Electronic Supplementary Information (ESI)

Planar Se multipod crystals with unusual growth directions:

Thoughts on the spontaneous growth of hexagonal Se

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Fig. S1. Typical SEM and TEM images (inset of panel b, SAED pattern) of one-dimensional (1D) Se nanowires prepared by our group.



Fig. S2. SEM and TEM images (inset of panel b, SAED pattern) of 1D Se nanotubes prepared by our group.



Fig. S3. SEM images of Se crystals prepared via the oxidation of Na_2Se and subsequent spontaneous crystallization of Se monomers in the presence of various thiol molecules: A) thiolglycerol, B) mercaptamine, and C) L-cysteine. The detailed experimental results have been published in Eur. J. Inorg. Chem.¹



Fig. S4. SEM image of nonspherical Se crystals formed from the EDTA-induced transformation of L-cys-capped CdSe nanoparticles. TEM image and the corresponding SAED patterns of the as-prepared Se crosshead. The detailed experimental results have been published in Cryst. Growth Des.²



Fig. S5. A) EDX spectrum of the as-prepared planar Se multipod crystals. This spectrum indicates that the product is highly pure Se (the signals of Cu detected in EDX should be attributed to TEM grids). B) The typical XRD pattern of planar Se multipod crystals obtained in the presence of TSC. All the sharp and strong diffraction peaks can be readily indexed to a hexagonal phase of selenium (JCPDS: 06-0362) with a cell constant a=4.35 Å and c=4.95 Å (no impurity was detected). C) The XRD pattern of 1D Se nanowires with the preferred [001] growth direction.

Fig. S6. (A) SEM image of a tripod and (B) the facile diagram showing the internal two-dimensional atomic arrangement and the pod growth directions of the tripod (here, the observation direction is along the [001] axis of hexagonal phase). For the Se tripod in panel A, its each arm has the similar length. As shown, when extending the topmost planes of three pods, the lines will intersect and form a hexagon with six same internal angles of 120°. This hexagon should be the same as the shape of the cross section of the crystal cell of hexagonal Se.



Fig. S7. The molecular structures of the small molecules used: trisodium citrate (TSC), ethylenediaminetetraacetic acid disodium salt (EDTA), succinic acid, glutaric acid, acetic acid, glycerol and mercaptamine (MA).



Fig. S8. SEM images of Se products obtained in the presence of various small molecules: (A) acetic acid, (B) succinic acid, (C) glutaric acid, (D) EDTA.



Fig. S9. A typical SEM image of Se product obtained from the oxidation of Na₂Se at pH=11 in the presence of glycerol (6 mM). The result obtained in the presence of mercaptamine has been shown in Ref. 1 and Fig. S3b (the flower-like particles).



Fig. S10. Schematic illustration of the interaction between citrate molecule and Se atoms on the surface of hexagonal Se crystal (in this case, the spatial structure of the citrate molecule in solution is a stable conformation³). The distance between the carboxyl groups in the stable citrate molecule (marked by <u>1</u> and <u>2</u> respectively) is close to the cell constant *a* of t-Se (a = 4.35 Å, namely, the distance between Se atom and six adjacent ones on the (001) plane). Thus, a single citrate molecule may cap two Se atoms on the (001) facet. Meanwhile, for t-Se seeds, there are a large density of Se atoms (3.05 Se atoms/nm²) and dangling bonds on their (001) planes. Hence, the small molecules containing more carboxyl groups might be more favorable to stabilize the Se atoms on the (001) facets of hexagonal Se crystals, resulting in a decrease in the growth rate of the (001) planes.



Fig. S11. The FT-IR spectra of free trisodium citrate (TSC) and the as-prepared planar Se crystals before and after washing by water.



Fig. S12. Typical SEM images of the intermediate samples taken from reaction dispersion at different aging time: A) 0.5, B) 1.5, C) 3.5 and D) 6.5 h. The SAED patterns (not shown) that when the aging time is 1.5 h, the reaction solution is a complicated mixture of amorphous Se particles and. small h-Se nanocrystallites. The small h-Se nanocrystallites serve as the cores for the growth of planar Se multipod crystals at the expense of dissolution of amorphous Se particles.

References

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