

Strong Additive-Surface Interaction Leads to the Unusual Revival of Growth at Solvent-Poisoned Faces of DL-Alanine Crystal

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Supporting Information

Confirmation of the salt-assisted morphological change at DL-alanine +c end. In our previous study¹, we found that a DL-alanine seed crystal practically does not grow along its polar c-axis in pure DL-alanine aqueous solutions at normal supersaturations ($C/C_{\text{sat}} < 1.75$, where C and C_{sat} are the actual

concentration and the solubility respectively). Such a dead growth was attributed to the preferential adsorption of solvent water at the polar +c and –c ends.

In the present study, we have observed that inorganic salts generally revive the solvent-poisoned dead growth¹ at both the –c and +c ends of DL-alanine seed crystals. Particularly, the salts promote the growth rates of the NH_3^+ -rich faces (namely, {001}, {201} and {011} faces) to different extents, causing a morphological change from a sharply pointed +c end to a blunt +c end. It was also noted that a similar morphological change at the +c end could be an outcome of crystal twinning (a phenomenon where two individual crystals are jointed through their pointed +c ends). For clarification, we present successive images (Figures S1 and S2) of growing DL-alanine seed crystals in the presence of typical inorganic salts (NaAc, $(\text{NH}_4)_2\text{SO}_4$ and NaCl) to show how the morphology at the +c end to change.

These images in Figures S1 and S2 typically depict the growth behavior at DL-alanine +c end in the presence of an inorganic salt while crystal twinning at the +c end did not occur. It can be observed that the {001} face at the +c end of a seed crystal, initially not existent, gradually appeared and became larger while the hemihedral {201} and {011} faces shrank, exhibiting a significant morphological change from a sharply pointed +c end to a blunt one (even to a rather flat +c end after a long period of time, Figure S1) though the pace of this morphological evolution varied with the conditions (e.g., type of inorganic salts, concentration of a given salt and the supersaturation). Such a morphological change was due to the fact that the salt-assisted growth rate of the {001} face was relatively slow compared with those of the hemihedral {201} and {011} faces. Nevertheless, the relatively fast growing hemihedral faces might not shrink so quickly and they could co-exist with the {001} face, with the +c end still remaining somewhat pointed for a period of time (Figure S2).

In conclusion, inorganic salts indeed generally accelerate the growth of the NH_3^+ -rich faces (namely, {001}, {201} and {011} faces) to different extents, causing the sharply pointed +c end to become a blunt +c end while crystal twinning does not occur. Without crystal twinning, the {001} face, newly appearing at the blunt (even flat) +c end, is not the {00-1} face which exposes at the flat –c end.

