Snapshots of Calcium Carbonate Formation – A Step by Step Analysis

Supporting Information

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1. Details on the collection of TEM and cryo-TEM snapshots

TEM snapshots were taken directly after the scattering intensity profile showed the characteristic transition from stage II to stage III. The lag time until a drop of the solution was put on the TEM grid was about 10 s. ACC was identified by the absence of ED diffraction peaks and by EDX. The initially formed 30-50 nm particles were too small for collecting usable EDX data (Figure SI 3a-c). They could however be undoubtedly identified as $CaCO_3$ by EDX after they had grown to sizes of about 100 nm (Figure SI 3d).

Cryo-TEM snapshots were taken by transferring 1 mL of the solution to the vitrobot. The lag time from the start of nucleation until quenching of the solution in liquid propane could be estimated to be about 60-70s.

We observed different species in the cryo-TEM experiments (Figure SI 4a). Possible artifacts could originate from formed ice particles or propane. We considered only these particles to be ACC which were persistent upon gentle heating to -100 °C (Figure SI 4b) or under continuous exposure from the electron beam (Figure SI 4c and d). In the cryo-TEM snapshots, ACC had already grown to sizes of about 100 nm due to the increased lag time between nucleation and quench.

2. Additional data of the precipitation experiments without additive

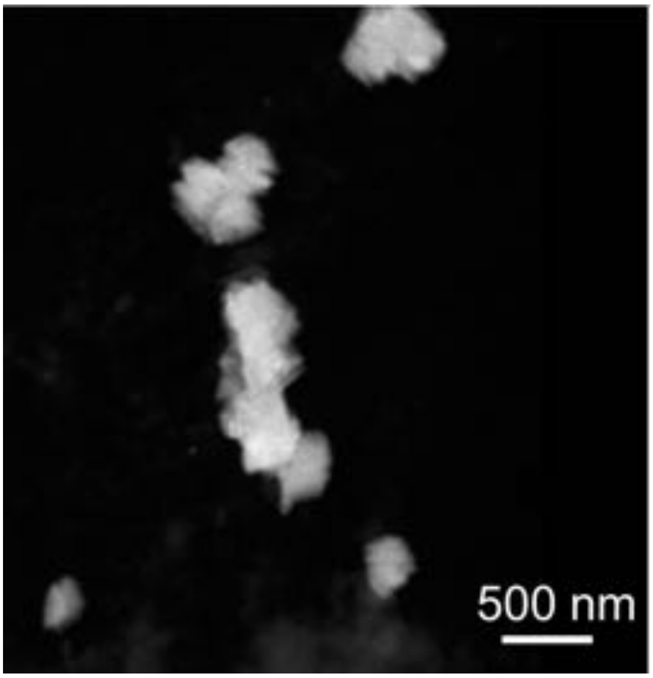

Figure S1. TEM snapshot taken after 18 minutes during the precipitation of $CaCO_3$. $[Ca^{2+}]$= [DEC]= 15 mM and [NaOH]= 12 mM.

