Gel-Network Incorporation into Single-Crystals: Effects of Gel Structures and Crystal-Gel Interaction

Liao Chen, Tao Ye, Yujing Liu, Wei Liu, Gang Wu, Hongzheng Chen and Hanying Li*

State Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China

Introduction

Gel-grown single-crystal composites where gel-networks are incorporated inside single-crystals have been reported in an increasing number of studies, with the composite structure similar to that of the biogenic biomacromolecule-incorporated single-crystals. However, the mechanisms of the gel incorporation are still not clear. In this work, we examined the growth of four types of crystals (NaF, NaCl, KBr and potassium dihydrogen phosphate (KDP)) in both silica gels and agarose gels to access the effects of crystal-gel interaction and gel structure on the gel incorporation.

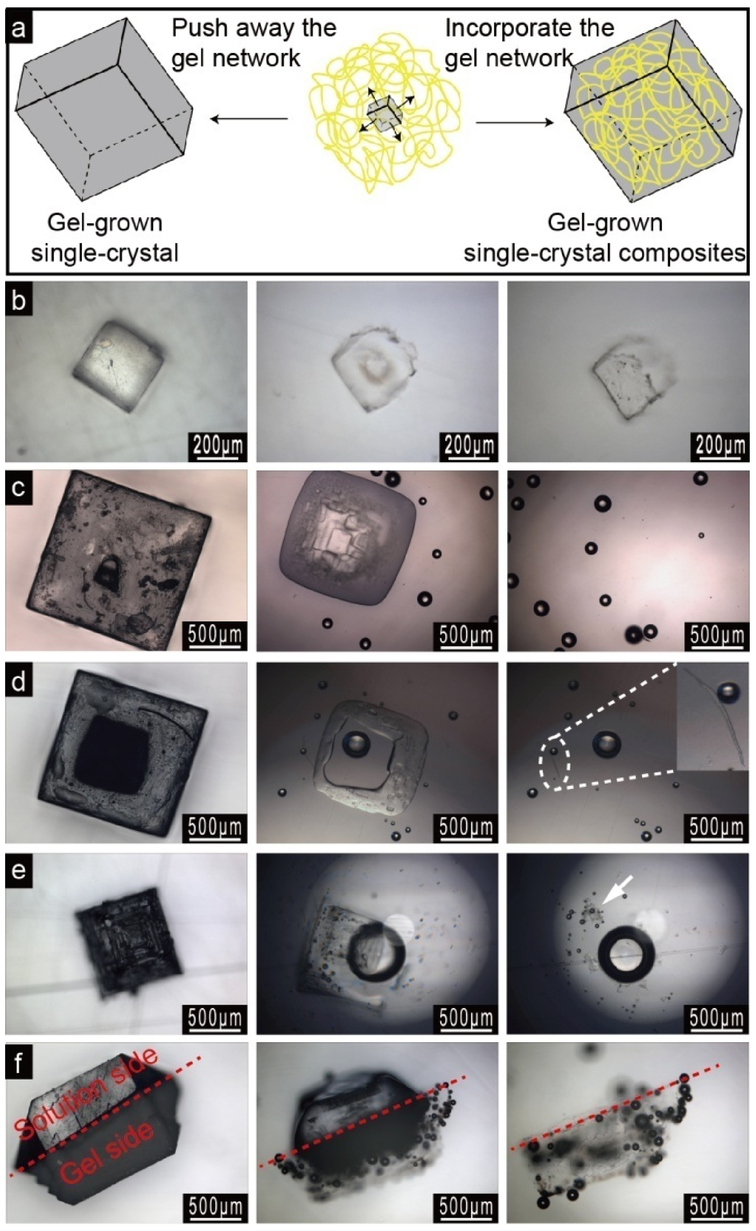

Fig. 1 **Optical microscopy (OM) images of crystals grown in silica gels before (left), during (middle) and after (right) dissolution of the crystals.** (a) A schematic representation of gel-grown crystals that may either incorporate or push away the gel-network. (b, c, d, e, f) OM images recording the dissolution processes of crystals: (b) NaF from silica gel; (c, d) NaCl from silica gels; (e) KBr from silica gel; (f) KDP from the interface of solution and silica gel. After dissolution of the crystal, the solution side disappeared while the gel side leaves a block of crystal-like gel. The inset in (d) and the white arrows in (e) highlight the gel fragments. The results show that NaF and KDP crystals can incorporate silica gel-network more probably.

