

Electronic Supplementary Information (ESI)

Calcium Carbonate Crystallisation at Charged Graphite Surfaces

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S1. Experimental

Crystal growth experiments

All aqueous solutions were prepared using ultrapure water (Milli-Q Reagent, Millipore) with a typical resistivity of 18.2 M Ω cm at 25 °C. This was used immediately, without equilibrating with the atmosphere. In each experiment, 2 mL of 5 mM CaCl₂ (Sigma Aldrich, \geq 97 %) and 2 mL of 20 mM NaHCO₃ (Sigma Aldrich, \geq 99.7 %) were pipetted directly onto the surface of interest, to create a supersaturated solution. Both solutions prepared fresh, immediately before starting the experiment, and were filtered using Minisart syringe filters with a 0.20 μ m pore (Sartorius). For all experiments, the measured pH of these solutions combined was 8.07, in agreement with that calculated by MINEQL+ (version 4.6, Environmental Research Software), assuming the system was closed to the atmosphere, as was the case at the start of the growth experiments. The calculated supersaturation with respect to calcite at the start of the experiments was 16.4.

Calcium carbonate crystallisation was investigated at a range of different surfaces, including plastic petri dishes (Polystyrene, 35 mm diameter, Greiner Bio-One) and circular borosilicate D-263 M glass slides (30 mm diameter, Thermo Scientific) fitted into Petri dishes (Willco Wells) equipped with a Perspex rim and lid. The latter exposed a circular area of 12 mm diameter to the growth solution. Both of these surfaces were cleaned thoroughly with ultrapure water, ethanol (VWR, \geq 99.9%), and then blown dry using nitrogen gas (BOC).

Highly Oriented Pyrolytic Graphite (HOPG) surfaces were produced by cleavage immediately before use by the Scotch tape method¹ from blocks of grade SPI-2, ca. 1 cm² area. Using double-sided tape, the thin piece of graphite on the Scotch tape was attached to the base of Petri dishes (Willco Wells) equipped with a Perspex rim and lid, with a 12 mm hole in the centre, exposing the cleaved HOPG side of the Scotch tape to the growth solution. To prevent the adhesive side of the Scotch tape also being exposed, Kapton tape was attached around the outer edges of the cleaved HOPG, as shown in Figure 1 in the main paper. A potential was applied to the HOPG surface by implementing a conventional three electrode setup using a potentiostat (CH Instruments, 1140B). A Pt wire (0.75 mm diameter) was used to connect the HOPG surface from above, serving as the working electrode. The majority of this wire was insulated, well before use, by covering it with a fast setting two-component epoxy (Araldite Rapid), leaving only the very end of the wire exposed to the growth solution (\sim 0.65 mm²) to allow for contact with the HOPG surface and connection as the working electrode. A commercial saturated calomel electrode (SCE) (CH Instruments-150) and a Pt mesh electrode were implemented as the reference and counter electrodes, respectively. Potentials of - 1.00, + 0.50 and + 1.00 V vs. SCE were applied to the HOPG/Pt surface over the period for which crystal growth was monitored. These potentials correspond to potentials of - 0.76, + 0.74 and + 1.24 V, with respect to the PZC, respectively, which has been measured as \sim - 0.24 V vs. SCE.² The open circuit potential was measured as 0.05 V.

Analysis of crystal morphologies

Crystal growth was monitored in situ for five hours for each experiment using a Leica DM4000 M optical microscope. A 40 \times objective water immersion lens was used, and either discrete images or a series of time-lapse images were taken throughout the crystal growth process. After five hours, the growth solution was removed and the samples were rinsed with ultrapure water (Milli-Q Reagent, Millipore) and blown dry using nitrogen gas (BOC). To resolve the morphologies of the crystals obtained at the HOPG surfaces at much higher magnifications, a Zeiss Supra 55-VP field emission

scanning electron microscope (SEM) was used in secondary electron (SE2) mode at an acceleration voltage of 5 kV.

Analysis of crystal polymorphs

Crystals with the same morphologies as those shown in SEM images were analyzed using Raman spectroscopy to determine the calcium carbonate polymorphs. Spectra were obtained using a Renishaw micro-Raman inVia spectrometer, and the crystals of interest were selected using an optical microscope with a 50× objective lens. The 633 nm line of a HeNe laser was used at 100 % power, with an acquisition time of 10 s for each spectrum. Due to the small laser spot size (515 nm radius), it was possible to resolve and obtain spectra for individual crystals. Spectral calibration was performed using the 520.7 nm peak of a silicon standard.

