

Supporting Information

Growth of Micro-Ikebana on a Floating Substrate: A Method to Monitor Local Supersaturation Levels

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1. Experimental Section

Materials Strontium chloride hexahydrate (Wako, 99.0%), sodium silicate solution (water glass; Wako 57.0%, mol ratio $\text{SiO}_2/\text{Na}_2\text{O}$: 2.06), dimethyl carbonate (Wako, 98.0%), sodium hydrogen carbonate (Wako, 99.5%) and sodium hydroxide (Wako, 97.0%) were purchased commercially and used without further purification. Conductivity water was used for the preparation of all required solutions.

Glass cover slides (Matsunami NEO micro cover glass, 25×50 mm, thickness 0.12~0.17 mm) was cut into 13.0~14.0×25 mm pieces which were used as the crystallization substrate. The substrate was intensively cleaned with acetone and 2-propanol prior to use.

Crystallization Experiments. Crystallization experiments were conducted in disposable petri dishes with a diameter of 8.5 mm. Stock-solutions of strontium chloride hexahydrate (0.1 M) and sodium silicate were used as the strontium carbonate and silica precursor respectively. The sodium silicate stock-solution was prepared by mixing 10 g of commercial water glass with 90 g of water and the addition of 15 μL of NaOH (1 M). The stock-solutions were replaced weekly.

Coprecipitation of $\text{SrCO}_3/\text{SiO}_2$ was conducted with three different (CO_3^{2-})-sources: 1. Diffusion controlled dissolution of CO_2 from air; 2. Forced nucleation by the addition of sodium hydrogen carbonate (10, 1 mM) and, 3. Controlled homogenous nucleation induced by slow hydrolysis of dimethyl carbonate.

1.) In a typical diffusion controlled crystallization experiment 2 mL of the strontium chloride solution were mixed with 17.8 mL of water followed by the addition of 200 μL of silica precursor (resulting pH = 11.0). The crystallization medium was stirred intensively with a glass rod and the glass substrate was gently placed at the water surface subsequently. The crystallization setup was covered with a Büchner funnel to avoid movement of the sample due to air movement (e.g. lab ventilation system) and contamination with dust on one side and to provide a gentle, homogenous air (CO_2) flow towards the water surface on the other side. The coprecipitation of SrCO_3 and SiO_2 occurred due the dissolution of CO_2 in the crystallization medium and the resulting *in situ* formation of CO_3^{2-} and 2H^+ . The precipitation reaction was terminated after 8 h. Therefore the sample was removed from the water surface and washed copious times with water and EtOH. The sample was allowed to dry in air for further investigations with optical and electron microscopy.

2.) To show that the location of crystal-nucleation be controlled by the addition of HCO_3^- the previously described crystallization medium was produced using a petri dish as a reaction container. Afterwards the glass slide was placed at the water surface followed by subsequent covering of the setup with a Büchner funnel. The sample was allowed to rest for 10 min at the water surface to establish an adsorption/desorption equilibrium of the precursor species. Subsequently a burst of 100 μL NaHCO_3 (10 or 1 mM) was gently released within 30 s towards one edge of the substrate (Figure S1). In total 3 burst of NaHCO_3 were added to the reaction in a time interval of 5 min. between

each NaHCO_3 -burst the setup was covered again with the Büchner funnel. After the last burst the substrate was allowed to rest for 5 min at the water surface and was then removed. The substrate was cleaned as described previously.

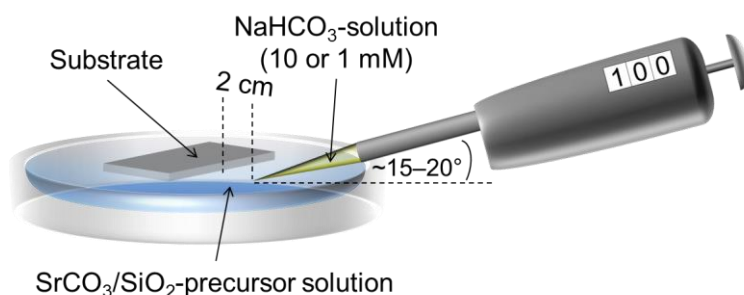


Figure S1. Experimental setup of the NaHCO_3 -burst experiments. The NaHCO_3 solution was released via Eppendorf pipette in a distance of 2 cm towards the edge of the substrate at an angle of approximately $15\text{--}20^\circ$. The pipette-tip was held at the air/water interface.

