Supplementary Information

Light-controlling nucleation, growth and patterning of metal carbonate crystals using resonant near-infrared laser heating

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Content:

1. Nucleation upon increasing light intensity

To investigate how the NIR light intensity determines the nucleation rate of $CaCO_3$, we fill four reaction cells with a freshly prepared precursor solution of fixed concentrations (1.5 mM $CaCl_2$, 1 mM Na_2CO_3, 300 mM NaCl, pH 10.7) and focus a NIR light beam with different light intensities on the substrates of the reaction cells. Per reaction cell, we use one NIR light intensity (90, 120, 150, or 180 mW) with which we subsequentially irradiate three light spots, each for 45 seconds. After the NIR light irradiation, we directly wash the cell with water and ethanol and let it dry in air. To analyse and compare the induced nucleation upon the irradiation with different light intensity, we use in-situ monitoring, light microscope imaging, and Scanning Electron Microscopy (SEM) imaging. For the freshly prepared solutions, we find the nucleation of mainly vaterite and aragonite in a small radius (35-110 µm) of the irradiated area with all light intensities. Within the regime of 90-180 mW, the area where nucleation is observed increases almost linearly for increasing light intensities (Fig. S1A-B). Furthermore, the results indicate a light intensity offset with respect to nucleation, since with 90 mW NIR light intensity almost no nucleation is observed, but for light intensities of 120 mW and higher, the nucleation density at the center of the light spot does not significantly differ within this time span of 45 seconds (Fig. S1C).

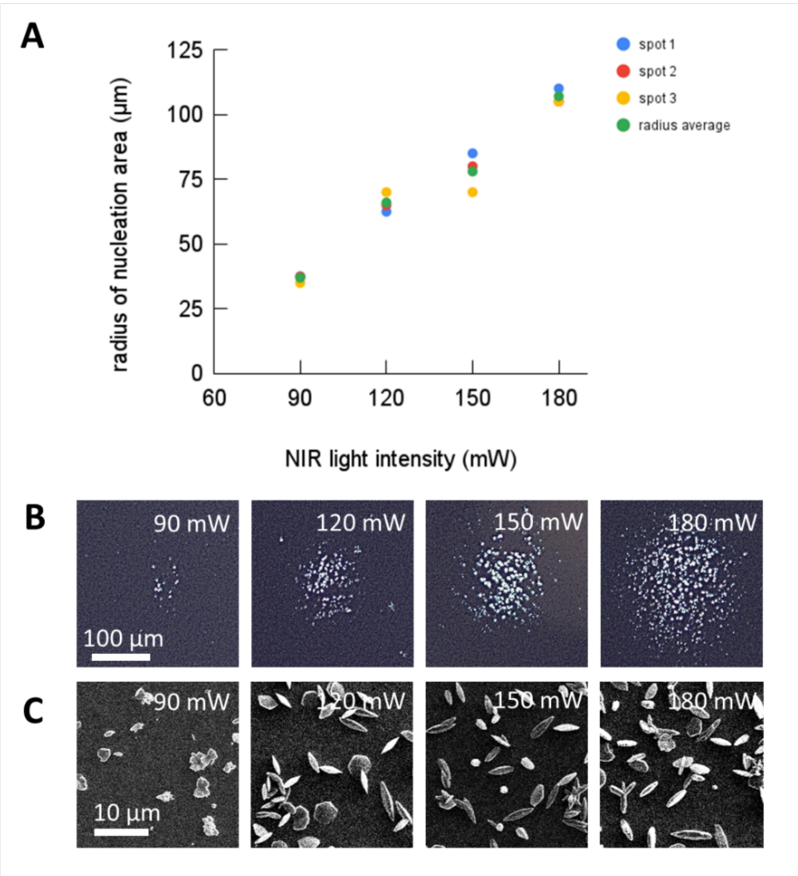

Fig. S1. Nucleation of $CaCO_3$ upon 45 seconds of irradiation with different NIR light intensities. **(A)** Plot of the area in which nucleation is observed upon NIR light intensity. **(B)** Light microscopy images of the NIR light induced nucleation. **(C)** SEM images of NIR light induced nucleation at the center of the NIR irradiated area.