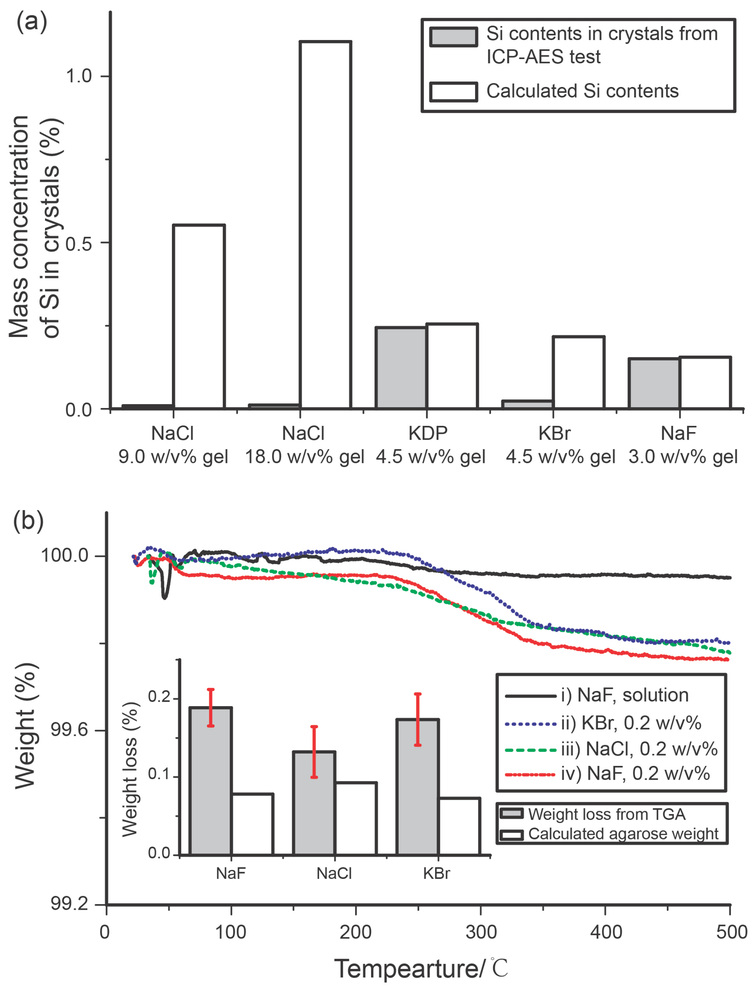

Fig. 2 **Quantification of the incorporated gel-networks in the crystals:** (a) Mass ratio of Si in crystals grown from silica gels; (b) TGA curves for NaF crystal grown from solution and NaF, NaCl and KBr crystals grown in 0.2 w/v% agarose gels; Inset in (b) is the amount of agarose in crystals from TGA (gray column) and calculation(blank column).