3.) To generate a homogenous nucleation dimethyl carbonate was used as a source of CO_3^{2-} . The crystallization medium was analogue to the previous experiments and poured into a petri dish. After substrate was placed at the air/water interface, $100\ \mu\text{L}$ ($1.19\ \text{mmol}$) of dimethyl carbonate were added to the crystallization medium. Subsequently the petri dish was sealed with parafilm to avoid diffusion of air (CO_2) to the water surface and the thereby affiliated formation of CO_3^{2-} and H^+ . The diffusion of the confined air within the petri dish could not be avoided (Figure S2). The reaction was terminated after 4 h and the sample was cleaned as described previously.

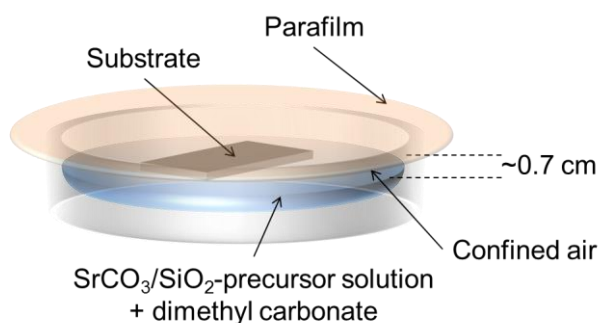


Figure S2. Experimental setup of $\text{SrCO}_3/\text{SiO}_2$ formation induced by the addition of Me_2CO_3 .

Image Processing and Analysis. The prepared samples were investigated by optical microscopy using an Olympus BX51 microscope attached with Olympus DP73 camera (Figure S3). Typically a digital bright-field image (Figure S3a) as well as an image using a cross-polarization filter (Figure S3b) was taken of the same region. The number of crystals N_d as well as the area cover by the crystals ($\text{CA} = \text{covered surface area}$) was determined by a graphical evaluation of the cross-polarized images using the computer program ImageJ (1.47v). Cross-polarized images were chosen since they exhibit a good contrast and crystalline morphologies can be observed easily, whereas some crystals e.g. leave like structures appear translucent in the normal bright-field image and thus are not recognized by the program. After setting a color threshold (Figure S3c) a black-and-white mask (Figure S3d) is generated and evaluated by the computer program. Comparing Figure S3b with

Figure S3d it can be recognized that the structures evaluated in the count-mask greatly matches the size, shape and surface area of the observed crystals in the cross-polarized image.