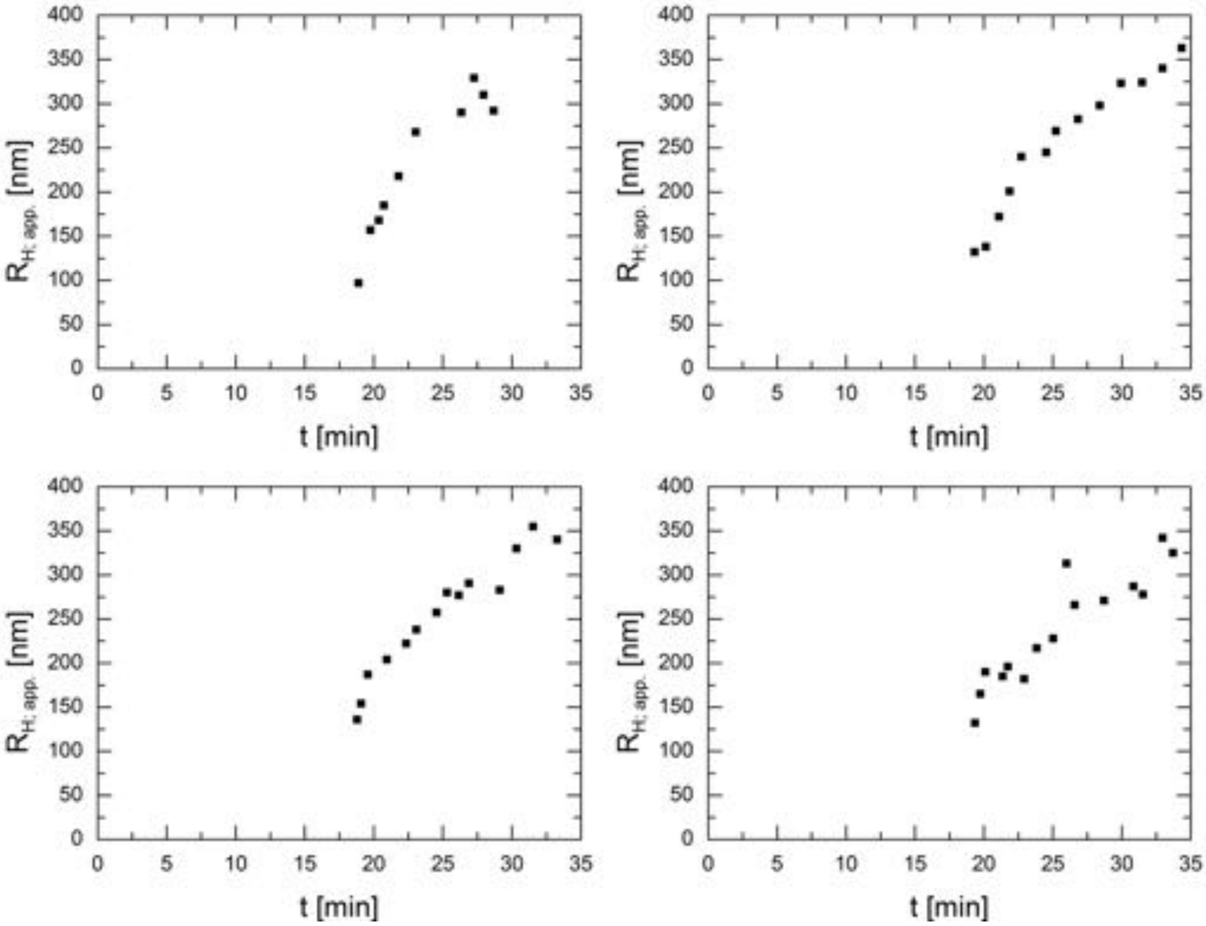

Figure S2. Growth curves acquired with DLS at concentrations of $[Ca^{2+}]$=[DMC]=10 mM and [NaOH]= 8 mM and a constant angle of $\theta = 30°$.

