

## Supporting Information

### Sub-nanometer Replica Molding of Molecular Steps on Ionic Crystals

Selim Elhadj<sup>1,‡</sup>, Robert M. Rioux<sup>2,‡</sup>, Michael D. Dickey<sup>2</sup>, James J. DeYoreo<sup>3,\*</sup>, George M. Whitesides<sup>2,\*</sup>

<sup>1</sup>*Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550, USA*

<sup>2</sup>*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St., Cambridge, Massachusetts 02138, USA*

<sup>3</sup>*The Molecular Foundry, Materials Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, California 94720, USA*

\*Email Addresses: [gwhitesides@gmwgroup.harvard.edu](mailto:gwhitesides@gmwgroup.harvard.edu), [jjdeyoreo@lbl.gov](mailto:jjdeyoreo@lbl.gov)

<sup>‡</sup>*These authors contributed equally to this work.*

## EXPERIMENTAL METHODS

**Synthesis of Potassium Dihydrogen Phosphate and calcite single-crystals.** The as-grown KDP {100} crystals (5 mm × 5 mm × 4 mm) were produced starting from a seed crystals (2 mm × 2 mm × 1 mm) cut from the {100} face of large KDP crystals. High-purity stock solutions of KDP salts (dissolved in water (18 MΩ cm resistivity)) were kept at 80 °C (overnight) in Teflon tanks and fed to a reactor vessel holding the KDP seed crystal. We determined the salt purity using inductively coupled mass spectrometry (ICP-MS) following separation of K<sup>+</sup> by ion exchange with a cation resin.<sup>21</sup> Total metal impurities in KDP ranged between < 0 – 500 ppb by weight; the level of any single impurity was ≤ 1ppm and typical tri-valent cation (Cr, Fe, Al) levels were below 100 ppb. We mixed the solutions at 80°C, filtered them for about 72 h through 0.02 μm polycarbonate filters and heated them at 80°C for ~72 h to ensure high solution stability.

Heating and continuous stirring (with a Teflon-coated magnetic stir bar) of the KDP solution prevented spontaneous crystallization and ensured a homogeneous solution. A Teflon-coated type-T thermocouple (inserted through the tubing just inside the outlet port of the fluid cell) monitored the temperature of the solution in the cell. A Peltier heater/cooler controlled the temperature of the fluid cell to within 0.1°C. We grew crystals in supersaturated KDP solutions (1-7 %) by decreasing the solution temperature from 30°C to 21°C.

The crystals grew until ~ 1 – 3 mm of new material had been added to the face of the crystal. We maintained the rate of rotation of the stirrers at 60 rpm (a tip speed of 60 cm/s) and periodically reversed the direction of rotation to avoid step bunching due to instabilities

associated with the depletion of solute behind the leading corners of the seed crystal. After completion of crystal growth, we withdrew the Teflon-coated stir bars—to which the seed crystals had been attached—through a stream of hexane warmed to the same temperature as the control bath.

Calcite crystal substrates were grown at room temperature under conditions of flowing supersaturated solutions starting from cleaved plates of Icelandic spar (Ward's Natural Science, Rochester, NY) mounted on glass cover slips in the fluid cell of an AFM. The calcium carbonate solutions were made by mixing  $\text{NaHCO}_3$  with  $\text{CaCl}_2$  to yield a supersaturation,  $\sigma \sim 1$ , where  $\sigma = \log[a(\text{Ca}^{2+}) a(\text{CO}_3^{2-})]/K_{\text{sp}}$ ,  $a(\text{Ca}^{2+})$  and  $a(\text{CO}_3^{2-})$  are the activities of the calcium and carbonate ions respectively, and  $K_{\text{sp}} = 4.4 \times 10^{-9}$  is the calcite solubility product, calculated using Geochemists Workbench.<sup>12</sup> The crystals were grown for two hours, resulting in a sufficient overgrowth of new material to ensure growth hillocks were present. The crystals were then removed from solution through a stream of nitrogen to remove the excess solution and stored in a nitrogen-purged dry box until use.