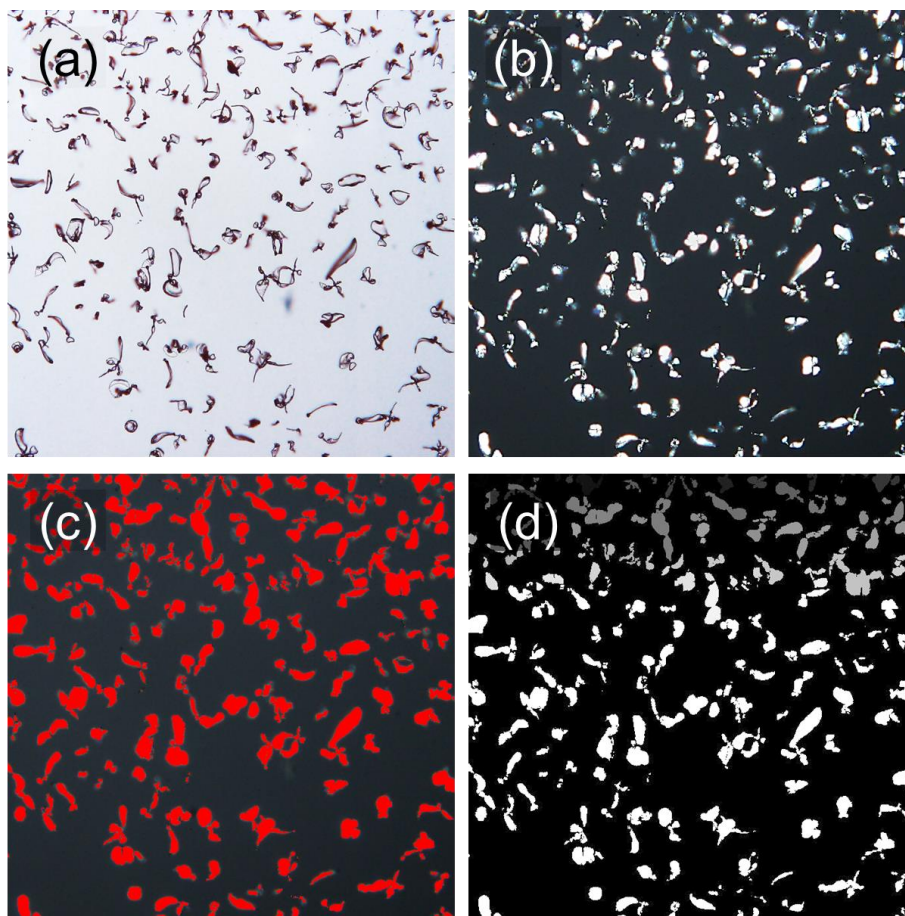


Figure S3. Typical evaluation of crystallization images. (a) Optical bright-field micrograph. (b) Corresponding image with cross-polarization filter. (c) Adjustment of color threshold. (d) Evaluated crystal-count-masks (black-and-white image) using ImageJ (1.47v). Dimensions of all images: 1.5×1.5 mm.

SEM measurements. After cleaning and drying of the substrate, the samples were investigated by scanning electron microscopy using a Keyence 3D-VE8800 or a JEOL JSM-7500F. We abstain from any coating or sputtering of the samples (e.g. carbon coating or gold sputtering) to provide a pure and not falsified surface structure.

EDX measurements. The $\text{SrCO}_3/\text{SiO}_2$ crystals were peeled off the glass substrate using a carbon tape. The EDX measurements of resulting carbon tape substrate were conducted using a JEOL JSM-7500F.

2. Additional Images and Diagrams

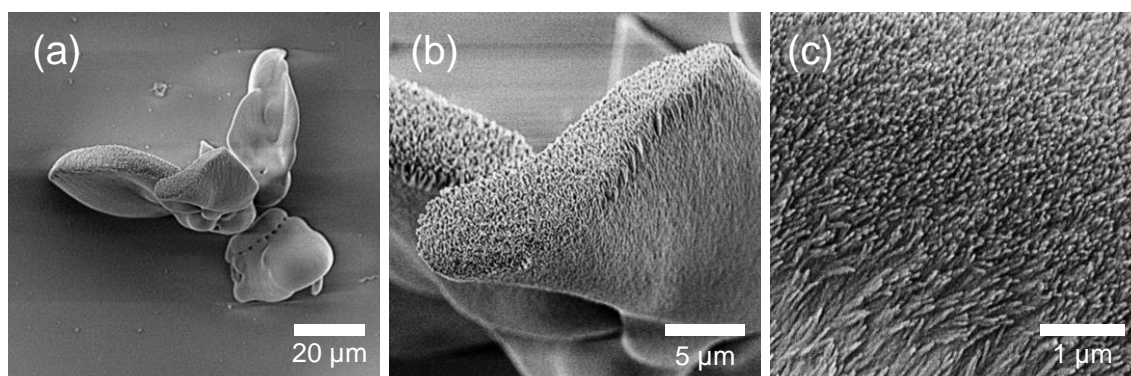


Figure S4. SEM micrographs of a typically obtained crystal morphology. The different magnifications show that the macroscopic crystal-system is generated by a self-assembled alignment of small fibrous units.

