Supporting Information

Growth and Morphology Control of Metastable KDP Crystals with Defect-free Seeds

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Optical Micrograph of KDP Crystal

The crystallization process of the KDP solution was monitored in situ using an OLYMPUS (SZX16) optical microscope. The scale for all micrographs was calibrated using a standard micrometer-scale graticule imaged under the same optical conditions and magnification as the crystal samples. This graticule serves as the spatial reference to convert pixel distances into absolute lengths (μm).

Calculation of the Critical Supersaturation Ratio for Monoclinic KDP Crystal Nucleation

In the experiment to determine the critical supersaturation ratio for the nucleation of the monoclinic phase of KDP, the solubility curve of the monoclinic phase was not yet available. Therefore, the established solution temperature and concentration were initially expressed using the supersaturation ratio relative to the tetragonal phase. The solubility curve of the KDP tetragonal phase was determined using tetragonal fiber seed crystals in our previous study:[1]

$$C_e = 12.06179 + 0.46147*T + 0.00176*T^2$$

T is temperature, and C_e is the equilibrium concentration. This equation allows for the calculation of the equilibrium concentration at different saturation temperatures. The equilibrium concentration of the solution at 0 °C relative to the tetragonal phase is 12.1 g KDP/100 g H_2O. The supersaturation ratio (S_T) relative to the tetragonal phase can be further calculated for solutions of various concentrations (C) at a given temperature(T) using the equation:

$$C = \frac{m_{KDP}}{m_{KDP} + m_{H_2O}}$$

$$S = \frac{C}{C_e}$$

The crystallization behavior at each supersaturation ratio in the experiment was tested across 10 replicate experiments, with the critical ratio showing an error margin of ± 0.05 (corresponding to 62 ± 2 °C undercooling).

Crystal Transition in Defective Seed Crystals

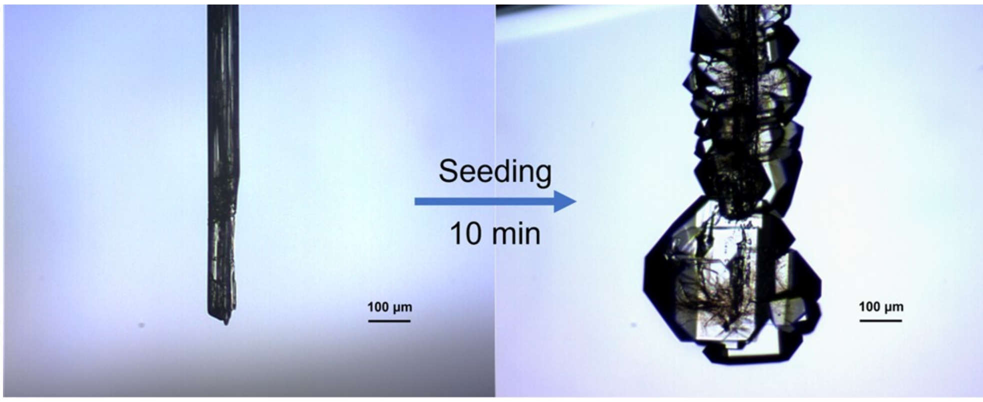

Figure S1. Tetragonal block crystals formed on the surface of a highly defective crystal seed by crystal transition in a supersaturated solution of the tetragonal phase (σ_T = 48.27 %).