2. Nucleation upon increasing light intensity

To investigate the absorption of the (ITO-coated) glass substrates at 1435 nm wavelength, steady-state absorbance measurements are carried out using a LAMBDA 750 UV/vis/NIR spectrophotometer (Perkin Elmer), equipped with a deuterium and tungsten excitation source, an InGaAs detector, and an integrating sphere. The absorbance measurements are done for the range of 1000-1600 nm (Fig. S2).

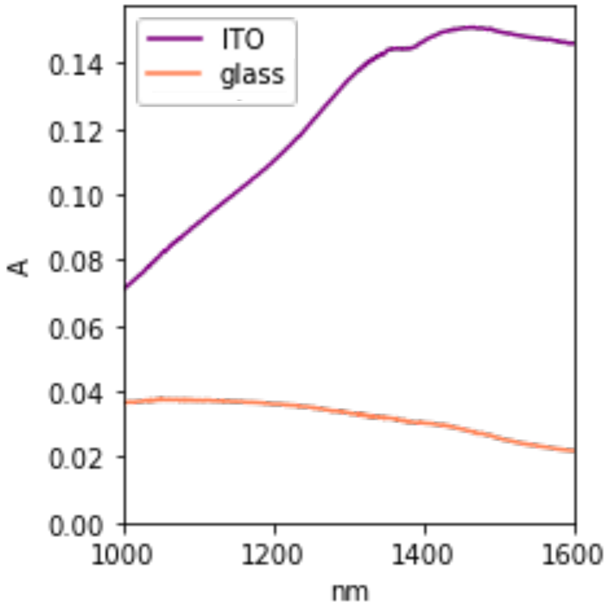

Fig. S2. Steady-state absorbance measurements of glass (orange line) and ITO-coated glass (purple line) in the range of 1000-1600 nm.

3. Dissolution test

To test if dissolution of NIR light induced crystals occurs when placed outside the NIR light spot, we closely monitor a reaction cell filled with a 2 days old $CaCO_3$ precursor solution (0.5 mM $CaCl_2$, 1 mM Na_2CO_3, 400 mM NaCl, pH 10.7) with and without NIR irradiation. First, we induce the nucleation and growth of $CaCO_3$ upon high intensity (180 mW). We continue NIR light irradiation until no further growth is observed (48 hours). We turn off the NIR laser light, but we continue to monitor the grown crystals (60 hours). After 60 hours, we observe no significant dissolution for neither the large grown crystals nor small nucleated calcite-like crystals (Fig. S2A), indicating that the NIR light grown calcite crystals remain stable and that the growth solution is only slightly undersaturated at room temperature after the NIR irradiation.
To test the thermodynamic stability between polymorphs after irradiation, we induce the nucleation of a mixture of calcite and vaterite with a freshly prepared precursor solution which contains rather high precursor concentrations (5 mM $CaCl_2$, 1 mM Na_2CO_3, 100 mM NaCl pH 10.7). We irradiate for several hours with high light intensity to induce nucleation and growth of mixed $CaCO_3$ (180 mW for 3 hours). Within 12 hours after switching off the NIR light spot, we observe slow dissolution of small vaterite crystals and further growth of calcite crystals (Fig. S3B), which indicates that the light induced small vaterite is thermodynamic less stable than calcite.

