Supporting Information for

Colloidal Synthesis of Metastable Zinc-Blende IV-VI SnS Nanocrystals with Tunable Sizes

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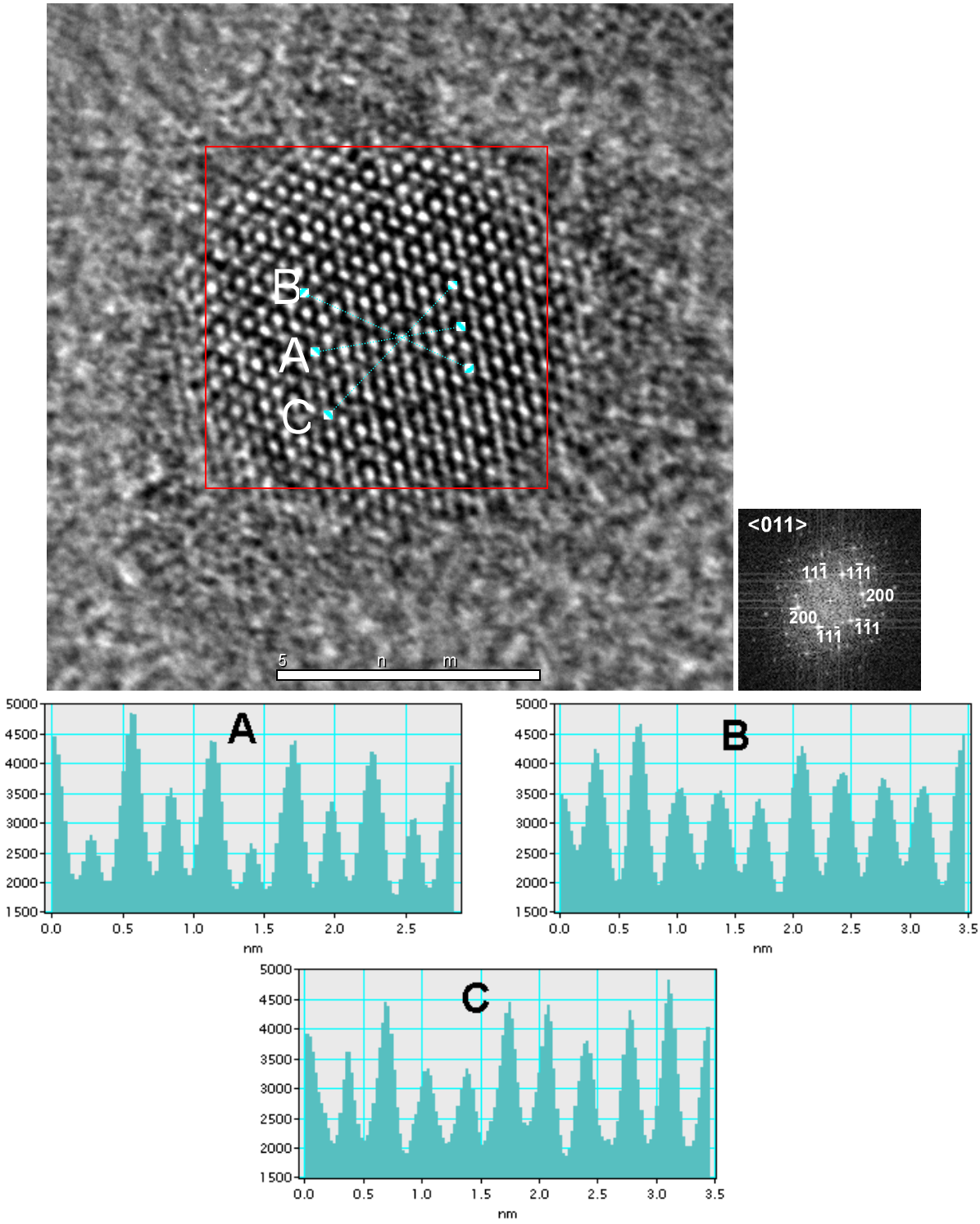

Figure S1. (**Top**) Enlarged high resolution TEM image of 8 nm nanocrystals (zoom in from Figure 1F) and the corresponding indexed fast Fourier transform (FFTs), indicating the electron beam is incident along the [011] direction of the crystal. (**Bottom A, B, C**) Line profiles of the thin green lines marked in the HR-TEM image.