Atomic Force Microscope (AFM)

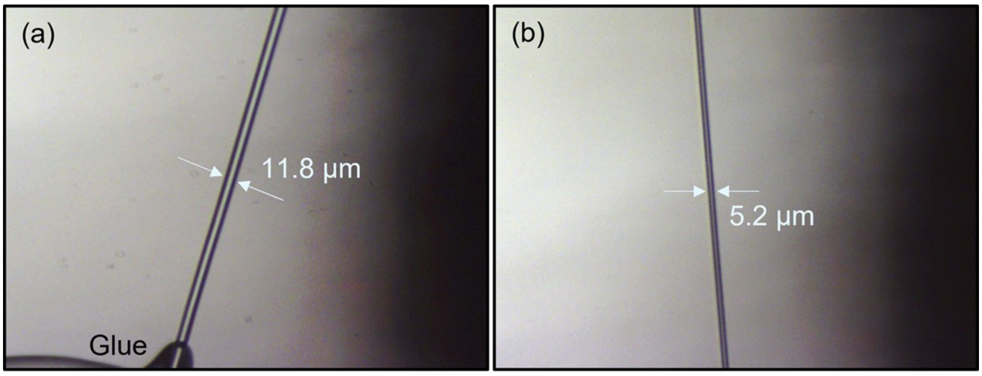

Figure S2. The microscope images of spontaneously nucleated monoclinic KDP fiber seeds with different widths for AFM observation. (a) typical W >10 µm; (b) typical W <10 µm.

Measurement of the Solubility and 1D Growth Curve of the KDP Monoclinic Phase

In the measurement, an in-situ microscopic observation method was adopted using a home-made microscopic imaging system. The temperature controlling of the solution was realized by a water bath circulator (Thermo Fisher heated immersion circulator S100). The accuracy of the temperature controller is ± 0.02 °C. The measurement of the solubility was started after the solution was kept at the set temperature for at least one hour until the temperature of the solution was stabilized. The microscopic observation of the dimensional change of the crystal length and width was typically lasted for over 12 hours. If the dissolution of the fiber tip is detected, the solution temperature will continue to drop by a step of 0.05 °C. The temperature at which no detectable dissolution of the fibers occurs was defined as the saturation point. The temperature points for the initiation of 1D growth of the metastable monoclinic crystal were obtained by further slow cooling the solution from the saturation points. The fitting function for initiating 1D growth curve of monoclinic phase in Figure 3 is

$$C = 28.94238 + 0.43973*T + 0.00441*T^2$$

T is temperature, and C is solution concentration. In addition to the water bath circulator, a monitor was also used to measure the practical temperature adjacent to the crystal. The accuracy of the monitor is 0.1 °C. Since the saturation and growth temperature points were determined by cooling, the resulting reading error should be less than -0.05 °C.

