

Supporting Information

for

Facile Synthesis of IV-VI SnS Nanocrystals with Shape and Size Control: Nanoparticles, Nanoflowers and Amorphous Nanosheets

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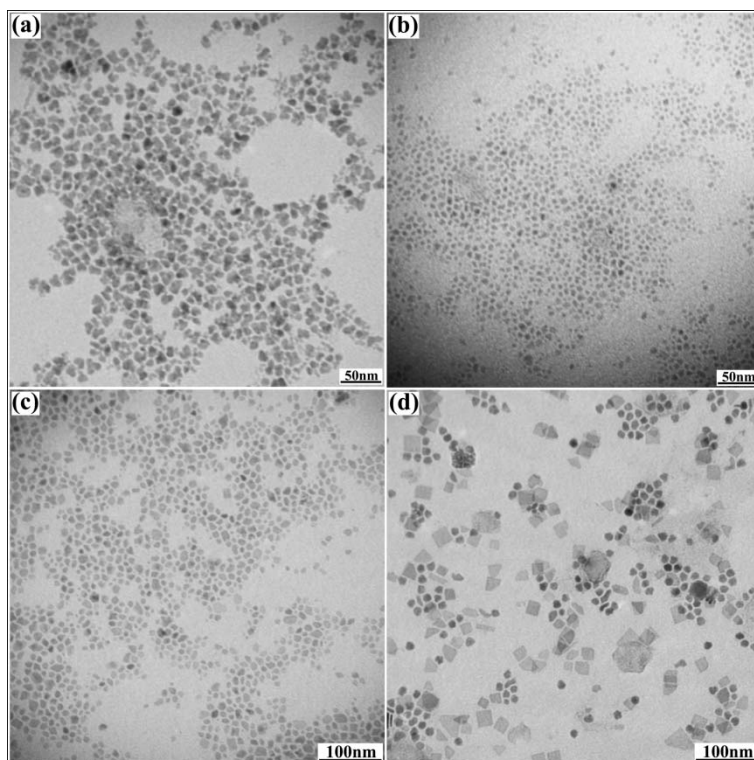


Figure S1. TEM images of samples produced at different reaction temperature and molar ratio of Sn/S. When the temperature of injecting S source was 120 °C, nanoflowers would be obtained with Sn/S molar ratio of 1:1 (a). With Sn/S molar ratio of 1:2, nanoparticles appeared and size was about 7 nm (b). When the temperature was 150 °C, we can get nanoparticles with 2:1 for Sn/S molar ratio (c). Nanosheets appeared with 1:2 for Sn/S molar ratio (d).

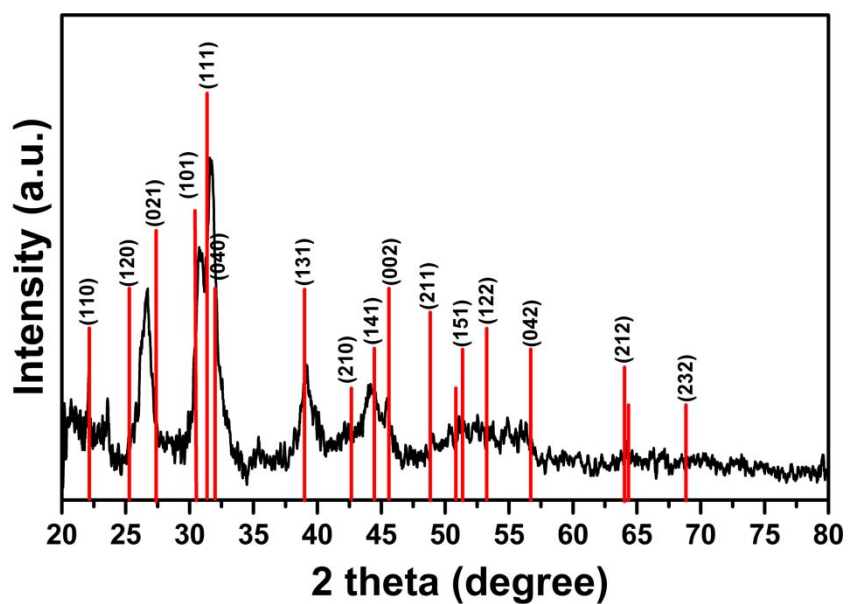


Figure S2. XRD patterns of produced SnS nanoparticles.

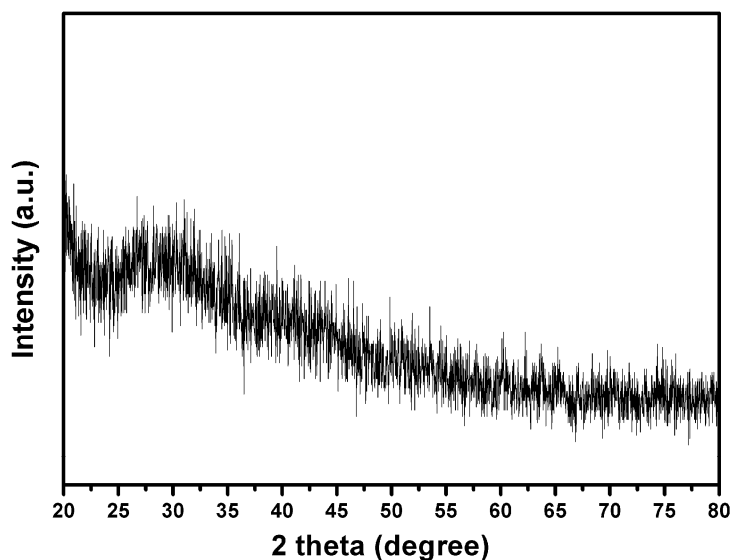


Figure 3. XRD patterns of nanosheets. No obvious diffraction peaks can be observed, the XRD further proved the amorphization process from SnS nanoflowers to nanosheets.

