ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Magnesium Ions Direct the Solid-State Transformation of Amorphous Calcium Carbonate Thin Films to Aragonite, Magnesium-Calcite, or Dolomite

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Table S1. Deposition periods of ACC films generated under different conditions.

$[Ca^{2+}]$ (mM)	$[Mg^{2+}]$ (mM)	[PAA] ($\mu g\ mL^{-1}$)	Film deposition time (min)
10	0	8	45
10	0	10	45
10	2	2	20
10	4	4	25
10	10	2	25
10	10	4	25
10	10	8	25
10	15	2	25
10	20	2	25
10	20	4	25
10	30	0	30
10	50	0	60
2	10	0	90
10	75	0	120
10	100	0	120

Table S2. Comparison of calculated and experimentally-determined Mg content of ACC and the product calcite films.

Mg content of ACC measured by ICP-OES (mol%)	Mg content of calcite measured by EDX (mol%)	Shrinkage of $d_{(104)}$ measured from HRTEM (%)	Mg content of calcite calculated from HRTEM (mol%)
9.94 ± 0.29	9.3	0.9 ± 0.1	9.0 ± 1.0
17.61 ± 0.46	16.7	1.6 ± 0.1	15.8 ± 1.0
21.62 ± 0.54	25.5	2.3 ± 0.2	22.8 ± 1.0
29.69 ± 0.67	29.5	2.8 ± 0.2	27.6 ± 2.0
42.21 ± 0.75	49.3	4.2 ± 0.2	42.0 ± 2.0