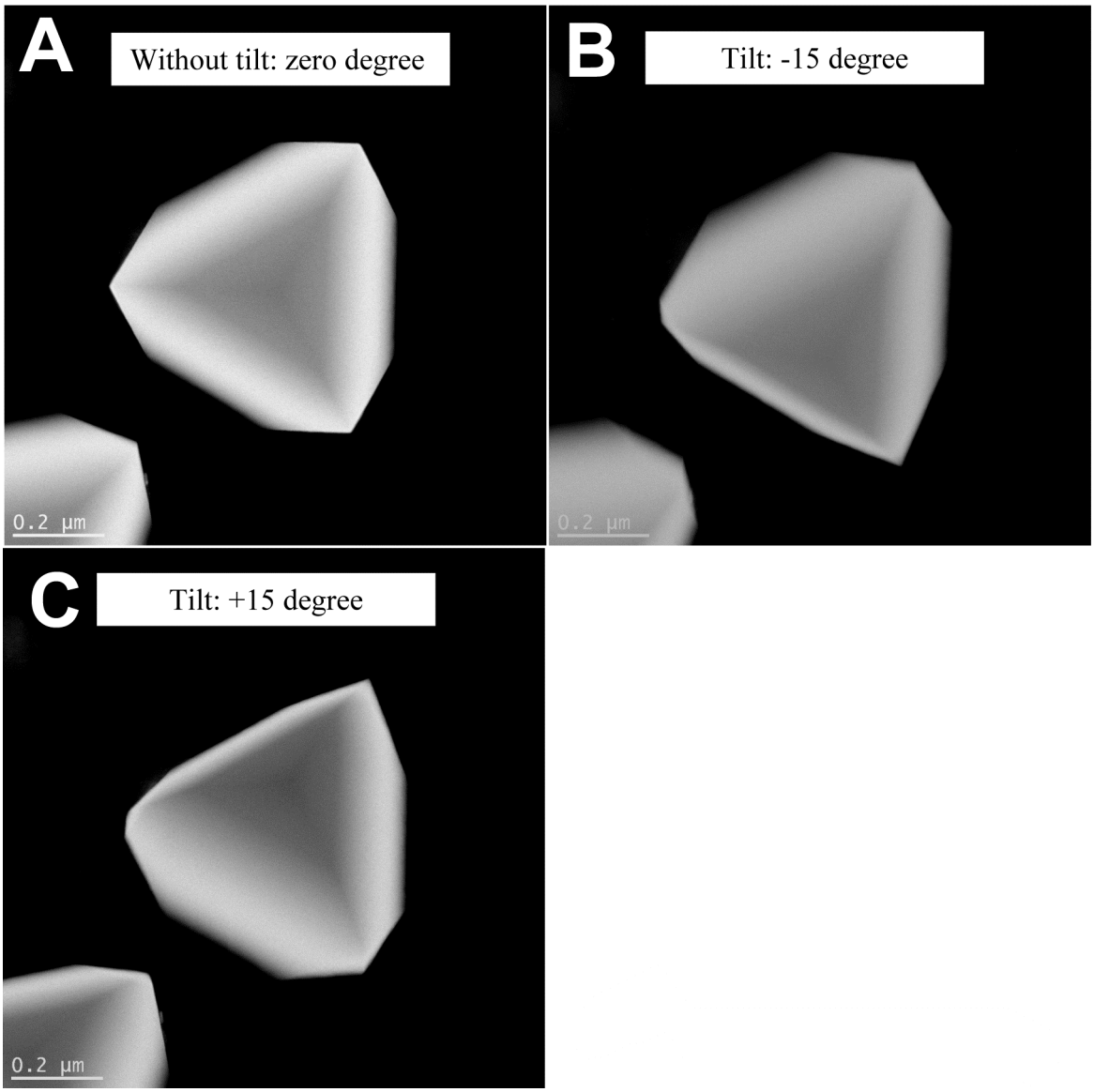

Figure S2. Incident beam angle-dependent STEM images for the sixteen-facet SnS polyhedral crystals on ultrathin carbon coated TEM grids. (A) no tilting, the electron beam is perpendicular to the surface of the substrate, where the bottom surface of the crystal lands on the substrate; (B) -15 degree tilting and (C) + 15 degree tilting along the horizontal axis of the sample.