S2. Currents obtained at the HOPG/Pt working electrode:

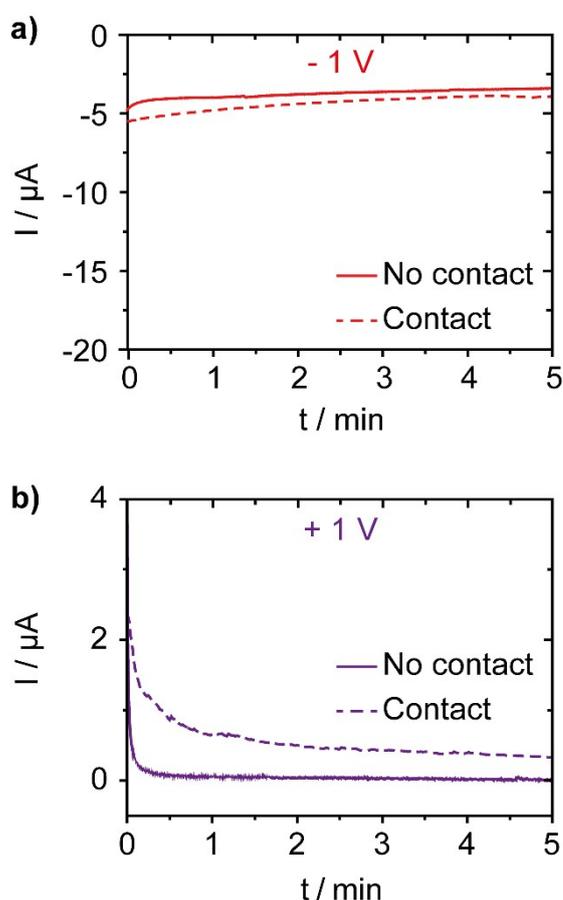
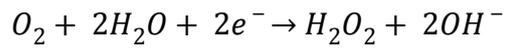
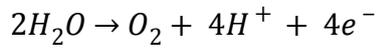


Fig. S1: Currents obtained at the partially insulated Pt wire working electrode when not in contact with the HOPG surface (solid lines) and when in contact with the HOPG surface (dashed) for applied potentials of (a) -1.00 V and (b) $+1.00 \text{ V}$ vs. SCE (electrolyte: 5 mM CaCl_2 and 20 mM NaHCO_3 , initial $\text{pH} = 8.07$).



Eq. S1: Hydrogen peroxide evolution occurring at cathodic potentials at the Pt wire surface.



Eq. S2: Oxygen evolution reaction (OER) occurring at anodic potentials at the Pt wire surface.