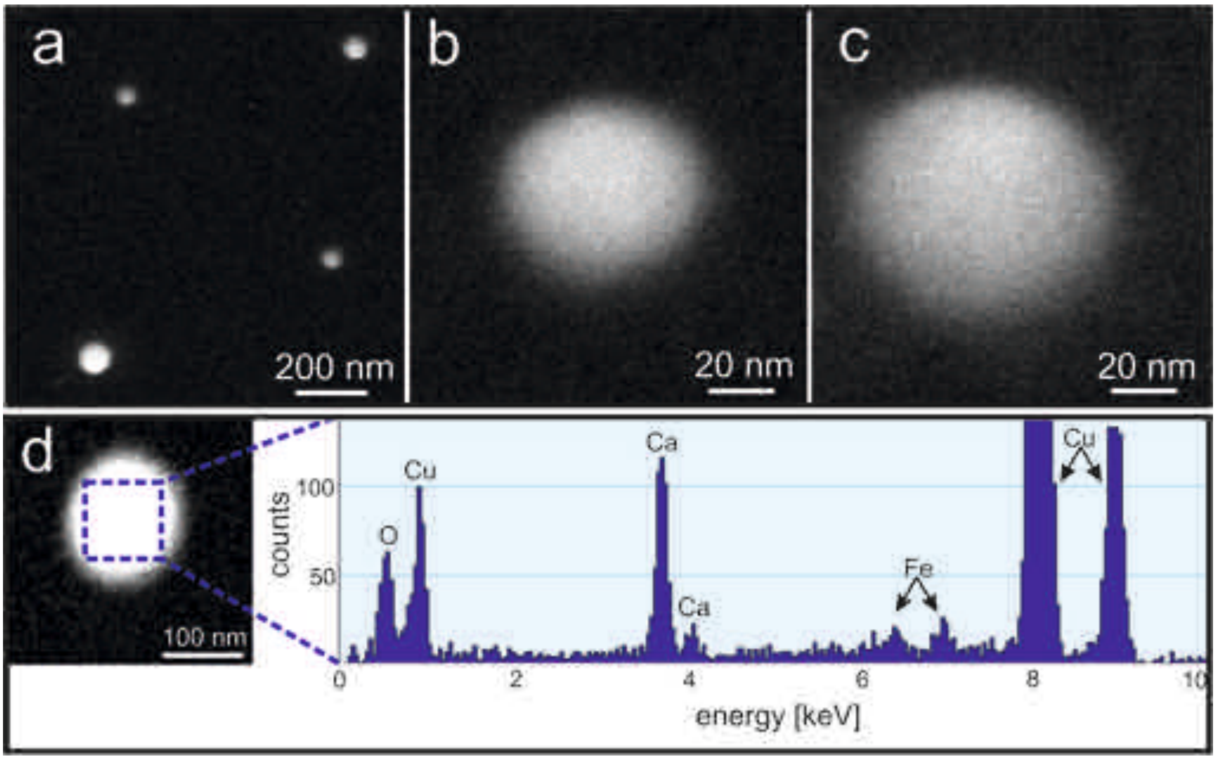

Figure S3. STEM images taken during the precipitation of $CaCO_3$ using $[Ca^{2+}]$= [DMC]= 10 mM, [NaOH]= 8 mM. (**a**)-(**c**) Snapshots taken directly after the beginning of stage III. The particles did not diffract. (**d**) Snapshot taken 1 minute after the beginning of stage III. EDX indicates the presence of $CaCO_3$. The Cu- and Fe-signal originate from the grid and the microscope, respectively.