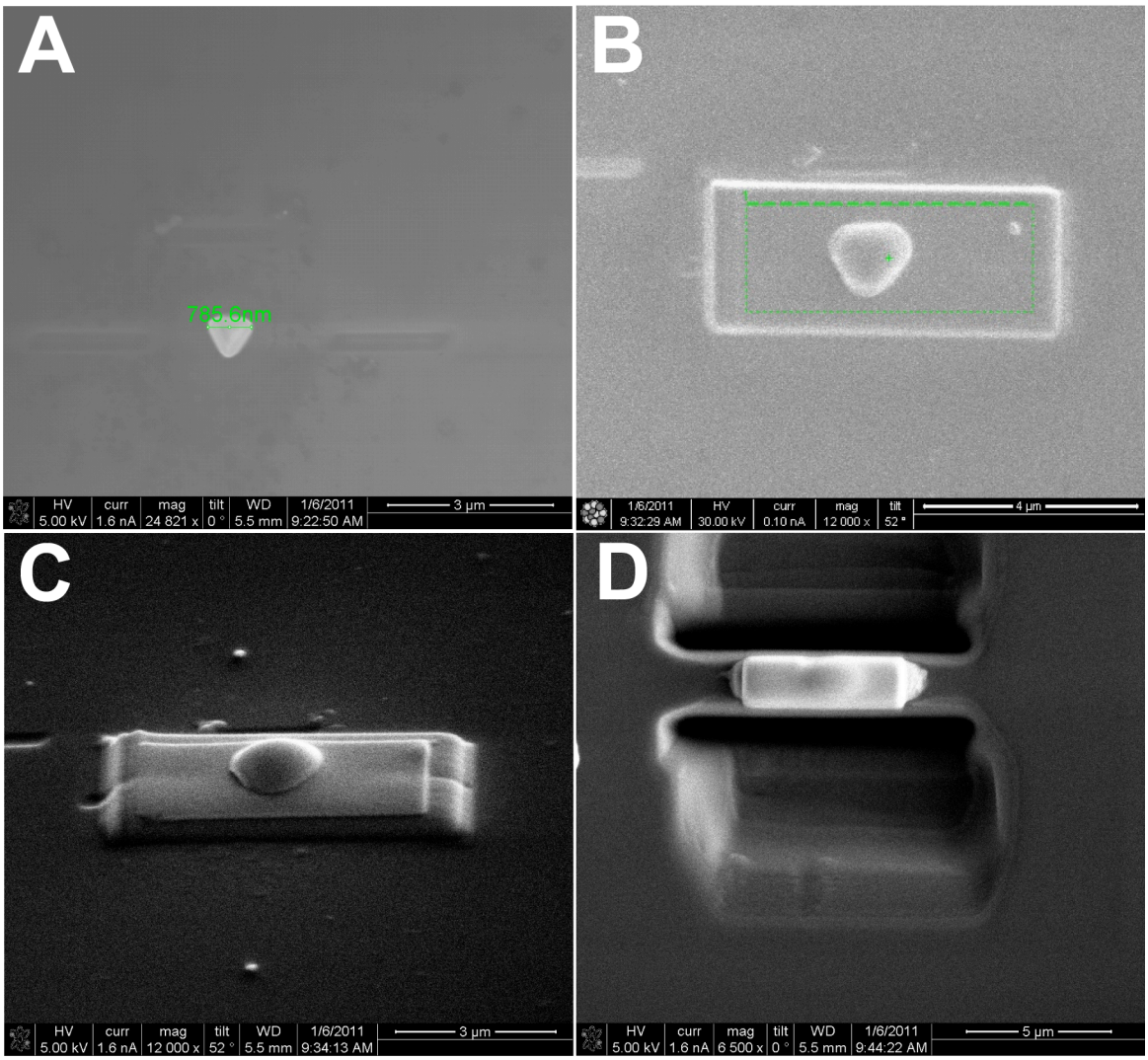

Figure S3. Additional SEM images of a sixteen-facet SnS polyhedral crystal during the FIB sectioning process. (A) A crystal deposited on silicon substrate was selected; (B) A thin (about 10 nm) Pt layer was deposited to pre-cover and stabilize the crystal, where the green dot marks the center of the coating; (C) A thick (about 200 nm) Pt layer was further deposited to fully cover the crystal; (D) The areas besides the crystal were removed from the substrate by FIB to prepare for lifting the Pt covered crystal for further sectioning.

