

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

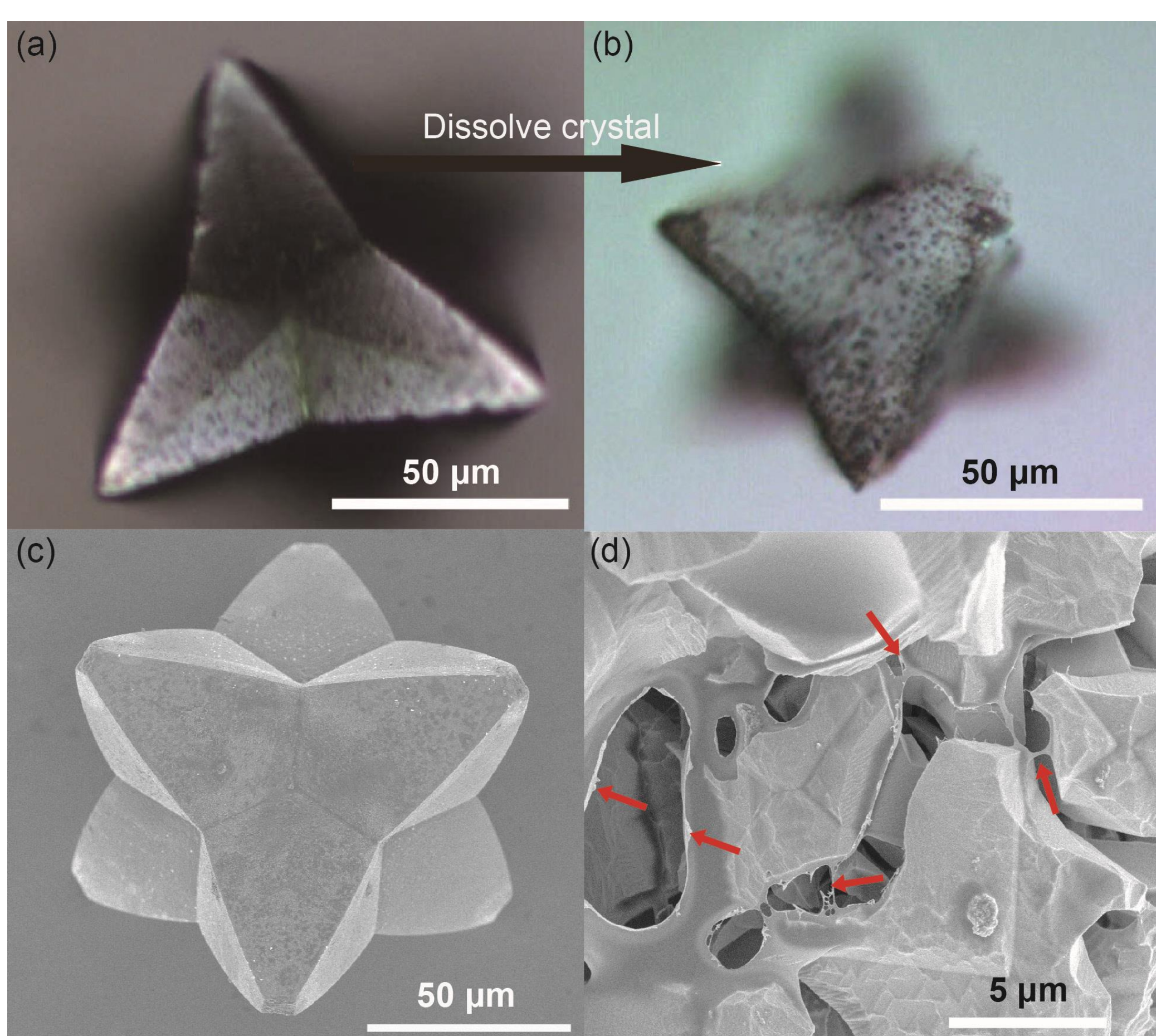
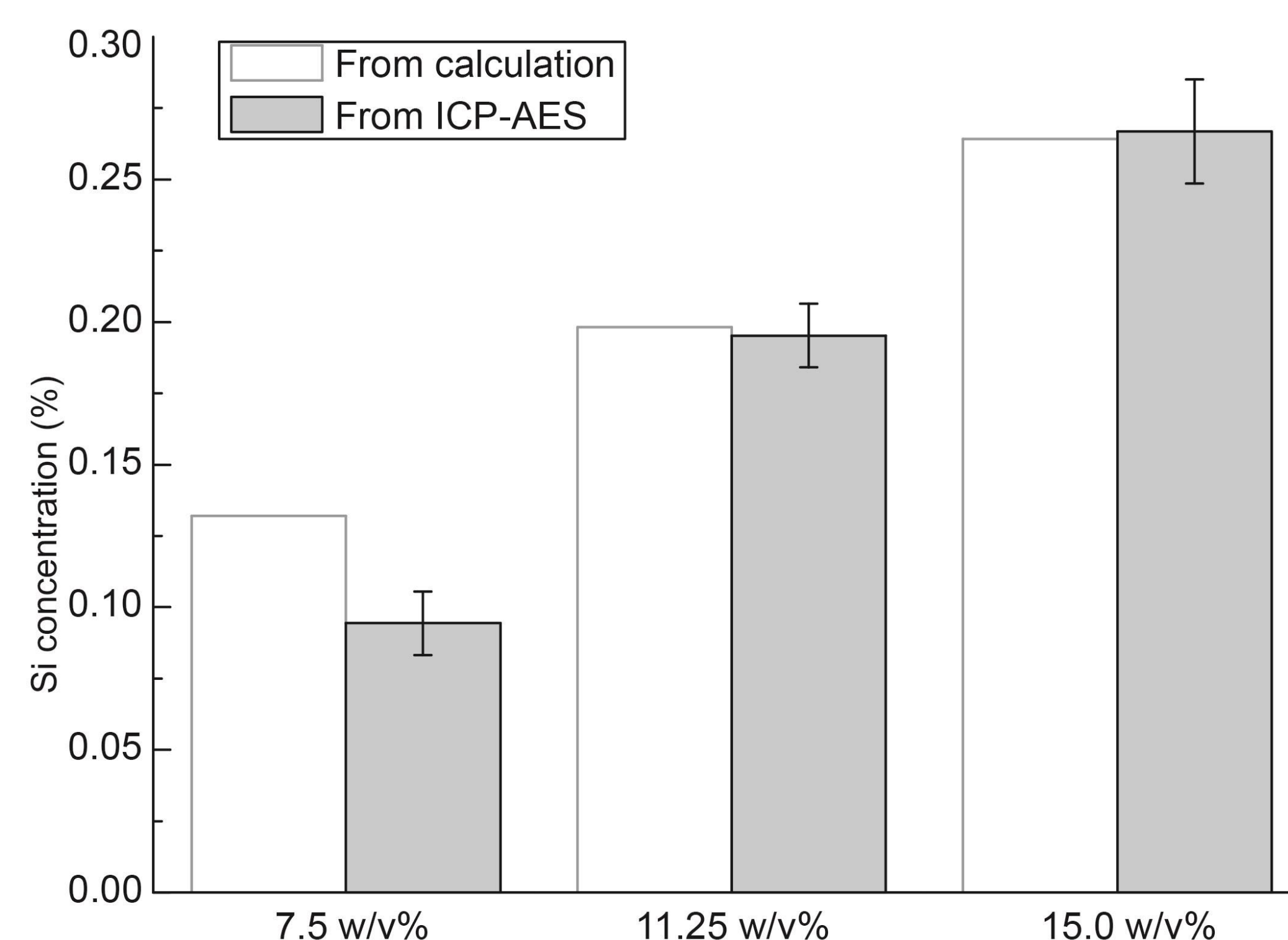


