# Pseudomorphic transformation of amorphous calcium carbonate films follows spherulitic growth mechanisms and can give rise to crystal lattice tilting

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## Electronic Supplementary Information

## Experimental Details

*Materials*

All chemicals ammonium carbonate, calcium chloride dihydrate, poly (acrylic acid) (PAA) sodium salt (typical molecular weight 5100 g/mol), poly (vinylpyrrolidone) (PVP) (typical molecular weight 10000 g/mol) sodium hydroxide and hydrochloric acid were used without further purification. Glassware was cleaned with deionised water, immersed in 1 M HCl for 5 minutes and subsequently rinsed with deionised water before air drying.

*Crystallisation*

In a typical experiment, $CaCO_3$ crystallisation was performed in a closed 21 litre volume desiccator at 25 °C for 1 to 4 days. A 9 cm diameter petri dish was used as a crystallisation vessel. This contained 25 ml of a 10 mM $CaCl_2{\cdot}2H_2O$, 100 µg ml$^{-1}$ PAA solution set to pH 5 by addition of HCl. The petri dish was covered with clingfilm which was punctured with one needle hole and placed in a closed desiccator. One glass vial (10 ml) containing 3 g of freshly crushed ammonium carbonate powder was covered with parafilm punctured with a single hole and placed at the bottom of the desiccator. The crystals were recovered from solution rinsed with ethanol and air dried.

*Characterisation*

Optical microscopy was performed on an Olympus BX51 polarised optical microscope equipped with an Olympus XC50 digital camera (Olympus, UK). Powder X-ray diffraction (PXRD) patterns were recorded on a Kristalloflex D500 diffractometer (Siemens, Mannheim, Germany) using monochromatic Cu Kα radiation, $\lambda = 1.54184$ Å) at a scan rate of 1°min$^{-1}$ between 5 and 70°. Raman spectra were obtained using a Nicolet Almega XR Raman microscope employing the HeNe laser with an emission wavelength of 532 nm. FT-IR spectra were obtained from ground samples pressed into KBr pellets. Spectra were recorded between 400 and 2000 cm$^{-1}$ using an Impact 420 Nicolet FT-IR spectrometer, (Thermo Scientific, Waltham, USA). Thermogravimetric analysis (TGA) profiles were obtained between 25 and 1000 °C using a Netzsch STA 449 F3 TGA/DSC from 20 mg samples at a heating rate of 5 °C min$^{-1}$.

*Solid State NMR*

All solid state NMR experiments were recorded on a Bruker Advance 400 DSX spectrometer at $^1$H frequency of 399.87 and $^{13}$C frequency of 100.55 MHz. A three channel commercial Bruker 4 mm probe head at spinning speeds of 8000 ± 2 Hz and a temperature of 20 °C was used for all measurements. At those moderate spinning frequencies additional heating effects caused by air friction are insignificant and a correction of the effective sample temperature has not been performed. The $^{13}$C single pulse (SP) direct excitation experiments were carried out for all samples by a 30° pulse with a length of 4 µs and repetition time of 20 s acquiring 1 k transients. Additionally, to ensure almost full relaxation, resp. to record quantitative $^{13}$C NMR spectra, a 30° pulse of 4 µs and a recycle delay of 2200 s have been used averaging 128 transients. The $^1$H-$^{13}$C cross-polarisation (CP) experiments were recorded with contact times of 1 and 8 ms, resp. collecting 50 k and 12 k transients. For all $^{13}$C NMR experiments a two pulse phase modulation (TPPM) heteronuclear decoupling scheme was used. All spectra prior to processing were zero filled to 16 k points. The $^1$H and $^{13}$C chemical shifts were referenced to external adamantine as a secondary standard at 1.63 ppm and resp. 38.48 ppm.

*AFM*

Atomic force microscopy images were measured by bimodal dual AC imaging using a MFP-3D Infinity (Asylum Research, an Oxford Instruments Company, Santa Barbara, USA) and AC160 Cantilevers (Olympus, Tokyo, Japan). The probes were excited at the fundamental and third resonant frequency, resulting in two amplitude and two phase images.[38] Information gained from higher resonant modes are not disturbed by feedback filters and feedback mechanisms while measured giving more detailed and contrast rich images. The surfaces of the spherulites were investigated without further treatment. AFM data was in general analyzed in IGOR (Wavemetrics Portland, USA) using the routines provides by Asylum Research (MFP-Software Version 14), additionally the grain analysis was performed by the watershedding algorithms provided within gwyddion (Okružní, Czech Republic, www.gwyddion.de).

For analysis of cross-sections, e.g. for determination of flake thickness by AFM and SEM, spherulites were embedded in a 7:1 w/w ratio of Specifix 20 epoxy to Specifix 40 curing agent. Samples were allowed to cure overnight prior to further preparation. Mirror-polishing was performed by lapping on Allied MultiPrep Polishing System (Allied High Tech Products, Inc., Rancho Dominguez, USA). The lapping process used a waning series of micron-sized diamond polishing films. To prevent etching during preparation, water-based lubricants and polishing agents were eliminated—instead, Allied alcohol based “blue” lubricant was employed.

