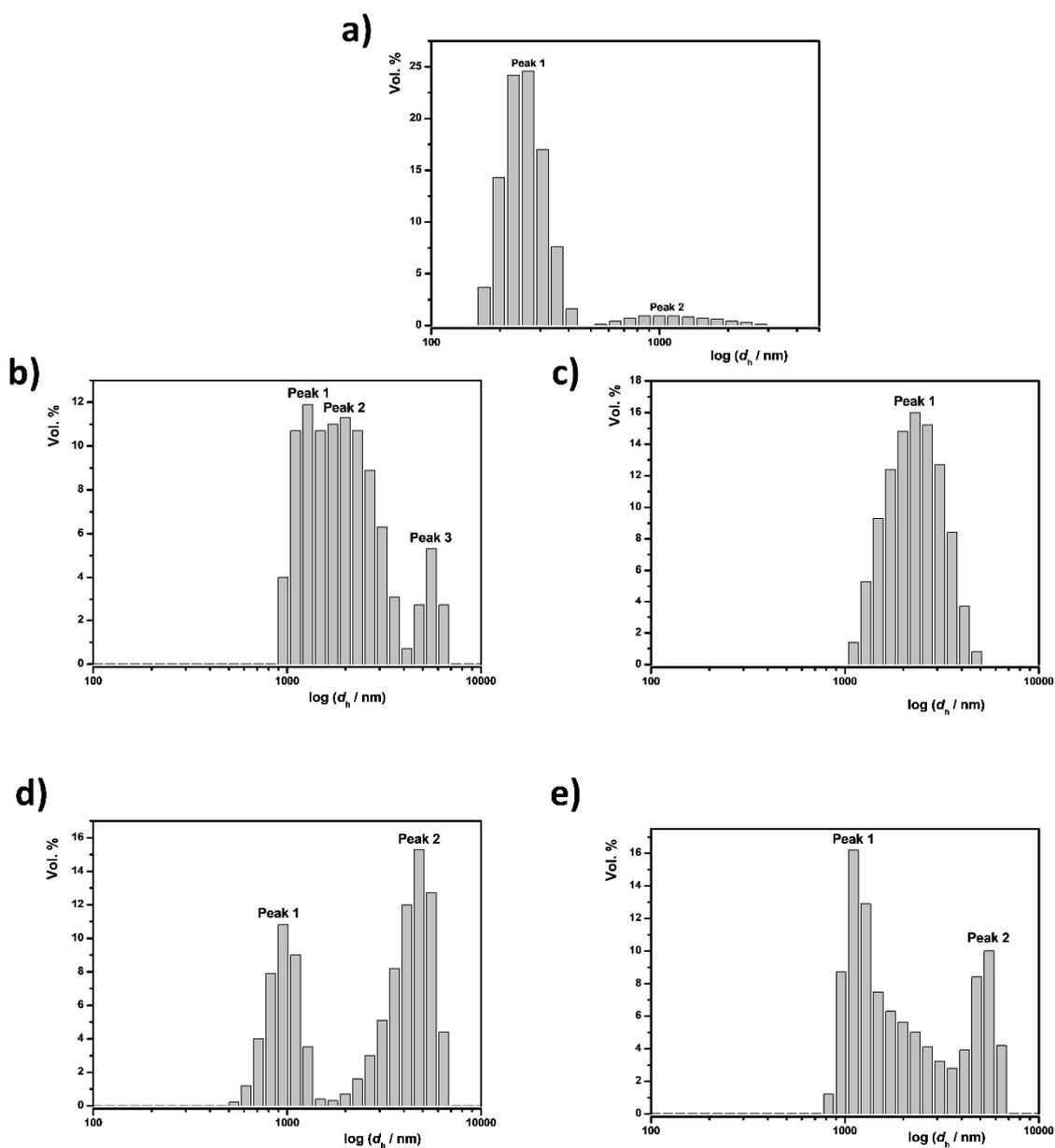


Figure S5. Distribution of particles' sizes obtained in system B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$, $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$) in a) DLS time-averaged experiment and b)-e) representative distributions obtained in time-resolved experiment at corresponding reaction times 15-17 min from the commencement of reaction.

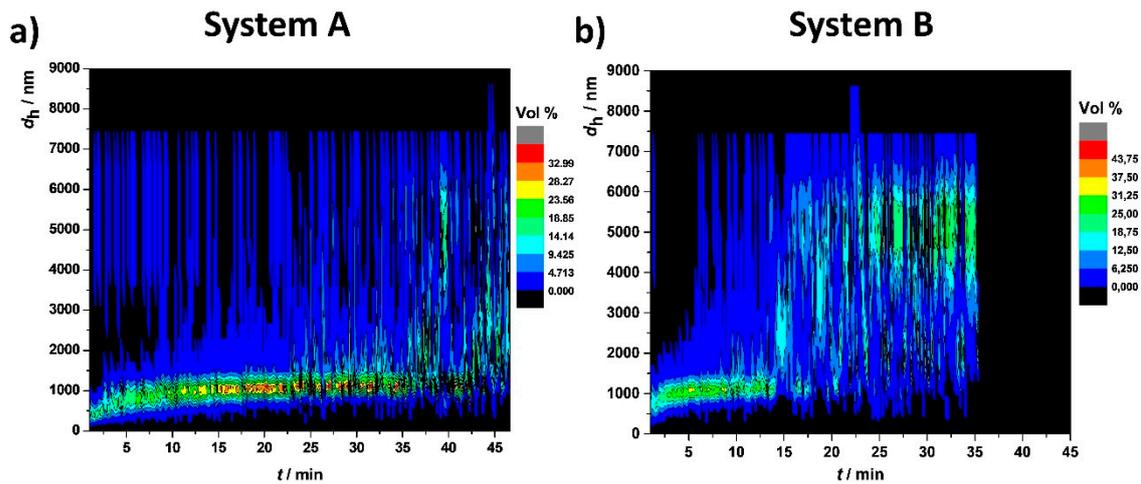


Figure S6. Changes of vol. % of particles formed in system a) A ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 3.5 \text{ mmol dm}^{-3}$) and b) B ($c(\text{CaCl}_2 \cdot 2\text{H}_2\text{O}) = c(\text{Na}_2\text{HPO}_4) = 4.0 \text{ mmol dm}^{-3}$) without stirring measured by DLS in time resolved experiment. $\text{pH}_{\text{init}} = 7.4$, $\vartheta = 25.0 \pm 0.1 \text{ }^\circ\text{C}$.