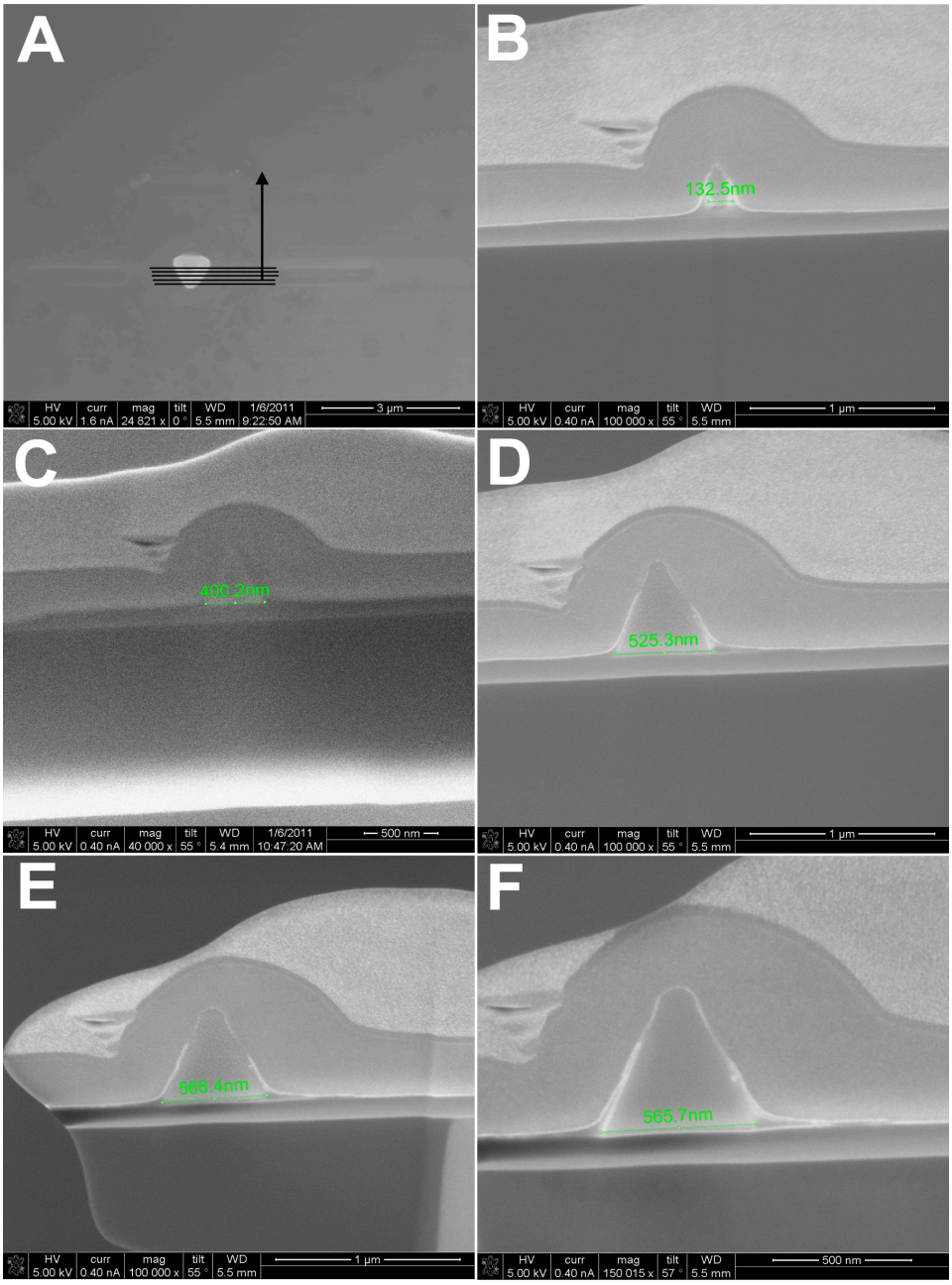

Figure S4. (**A**) The section lines are labeled on the image of the selected crystal. The arrow indicates the sequence of step-wise sectioning; (B-F) Additional SEM images of a sixteen-facet SnS polyhedral crystal after the stepwise FIB sectioning process. Note that the directions of all the above sections are parallel to the edge of a typical hexagonal facet as indicated by the black lines in (**A**).