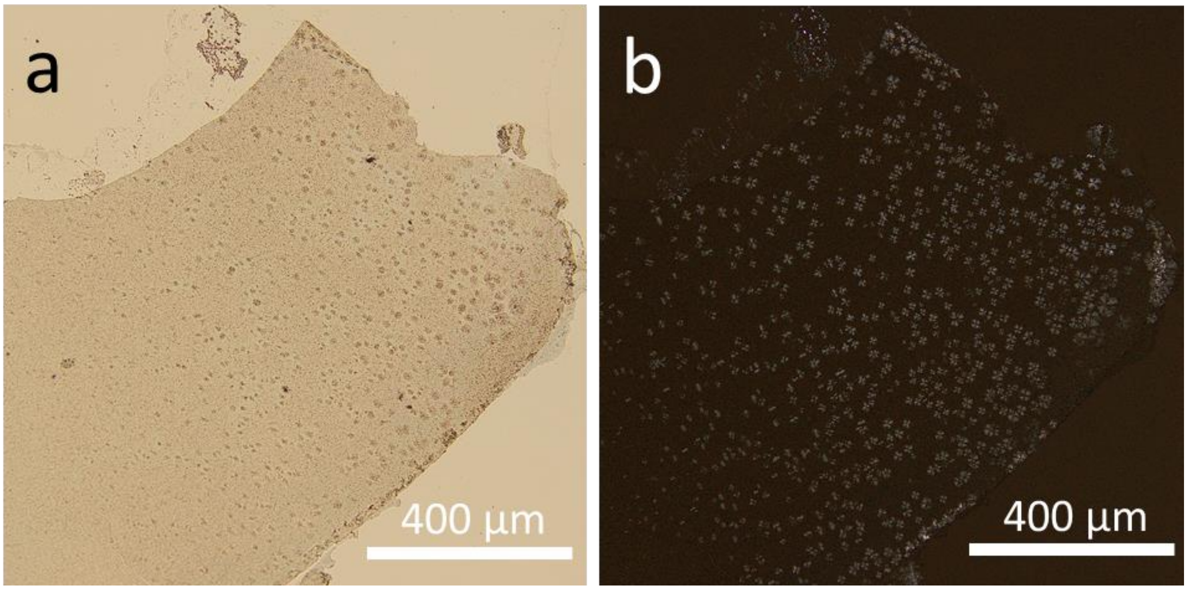

**Figure S1**. **a**) Optical micrograph of dried film formed at the air-water interface removed from the reaction solution after 40 hours. **b**) Optical microscopy image of the same film taken with crossed polarizers. Maltese crosses observed within the film indicate formation of crystalline birefringent calcium carbonate domains.

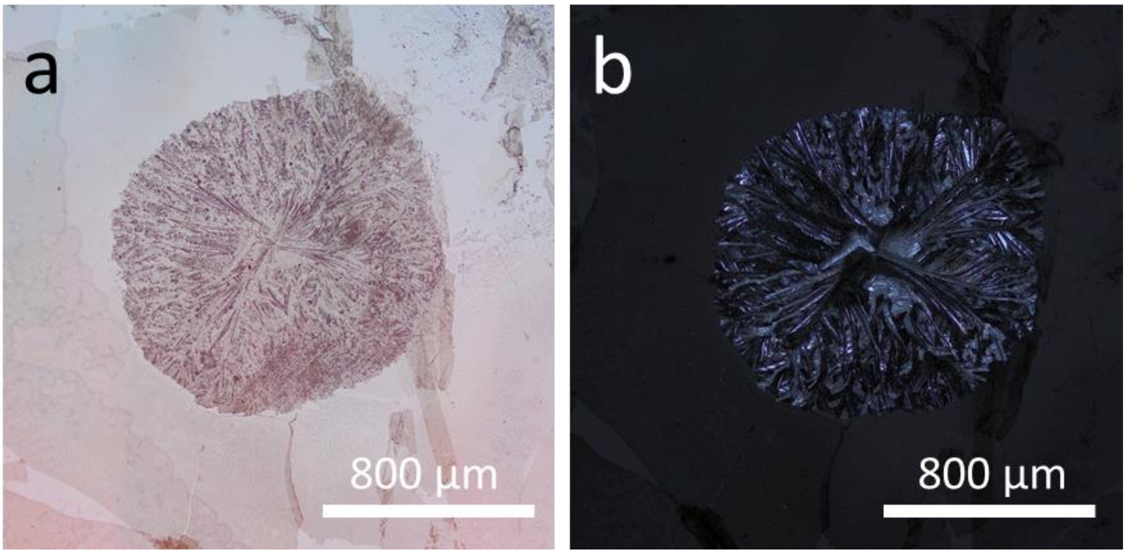

**Figure S2**. **a**) Optical micrograph of spherulite formed within an amorphous film at the air-water interface, removed from the reaction solution after 47 hours. **b**) Optical microscopy image of the same film taken with crossed polarizers at 40°, crystalline birefringent calcium carbonate spherulite evident within the non-birefringent amorphous film.