S3. Background crystal growth experiments

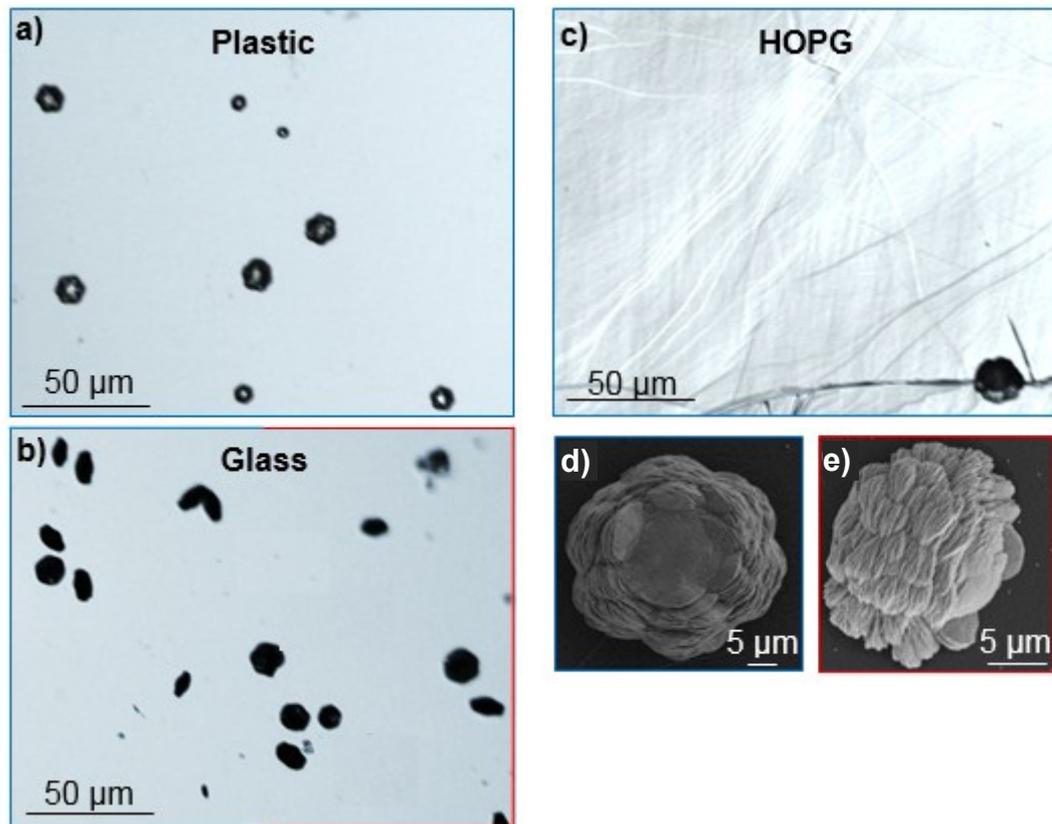


Fig. S2: Optical images of CaCO₃ growth after 5 hr on (a) plastic (polystyrene), (b) glass and (c) HOPG surfaces with no applied potential (PZC of HOPG ~ - 0.24 V) for 5 mM CaCl₂ and 20 mM NaHCO₃ at an initial pH of 8.07 (OCP = + 0.05 V). The different crystal orientations obtained on glass are shown at higher magnifications in the SEM images, (d) and (e).

S4. Raman analysis of crystals obtained in background experiments

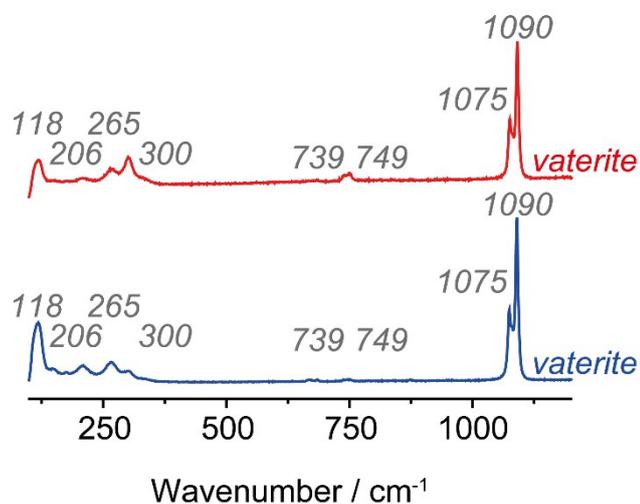


Fig. S3: Raman spectra obtained for the crystals shown in Fig. S2d (blue) and Fig. S2e (red), both of which correspond to vaterite.

S5. Crystal growth at a HOPG surface biased at + 1 V



Fig. S4: Optical image of resulting crystal growth for an applied potential of + 1.00 V vs. SCE at the HOPG/Pt working electrode at a time of 5 hours

S6. Videos of crystal growth

video_-1V.avi:

Crystallisation of CaCO_3 over a 5 hr period in 5 mM CaCl_2 and 20 mM NaHCO_3 (initial pH = 8.07) at a HOPG surface biased at - 1.00 V vs. SCE. Video obtained from a series of optical microscopy images using a 40x objective water immersion lens, using the setup described in the experimental section, and shown in Fig. 1.

video_+1V.avi:

Crystallisation of CaCO_3 over a 5 hr period in 5 mM CaCl_2 and 20 mM NaHCO_3 (initial pH = 8.07) at a HOPG surface biased at + 1.00 V vs. SCE. Video obtained from a series of optical microscopy images using a 40x objective water immersion lens, using the setup described in the experimental and shown in Fig. 1.

References

1. A. N. Patel, M. Guille Collignon, M. A. O'Connell, W. O. Y. Hung, K. McKelvey, J. V. Macpherson, P. R. Unwin, *J. Am. Chem. Soc.*, 2012, **134**, 20117-20130.
2. K. R. Kneten, R. L. McCreery, *Anal. Chem.*, 1992, **64**, 2518-2524.