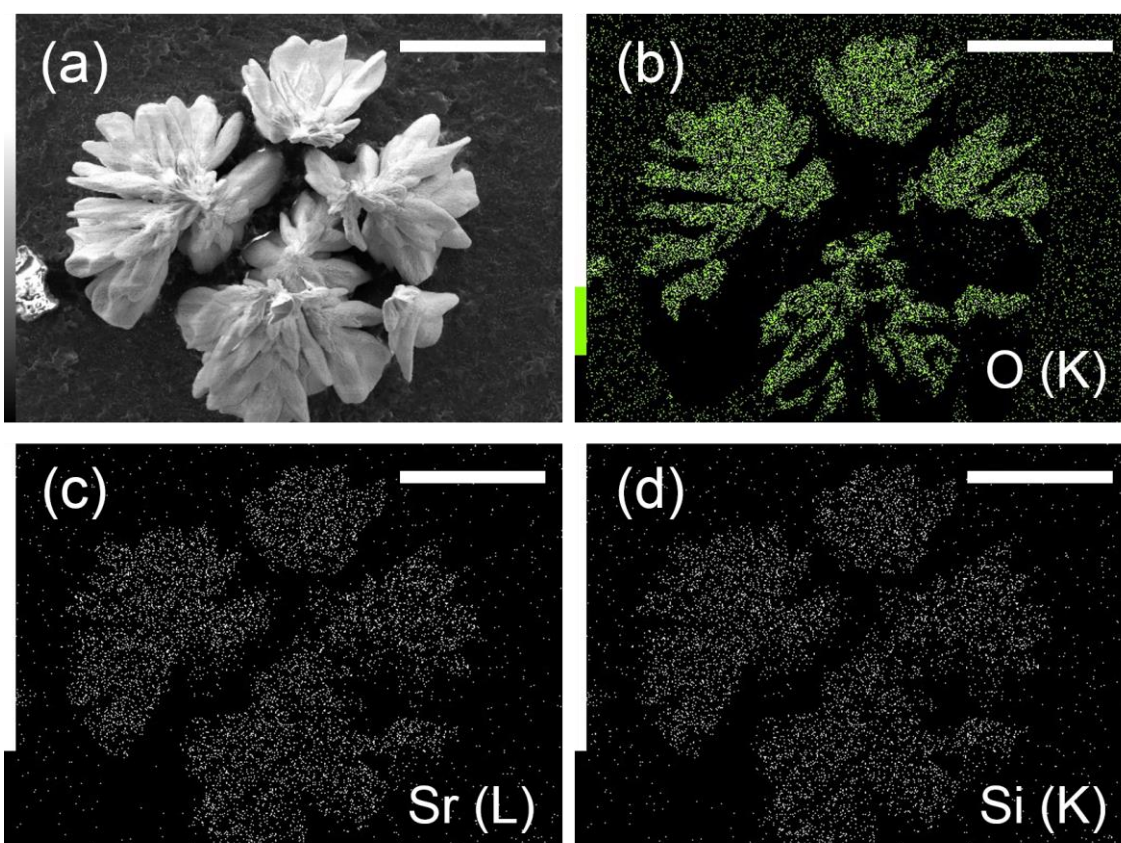


Figure S5. (a) Secondary electron SEM micrograph of peeled-of $\text{SrCO}_3/\text{SiO}_2$ crystal architecture. Elemental mapping of the same area for (b) oxygen, (c) strontium and (d) silicon. The elemental mapping shows that SrCO_3 and SiO_2 are equally distributed in the crystal architecture. The carbon mapping is not shown since the crystal structures were peeled of using a carbon tape. (Scale bars = 20 μm)

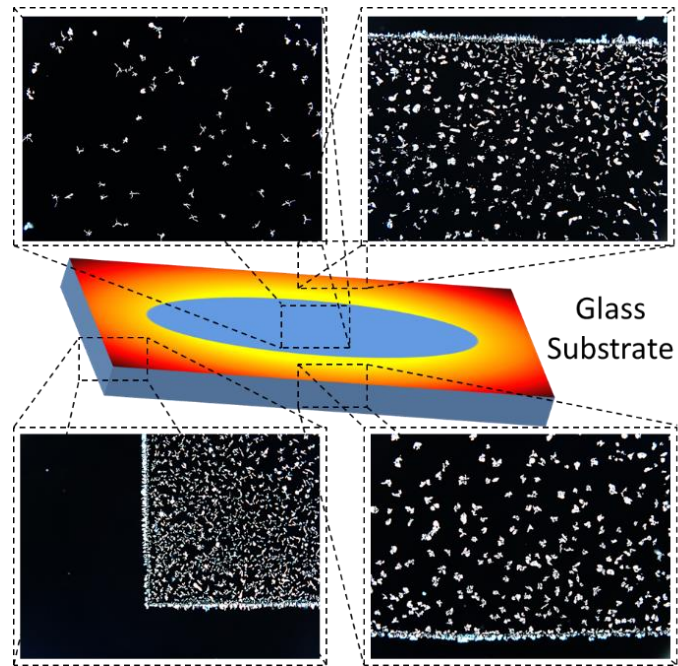


Figure S6. Optical micrographs of the rectangular substrate at different positions (Image width = 3.56 mm). The Images were taken by an optical microscope using a cross polarization filter. The center of the substrate represents a crystal-poor and the edges/corners a crystal-rich area. The coloration of the substrate depicts a schematic heat map of crystal density.