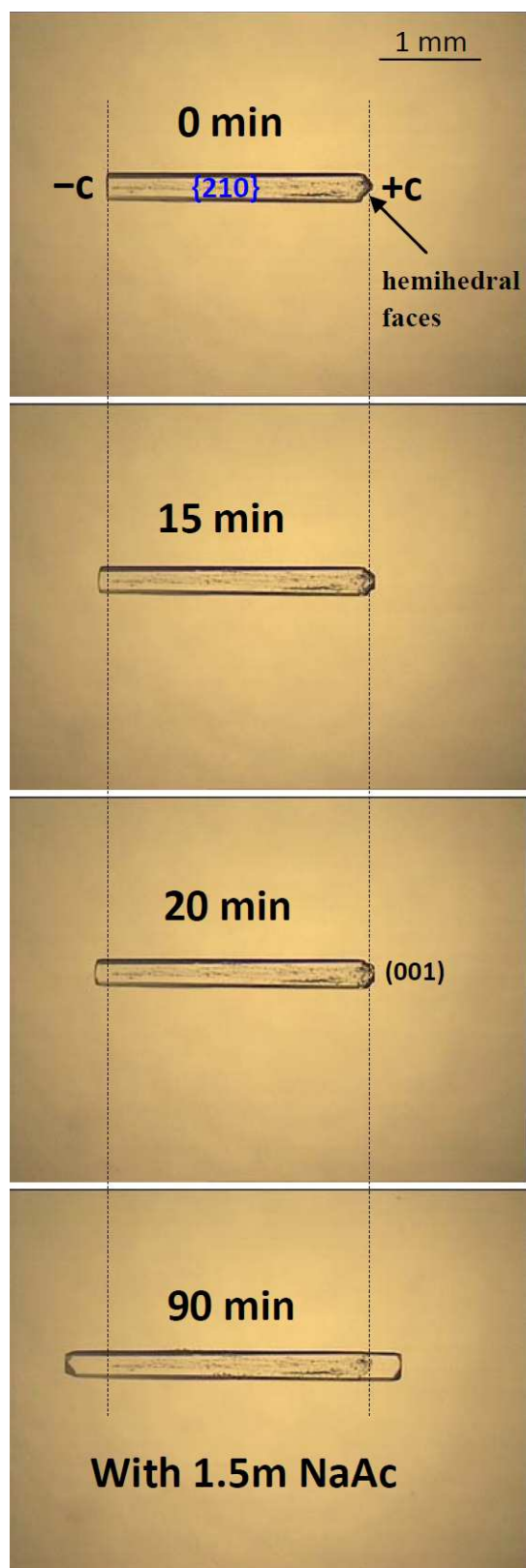


Figure S1. Successive images of a DL-alanine seed crystal growing in a solution in the presence of NaAc at supersaturation $\sigma = 1.3$ at 23°C, showing the morphological change at the $+c$ from sharply pointed to blunt while crystal twinning at the $+c$ end was not observed.