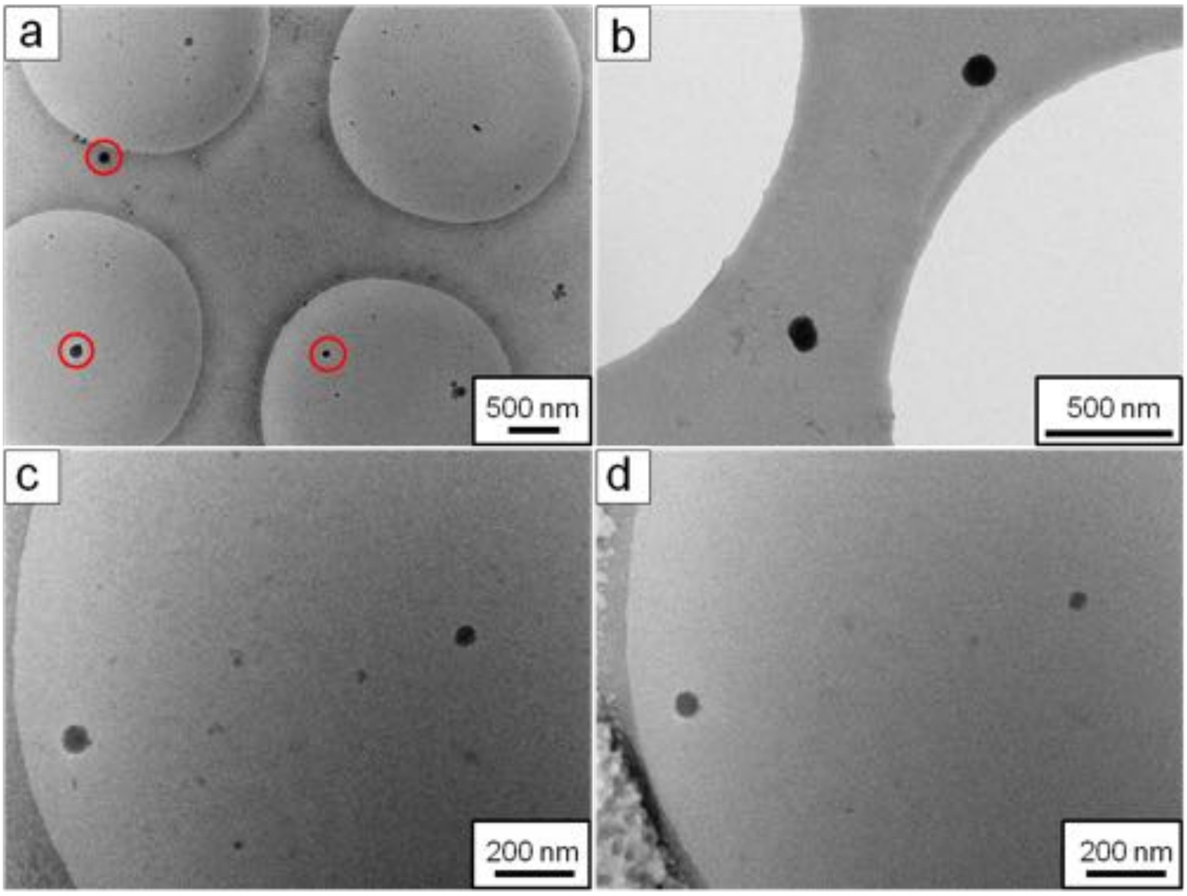

Figure S4. Snapshots taken 60 seconds after the beginning of stage III using [Ca^{2+}]= [DMC]= 10 mM, [NaOH]= 8 mM. (**a**) Cryo-TEM overview picture. The family of particles with higher contrast and sizes between 50-100 nm could be identified as ACC and are marked with a red circle. (**b**) ACC after slow unfreezing of the cryo-TEM specimen in vacuum. (**c**) and (**d**) ACC imaged in cryo-TEM is persistent after continuous exposure to the electron beam.

3. Additional data of the precipitation experiments with Na-PMA

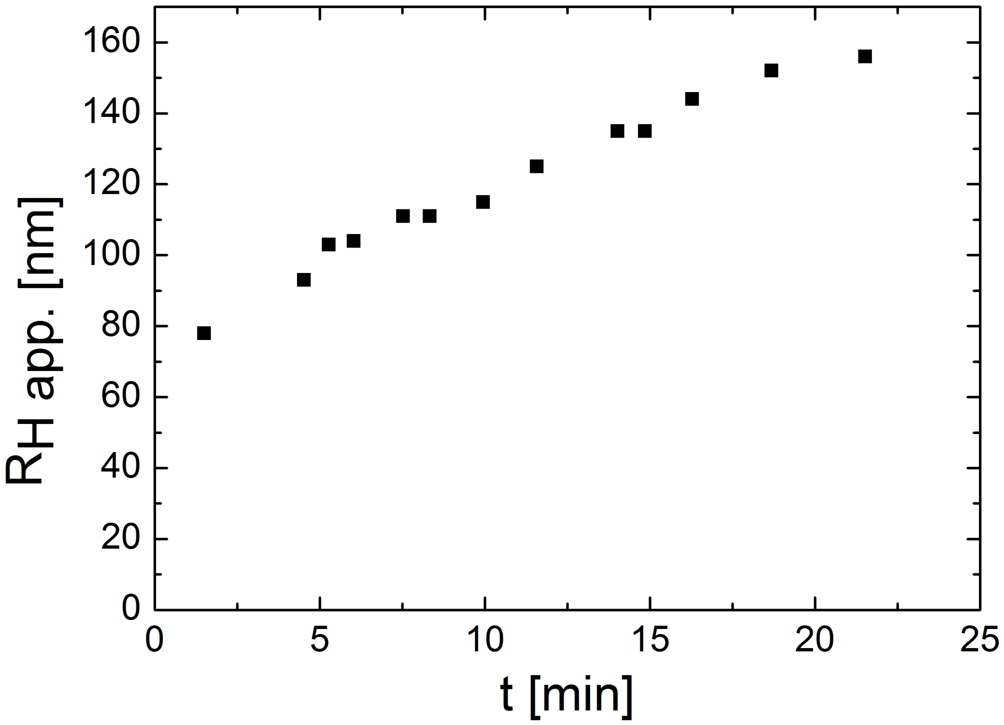

Figure S5. Apparent hydrodynamic radius of Ca-PMA aggregates formed in the absence of carbonate (DMC). [$CaCl_2$]= 10 mM, [Na-PMA] (M_w= 8300 g/mol)= 3 mM