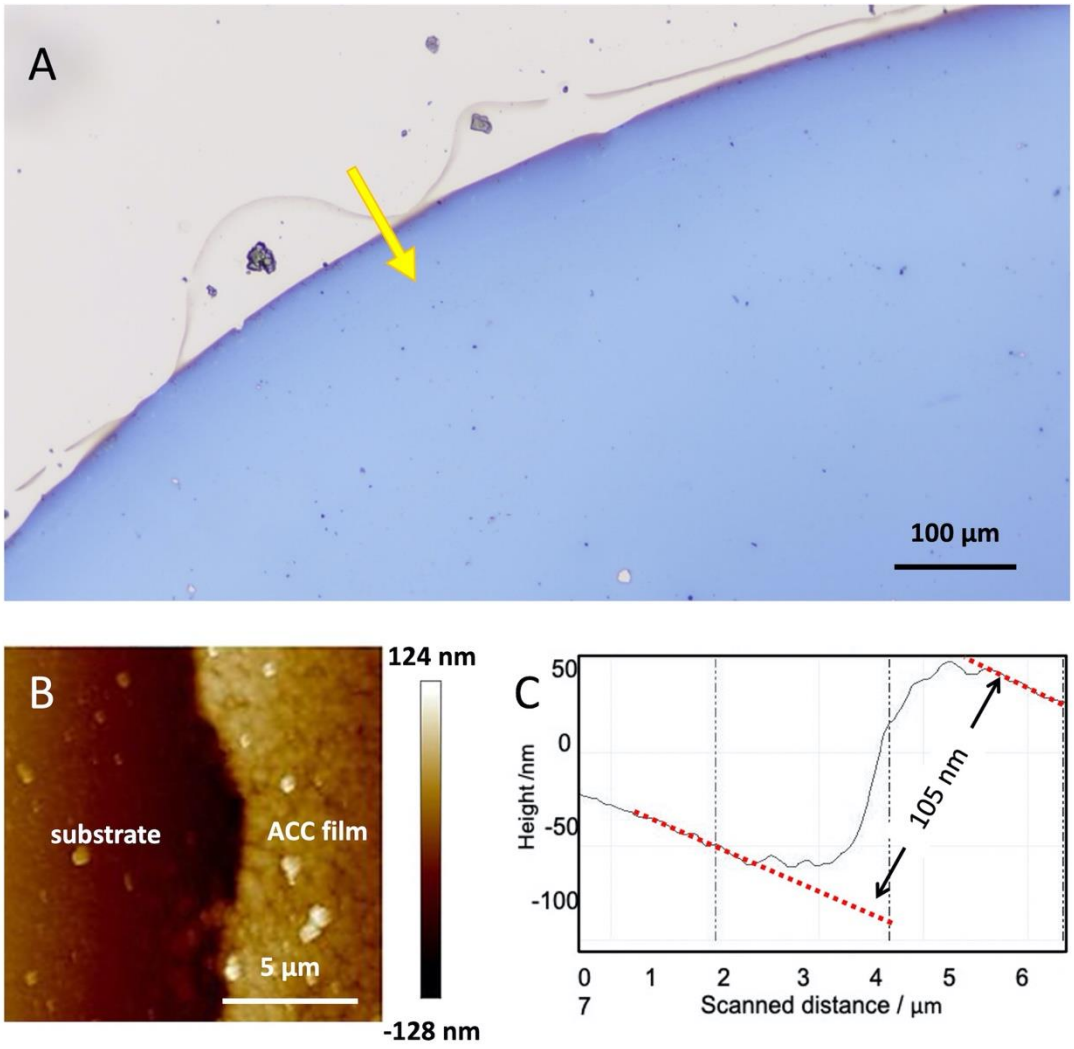

Figure S1 (A) Optical micrograph and (B) atomic force microscopy (AFM) image of ACC films prepared from solutions comprising [Ca^{2+}] = 10 mM, [Mg^{2+}] = 20 mM and [PAA] = 2 µg mL^{-1}. (C) Height profile along the direction of the yellow arrow in (A), showing that the overall thickness of the ACC film is around 100 nm.

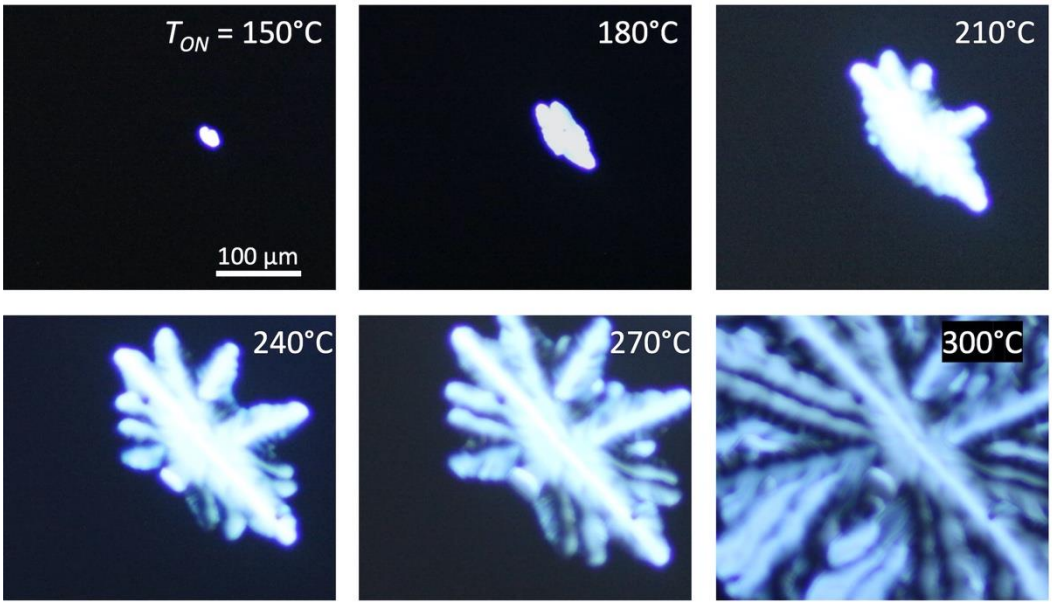

Figure S2. Sequential Polarized Optical Microscopy (POM) images of ACC films incubated under a continuous heat ramp from T_{ON}. The ACC films were prepared from solutions comprising $[Ca^{2+}] = [Mg^{2+}]$ = 10 mM and [PAA] = 2 µg mL^{-1}, and crystallized above T_{ON} (150 °C). POM images were captured at 180, 210, 240, 270 and 300 °C.

