

Supporting Information

Opposite Particle Size Effect on Amorphous Calcium Carbonate Crystallization in Water and during Heating in Air

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Table S1 Summary of Experimental Conditions.

approximate particle size	CaCl ₂ solution		Na ₂ CO ₃ solution		Solution after mixing and prior to precipitation		
	CaCl ₂ (mol/l)	Volume (ml)	Na ₂ CO ₃ (mmol)	Volume (ml)	CaCl ₂ (mM)	Na ₂ CO ₃ (mM)	Volume (ml)
200 nm	1	0.25	0.25	49.75	5	5	50
120 nm	1	0.5	0.5	49.5	10	10	50
87 nm	1	1	1	49	20	20	50
73 nm	1	2	2	48	40	40	50
66 nm	1	5	5	45	100	100	50

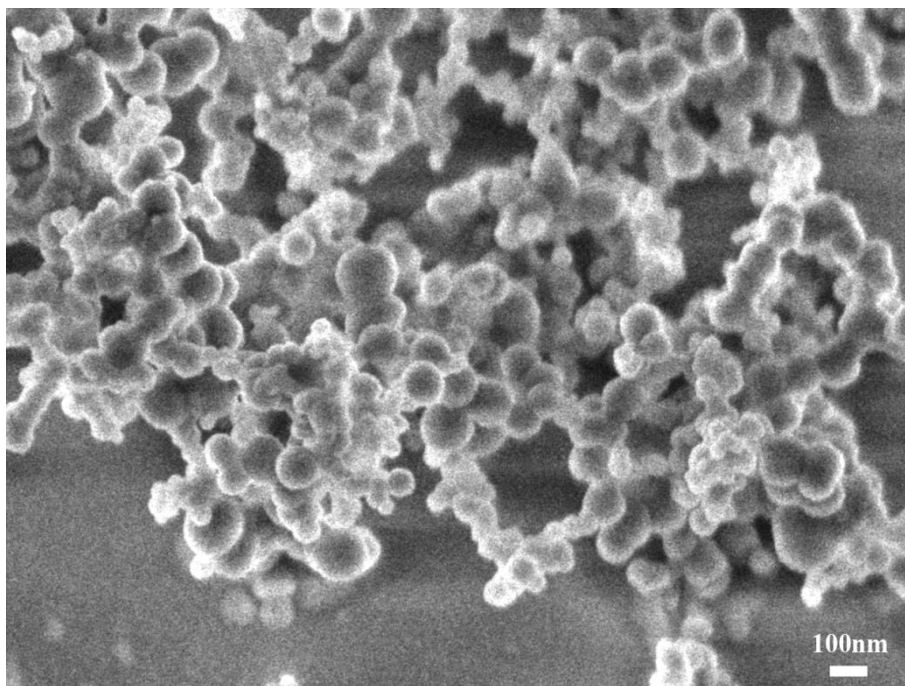


Figure S1. Cryo-SEM image of 73 nm sized sample. The reaction solution droplet was frozen using the liquid nitrogen and then cut for observation. The measured average diameter is 72.5 ± 28.0 nm, which suggests that the sample preparation procedure does not influence the particle size.

