Electronic Supplementary Information

Ultra-smooth and space-filling mineral films generated via particle accretion processes

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Experimental Details

Materials

Sodium poly(acrylate) Mw 5100 (Fluka), calcium chloride 1.0 M solution (Carl Roth), magnesium chloride hexa-hydrate (Sigma Aldrich), 2-(N-morpholino) ethanesulfonic acid and fluorescein glycine amide (Thermofisher Scientific), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (Sigma Aldrich), hydrochloric acid (Carl Roth) and ammonium carbonate (Carl Roth) were used as received 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.

Film preparation by

slow-diffusion mineralization

In a typical experiment, film precipitation was performed in a closed 21 litre volume desiccator at 25 °C for 42 hours.[1] A 9 cm diameter petri dish was used as a crystallisation vessel. This contained 25 ml of a 10 mM CaCl2, 0 to 15 mM MgCl₂·6H₂O, 200 µg ml-1 PAA solution. The petri dish was covered with clingfilm which was punctured with one 1 mm diameter needle hole, this was sealed in a desiccator with two glass vials (10 ml) each containing 3g of freshly crushed ammonium carbonate powder. Each vial was covered with parafilm punctured with a single 1 mm diameter needle hole placed at the bottom of the desiccator. The number of glass vials bearing ammonium carbonate or, alternatively, the number of needle holes in the vial(s) affect the escape rate of carbon dioxide and ammonia released from the decomposing ammonium carbonate powder to the desiccator's gas phase This provides a very simple but efficient control over the rate by which the composition of the gas phase is saturated with respect to carbon dioxide and ammonia. This, in turn, affects the rate of ammonium carbonate uptake in the reaction solution, eventually controlling the pH and supersaturation profile of the reaction. Alternatively, the desiccator size can be altered; see Harris et al. (2017) for more details [1].

The films were recovered from solution, rinsed with ethanol, and air dried. The defectfree films could be easily extracted from the interface using a microscope coverslip; optical microscopy under cross-polarization, FT-IR, and XRD analyses indicated absence of crystalline polymorphs in case of Mg-doped films.



Preparation of fluorescein glycine amide-tagged PAA

A 2.5 mg ml⁻¹ sodium poly(acrylate) was prepared in a 100 mM MES buffer at pH 4.9. A 4 ml volume of this solution was used to dissolve 1 mg fluorescein glycine amide. A volume of 0.1 ml of EDC solution (0.19 M) in MES buffer at pH 4.9 was added to the sodium poly(acrylate)/fluorescein glycine amide solution. The reaction was stirred for 4 hours in the dark to yield fluorescein-labelled poly(acrylate). Unreacted EDC and fluorescein glycine amide, and buffer molecules were removed by dialysis (M_w cut off 3500 Da) against deionized water for 48 hours in the dark with regular changes of water. The fluorescein-labelled poly(acrylate) solution was then lyophilized in the dark to yield dry fluorescein-labelled poly(acrylate) which was stored in the dark prior to further use. Coupling efficiency was determined by UV-Vis spectroscopy (fluorescein glycine amide $\varepsilon_{(490)} = 60738 \text{ M}^{-1} \text{ cm}^{-1}$).

General characterisation methods

Optical microscopy was performed using an Olympus BX51 polarized optical microscope equipped with an Olympus XC50 digital camera (Olympus, UK). Powder X-ray diffraction (PXRD) patterns recorded were on Kristalloflex D500 diffractometer (Siemens, Mannheim, Germany) using monochromatic Cu K α radiation, $\lambda = 1.54184$ Å) at a scan rate of 1°min⁻¹ between 5 and 70°. FT-IR 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 10 mg samples at a heating rate of 5 °C min⁻¹. Confocal fluorescence microscopy measurements were performed with a Leica SP5 II Fast Resonant Scanner (excitation at 496 nm, signal detection at 520 - 530 nm) on sections of film removed from the air-water interface. Prior to microscopy, the films were rinsed with ethanol, and then left in 5% NaOCl solution for 1 hour, before being rinsed again with ethanol to remove surface absorbed polymer.