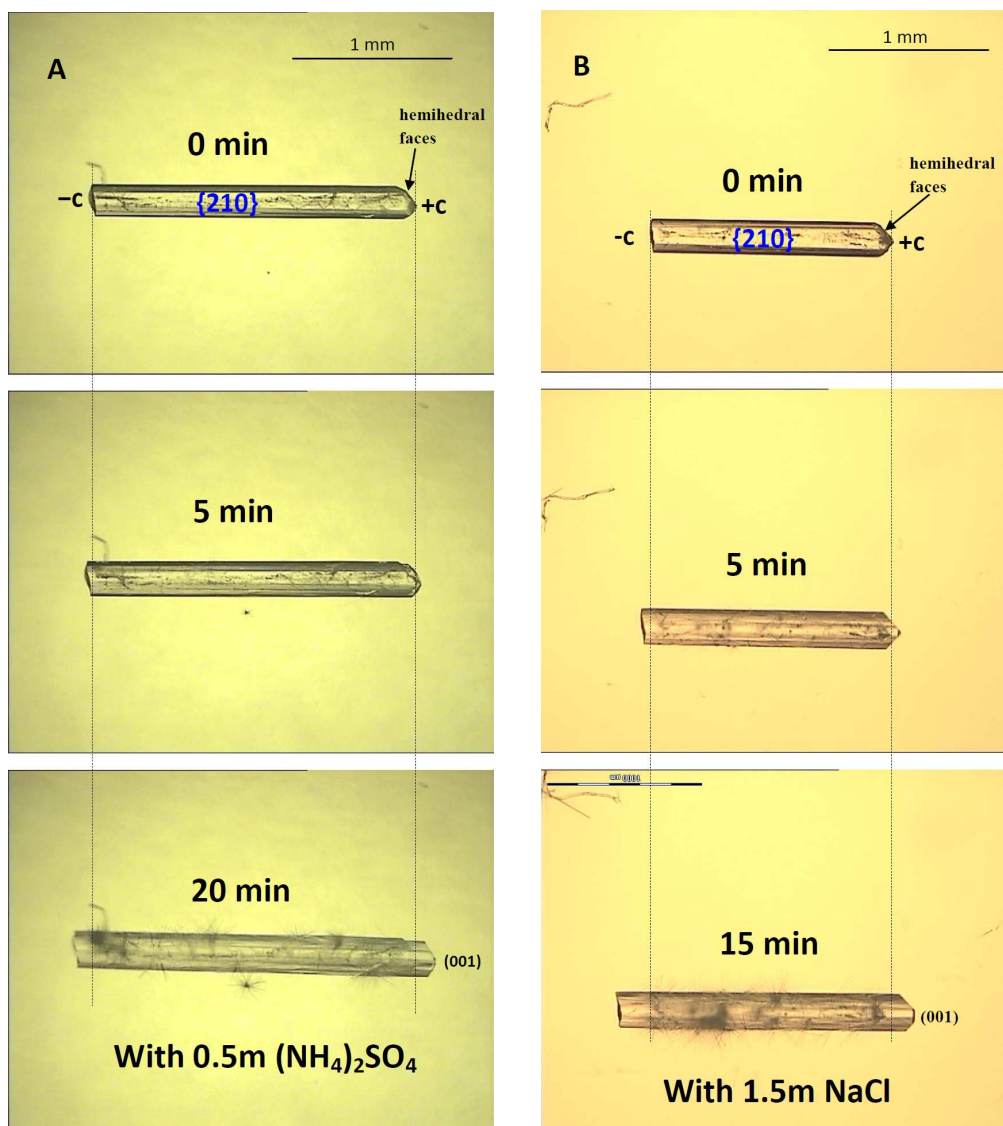


Figure S2. Successive images of DL-alanine seed crystals growing in a solution in the presence of 0.5m $(\text{NH}_4)_2\text{SO}_4$ and 1.5m NaCl, respectively, at supersaturation $\sigma = 1.4$ at 23°C , showing the morphological change at the +c from sharply pointed to blunt while crystal twinning at the +c end was not observed.

Confirmation of DL-alanine solid form. Our measured PXRD patterns (Figure S3) of the needle-like DL-alanine crystals, spontaneously formed in various salt solutions, are practically the same as the simulated PXRD pattern (CSD ref. code DLALNI01). Since the simulated PXRD pattern represents the sole crystalline structure¹ of DL-alanine crystals which can exhibit different habits, it is confirmed that

all these inorganic salts used in this study, acting as additives, do not induce different solid forms (i.e., polymorphs) of DL-alanine crystals.

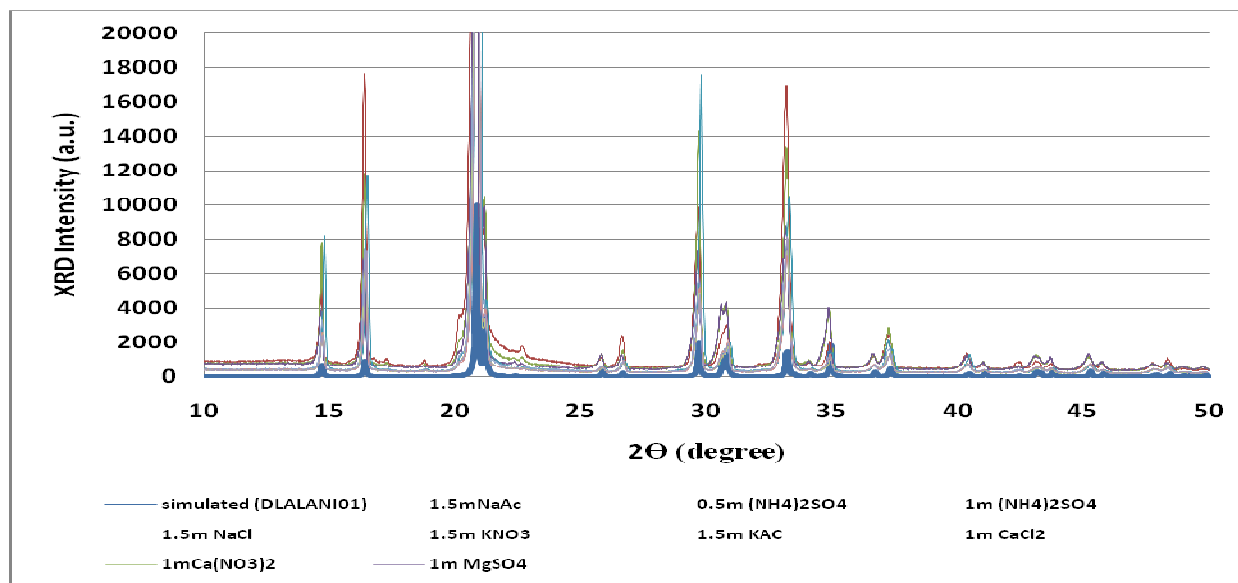


Figure S3. Identical PXRD patterns of the DL-alanine crystals spontaneously formed in various salt solutions, showing that all these crystals are the same in crystalline structure.

REFERENCES

1. Han, G.; Chow, P. S.; Tan, R. B. H. Cryst. Growth Des. 2011, 11, 3941–3946.