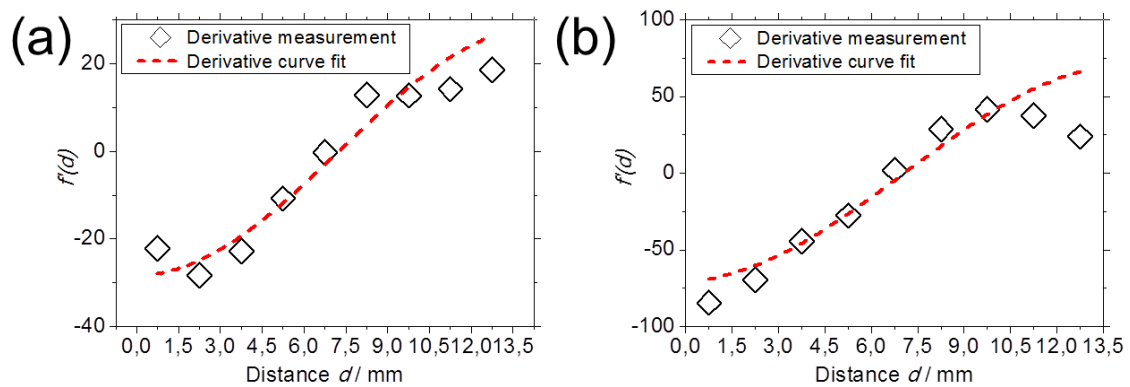


Figure S7. Derivative of the nucleation events (N_d) in dependency of the distance d from the edge of the substrate; showing the numerical derivative of the measurement, obtained from the graphical evaluation (diamonds), and the derivative of the theoretical curve fit (dashed, red line). It can be seen both curves show a good overlap. (a) Measurements from the center of the substrate and (b) at the corner of the substrate.

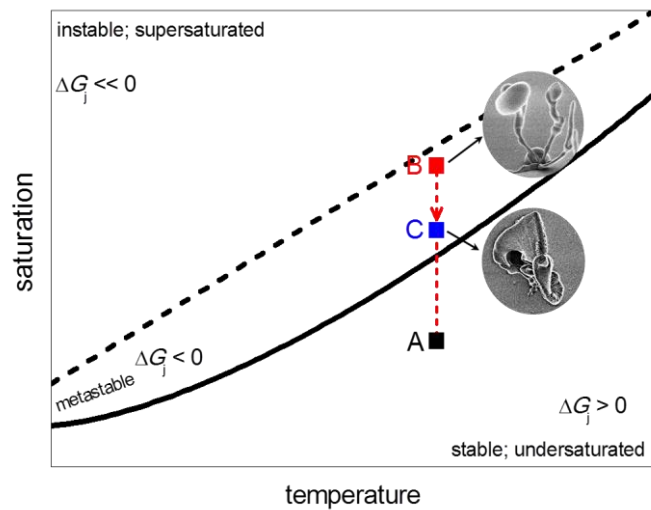


Figure S8. Solubility – supersaturation diagram.¹ The diagram shows three regions: In the first region the system is undersaturated thus nucleation is not probable and the nucleation enthalpy is $\Delta G_j > 0$. The second region shows the supersaturated state with $\Delta G_j \ll 0$, so homogenous nucleation in bulk is probable to happen. The third region constitutes a metastable sector with $\Delta G_j < 0$. In this region the system is slightly supersaturated and mostly heterogeneous occurs (secondary nucleation is also possible).