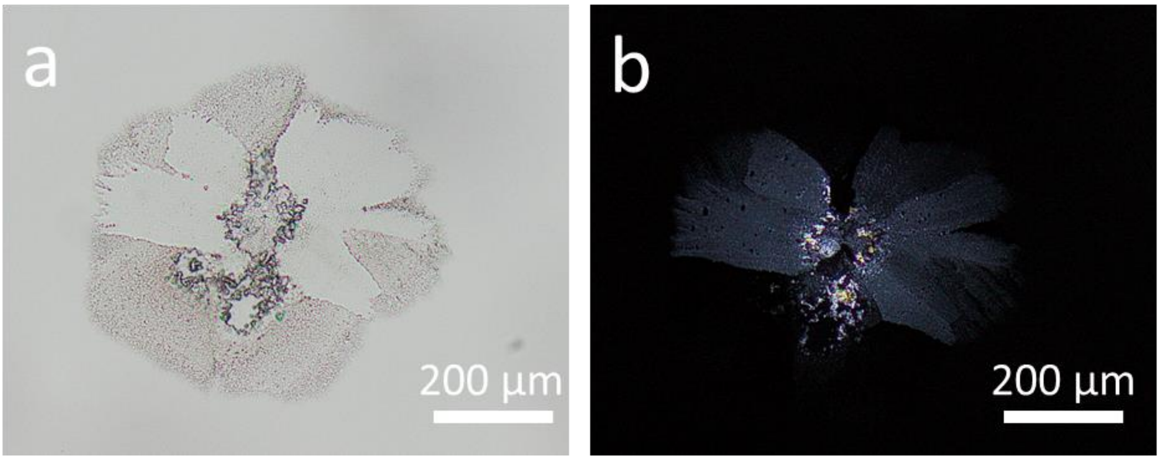

**Figure S3**. **a**) Optical micrograph of partially crystalline spherulite formed within an amorphous film at the air-water interface, removed from the reaction solution after 45 hours. **b**) Optical microscopy image of the same film taken with crossed polarizers, some domains within the calcium carbonate spherulite are crystalline as evidenced by birefringence, whereas other domains remain non-birefringent and amorphous.

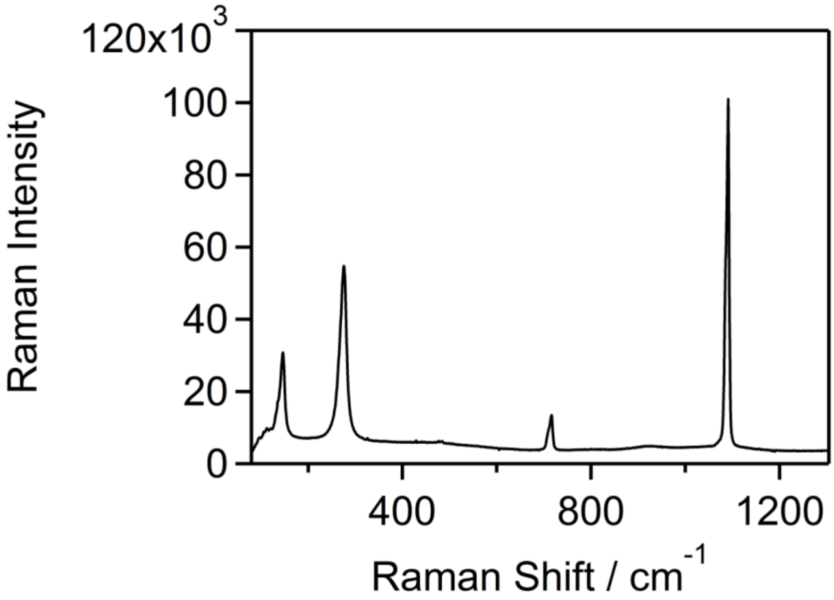

**Figure S4**. Raman spectra of calcium carbonate spherulites within amorphous film obtained after 52 hours of reaction time, Raman absorbance bands (1091 cm$^{-1}$, $v_1$ symmetric stretch), (716 cm$^{-1}$, $v_4$ in-plane bending), (276 and 146 cm$^{-1}$, lattice modes) are concordant with calcite.

