Supporting Information for:

Synthesis and Properties of Nanocrystalline π-SnS – A New Cubic Phase of Tin Sulphide

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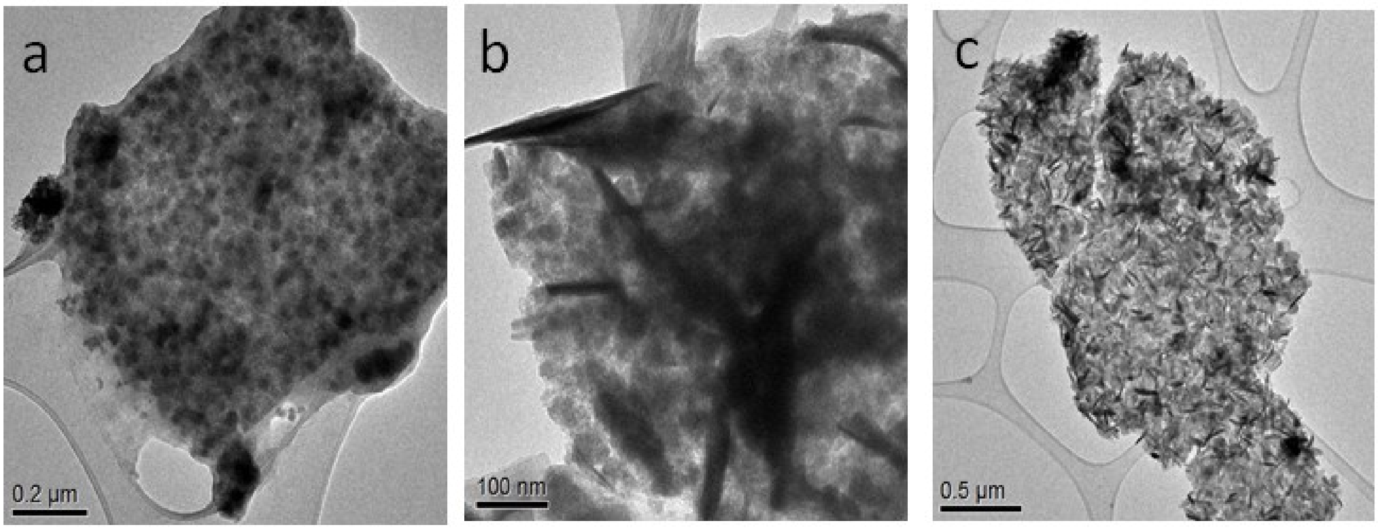

Figure S1. Shape evolution of SnS nanoparticles synthesized using tin-ethylxanthate precursor. The bright field TEM micrographs show nanoparticles synthesized at (a) 140 ºC (b) 160 ºC (c) 220 ºC. All samples were synthesized in the presence of 0.4ml HMDS.