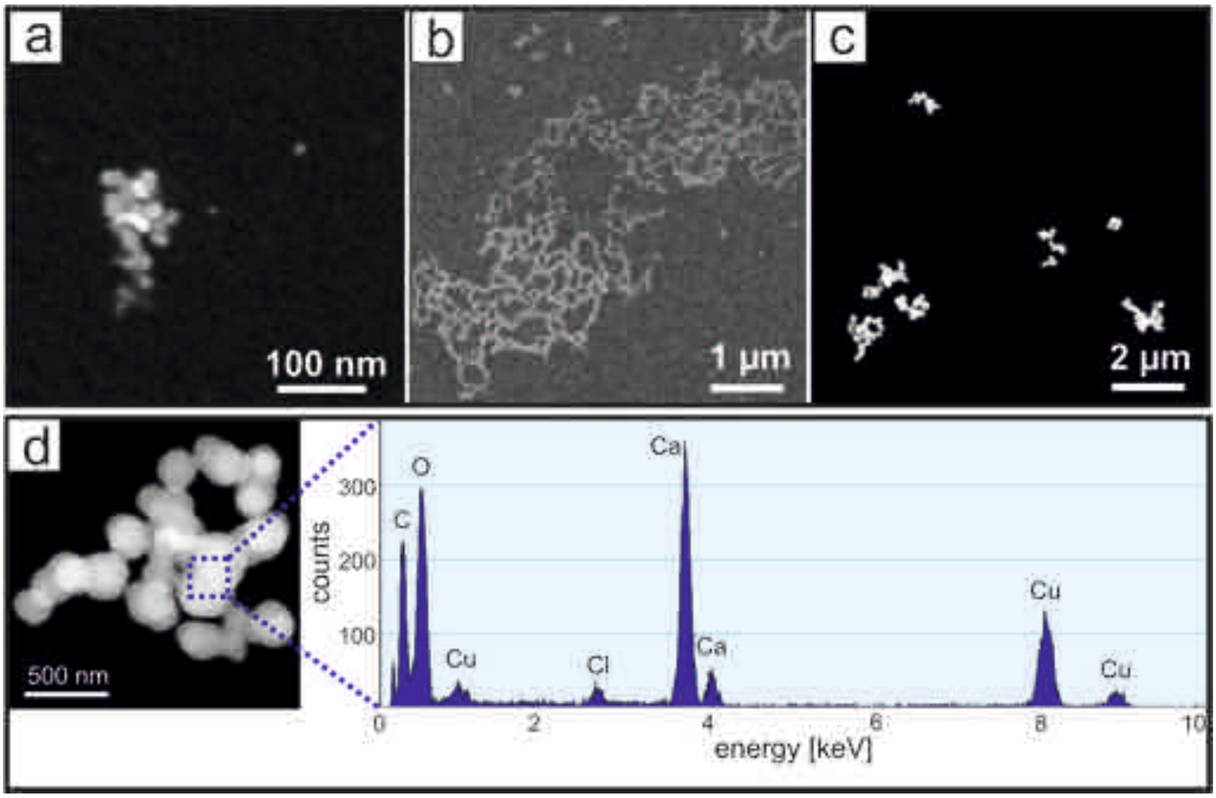

Figure S6. STEM images of critical intermediates during the precipitation of $CaCO_3$ in the presence of the short chain Na-PMA (M_w= 1200 g/mol) at a polymer concentration of 3 mM. (**a**) Ca-PMA aggregate during the prenucleation stage. (**b**) extended liquid $CaCO_3$ networks in the postnucleation stage. (**c**) and (**d**) ACC formation alongside the network structure.