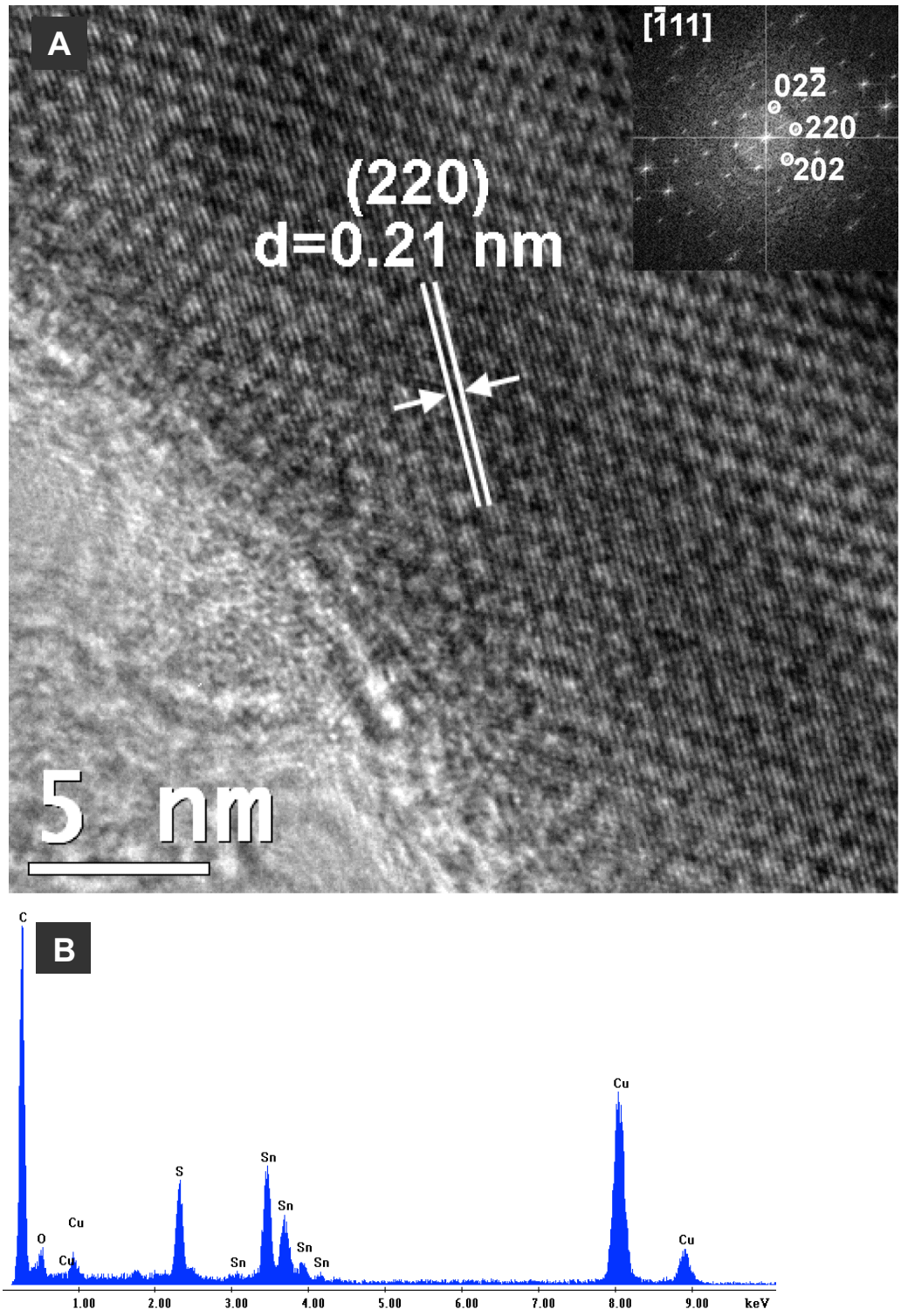

Figure S5. (**A**) Enlarged high resolution TEM image of Figure 3H (zoom in from boxed area in Figure 3G in main text) and the corresponding indexed fast Fourier transform (FFTs), indicating the electron beam is incident along the [111] direction of the crystal. (**B**) Energy dispersive X-ray spectroscopy (EDS) of sixteen-facet SnS polyhedral crystals revealing the atomic ratio of Sn:S is close to 1:1.