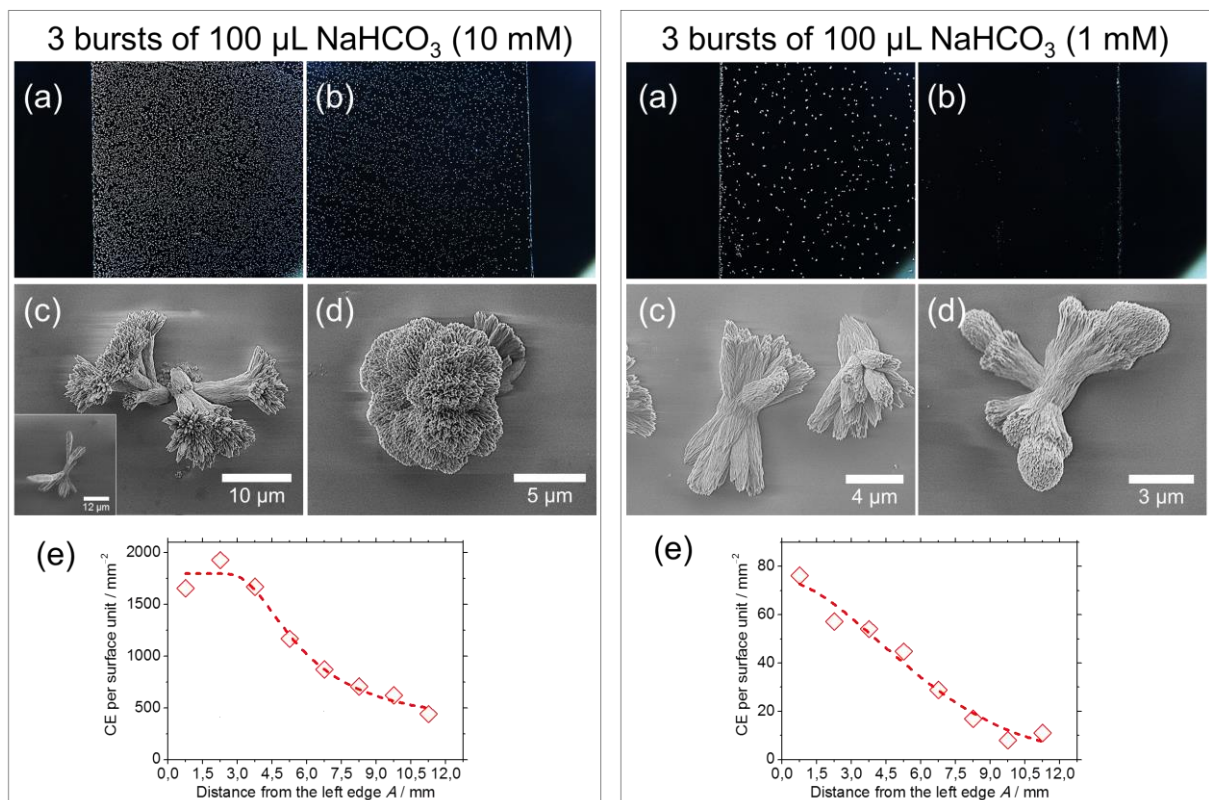


Figure S9. Coprecipitation of SrCO₃ and SiO₂ induced by the addition of NaHCO₃ of different concentrations: 10 mM (left column) or 1 mM (right column). (a) Cross-polarized images of the left edge of the substrate, where the NaHCO₃ solution was inserted. (b) Cross-polarized images of the right edge. (c) SEM micrograph of left edge. The inset in image (c) (left column) show the morphology of surface nucleated SrCO₃. (d) SEM micrograph of right edge. (e) Crystallization events per surface unit in dependency to the distance of the left edge.

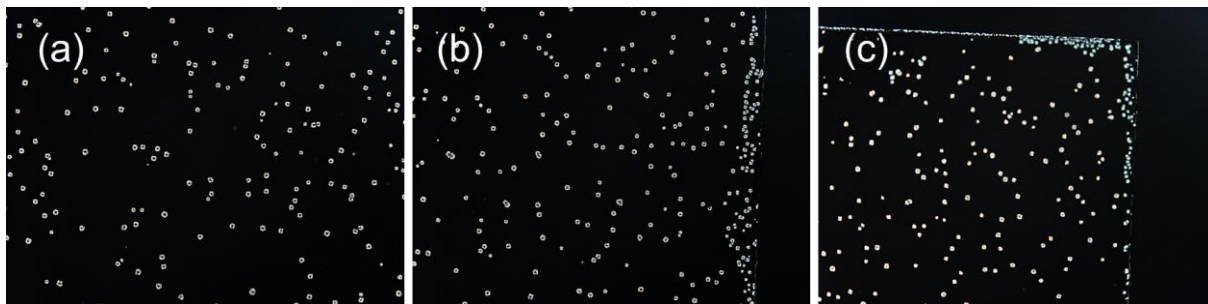


Figure S10. Cross-polarized optical images of SrCO₃/SiO₂ crystals obtained using dimethyl carbonate as a CO₂ source. The images were taken from different positions of the substrate: (a) center, (b) edge and (c) corner. The images are showing no difference in the amount of crystallization events at every position of the substrate. Only at the very edge some points of preferential crystallization can be observed (b, right or c top right corner).

Reference

1. J. W. Mullin, *Crystallization*, Elsevier Science, 2001.