BET analysis

The specific surface areas were determined by gas sorption at 77 K with nitrogen and the calculations was done from the adsorption branch of the isotherm using the method of Brunau, Emmet and Teller (BET)[2].

In case of geological calcite and biogenic calcite extracted from *P. nobilis*, the specific surface area was additionally determined by adsorption of krypton at 77 K because of their low surface area.

	nitrogen	krypton
Geo-Calcite	0.9422 m²/g	0.9201 m²/g
Bio-Calcite	1.4413 m²/g	0.7648 m²/g
Films	35.2752 m²/g	n.a.

Atomic force microscopy

force microscopy Atomic (AFM) was conducted on a JPK NanoWizard 4 (JPK Instruments, Berlin, Germany) using intermittent contact mode in air. All samples were measured with the same Olympus AC 160 cantilever. Images were recorded with a resolution of 1024 x 1024 px, all images were flattened by applying a polynomial of second degree to every line and setting the mean value of the image as zero point prior to roughness analysis. root mean square roughness was calculated within Gwyddin 2.4 (open source software, Okružní, Czech Republic, www.gwyddion.de), power spectral density analysis was performed within MATlab (Mathworks, Masachusetts, USA) utilizing selfwritten algorithms.



Figure S1. Left - Optical microscopy image of vaterite and calcite crystals extracted from the air-water interface after 42 hours. Initial solution composition [Ca] = 10 mM, [Mg] = 15 mM. Scale bar 200 μ m. Right - Optical microscopy image of an amorphous calcium carbonate film and calcite crystals extracted from the air-water interface after 42 hours. Initial solution composition [Ca] = 10 mM, PAA = 200 μ g ml⁻¹. Scale bar 200 μ m.



Figure S2. TGA (black line) and DSC (red line) profiles of calcium carbonate films.



Figure S3. PXRD, IR analysis, and a SEM micrograph of ultra-smooth films. (A) The diffractogram demonstrates that the films are X-ray amorphous. (B) The IR spectrum gives no evidence for basic magnesium carbonate as the characteristically sharp bands arising from O-H vibrations are absent at ~3650 cm⁻¹ [3–5]. (C) An enlarged view on the cross-section of the film shows, besides the very smooth top side, no evidence of internal pores.



Figure S4. TGA analysis of ultra-smooth films prepared with varying Mg content.



Figure S5. Reaction profile showing the evolution of pH calcium concentration as a function of time in a slowdiffusion setup, starting with a 20 mL 10 mM/L CaCl₂, incubated together with 3 g ammonium carbonate in a desiccator of a volume of about 0.27 L. The apparent in calcium concentration beyond the nominal calcium concentration of 10 mM/L is caused by the fact that the ion-selective electrode is not only sensitive to Ca ions but also to protons and ammonium ions.



Figure S6. Intensity line profiles of the fluorescence maps. The signal variation between the three regions of interest (ROI) is due to different sample thickness. It probably also accounts for the small gradient observed in the ROIs on the length scale of hundreds of micrometers. The inherent anisotropy of fluorescence microscopy, caused by unequal polarization, also contributes to this fading signal intensity. The variation on low length-scales, in the range of few nanometers, is due to non-Nyquist sampling, the resolution was chosen to be higher than the Nyquest limit. Thus, the pixel size is relatively big and causes the large variation between neighboring pixels. Overall, the polymer distribution is homogenous, at least within the resolution limit of the chosen approach.

Table S1. Overview of selected procedures for preparing ultra-smooth surfaces, and the associated roughness values.

Procedure	RMS roughness	Reference
Chemomechanically polished Si(001) wafer	1.10 nm	[6]
Chemomechanically polished Si(001) wafer	0.115 nm	[6]
with a final etching with a reductant agent		
Freshly cleaved calcite (104)	0.32 ± 0.2 nm	[7]
Native Si-Wafers	0.7 nm	[8]
Si-Wafer after KOH etching	4.0 to 12.2 nm	[8,9]
Thermally evaporated gold films	1.45 nm	[10]
Template stripped gold	0.20 nm	[10]
Polymer films evaporated by matrix-assisted pulsed	3 - 9 nm	[11]
laser evaporation		

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