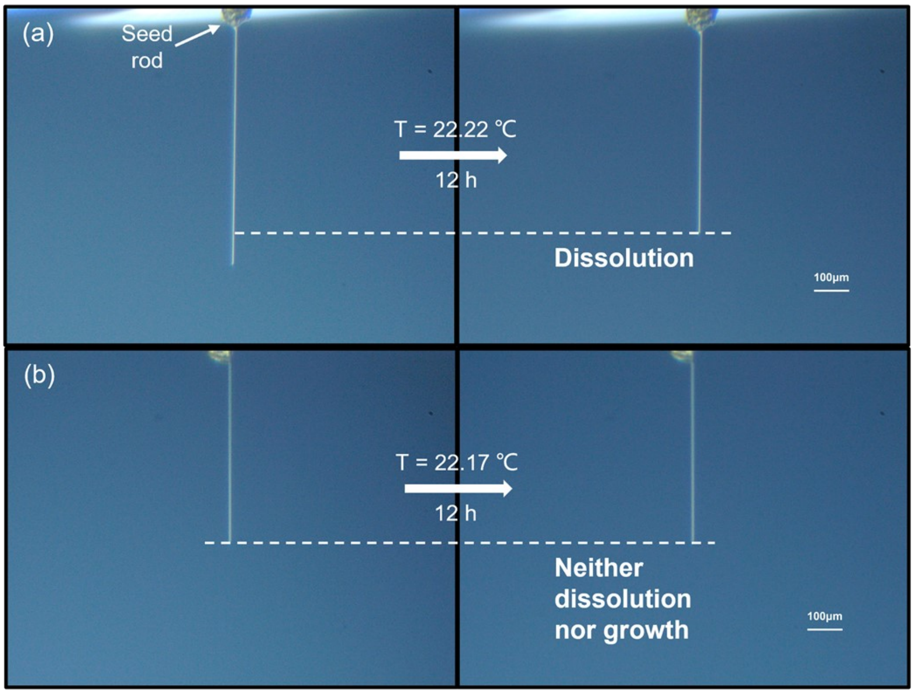

Figure S3. In situ micrographs captured during the solubility measurement of the monoclinic KDP fiber seeds. (a) Dissolution of a seeded fiber at 22.22 °C in a solution with a concentration of 40 g KDP/100 g H_2O. (b) After further cooling by 0.05 °C, the length of the fiber remained unchanged within 12 hours.

The Definition of Relative Supersaturation

The calculation formula of relative supersaturations (σ) is as follows.

$$\sigma = \frac{C - C_e}{C_e} \times 100\%$$

The supersaturation ratio (S) and relative supersaturations (σ) of different concentration solutions (C) were calculated based on the solubility (C_e) of monoclinic phase and the tetragonal phase at 25 °C respectively. The results were summarized in Table S1.

Table S1. The relative supersaturation (σ) and supersaturation ratio (S) of KDP solutions of different concentrations relative to the monoclinic phase (M) and the tetragonal phase (T) at 25 °C respectively.

KDP (g) in 100 g H_2O	Supersaturation relative to the monoclinic phase (σ_M, %)	Supersaturation relative to the tetragonal phase (σ_T, %)	Supersaturation ratio relative to the monoclinic phase (S_M)	Supersaturation ratio relative to the tetragonal phase (S_T)
43.0	2.29	51.82	1.02	1.52
44.0	3.94	54.27	1.04	1.54
45.0	5.57	56.69	1.06	1.57
46.0	7.18	59.07	1.07	1.59
47.0	8.76	61.42	1.09	1.61
48.0	10.33	63.75	1.10	1.64
49.0	11.87	66.04	1.12	1.66

Determination of the Supersaturations Required to Initiate One-Dimensional and Prismatic Growth of Monoclinic KDP Fibers at Room Temperature

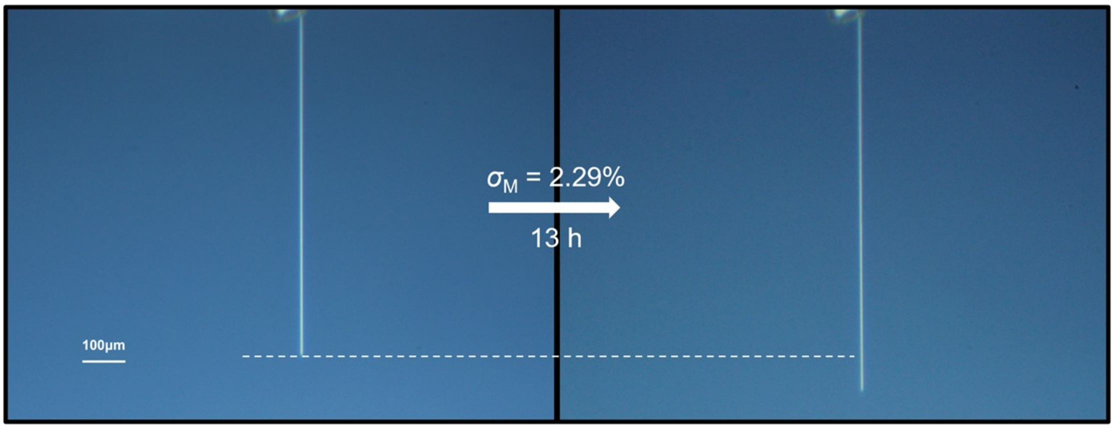

Figure S4. The micrographs of the monoclinic fiber initiating 1D growth in solution with the critical supersaturation of 2.29 %. The left picture was taken at the moment of seeding. The right picture was obtained after 13-hours observation.