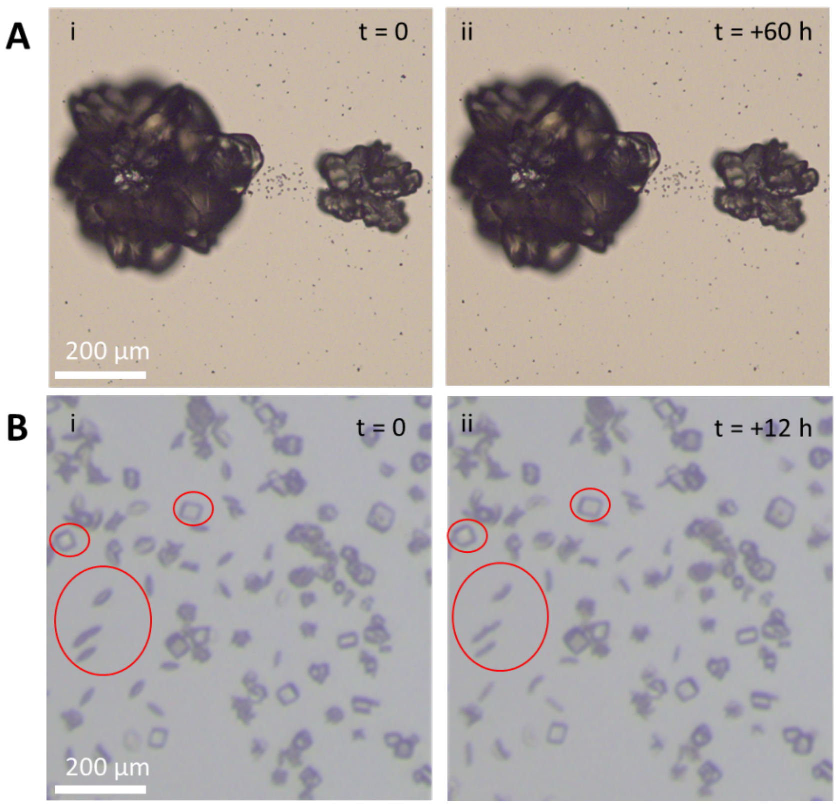

Fig. S3. Monitor of NIR light induced $CaCO_3$ when placed outside the NIR light spot. **(A)** Light microscopy image of NIR light induced $CaCO_3$ crystals at (i) t=0, directly, placed outside the NIR light spot and (ii) t= + 60 hours. No dissolution is observed. **(B)** Light microscopy image of NIR light induced vaterite and calcite crystals at (i) t=0, directly placed outside the NIR light spot, and (ii) t= + 12 hours. Red circles point out the dissolution of vaterite and growth of calcite.

4. Raman spectroscopy

To confirm the crystal structure and Raman spectroscopy measurements are carried out on the NIR light induced grown MCO_3 crystals using a confocal Raman microscope. Excitation is done with a 532nm laser. Spectra are dispersed on a 600 l/mm^{-1}. The spectra are each 20 times averaged with an integration time of 1 second (Fig. S4,S5).