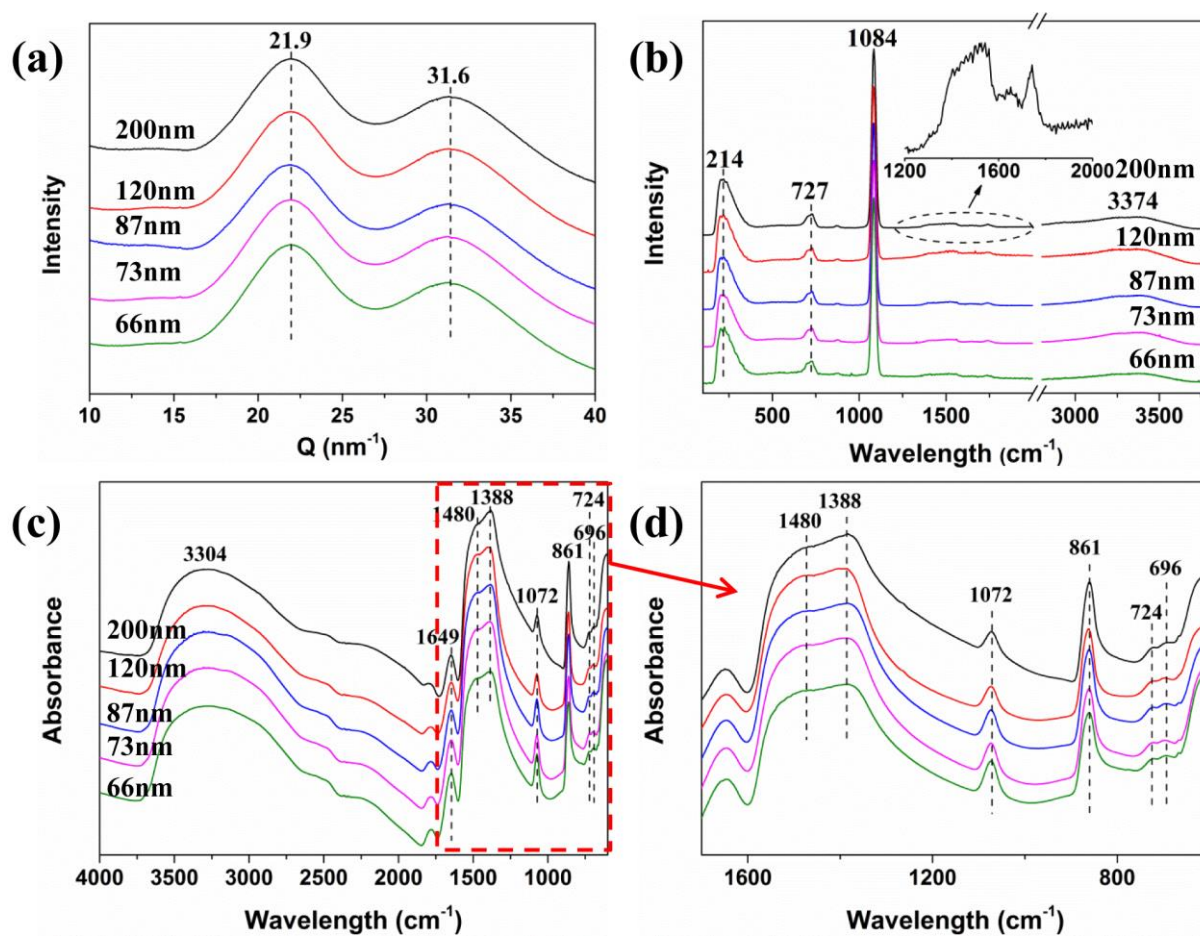


Figure S2. WAXS patterns (a) and Raman (b) and IR spectra (c-d) of ACC spheres with different particle sizes. No detectable differences among all samples could be found.

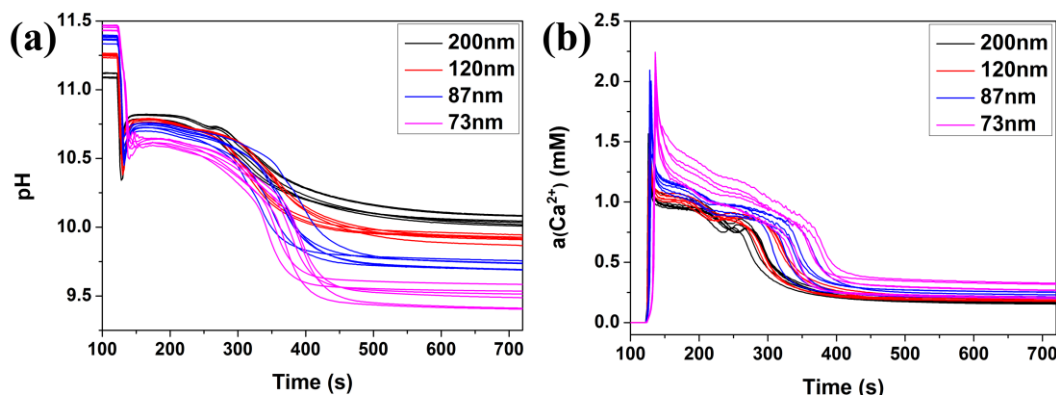


Figure S3. Reproducibility of the pH and Ca^{2+} activity measurement. With the accurate control over many parameters, both the changes of pH and calcium activity showed very good reproducibility.