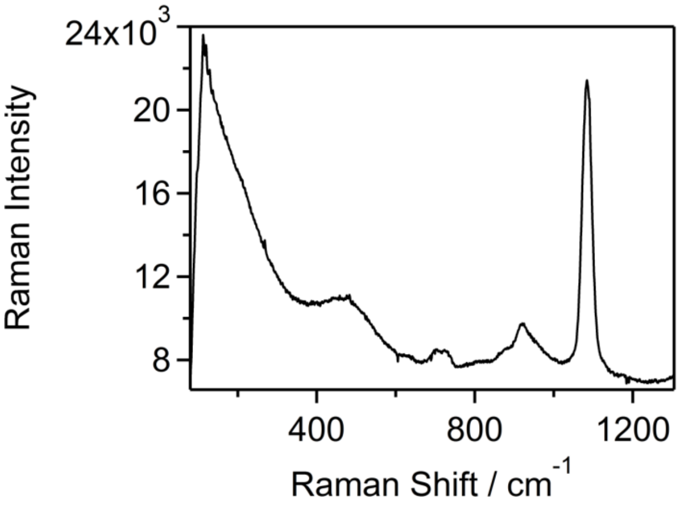

**Figure S5**. Raman spectra of amorphous calcium carbonate film obtained after 52 hours of reaction time, broad Raman absorbance bands present at 1082and 712 cm$^{-1}$ correspond to the $v_1$ and $v_4$ modes of calcite respectively, the peaks at 112, 924 and 475 cm$^{-1}$ arise from PAA which is also present within the amorphous film.

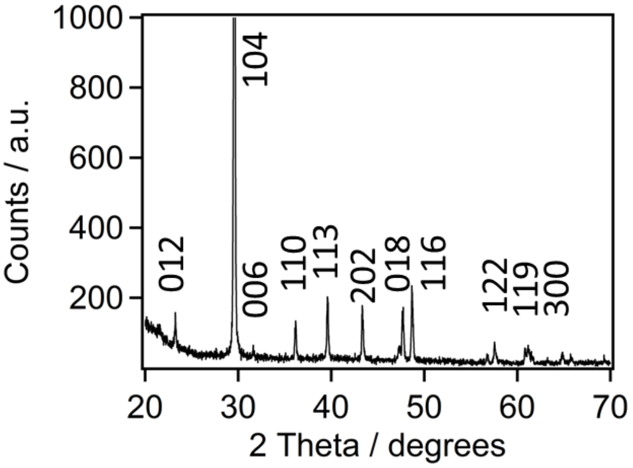

**Figure S6**. Powder XRD pattern of calcium carbonate spherulites removed from solution after a reaction time of 96 hours. Reflections at values of 2θ = 23, 29.5, 31.8, 36.1, 39.5, 43.2, 47.2, 47.6, 48.6, 56.6, 57.5, 60.7, 64.7 and 65.7° correspond to the (012), (104), (006), (110), (113), (202), (024), (018), (116), (211), (122), (214), (300) and (0012) lattice planes of the calcium carbonate polymorph calcite respectively.

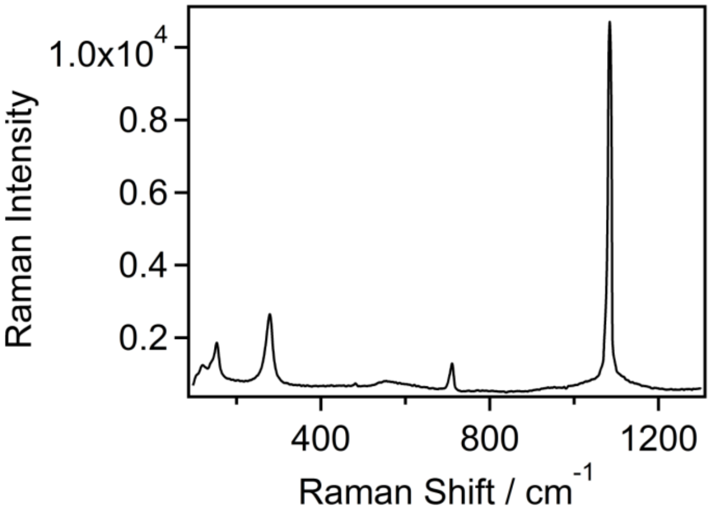

**Figure S7**. Raman spectra of calcium carbonate spherulites obtained after 96 hours of reaction time, Raman absorbance bands present (1085 cm$^{-1}$, $v_1$ symmetric stretch), (711 cm$^{-1}$, $v_4$ in-plane bending), (278 and 153 cm$^{-1}$, lattice modes) are concordant with calcite.

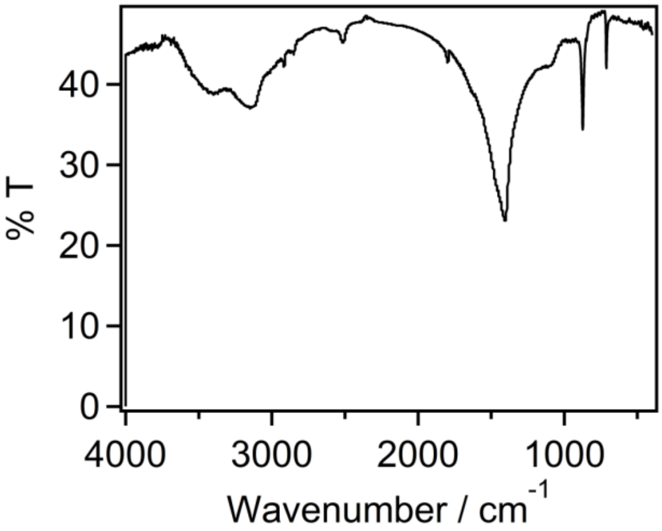

**Figure S8**. FTIR spectra of calcium carbonate spherulites removed from the reaction solution after 96 hours, absorbance bands present at 1400, 872 and 712 cm $^{-1}$ correspond to the $v_3$, $v_2$ and $v_4$ $CO_3^{2-}$ bands of calcite respectively.