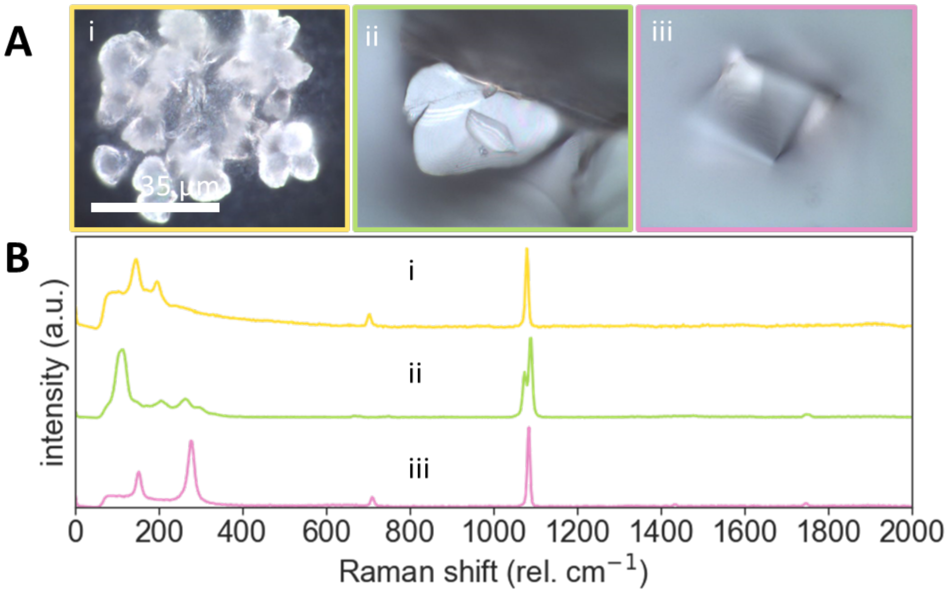

Fig. S4. Raman spectra of NIR light induced CaCO3 polymorphs. (A) Light microscope imaging of the probed area for Raman spectroscopy of (i) $CaCO_3$ grown in presence of $MgCl_2$, (ii) $CaCO_3$ grown in presence of NaCl without equilibration time, and (iii) $CaCO_3$ grown in presence of NaCl after 3 hours of equilibration time. **(B)** Raman spectra of $CaCO_3$ indicated by colored boxes and indices corresponding with (Ai-iii).

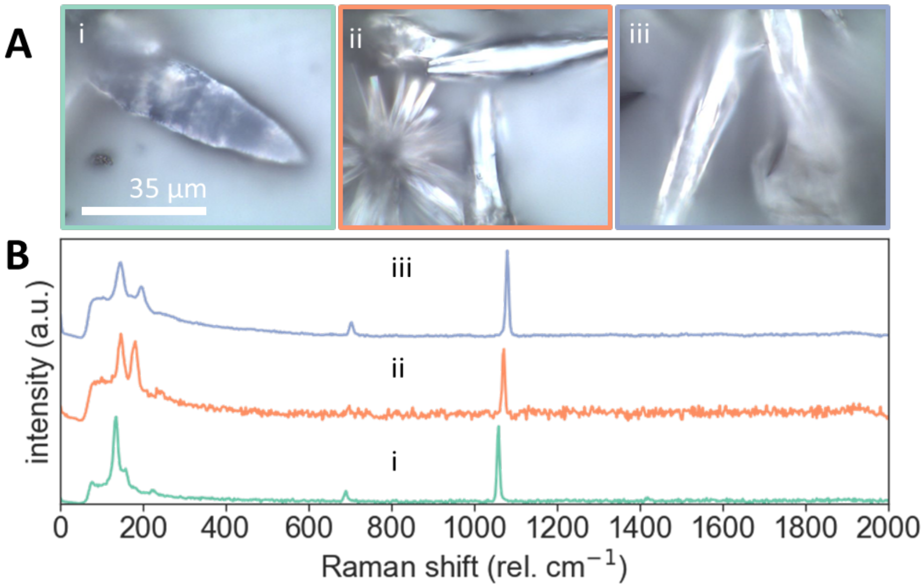

Fig. S5. Raman spectra of NIR light induced MCO3 crystals. (A) Light microscope imaging of the probed area for Raman spectroscopy of (i) $BaCO_3$ (ii) $SrCO_3$, and (iii) $CaCO_3$. **(B)** Raman spectra of the MCO_3 crystals indicated by colored boxes and indices corresponding with (Ai-iii).

5. Movie S1: NIR light induced nucleation and growth of $CaCO_3$ crystals

In this movie, the nucleation and growth of $CaCO_3$ crystals positioned in a line (described in the main text) are presented. The red dashed circle represents the location of NIR light spot. The total movie consists of 453 frames that cover a time span of 61 hours real-time growth. Due to the long timespan the video contains some time jumps. The real-time of crystallization per crystal as numbered in the movie is (times of nucleation are an estimation):

1. 16 hours (growth 120 mW, nucleation within first minute with 180 mW)
2. 6 hours (growth 120 mW, nucleation within first hour as well with 120 mW)
3. 14 hours (growth 130 mW, nucleation within first hour with 140 mW)
4. 9 hours (130 mW, nucleation withing first 2 hours as well with 130 mW)
5. 17 hours (120 mW, nucleation withtin first 3 hours as well with 120 mW)