Colloquium on Polymer Science and Molecular Engineering Zhejiang University and the University of Chicago
12-16 April 2017

Programming the internal structure of single crystals by gel incorporation

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Abstract: In nature, assembling crystals with foreign materials in a programmed fashion is a strategy to realize properties beyond what pure crystals intrinsically possess.. However, it is challenging to adopt this bioinspired strategy for the design of synthetic single crystalline materials partially because single crystals are typically homogeneous. Here, controlling crystallization conditions are demonstrated to switch single crystals of potassium dihydrogen phosphate between two states: crystals with or without incorporated gel-networks (termed as state “1” or “0”). Fast growth rate leads to state “1”, whereas slow crystallization results in state “0”. In addition, these two states can be obtained by changing crystallization media (solution for “0”; gel for “1”). Oscillating crystallization condition induces switching between the two states within individual crystals. Consequently, programmed crystals, such as “010”, “001”, “011”, “100”, “110”, “101”, have been demonstrated. As such, our work provides a facile way to prepare single crystals with programmable structures and properties.

Controlling the internal structure of KDP single crystals grown in silica gel by regulating growth kinetics

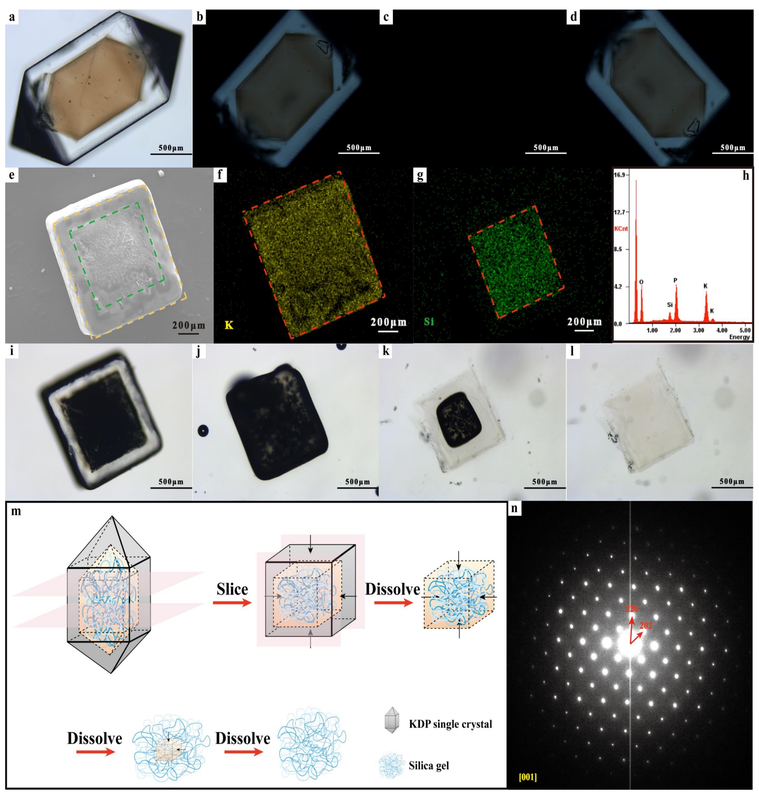
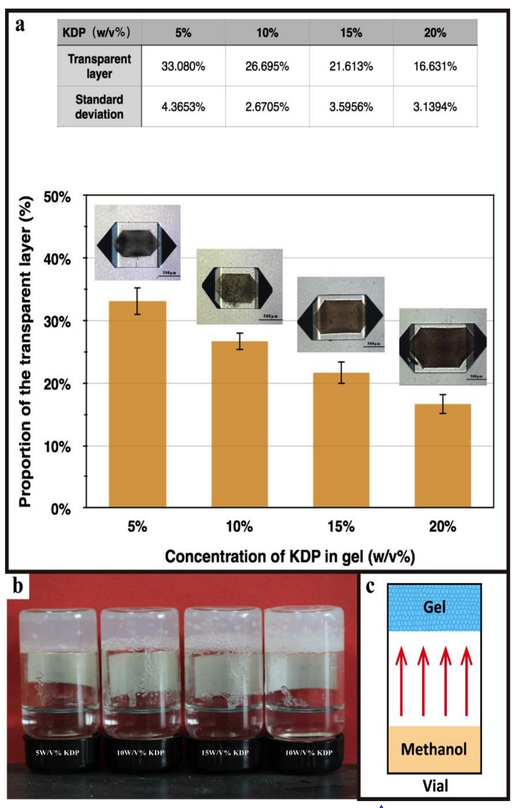


Fig.1. Two-layer KDP crystal was characterized by OM, SEM, EDS and TEM. Schematic diagram represents the dissolution process of a cuboid cut from the crystal. The SAED pattern suggests its single-crystallinity.



