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Supporting Information for:

Porous Calcite Single Crystals Grown From Hydrogel Media

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Experimental Section:

Gel preparation: The 1 w/v% agarose solution was prepared by dissolving agarose powder (Type IB, Sigma) in a hot solution of 7 mM $CaCl_2 \bullet 2H_2O$ (99+%, Sigma-Aldrich). 3 mL of the solution was then filtered (syringe filter; 0.2 μm, Nylon, Millipore), into a Petri dish (35 mm x 10 mm). After gelation (about 30 minutes), the Petri dishes were covered with aluminum foil with one small hole. The 2 w/v% gel was prepared via the same procedure except using a different filter (syringe filter; 0.45 μm, PVDF, Millipore) because the 2 w/v% agarose solution was more viscous than the 1 w/v% solution.

SAM-gel matrix preparation: To form the SAMs, pieces of gold-coated glass slides (40 nm of Au on 3 nm of Cr, Veeco 7700 Bell Jar Evaporator, base pressure 10^{-6} Torr) were incubated overnight in a 10 mM solution of 16-mercaptohexadecanoic acid (16-MHDA; Aldrich) in ethanol. After rinsing with ethanol and deionized (DI) water (18.2 mΩ, Barnstead EASYpure® RoDi), the slides were transferred to Petri dishes (35 mm x 10 mm) and covered with 3 mL of a filtered (syringe filter; 0.45 μm, PVDF, Millipore), warm solution of agarose

(2 and 3 w/v%) in 7 mM $CaCl_2 \bullet 2H_2O$. After gelation (about 30 minutes), the Petri dishes were covered with aluminum foil with one small hole.

Crystallization: The Petri dishes with the gel or SAM-gel matrix were placed in a closed desiccator containing one vial of ammonium carbonate ($(NH_4)_2CO_3$, Sigma-Aldrich). After 24 hours in the desiccator, crystals grew in the bulk gel (Type I) and on the SAM in gel (Type II). Type I crystals were removed from the gel by dissolving the agarose in boiling DI water. Type II Crystals were removed from the gels by peeling the gels away from the slides and the crystals on slides were rinsed with DI water.

Etching: The crystals were etched in DI water (Type I: etching for two days; Type II: four days. The difference in etching time is due to the different sizes of the two types of crystals.). During this time, the Petri dishes with the crystals were gently rocked on a rocking platform. After etching, the etched crystals were air-dried. For complete etching, Type II crystals were dissolved in 0.1M HCl for approximately 10 minutes. The slide was then rinsed with DI water and air-dried.

Characterization: The morphology of both the as-grown and the etched crystals was examined by scanning electron microscopy (SEM, STEREOSCAN 440, LEICA, 25 kV, 600 pA) after being sputter-coated with Au/Pd. The elemental composition was identified by Energy Dispersive X-ray Analysis (detector: Kevex; analyzer and software: Evex).

The internal structure of type I crystal was observed by transmission electron microscope (TEM, JEOL 1200EX, 120 kV) after being embedded in epoxy (Unicryl embedding kit, EMS, Cat #14660) and microtomed (diamond knife) into slices of 50 nm thick. The details of sample preparation are described below. Step 1: Embed the crystals in agarose hydrogel; Step 2: Sequentially replace the water in the hydrogel with ethanol/water mixtures (1:3, 1:1, 3:1) and then absolute ethanol; Step 3: Replace the ethanol in the gel with an epoxy

monomer/ethanol mixture (1:1) and then pure monomer; Step 4: Polymerize the epoxy at 100°C; Step 5: Microtome with diamond knife.

The incorporated gel fibers were observed by optical microscopy (Olympus BX51) after completely etching type II crystals in 0.1 M HCl.

Figure S1. TEM images and SAED pattern: Calcite crystals were grown in a 1 w/v% agarose gel and then microtomed into slices of 50 nm thick as described in experimental section. The slices were examined by TEM (Figure S1).

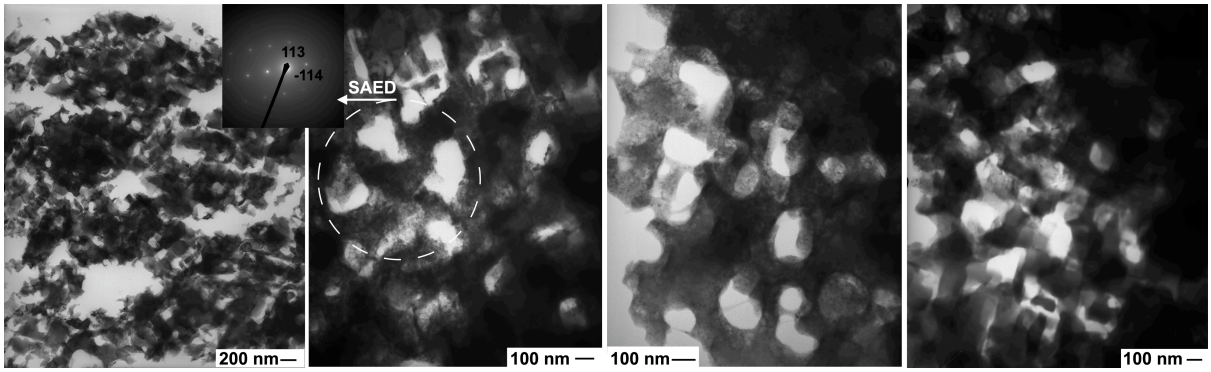

Figure S1. TEM images of a 50 nm thin slice of an epoxy-embedded calcite crystal which is grown in a 1 w/v% agarose gel. The slice was cut by microtome. Inset: An indexed SAED pattern of the area indicated by the dashed line.