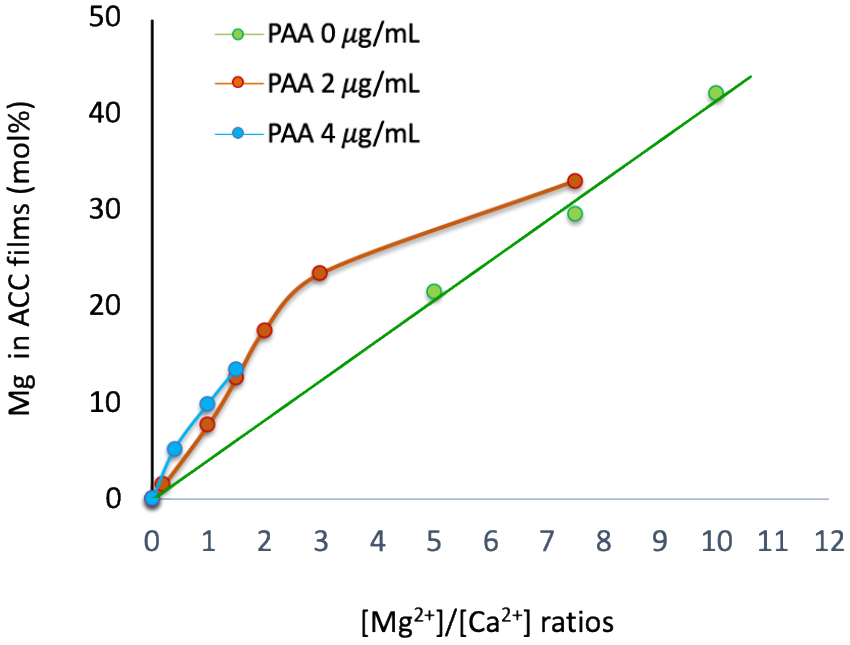

Figure S3. Mg content of calcite films formed in the presence of 0, 2 and 4 μg mL^{-1} PAA at different $[Mg^{2+}]/[Ca^{2+}]$ ratios, as determined using ICP-OES.

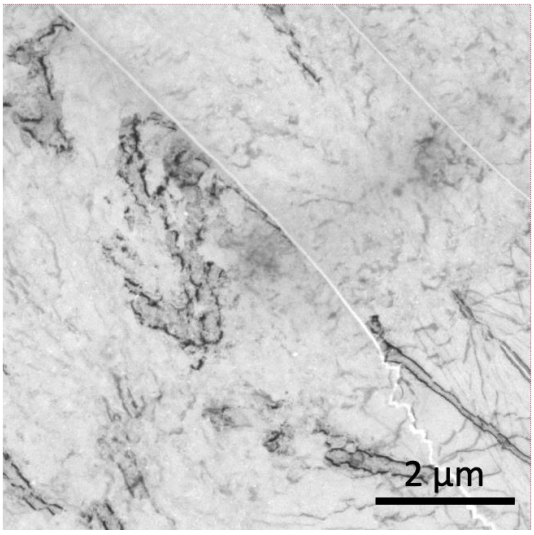

Figure S4. Bright field TEM image of a calcite film prepared at $[Ca^{2+}]$ = 10 mM, $[Mg^{2+}]$ = 20 mM and [PAA] = 4 µg mL^{-1}, and crystallized at 260 °C.

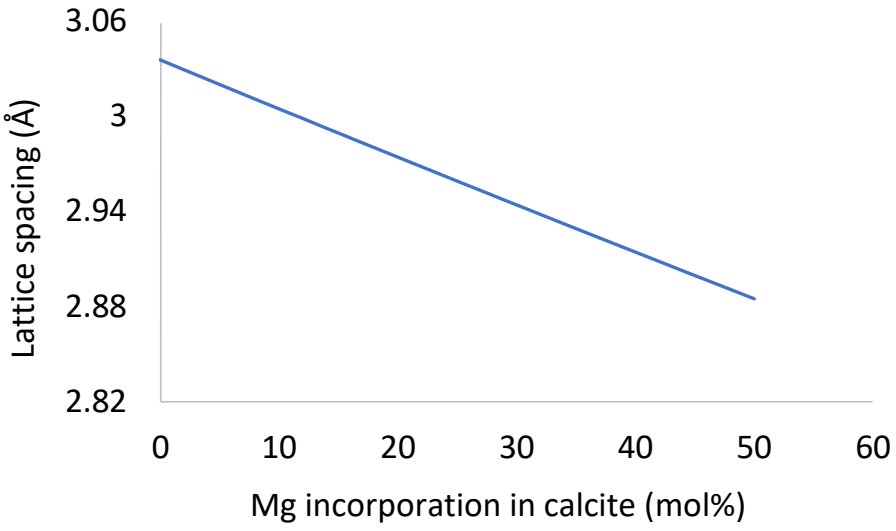

Figure S5. Calculated lattice spacing of (104) planes of Mg-calcite as a function of the Mg content. This was calculated using the parabolic functions of generalized Vegard's law [1-3]:

$$a=4.98964-0.4287733\eta+0.07309\eta^2$$

$$c=17.06728-2.0291349\eta-0.02223\eta^2$$

and follows $d_{(104)} = -0.003\eta + 3.0354$.