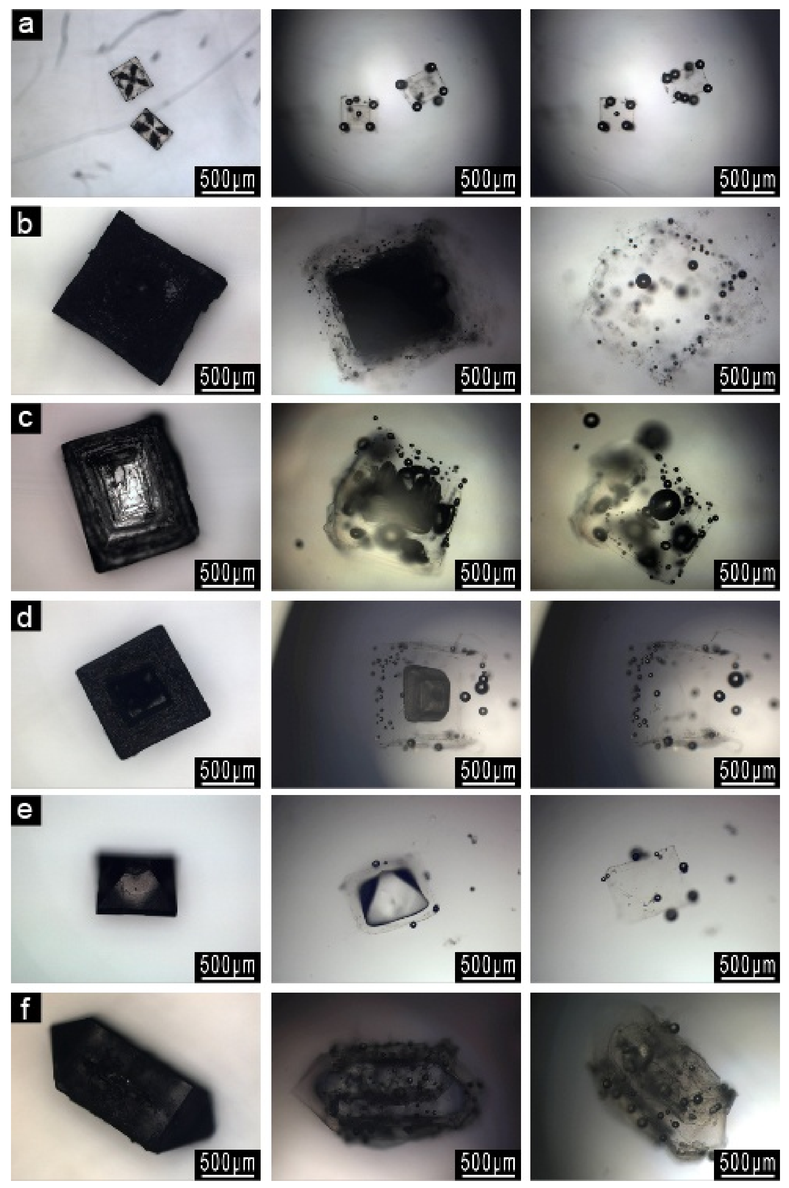

Fig. 3 **OM images of crystals grown in agarose gels before (left), during (middle) and after (right) dissolution of the crystals.** (a) NaF in 0.2 w/v% agarose gel; NaCl in (b) 0.2 w/v% and (c) 0.5 m/v% agarose gel; (d) KBr in 0.2 w/v% agarose gel; KDP in (e) 0.2 w/v% and (f) 1 w/v% agarose gel. The crystal-shape residuals indicate that all the crystals grown in agarose gels can incorporate the gel-networks.

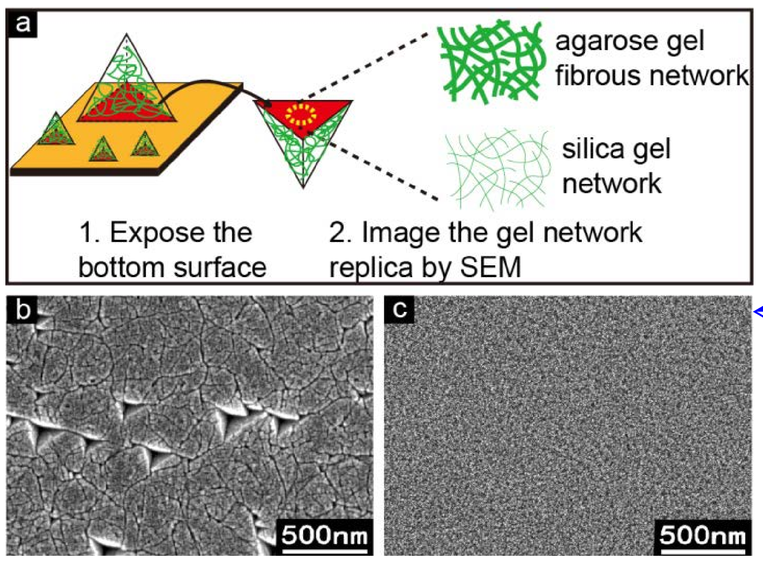

Fig. 4 **Characterization of the gel structure of agarose and silica gels:** (a) A schematic representation of the replica method used to image the gel structures. The well-oriented calcite crystal on the SAM-modified Au substrate incorporated the gel and the flat bottom surface became a replica of the gel-network. (b, c) SEM images of the bottom surfaces of calcite grown from (b) an agarose gel and (c) a silica gel.

Conclusions

For a gel with mechanically weak gel-network like the silica gel, strong crystal-gel interaction of hydrogen bond was necessary to promote the gel-incorporation in the NaF and KDP crystals. In contrast, the fibrous structure in agarose gel resulted in strong gel-network and the four gel-grown crystals all incorporated the agarose gel-network even if the hydrogen bond was relatively weak. As such, this work demonstrates the critical effects of the gel structures and the crystal-gel interactions on the gel-incorporation inside gel-grown crystals and may help to prepare single crystal polymer composites with desired structures and properties.

References

[1] H. Y. Li and L. A. Estroff, *Adv. Mater.*, 2009, **21**, 470-473;
[2] H. Y. Li et al., *Science*, 2009, **326**, 1244-1247;
[3] J. A. Gavira et al., *Crystal Growth & Design*, 2013, **13**, 2522-2529;
[4] Y. J. Liu et al., Angew. Chem., Int. Editi., 2014, **53** 4127-4131