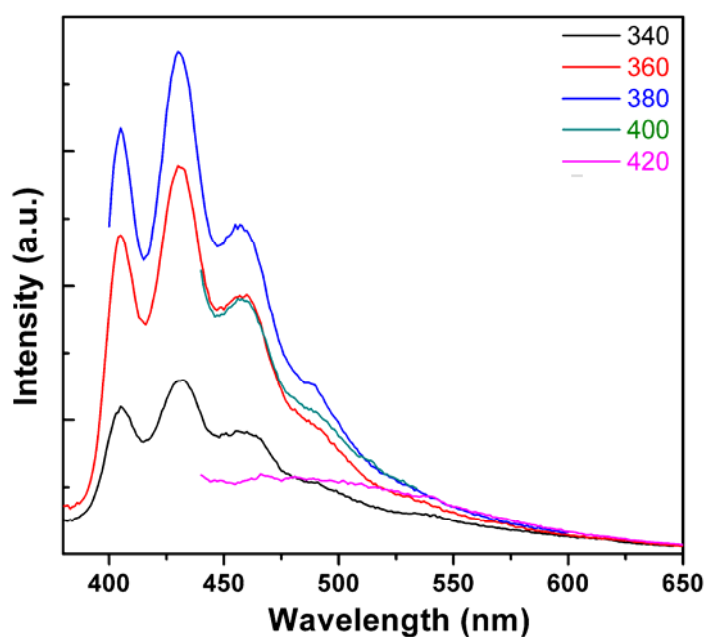


Figure S4. Emission spectra of SnS nanoparticles with different excitation wavelength.

The description of Gibbs free energy at different crystal states:

The nucleation and growth of nanocrystals in solution would couple with the increase of Gibbs free energy. The Gibbs free energy of nanocrystals includes two parts, one is the increase of atomic chemical potential and the other is the surface tension of nanocrystals, as shown in the following equation¹:

$$\Delta G = n(\mu_n - \mu_s) + S_n \sigma_n$$

The n is the amount of atoms, μ_n is the chemical potential of one atom in nanocrystals (dependent on the

chemical bond of atoms in nanocrystals), μ_s is the chemical potential of an atom in solution, σ_n is the surface tension of nanocrystals. We think the drive force of the amorphization in the shape evolution of SnS nanocrystals is decreasing the free energy. The SnS nanoflowers have many defects, and they transformed to amorphous nanosheets by oriented attachment. Compared to the atoms in the solution, the Gibbs free energy at defective nanoflowers (ΔG_{NFs}) and amorphous nanosheets (ΔG_{ANS}) can be shown as following:

$$\Delta G_{NFs} = n(\mu_{NFs} - \mu_s) + S_{NFs}\sigma_{NFs}$$

$$\Delta G_{ANS} = n(\mu_{ANS} - \mu_s) + S_{ANS}\sigma_{ANS}$$

μ_{NFs} is the chemical potential of an atom in defective nanoflowers, S_{NFs} is the surface of nanoflowers which include n atoms, σ_{NFs} is the surface tension of nanoflowers, μ_{ANS} is the chemical potential of an atom in amorphous nanosheets, S_{ANS} is the surface of nanosheets which include n atoms, σ_{ANS} is the surface tension of nanosheets. The change of free energy from nanoflowers to amorphous nanosheets can be shown (the amount of atoms is constant):

$$\Delta G = n(\mu_{ANS} - \mu_{NFs}) + (S_{ANS}\sigma_{ANS} - S_{NFs}\sigma_{NFs})$$

Because both of the defective nanoflowers and amorphous nanosheets have many defect and dangling bond in the surface, we can get $\sigma_{NFs} \approx \sigma_{ANS} = \sigma$, so the ΔG from defective nanoflowers to amorphous nanosheets can be described as:

$$\Delta G = n(\mu_{ANS} - \mu_{NFs}) + (S_{ANS} - S_{NFs})\sigma$$

As we know, the amount and intensity of the chemical bond between atoms in defective nanoflowers are more than that in amorphous nanosheets ($\mu_{ANS} < \mu_{NFs}$). If the amount of atoms (n) is constant in the shape transition, the aggregation of nanoflowers to bigger nanosheets would reduce the surface of nanocrystals, so $S_{ANS} < S_{NFs}$. Based on the above relations, we can get:

$$\Delta G = n(\mu_{ANS} - \mu_{NFs}) + (S_{ANS} - S_{NFs})\sigma < 0$$

So the shape evolution from defective nanoflowers to amorphous nanosheets is favorable in thermodynamic, and the drive force of this transition is reducing the free energy of nanocrystals.

1. S. Kudera, L. Carbone, L. Manna, W. J. Parak, Semiconductor Nanocrystal Quantum Dots Synthesis, Assembly, Spectroscopy and Applications: Growth mechanism, shape and composition control of semiconductor nanocrystals, *Springer*, **2008**, page 5-6.