KDP (w/v%)	5%	10%	15%	20%
Transparent layer	33.080%	26.695%	21.613%	16.631%
Standard deviation	4.3653%	2.6705%	3.5956%	3.1394%

Fig.2. 40 crystals at each KDP concentration from different vials were calculated for the width proportion of the transparent layer. Higher KDP concentrations lead to larger translucent cores.

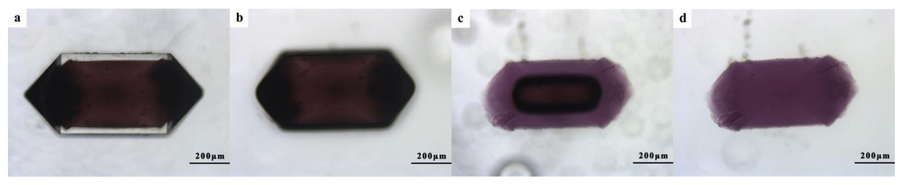
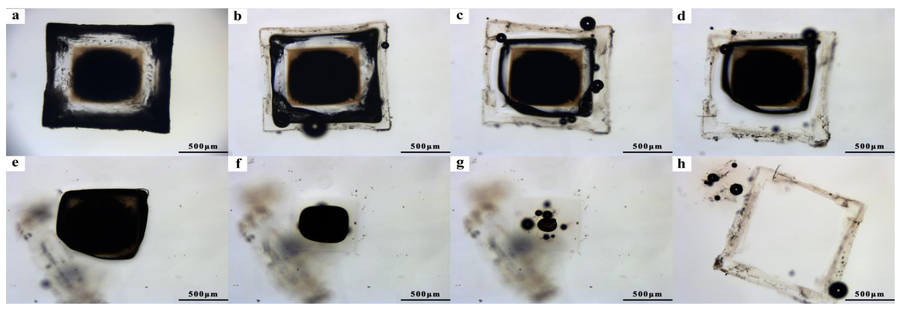


Fig.3. Two-layer KDP crystal with Gold nanoparticles incorporated[4,5] merely in the core.

Fig.4 Further raise of growth rate on the basis of the two-layer crystal “10” caused a third translucent layer.



Controlling the internal structure of KDP single crystals grown in agarose gel by switching growth media

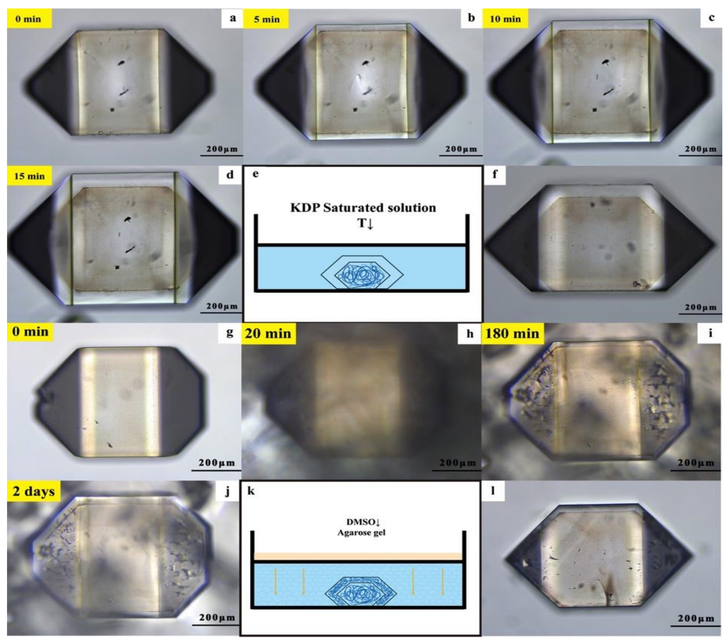


Fig.5. Thickness of each layer can be controlled precisely by manipulating growth time under optical microscope.