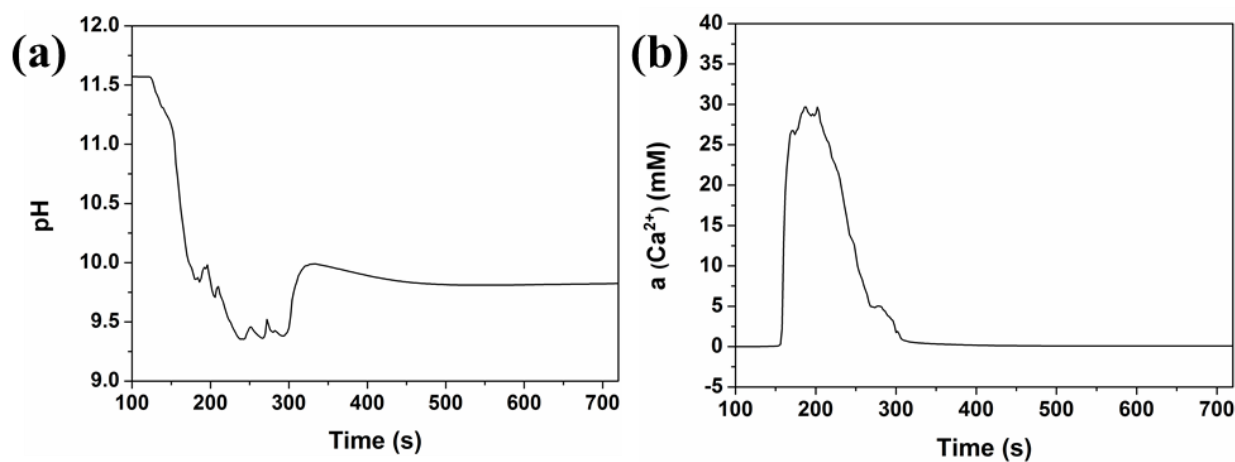


Figure S4. The pH (a) and calcium activity (b) evolution of the solution for experiment with ACC particle sizes of 66 nm. Here during the precipitation of ACC and its transformation until ~ 350 s both pH and Ca^{2+} -activity show an abnormal behavior, most likely caused by ACC precipitate on the electrodes themselves. The shocky pattern in both electrodes and high Ca^{2+} -activities/low pH could reflect local dissolution-reprecipitation events, though doesn't reflect the pH/ Ca^{2+} -activity in the bulk solution. For example, the 30 mM Ca^{2+} -activity in the right graph would correspond to a Ca^{2+} -concentration ~ 100 mM, indicating that nothing precipitated. Finally, after ~ 350 s the values for both pH and Ca^{2+} -concentration are comparable to the 40 mM samples, indicating that from here on the electrodes are free from precipitate.