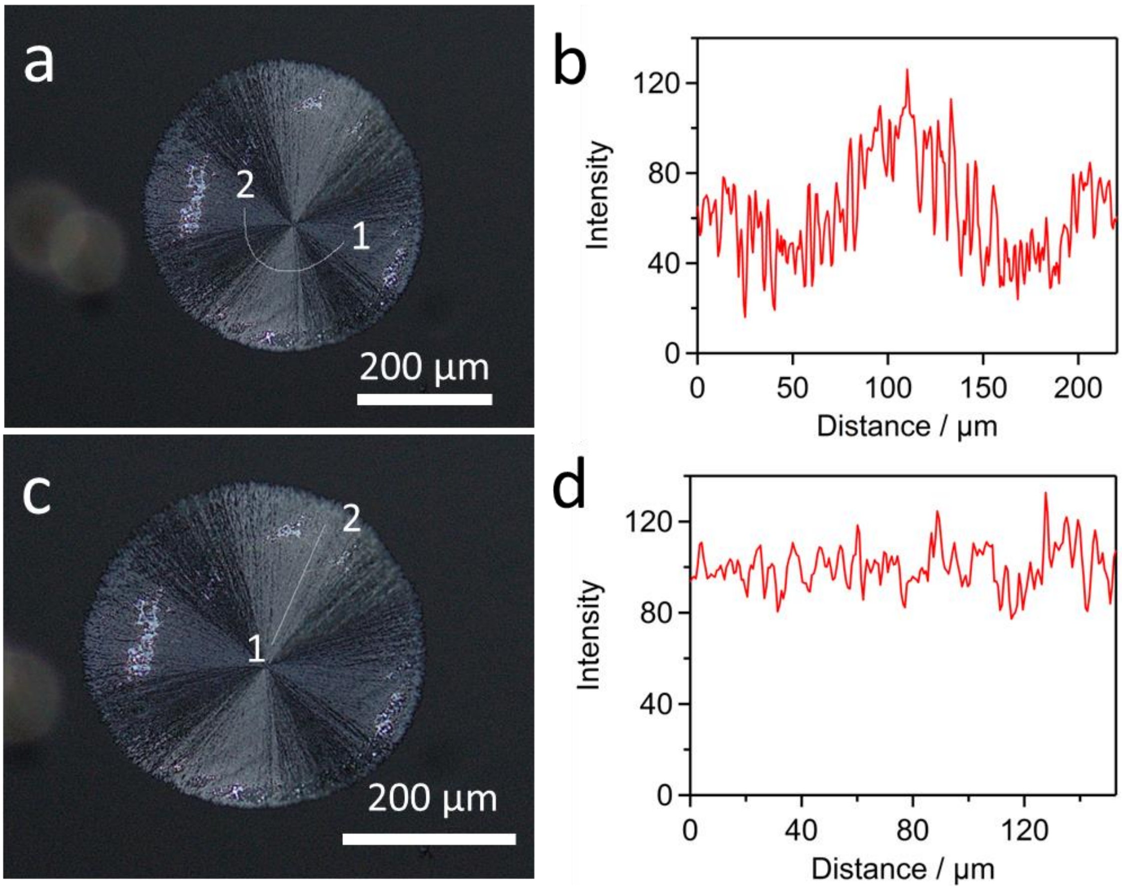

**Figure S9**. **a**) Optical micrograph of coarse closed spherulite depicting curved line from which intensity line profile in **b** was obtained. **b**) Line profile obtained from curved line between points 1 and 2 in **a**, 5 distinct areas of intensity are observed. **c**) Optical micrograph of coarse closed spherulite depicting straight line from which intensity line profile in **d** was obtained. **d**) Line profile obtained from straight line between points 1 and 2 in **c**, approximately constant intensity is indicative of crystalline alignment in c-axis of calcite.