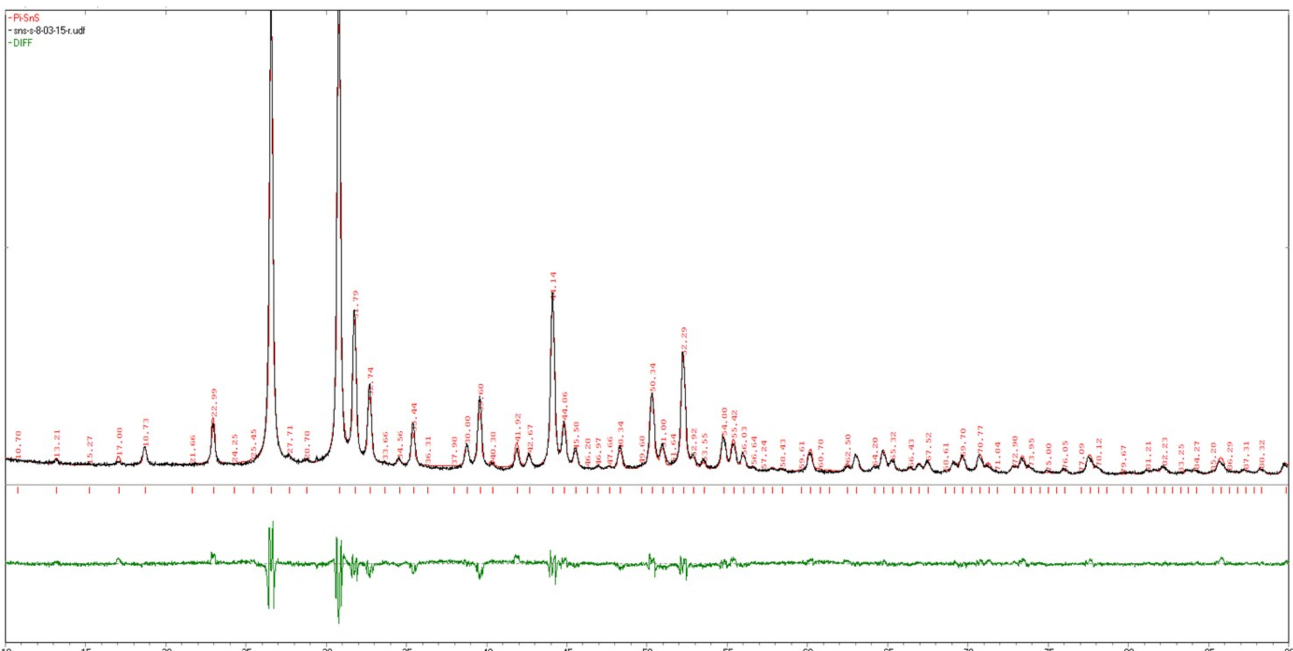

Figure S2, Rietveld refinement performed using "PowderCell" software v.2.4[1] . R_p=**6.65**, R_{wp}=**8.57**, R_{exp}=**3.46**. XRD pattern for π-SnS phase fitted model (red curve), experimental XRD pattern of π-SnS phase (black curve) and subtraction of the experimental XRD curve from the fitted model curve (green curve). The difference curve indicates a considerably good match of the fitted crystallographic model to the experimental results.

Rhombic dodecahedron shape determination

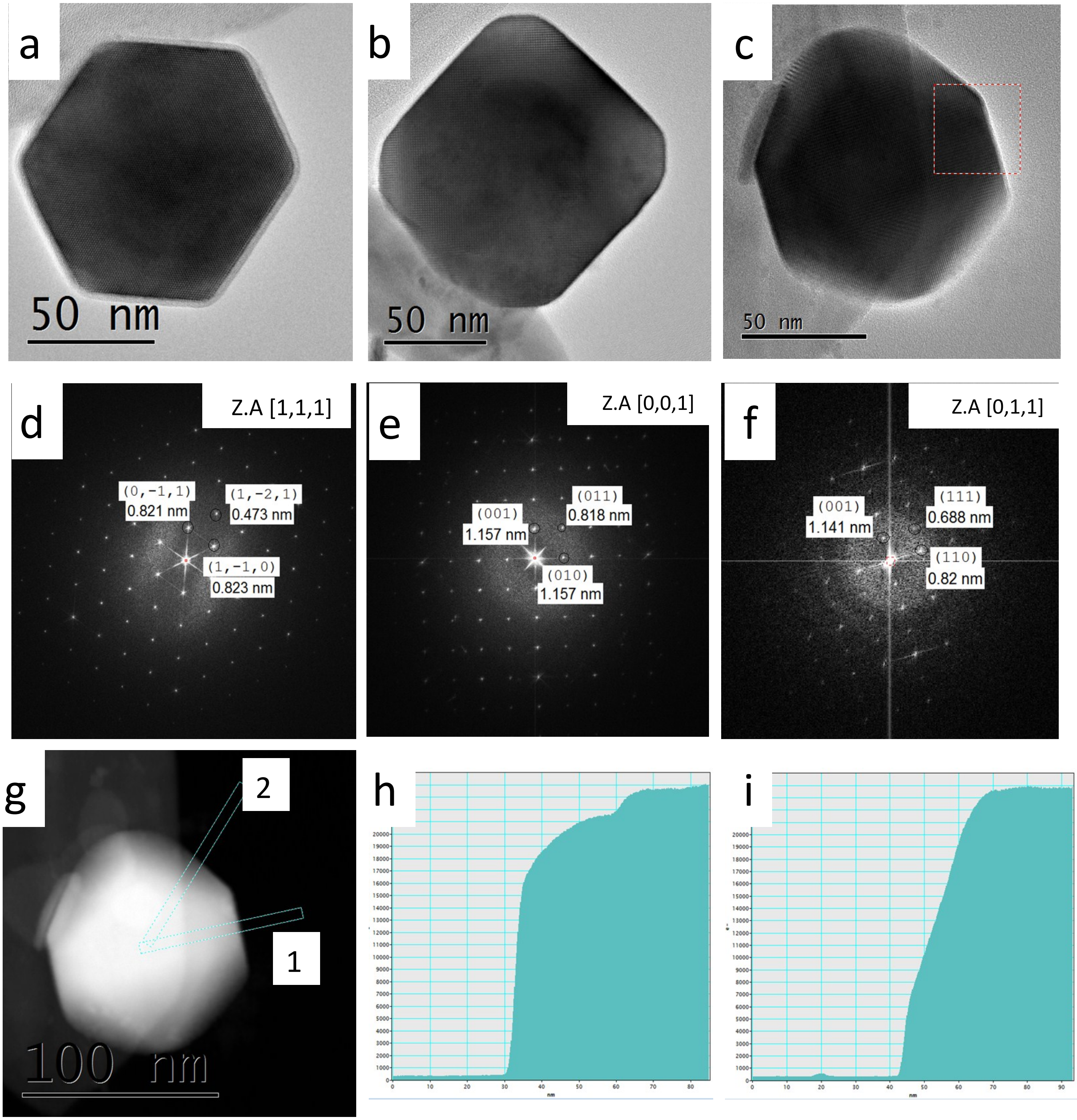

Figure S3, π-SnS rhombic dodecahedra shaped nanoparticles viewed at different orientations. (a-c) HRTEM micrographs of select nanoparticles. (d-f) Corresponding FFT micrographs, respectively. (g) STEM micrograph of nanoparticle seen in (c). (h) line profile of the selected area labeled "1" in (g). (i) line profile of the selected area labeled "2" in (g).