Figure 1. (a, b) OM images of PbS crystals grown in a silica gel (7.5 w/v %): (a) as prepared; (b) after dissolving the crystal with 12 M HCl. (c, d) SEM images of PbS crystals grown in a silica gel (11.25%v/v): (c) as prepared; (d) after slightly etched by 8M HCl. The arrows highlight the exposed gel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



Mass ratio of Si in PbS crystals grown in silica gels with varied concentrations

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 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).

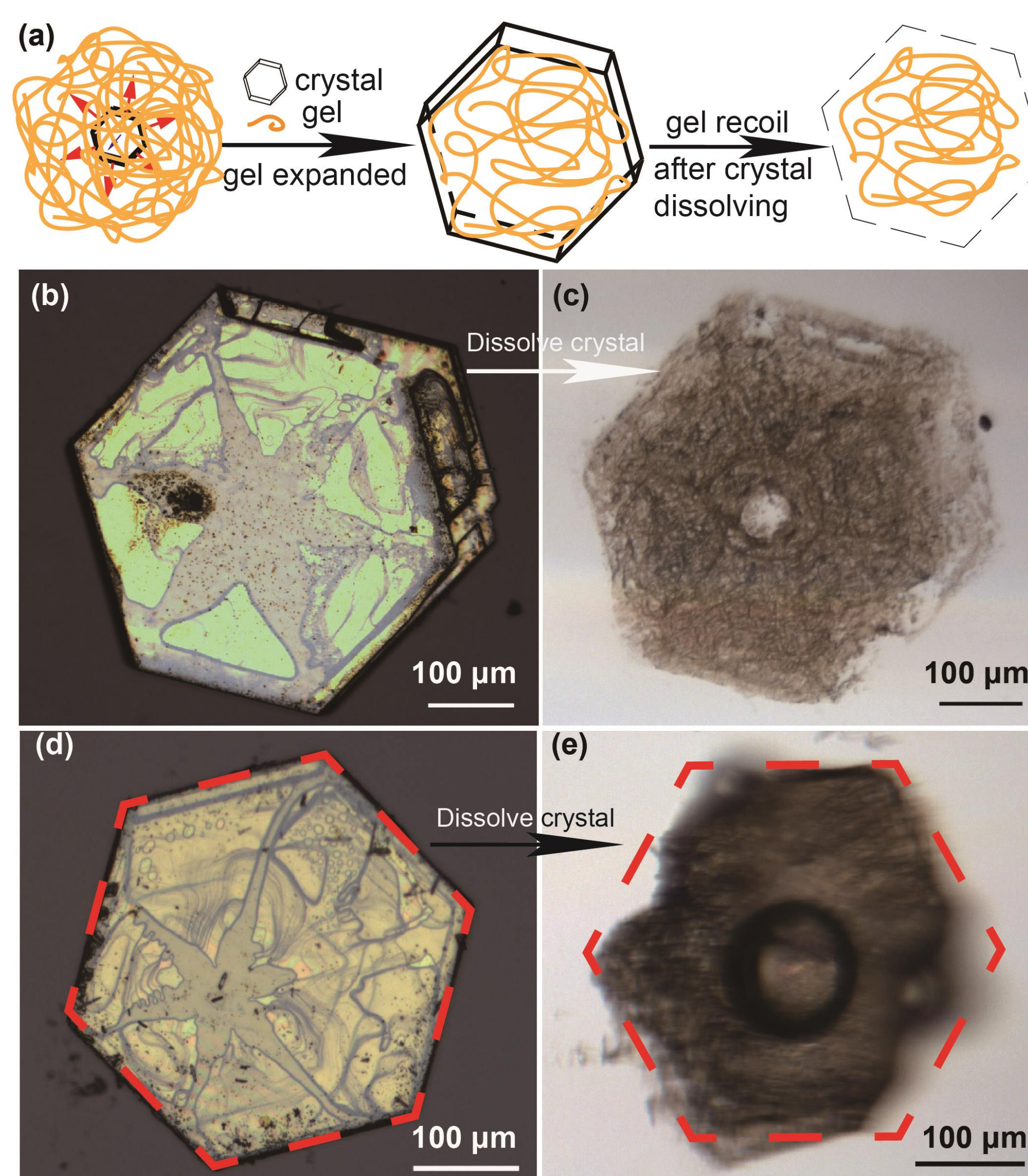
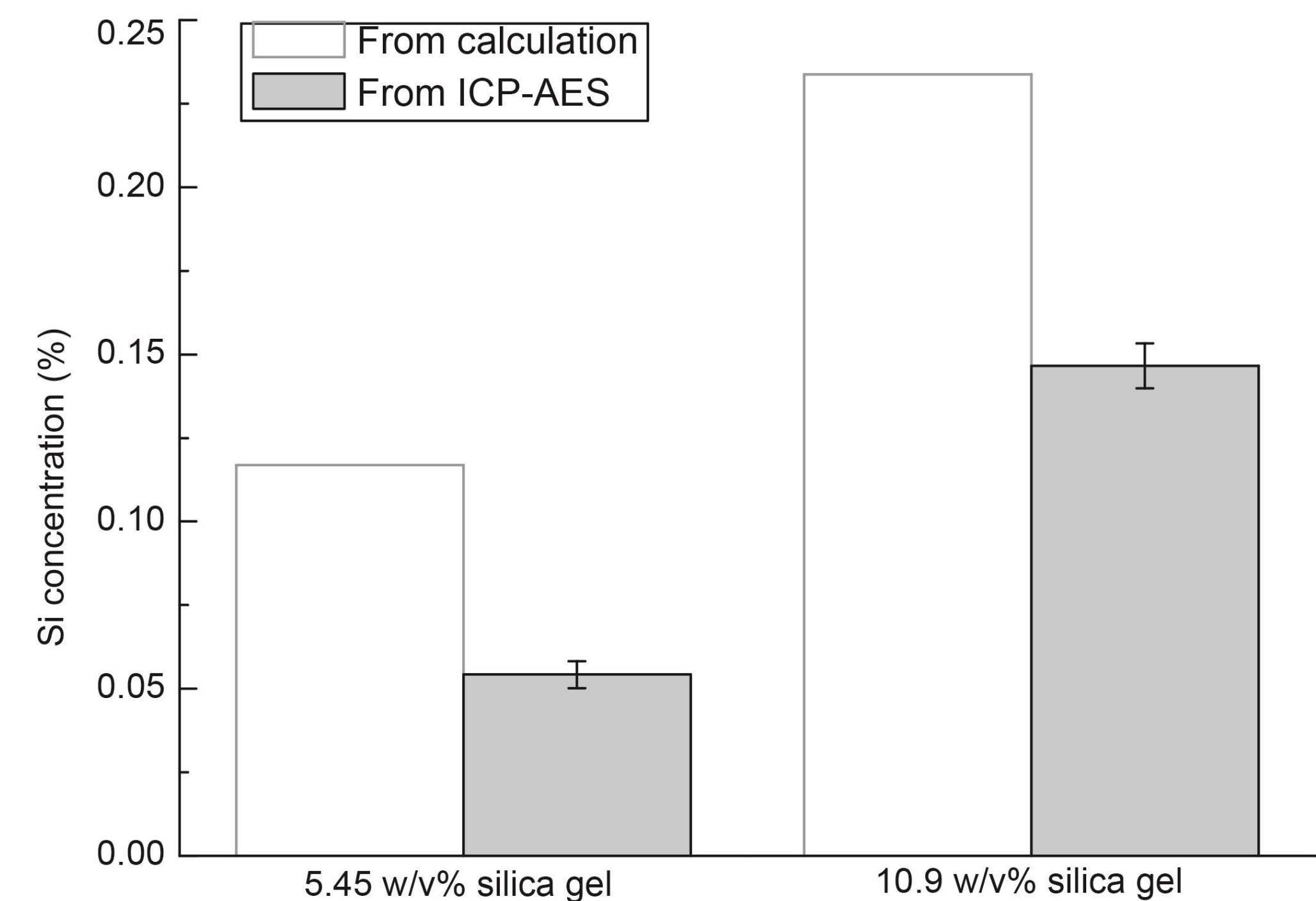