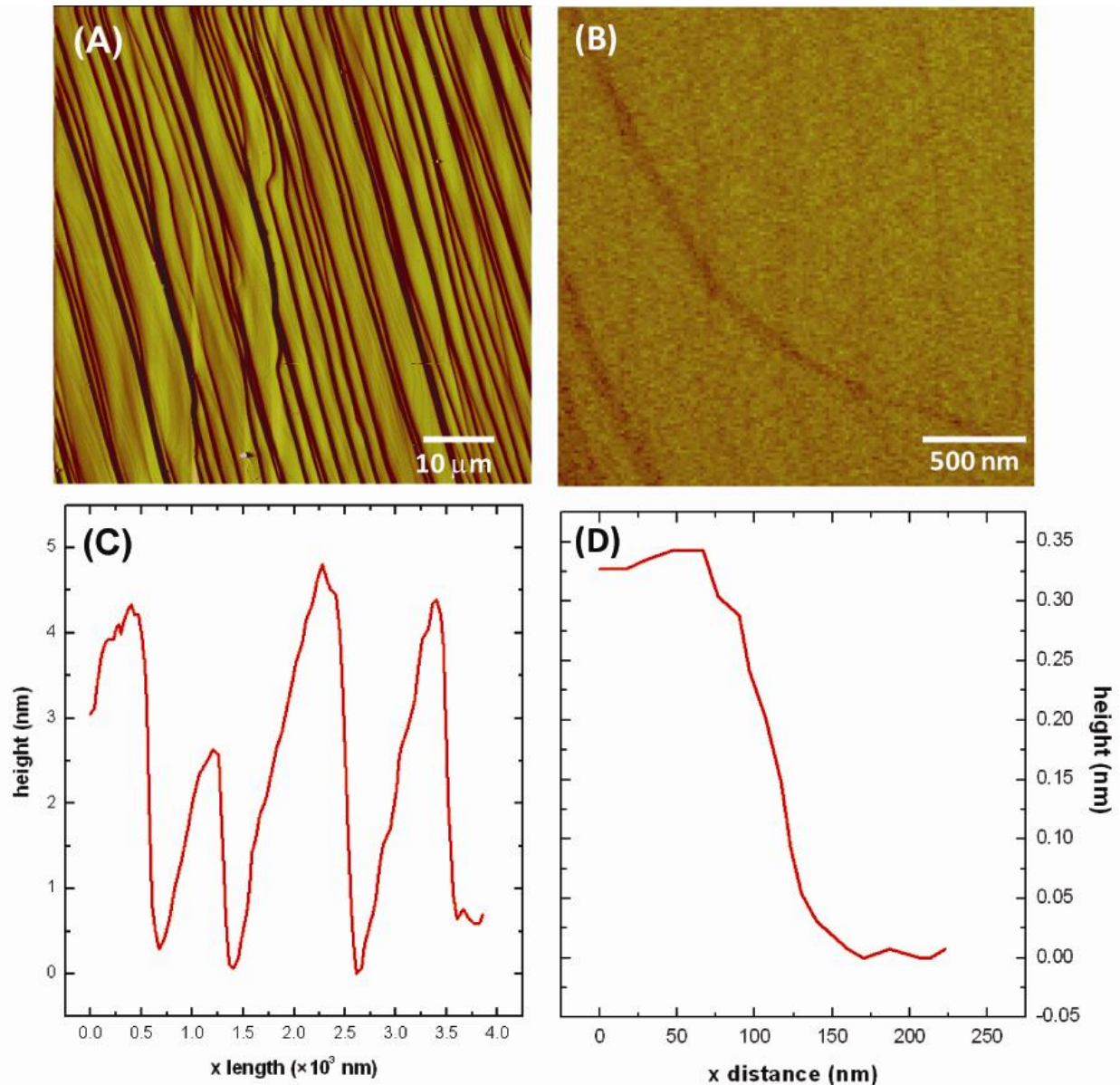
**Replication of crystal in poly(dimethylsiloxane) (PDMS) and polyurethane (PU).** **Figure 2A** is a schematic of the simple procedure used to replica mold a KDP surface (**Figure 2B**) (the same procedure was used for calcite with a freshly prepared crystal). To prepare *h*-PDMS, we mixed and degassed the following chemicals: 3.4 g of a vinyl PDMS prepolymer (VDT-731, Gelest Corp.), 18  $\mu\text{l}$  of a Pt catalyst (platinum divinyltetramethyldisiloxane, SIP6831.1, Gelest Corp.), and one drop of a modulator (2,4,6,8-tetramethyl-tetravinylcyclotetrasiloxane, 87927, Sigma-Aldrich). We then gently stirred 1 g of a hydrosilane prepolymer (HMS-301, Gelest

Corp.) into this mixture. Immediately (within 30 s of stirring), we spin-coated a thin layer (30-40  $\mu\text{m}$ ) of *h*-PDMS onto the crystal (1000 rpm, 40 s) affixed to a silicon wafer by double-sided tape and cured the *h*-PDMS coated crystal for 10 min at 60 °C. We then poured a liquid prepolymer layer (~ 3 mm) of Sylgard 184PDMS (Dow Corning) onto the *h*-PDMS layer and cured it for 4 h at 60 °C. We released the composite stamp from the surface by cutting and carefully peeling the stamp from the surface while still warm.