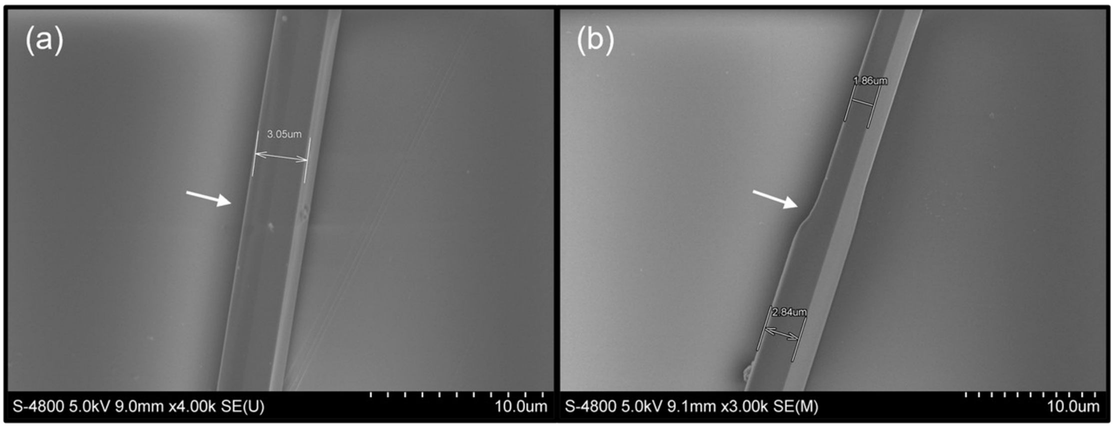

Figure S5. SEM images of KDP monoclinic fiber seeds grown in different supersaturated solutions for 10 minutes. (a) Fiber with unchanged width in solution with σ_M = 9.70 %. (b) Fiber widened by approximately 1.0 microns after growing for 10 minutes in solution with σ_M = 11.87 %. The white arrow labels the location of the interface between the solution and air.

Growth Rate and Driving Force of Monoclinic KDP Fiber Seeds at Different Supersaturation Levels

Growth of a monoclinic fiber seed in solutions of varied concentrations was recorded in situ using microscopy. The length increment in 1D growth over specific time intervals was measured to calculate the average growth rate. Thus, the crystal growth rate on different concentration and supersaturation were obtained.

The corresponding growth driving force data was calculated using the formula $\Delta\mu = kT\ln(C/C_e)$, C is the concentration at supersaturation, C_e is the equilibrium saturation concentration at the corresponding experimental temperature, k is the

Bolzman constant, and T is the temperature for seeding growth. The fitting accuracy and kinetics coefficients are listed in Table S2.

Table S2. Fitting details of the growth rate versus supersaturation curve for the 1D growth of monoclinic KDP fiber at 25 °C in Figure 5c.

Equation	$R = C_1\sigma^{2/3}[\ \ln(1+\sigma)\ ]^{1/6} \exp\{-C_2 / [298^2 \times \ln(1+\sigma)]\}$
Plot	Growth rate
C_1	334.3076 ± 71.88242
C_2	1200776.28351 ± 45562.99197
R-Square (COD)	0.99906

Movie S1 (separate file). Crystal transition of a defective seed crystal in the supersaturated region of the stable tetragonal phase. (sped up 14x)

Movie S2 (separate file). Monoclinic and tetragonal KDP fiber seeds simultaneously seeding into a solution slightly undersaturated relative to monoclinic phase. (sped up 25x)

Movie S3 (separate file). Monoclinic and tetragonal KDP fiber seeds simultaneously seeded into a solution at σ_M = 4.18 %. (sped up 15x)

References

1. C. Li, X. Liu, Z. Gao, J. Song, C. Zhang and Y. Ren, *Inorg. Chem.*, 2023, **62**, 19159-19163.