Fig. 2 (a) schematic representation of plate-like crystal growing in gel media: A growing crystal exerts anisotropic pressures on the surrounding gel networks and expands them; The gel networks incorporated inside the crystal recoil and shrink after the crystal is dissolved. (b, c) OM images of PbI₂ 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.



Mass ratio of Si in PbI₂ crystals grown in silica gels with varied concentrations

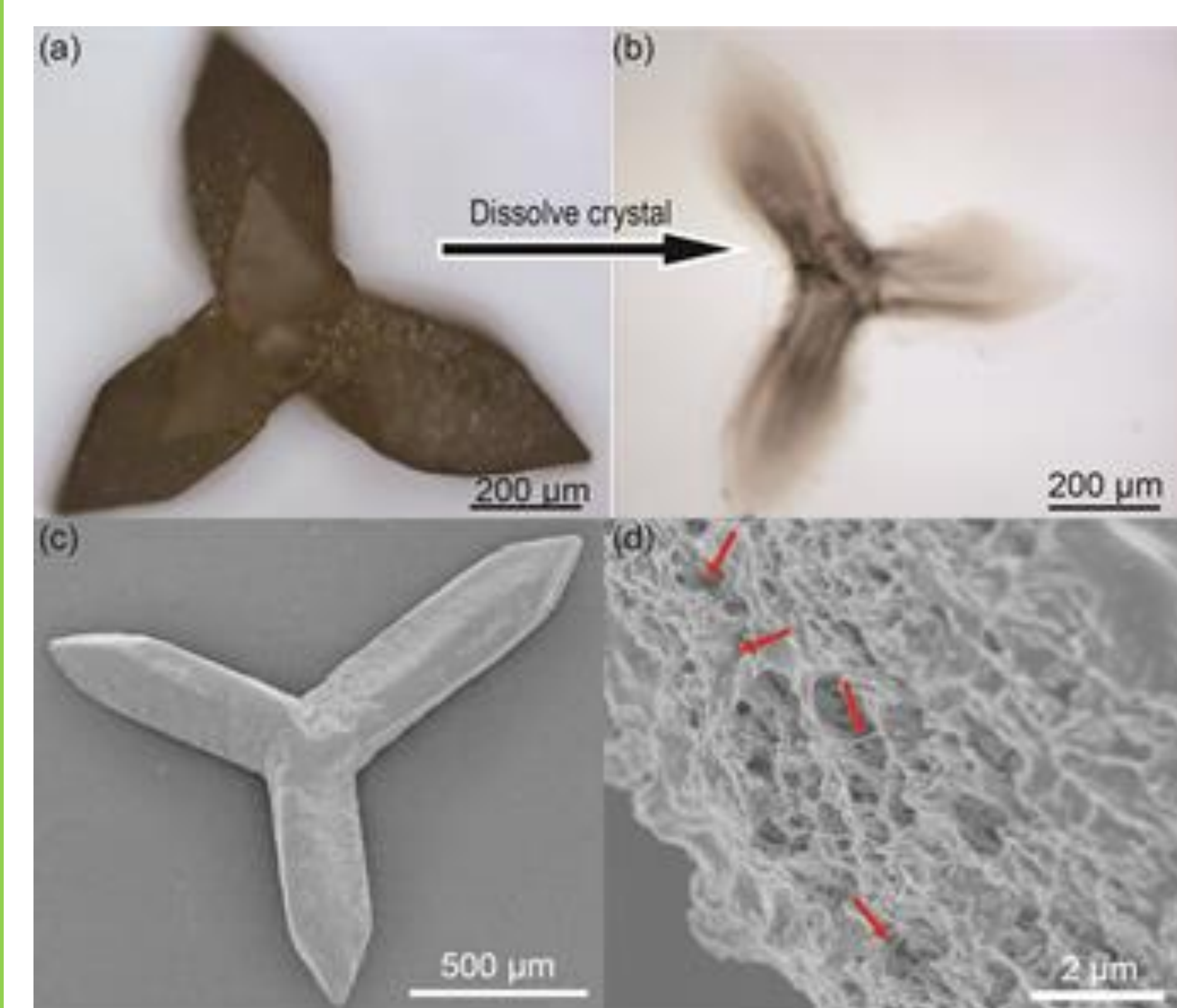


Fig. 3 (a, b) OM images of PbI₂ crystal grown in 0.2 w/v % agarose gels: (a) as prepared; (b) after the crystal was dissolved in 4 M Na₂S₂O₃, with gel left. (c, d) SEM images of PbI₂ crystals grown in 0.2 w/v% agarose gels: (c) as prepared; (d) after the crystal was slightly etched by 4 M Na₂S₂O₃. The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