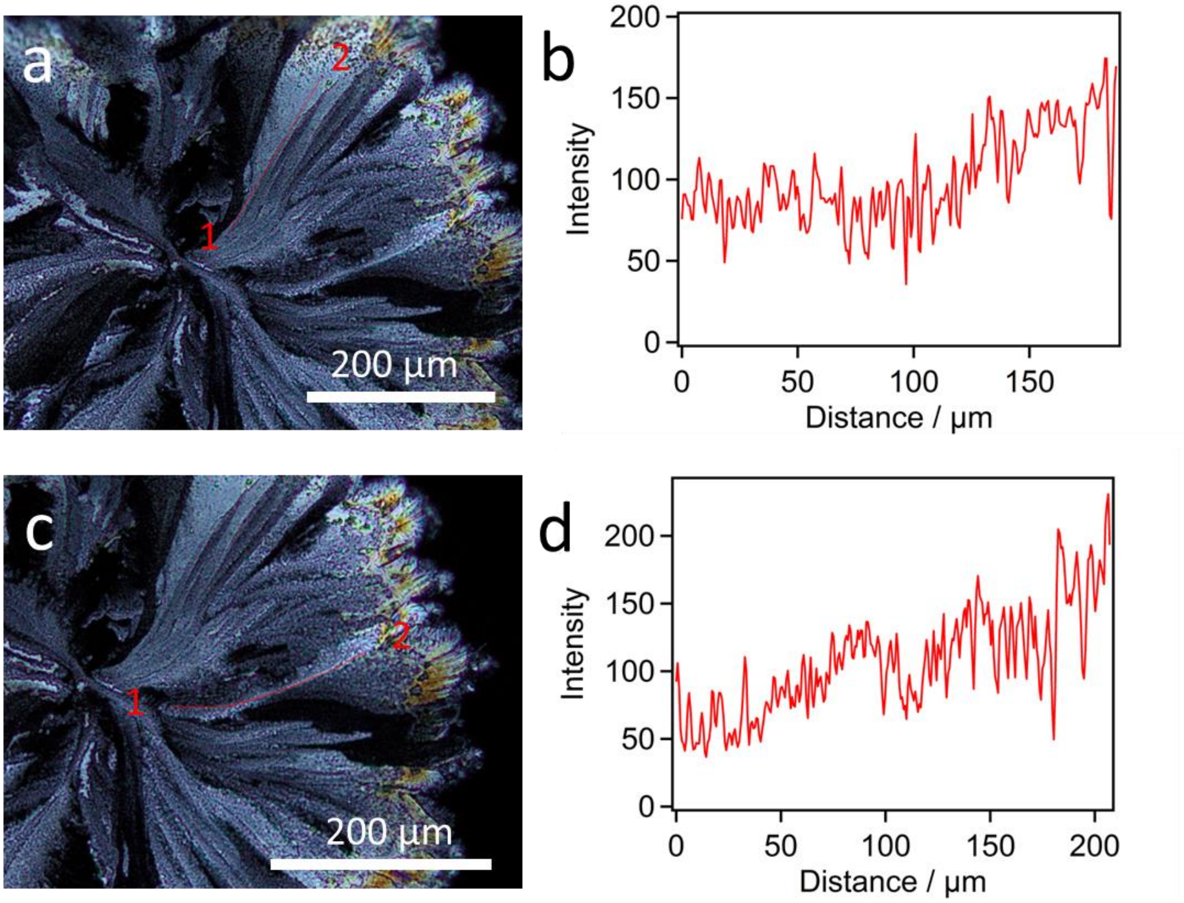

**Figure S10**. **a**) Optical micrograph of coarse closed spherulite depicting straight line from which intensity line profile in **b** was obtained. **b**) Line profile obtained from curved line between points 1 and 2 in **a**, alteration in intensity is indicative of a change in alignment of the calcite c-axis. **c**) Optical micrograph of coarse closed spherulite depicting curved line along spherulitic fibre from which intensity line profile in **d** was obtained. **d**) Line profile obtained from curved line between points 1 and 2 in **c**, alteration in intensity is indicative of a change in alignment of the calcite c-axis.