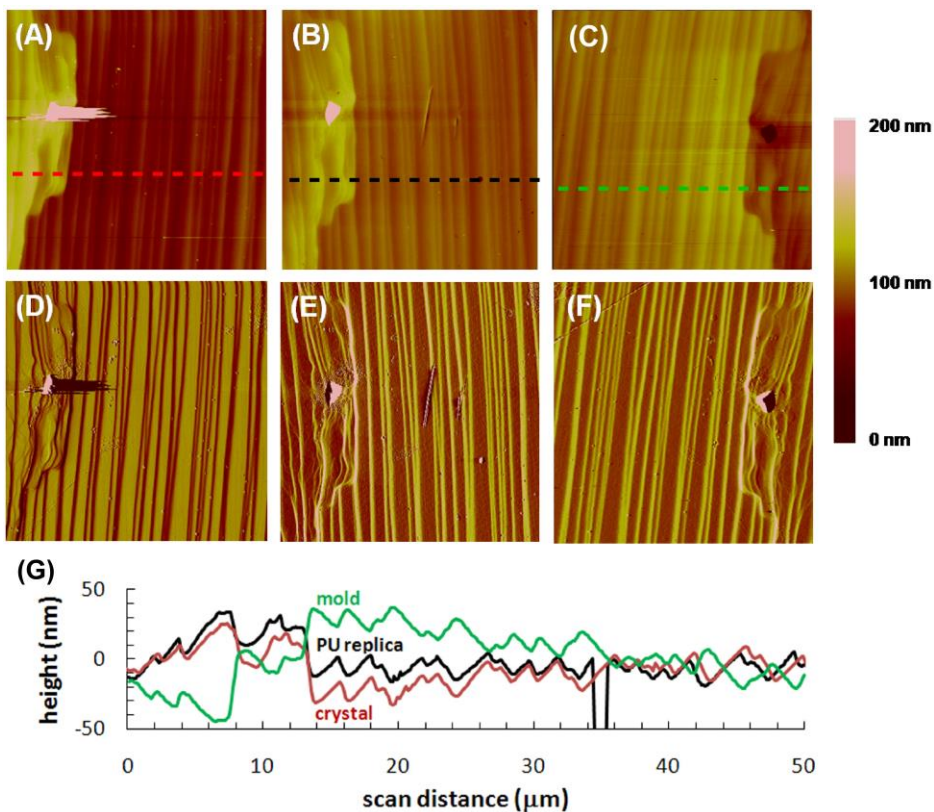
We photopolymerized polyurethane (PU, Norland Optical Adhesive 73) directly on top of the *h*-PDMS replica for 20 min under a Hg-arc lamp (100 W bulb, 10 cm sample-to-lamp distance). We gently peeled the PU from the mold to produce a crystal replica (**Figure 2C**).

**AFM imaging of crystal and polymeric replica and step height measurement.** For high resolution imaging of crystal and replica surfaces we used a Veeco Instrument Nanoscope E force microscope in contact-mode with a standard Si tip and SiN cantilever having a nominal force constant of 0.035 nN/nm, under ambient conditions, with a typical scanning frequency between 2-6 Hz. We avoided any damage to the surface by reducing the set point deflection (to the point where the imaging is just stable<sup>22</sup>) to minimize the force exerted on the sample by the tip. The height and deflection images were captured simultaneously. *Ex-situ* images were obtained under ambient conditions. Replica and mold surfaces were stable and could be re-imaged for months following preparation without loss of resolution. For measurement of actual step heights, images were first leveled with respect to the terraces using Veeco Nanoscope software. In addition, images of the PU replicas of calcite (**Figure 4C**) were processed to remove some scattered high features that arose from bubbles in the PDMS mold. Specifically,

high points due to bubbles in the PDMS mold were removed from the images of the replica by first defining a circular region containing the bubble and applying an in-filling routine that assigns a value to the bubble that is an average of the pixels around the perimeter. These did not affect the replication of steps or the measurements of step heights. The displacement of the AFM piezoelectric vertical scanner was calibrated by using the KDP {100} crystal surface elementary steps as reference and scaling the measured displacement accordingly based on the reported value for KDP. This correction represented ~20% of nominal value. Calcite AFM images were obtained in the solution using the standard Veeco AFM flow cell because calcite steps degrade under ambient air conditions. Consequently, this measurement could not be used as a vertical calibration standard for measurements on the replica, which was imaged in air. Thus, the values for step heights on the two surfaces were compared directly. In all cases, the quoted standard deviations are due to both the inherent error of the measurement, which is less than 0.1 nm, and real variations in height due to either master, mold and replica granularity or fidelity of replication.



**Figure S1. Representative AFM deflection images of the KDP {100} surface.** (A) macrosteps corresponding to a series of bunched elementary steps (on some terraces, elementary steps are also apparent) and (B) a single elementary step on a terrace. Line scans from AFM height images for (C) macrosteps and a (D) single elementary show an inclination of the terrace with respect to the horizontal of  $\sim 0.3^\circ$  as expected for the KDP {100} face (The x- and y- axes are not to scale.).



**Figure S2.** AFM images and height profiles of KDP crystal  $\{100\}$  surface, replica and mold. AFM height (A-C) and deflection (D-F) images of original KDP crystal (A and D), PU replica (B and E) and PDMS mold (C and F). Images demonstrate replication of macrosteps ( $\sim 5$ - $110$  atomic steps,  $\sim 2$ - $40$  nm in height) on the PDMS mold and PU replica over the entire  $45 \mu\text{m}$ . Note that the original crystal surface and replica are mirror images of the mold; high (bright) features in height images of replica and crystal appear as low (dark) features in the mold, as expected. All images are  $50 \mu\text{m} \times 50 \mu\text{m}$ . (G) Height profiles along the dashed lines in (A, B, and C, for C axis direction was reversed). The individual elementary steps in the macrosteps are too close to be resolved by AFM at this scan size.