Gel-incorporated PbS and PbI₂ single-crystals

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Introduction

Gel-incorporated single-crystals provide unique combinational properties of long-range order and composite structures, which is desired for semiconducting and conducting materials. However, the reported gel-incorporated single-crystals are limited to insulating crystals. Here, we examine crystals of two typical semiconductors, lead sulfide (PbS) and lead iodide (PbI₂), grown from both silica gels and agarose gels, and obtain gel-incorporated single-crystals for all the four crystal-gel pairs. As such, this work creates a facile strategy to construct 3D heterostructures inside semiconducting single-crystals without destroying their long-range order.

Results and discussion

![Figure 1](image1.png)

**Figure 1.** (a, b) OM images of PbS crystals grown in a silica gel (7.5 w/v %): (a) as prepared; (b) after dissolving the crystal with 12 M HCl. (c, d) SEM images of PbS crystals grown in a silica gel (11.25% w/v): (c) as prepared; (d) after slightly etched by 8M HCl. The arrows highlight the exposed gel materials.

![Figure 2](image2.png)

**Figure 2** (a) schematic representation of plate-like crystal growing in gel media: A growing crystal exerts anisotropic pressures on the surrounding gel networks and expands them; The gel networks incorporated inside the crystal recoil and shrink after the crystal is dissolved. (b, c) OM images of PbI₂ crystals grown in a silica gel (10.9 w/v %): (b) as prepared; (c) after dissolving the crystal with 4 M Na₂S₂O₃. (d, e) OM images of PbI₂ crystals grown in a silica gel (5.45 w/v %): (d) as prepared; (e) after dissolving the crystal with 4 M Na₂S₂O₃. The outline of the crystal is highlighted by dash lines.

The measured ratio is much lower than the calculated values. One possible explanation is associated with the hexagonal plate-like morphology. During crystallization, the crystals exert anisotropic pressures on the surrounding gel networks. As a result, the gel network is expanded and “diluted” (Fig. 2a). The gel networks shrinkage as they were released is a supporting evidence. (Fig. 2e).

![Figure 3](image3.png)

**Figure 3** (a, b) OM images of PbI₂ crystal grown in 0.2 w/v % agarose gels: (a) as prepared; (b) after the crystal was dissolved in 4 M Na₂S₂O₃, with gel left. (c, d) SEM images of PbI₂ crystals grown in 0.2 w/v % agarose gels: (c) as prepared; (d) after the crystal was slightly etched by 4 M Na₂S₂O₃. The arrows highlight the exposed gel fibers.

![Figure 4](image4.png)

**Figure 4** (a, b) OM images of PbS crystals grown in 0.5 w/v % agarose gels: (a) as prepared, (b) after the crystals were dissolved in 12 M HCl. (c, d) SEM images of PbS crystals grown in 1 w/v % agarose gels: (c) as prepared; (d) after the crystals were slightly etched by 3 M HCl. The arrows highlight the exposed gel fibers.

Conclusion

We have prepared PbS and PbI₂ single-crystal grown from both silica and agarose gels and demonstrated that the obtained crystals were gel-incorporated single-crystals for all the four crystal-gel pairs. This work provides a possible way to construct internal hybrid structure inside semiconducting single-crystals. One of the future directions is to prepare semiconducting single-crystals with incorporated semiconducting gels to make high-performance electronic applications.

References

4. L. Chen et al., *CrystEngComm*, 2014, 16, 6901-6906