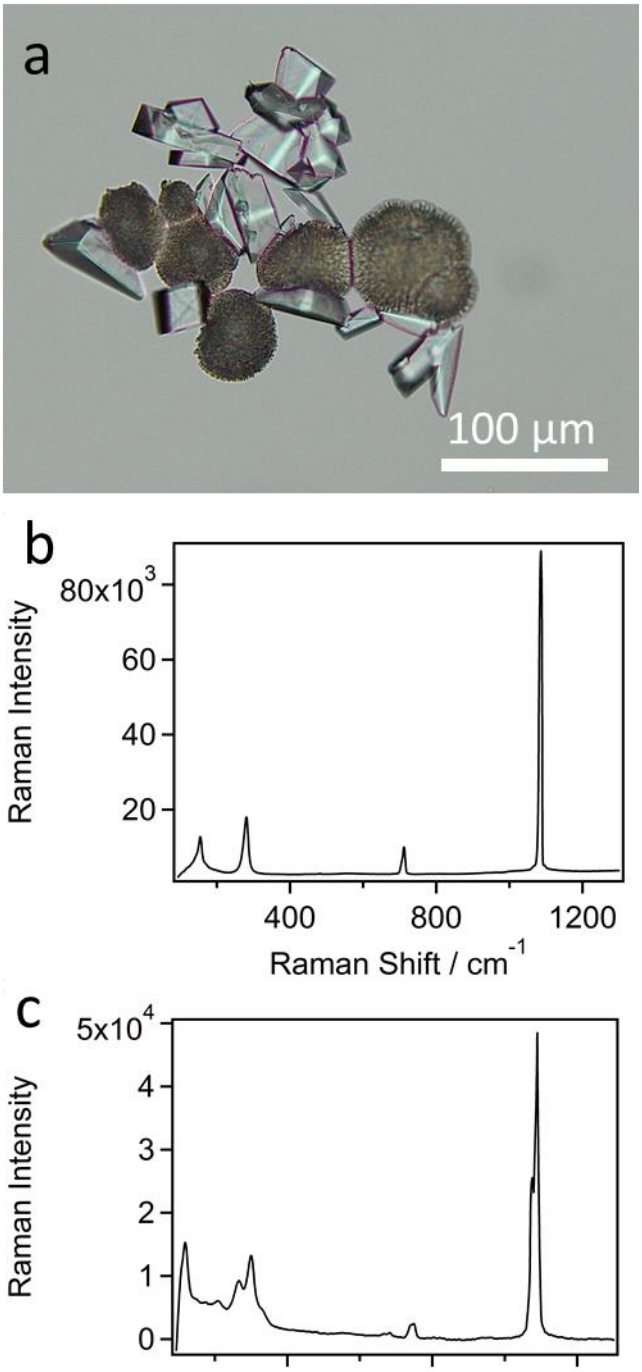

**Figure S11**. **a**) Optical micrograph of calcium carbonate particles present at the air water interface after 96 hours, particles were synthesized from a solution of 10 mM $CaCl_2$ in absence of PAA. **b**) Raman spectra of angular calcium carbonate particles present in **a**, Raman absorbance bands (1086 $cm^{-1}$, $v_1$ symmetric stretch), (712 $cm^{-1}$, $v_4$ in-plane bending), (281 and 155 $cm^{-1}$, lattice modes) are concordant with calcite. **c**) Raman spectra of spherical particles present in **a**, peaks (1090 and 1075 $cm^{-1}$, $v_1$ symmetric stretch), (747 $cm^{-1}$, $v_4$ in-plane bend) (300, 267 and 118 $cm^{-1}$, lattice modes) are concordant with vaterite.