In order to determine the shape of the nanoparticles, a series of HRTEM micrographs were taken with respect to the main crystallographic axes of the nanocrystal. The analysis is based on the relation between the atomic structure of a crystal and its shape and orthogonal projection. Figure S3 (a-f) presents a series of HRTEM micrographs of π-SnS nanoparticles with different orientations, along with their corresponding FFT patterns. Since the FFT was taken directly from the HRTEM micrograph, the crystallographic directions correspond to directions in real space. In the pair of FFT and HRTEM micrograph (a) and (d), the 2D projection of the particle appears to be a hexagon. In addition, the zone axis (ZA) in the FFT was found to be [111]. There are several nanocrystal shapes that give the hexagonal projection and ZA[111]. The tetrahedral shape is not possible here. As was determined in our previous work, tetrahedral crystals oriented along ZA [111] possess a triangular shape[2] . Therefore, tetrahedral shape is ruled out. Examining the pair (b) and (e) shows that the orthogonal projection is square shaped. Since the crystallographic directions of the FFT are shared with the HRTEM, we note that if the particle was indeed cubic, the {010} reflection direction should coincide with the normal to the particle facets. This is not the case here. The {010} reflections are tilted by 45^{o} with respect to the normal of the particle facets. Therefore a cube shape is also ruled out. The last pair, (c) and (f), indicates that particle shape projection at ZA [011] could well-match a rhombic dodecahedron. STEM micrograph taken from the same area provides complementary information. The contrast in STEM micrographs is mass-thickness but since the particle composition is known, the contrast of the STEM micrograph is narrowed only to thickness. Examining the line plots in Fig. S3h and Fig. S3i suggests that there is a plateau in the central region of the particle, this mean that this area is one of the particle facets. Combining this information with the fact that the ZA is [011] identifies this facet as belonging to {011}. In addition, the fact that in Fig. 3i a sharp increase in the thickness of the sample is observed, suggests a facet parallel to the electron beam direction. Examination of the corresponding FFT shows that the normal to that facet coincides with the reflection direction {011}. This proves that another facet is terminated by {011}, overall suggesting that the dominant terminating facet is {011}. The highest symmetry orthogonal projections of a rhombic dodecahedron are presented in Fig. S4. Comparing these projections with those observed in HRTEM shows resemblance. A rhombic dodecahedron has 12 congruent rhombic faces. This number of faces is shared with the number of available planes in {011}. These arguments support our hypothesis that these nano-particles are indeed shaped as a dodecahedra.

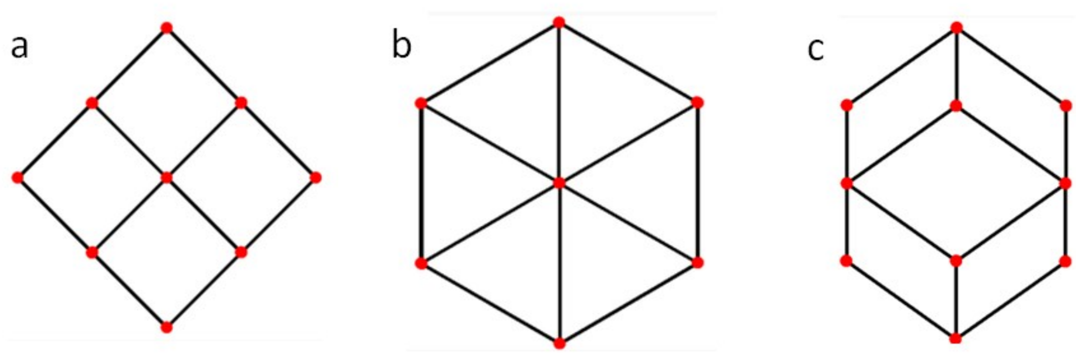

Figure S4. Highest symmetry orthogonal projection of a rhombic dodecahedron. (a) 4. (b) 6. (c) 2. These projections well match to the empirical data presented in Figure S3.

1. Kraus, W.; Nolze, G., "Powder Cell for Windows, Version 2.4". Federal Institute for Materials Research and Testing,Rudower Chaussee 5, 12489 Berlin, Germany: 2000.
2. Rabkin, A.; Samuha, S.; Abutbul, R. E.; Ezersky, V.; Meshi, L.; Golan, Y. *Nano Lett.* **2015,** 15, (3), 2174-9.