Fig.7. Different pathways lead to crystals with various inner structures such as “010”, “001”, “011”, “100”, “110”, “101” or even more layers like “01010” by freely switching growth media between gel and solution.

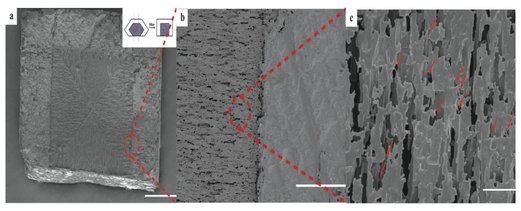
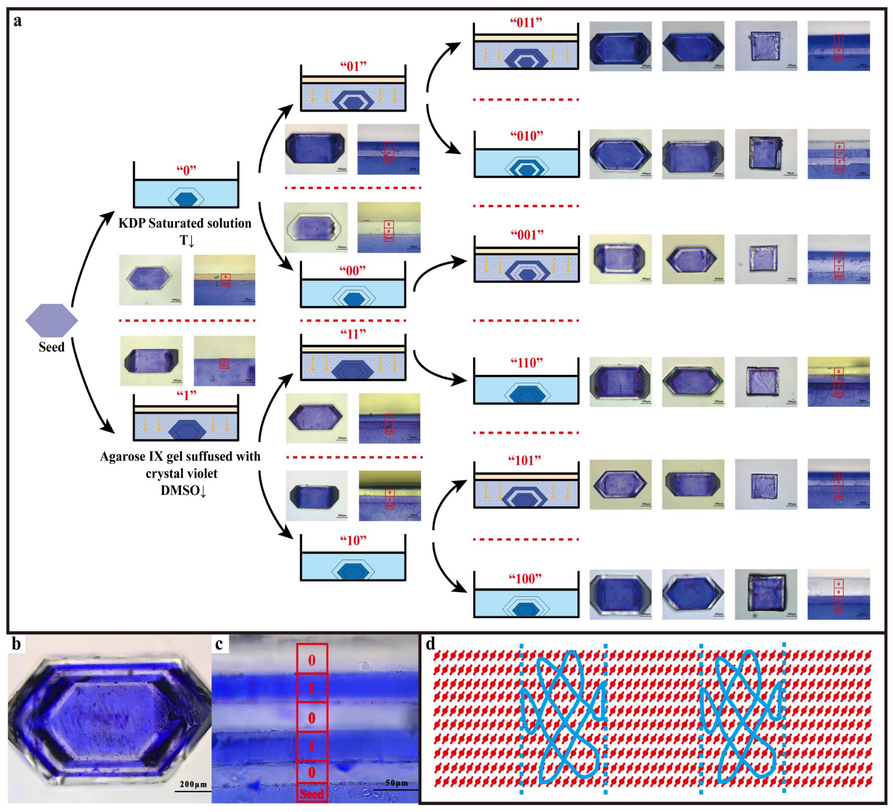


Fig.6. SEM images of the transverse section of a cuboid cut from an etched KDP crystal. Clear boundary can be seen between the coarse seed and the smooth layer “0”. Nanofibers can be found in the etched holes of the seed.



Conclusions： For the first time, this work provides practical and facile ways to manipulate the internal structure of individual single crystals in a programmed manner and expands potential applications for these biomimetic composites.

Acknowledgement： This work was supported by 973 Program (2014CB643503), National Natural Science Foundation of China (51373150, 51461165301), and Zhejiang Province Natural Science Foundation (LZ13E030002).

References： [1] AP Jackson et al. *Proc. R. Soc. Lond. B.* **1988**, 234, 415-440; [2] F Nudelman et al. *Faraday Discuss*. **2007**, 136, 9-25; [3] HY Li et al. *Adv. Mater*. **2009**, 21, 470-473; [4] YJ Liu et al. *Angew. Chem. Int. Ed*. **2014**, 53, 4127-4131; [5] YJ Liu et al. *Chem. Mater*. **2016**, 28, 7537−7543.