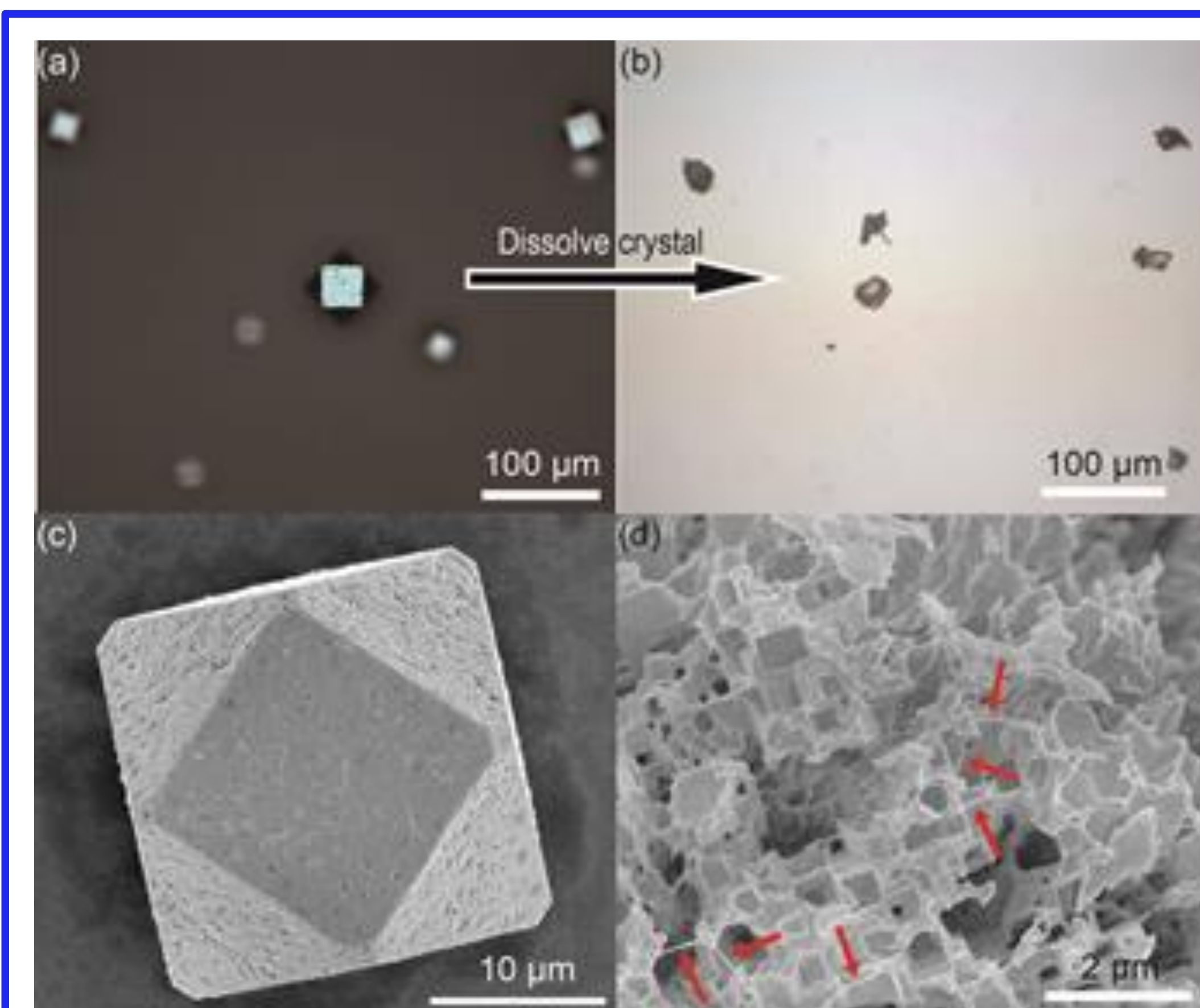


Fig. 4 (a, b) OM images of PbS crystals grown in 0.5 w/v% agarose gels: (a) as prepared, (b) after the crystals were dissolved in 12 M HCl. (c, d) SEM images of PbS crystals grown in 1 w/v% agarose gels: (c) as prepared; (d) after the crystals were slightly etched by 3 M HCl. The arrows highlight the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

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