Figure S2. Optical micrographs under cross-polarized light: The crystals grown from 1 w/v% gel were observed in optical microscopy (Olympus BX51). Individual crystals extinguish simultaneously as single crystals when rotated under cross-polarized light (Figure S2).

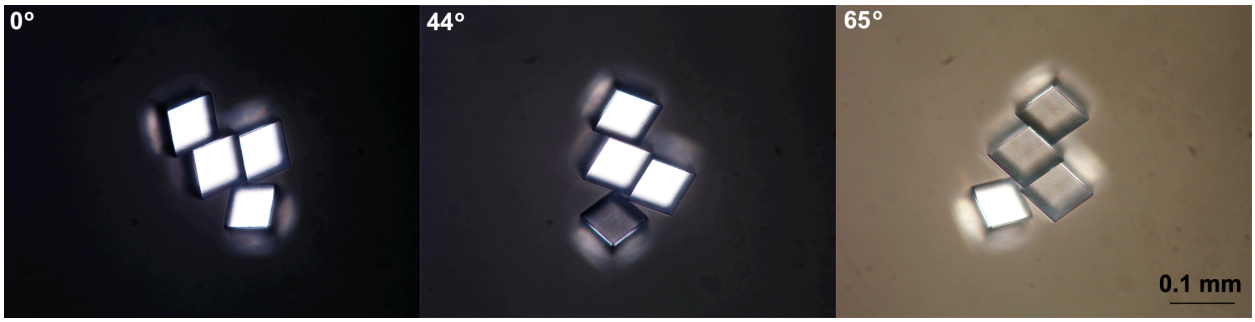

Figure S2. Micrograph series of crystals grown in 1 w/v% gel that are rotated under cross-polarized light.

Figure S3. EBSD Orientation mapping: Crystal orientation maps of a 50 micron by 50 micron, square area (Figure S3 blue area) with a step of 5 micron was obtained via electron back-scattered diffraction (EBSD, detector: Nordlys II, HKL; Software: Channel 5). Before the EBSD experiment, the crystals on a glass slide were coated with a very thin carbon film (~several nm) by a thermal evaporator (Edwards, Auto-306). To collect the data, the sample stage was tilted at 70° from the horizontal. The result shows that in this area, all of the crystalline components have the same orientation with a misalignment less than 1 degree (Figure S3, inset), which means the solid under investigation is a single crystal.

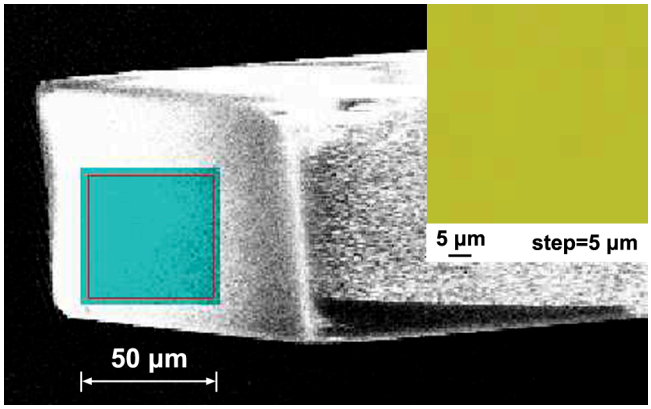

Figure S3. EBSD orientation map of a crystal grown in agarose gel (1 w/v%; 7 mM $CaCl_2$). The scanning area is blue-marked; the orientation mapping is shown in top right corner. Each crystallographic direction is allocated a specific color during mapping. The uniformity of the color in the inset means that all of the crystalline components in this area have the same orientation.

Figure S4. The crystal grown in 2 w/v% gel: Calcite crystals were grown in a 2 w/v% agarose gel as described in the experimental section. The morphology of both the as-grown and the etched crystals was examined by SEM (Figure S4).

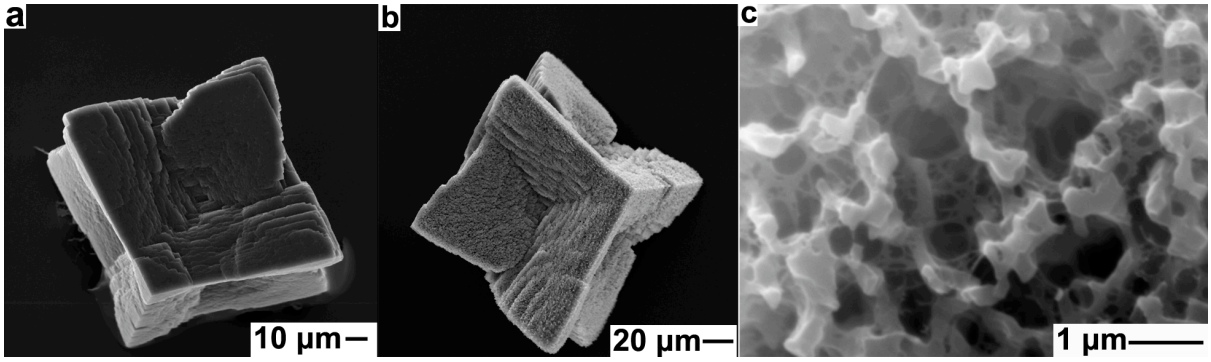

Figure S4. SEM images of a calcite crystal grown in an agarose gel (2 w/v%; 7 mM $CaCl_2$): (a) as-grown; (b,c) after etching in DI water for 4 days.