Constructing bulk-contact inside single crystals of organic semiconductors through gel incorporation

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Abstract: Single crystals of organic semiconductors are promising for high-performance semiconducting materials by virtue of their superior charge mobilities. Interfacing these single crystals with other foreign materials is needed to fabricate varied electronic devices. However, it is difficult to construct interfaces inside a single crystal that is typically homogeneous. In this work, single crystals of two typical organic semiconductors, anthracene and 9,10-diphenylnanthracene (DPA), were grown from both silica gels and phenyl-modified silica gels. X-ray diffraction analysis demonstrated their single-crystallinity. Examination of the residues remained after the sublimation of the gel-grown crystals revealed that single crystals grown from phenyl-modified silica gels incorporated the gel networks, with the gel networks penetrating through the crystal in three-dimensional space, whereas the silica-gel-grown crystals did not. This discrepancy suggests that the affinity between crystal and gel network favours gel incorporation. As such, our work provides a potential way to fabricate bulk contact between single crystals of organic semiconductors and foreign materials through gel crystallization.

Figure 1. (a) A schematic representation of two ways to interface organic single crystals with foreign materials. Route A: Planar contact is made from the outer surfaces of a single crystal. Route B: Bulk contact is constructed inside a single crystal as foreign materials are incorporated into the crystal; (b) The chemical structures of the two gelators (TMOS and PTMS), the corresponding gels, and the two crystals (anthracene and DPA); (c) A schematic representation of a crystal growing in gel media.

Figure 2. (a, b) Optical microscope (OM) images of anthracene single crystals grown from silica gel (a) and phenyl-modified silica gel (b) before (left), during (middle) and after (right) sublimation; (c, d) OM images of DPA single crystals grown from silica gel (c) and phenyl-modified silica gel (d) before (left), during (middle) and after (right) sublimation ; (e) OM images of a relatively large DPA crystal: before sublimation (left), top view after complete sublimation (middle), and side view after complete sublimation (right); (f-h) SEM images and EDX analyses and maps (Si element) of anthracene crystals grown from phenyl-modified silica gels: (f) as-grown; (g) partially sublimated; (h) fully sublimated. The EDX spectra were taken at the positions of the crosses and the blue line and square point out where the Si element peak should be; (i) The measured / calculated mass ratio of Si incorporated into the anthracene crystals grown from gels with different Cphen values (the proportion of phenyl groups in all the side groups of TMOS and PTMS ) and the relative Si content.

Figure 3. OM images of the multi-step sublimation process of anthracene crystals grown from phenyl-modified silica gels: (a) as-grown; (b, d, f, h) after sublimation in each step, with an inset to highlight an edge of the partially sublimated crystal; (c, e, g) after being washed with 5 M aqueous NaOH in each step.

Conclusion: In summary, we have prepared anthracene and 9,10-diphenylnanthracene (DPA) single crystals in silica gels and phenyl group-modified silica gels. The crystals grown from silica gels without modification could hardly incorporate the gel matrices, while those obtained from modified silica gels with different concentrations of phenyl groups exhibited various degrees of incorporation. With the concentration of phenyl groups in the gels increasing, the amount of incorporated gels rose significantly, and thus bulk-contact between the single crystals and the gel networks was formed, with the gel networks penetrating the crystals in three-dimensional space. This transition is attributed to an improvement in the affinity between the crystal and the gel network. Because such gel–crystal interaction plays a critical role in the process of gel incorporation into single crystals, it can be inferred that gels formed from conjugated molecules will provide stronger affinity to the crystals of organic semiconductors and further favor gel incorporation and the formation of bulk-contact inside the crystals.

References
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