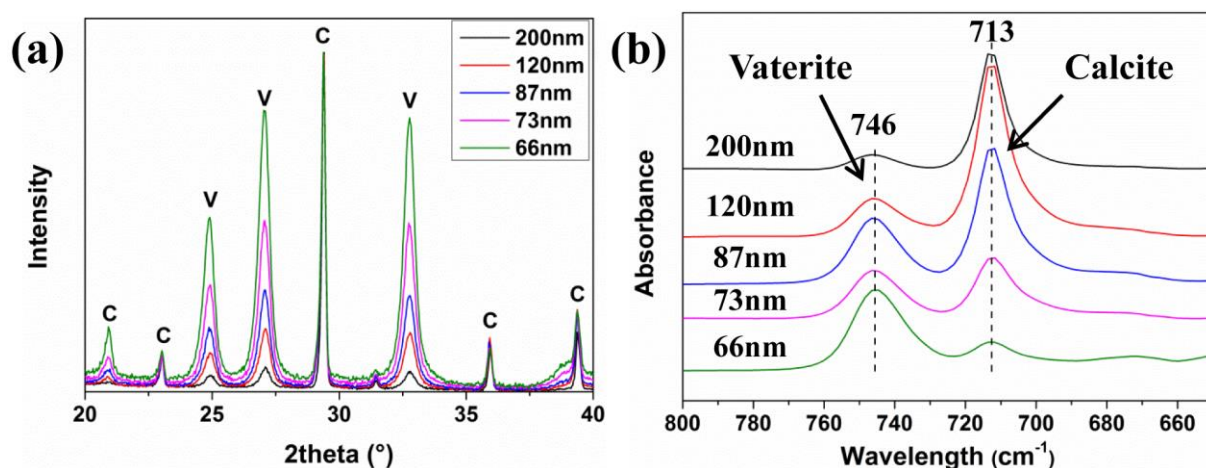


Figure S5. XRD patterns (a) and Infrared spectra (b) of the crystallized products from ACC particles with diameter of approximately 200 nm, 120 nm, 87 nm, 73 nm, and 66 nm. C and V in (a) stand for calcite and vaterite, respectively. The ratio between the intensity of peaks at 712 cm^{-1} (calcite) and 746 cm^{-1} (vaterite) in (b) decreased by ~ 30 times as particle size decreased from about 200 nm to 66 nm.

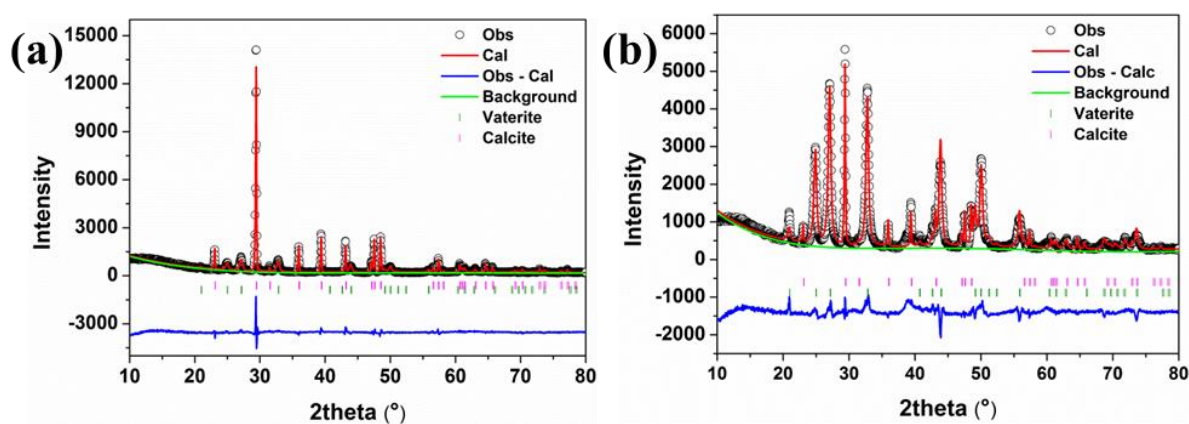


Figure S6. Rietveld refinement fits of the XRD pattern of the crystallized products from ACC particles with diameter of approximately 200nm (a) and 66nm (b). Obs and Cal in (a) stand for data observed from the XRD pattern and data calculated after rietveld refinement, respectively.