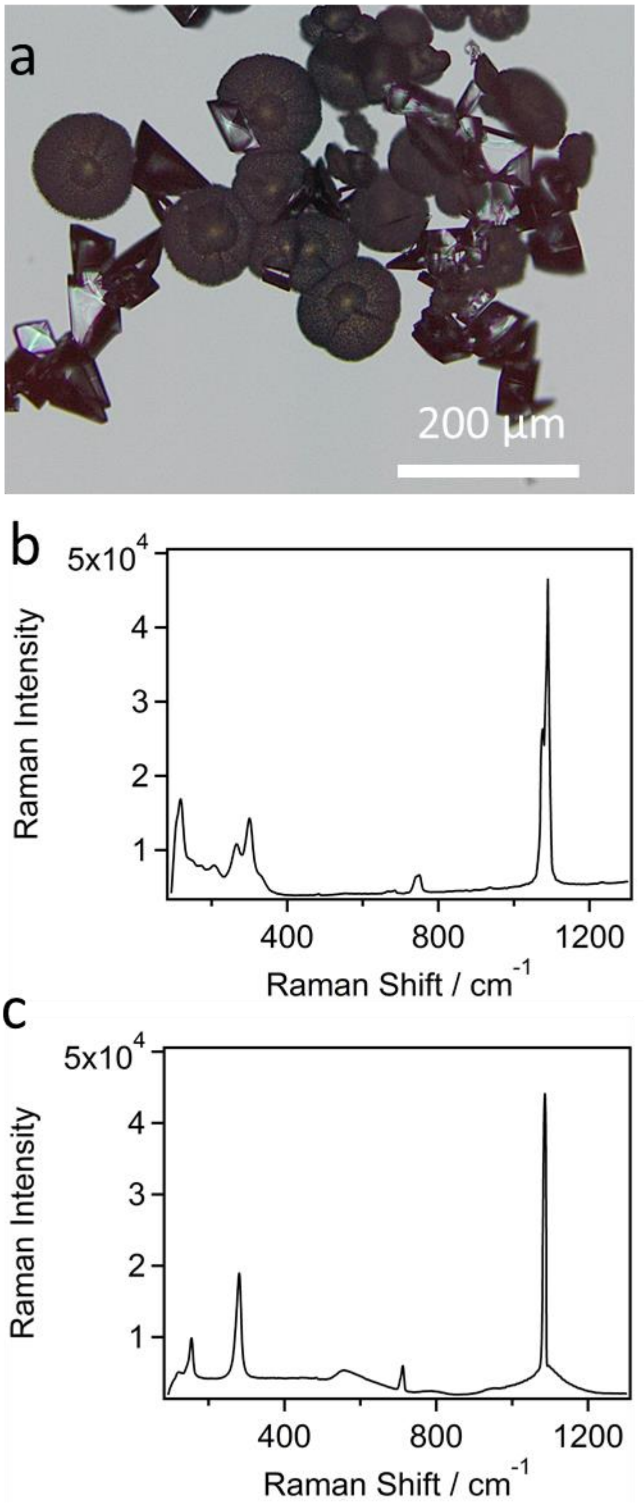

**Figure S12**. **a**) Optical micrograph of calcium carbonate particles present at the air water interface after 96 hours, particles were synthesized from a 10 mM $CaCl_2$ aqueous solution containing 100 µg/ml PVP. **b**) Raman spectra of spherical particles present in **a**, peaks (1090 and 1076 $cm^{-1}$, $v_1$ symmetric stretch), (745 $cm^{-1}$, $v_4$ in-plane bend), (299, 265 and 118 $cm^{-1}$, lattice modes) are concordant with vaterite. **c**) Raman spectra of angular particles present in **a**, Raman absorbance bands (1087 $cm^{-1}$, $v_1$ symmetric stretch), (712 $cm^{-1}$, $v_4$ in-plane bending), (280 and 155 $cm^{-1}$, lattice modes) are concordant with calcite.

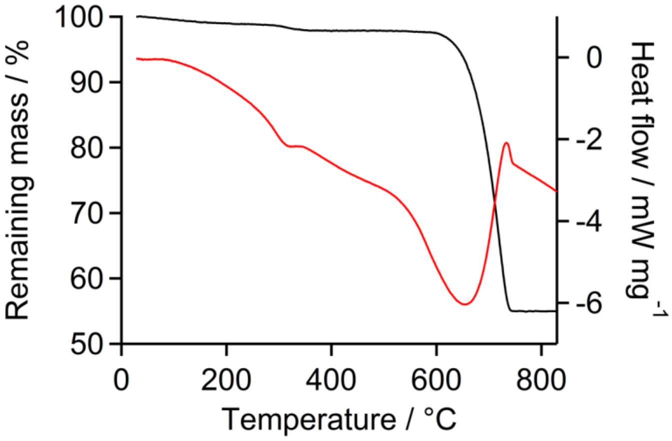

**Figure S13**. TGA (black line) and DSC (red line) profiles of calcium carbonate spherulites removed from solution after a reaction time of 96 hours.

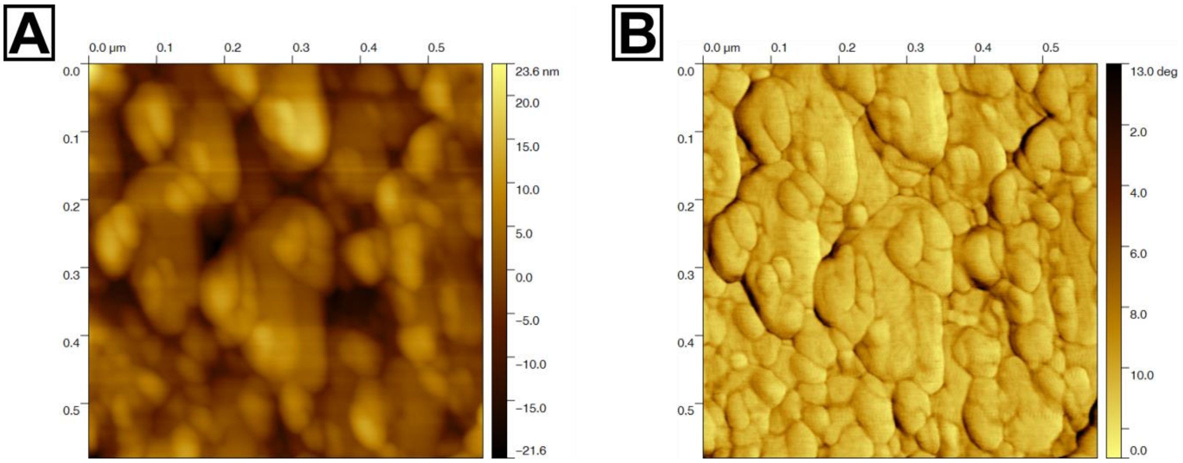

**Figure S14**. Standard AFM micrograph of the amorphous film obtained after 40 h. **A** height profile **B** phase image.

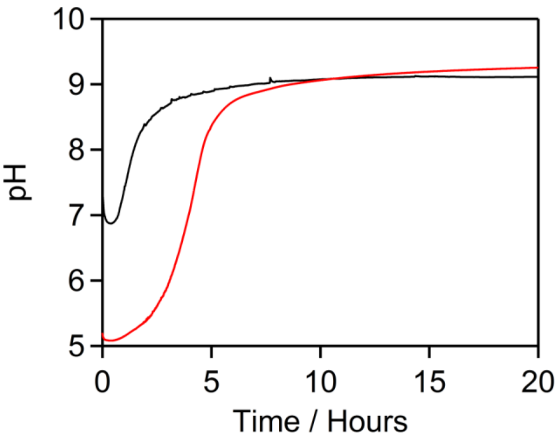

**Figure S15**. Reaction profile showing pH as a function of time for reaction solutions of differing initial pH. Black curve: starting pH of 7, red curve: starting pH of 5.