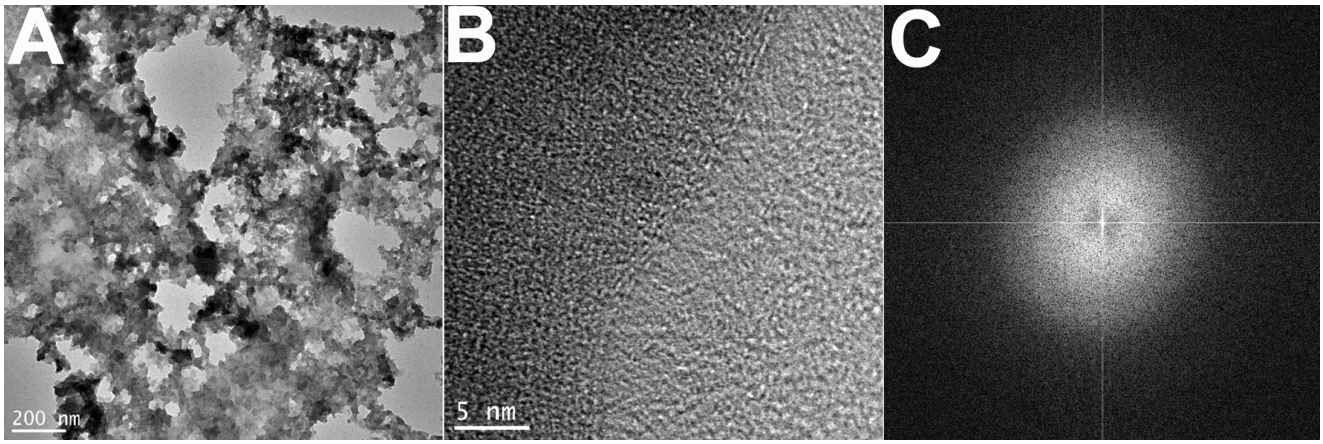

Figure S6. Characterization of the sample obtained with a reaction temperature of 160 ^{o}C in the absence of HMDS, while all other reaction conditions were held constant the same as that for 8nm SnS nanocrystal. (**A**) TEM image, (**B**) HRTEM image and (**C**) the corresponding indexed fast Fourier transform (FFT). These results indicate that the sample is amorphous.