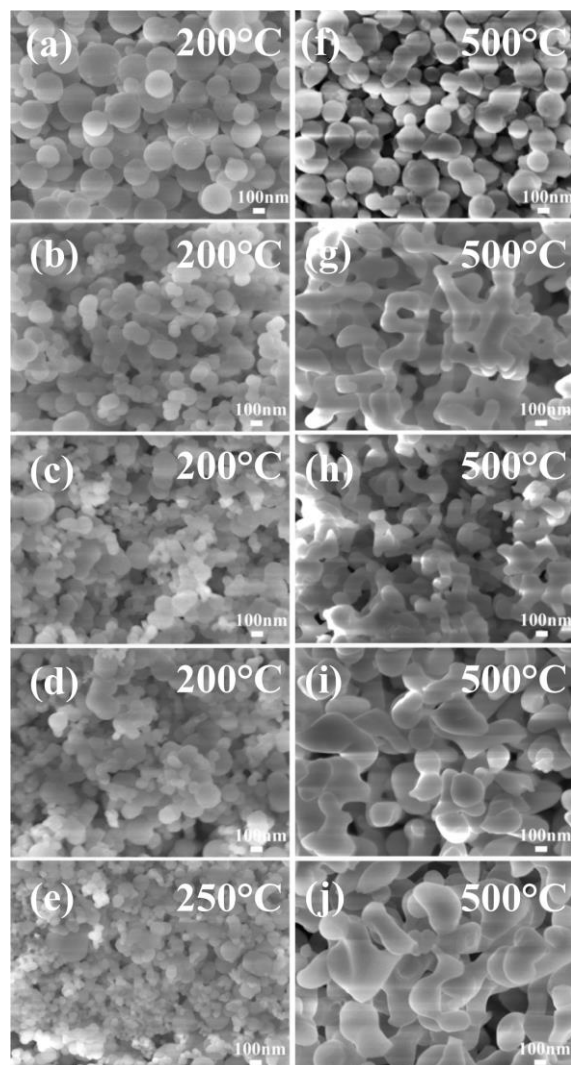


Figure S7. SEM micrographs of the sample taken after the 1st (a-e) and 2nd (f-j) crystallization of ACC with different particle size: 200 nm (a, f), 120 nm (b, g), 87 nm (c, h), 73 nm (d, i) and 66 nm (e, j).

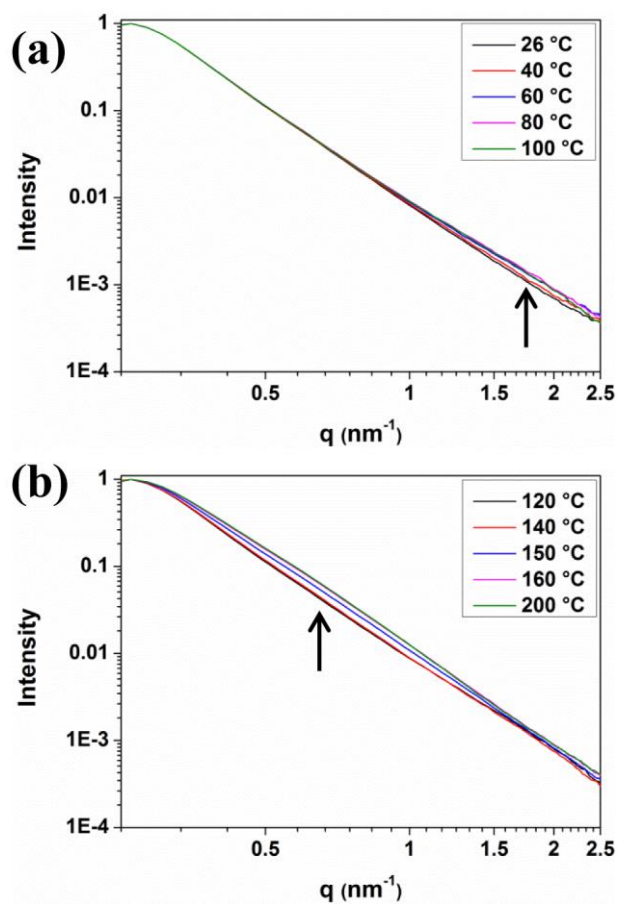


Figure S8. Stacked temperature series of selected SAXS patterns from 200 nm sized sample experiment (a-b), with the arrows illustrating the position of the peaks.