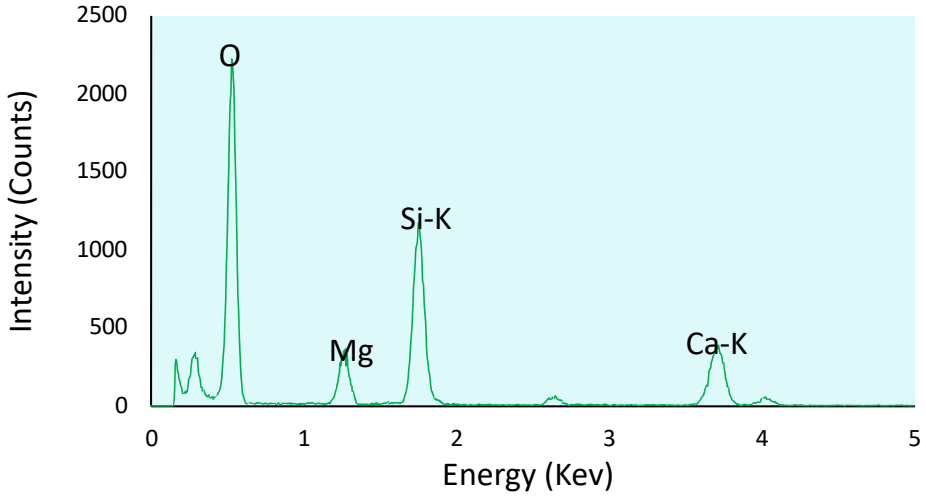

Figure S6. STEM-EDX spectrum of dolomite films showing a Mg content of ≈ 49 mol% Mg. The dolomite film was formed by heating ACC films prepared from solutions comprising $[Ca^{2+}]$ = 10 mM and $[Mg^{2+}]$ = 100 mM.

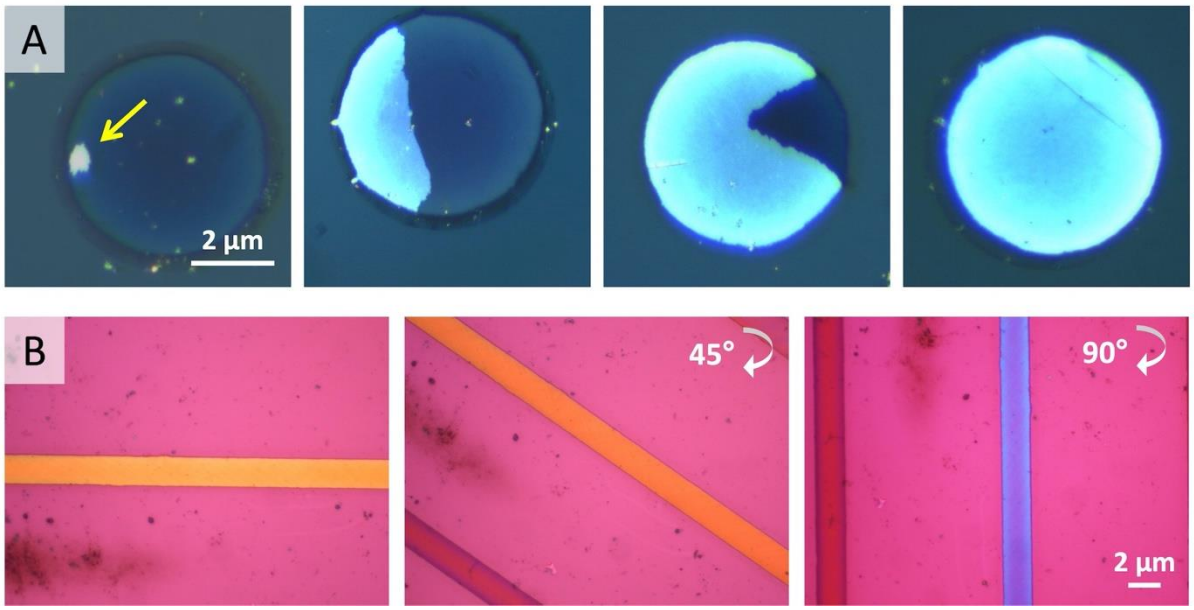

Figure S7. POM images of the patterned calcite films prepared under conditions [Ca^{2+}] = 10 mM, [Mg^{2+}] = 2 mM and [PAA] = 2 µg mL^{-1}, and crystallized at 150 °C. (A) Crystallization of ACC disc with diameter of 5 µm, where a single nucleation point is observed (marked by the yellow arrow), and which grows to generate a single crystal calcite disc. (B) Single crystal calcite strip with width of 5 µm.

References

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