Facile solvothermal approach to pristine tetrahedrite nanostructures with unique multiply-voided morphology

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Supporting Information

Table S1. Cu–Sb–S phase produced by solvothermal decomposition of copper and antimony dithiocarbamate precursors* in varying solvent ratios at 200 °C (heated in a sealed autoclave for 16 h).

Solvent/Solvent Mixture† **(Total Volume = 10 mL)**	**OM/DDT molar ratio**	**Cu–Sb–S phase**	**XRD pattern**
A. OM (10 mL)	1/0	Cu_3SbS_4 (famatinite)	Figure 1a
B. OM (7.5 mL)+ DDT (2.5 mL)	2.18/1	$Cu_{12}Sb_4S_{13}$ (tetrahedrite) + traces of Cu_3SbS_4 (famatinite)	Figure S4a
C. OM (5 mL) + DDT (5 mL)	0.73/1	$Cu_{12}Sb_4S_{13}$ (tetrahedrite)	Figure 1c
D. OM (2.5 mL)+ DDT (7.5 mL)	0.24/1	$Cu_{12}Sb_4S_{13}$ (tetrahedrite) + Cu_3SbS_3 (skinnerite)	Figure S4b
E. DDT (10 mL)	0/1	Cu_3SbS_3 (skinnerite) + $Cu_{12}Sb_4S_{13}$ (tetrahedrite)	Figure 1b

*Precursors: 0.3 mmol $Cu(dedtc)_2$ and 0.1 mmol $Sb(dedtc)_3$. Note that dedtc = diethyldithiocarbamate (S_2CNEt_2).
†OM = oleylamine; DDT = 1-dodecanethiol.

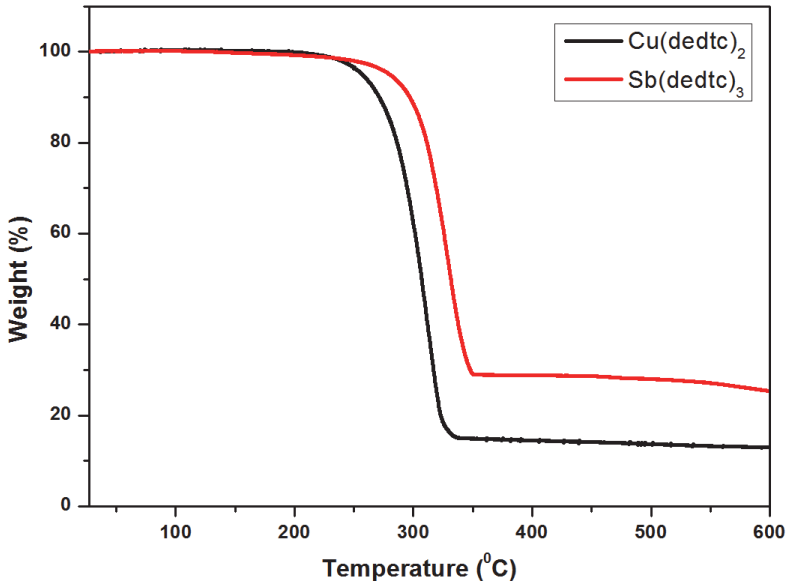

Fig. S1 Thermogravimetric analysis of $Cu(dedtc)_2$ and $Sb(dedtc)_3$, where dedtc = diethyldithiocarbamate (S_2CNEt_2).

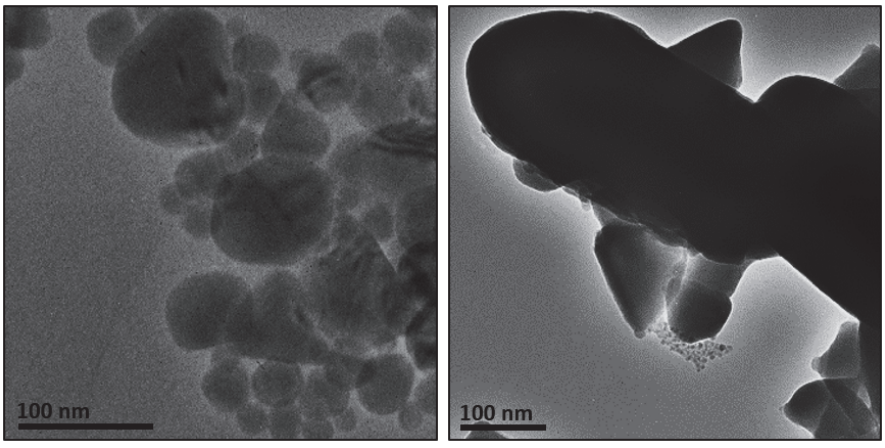

Fig. S2 TEM images of the products obtained when a mixture of 0.3 mmol $Cu(dedtc)_2$ and 0.1 mmol $Sb(dedtc)_3$ were solvothermally decomposed at 200 °C for 16 h using 10 mL OM (left image), and 10 mL DDT (right image).

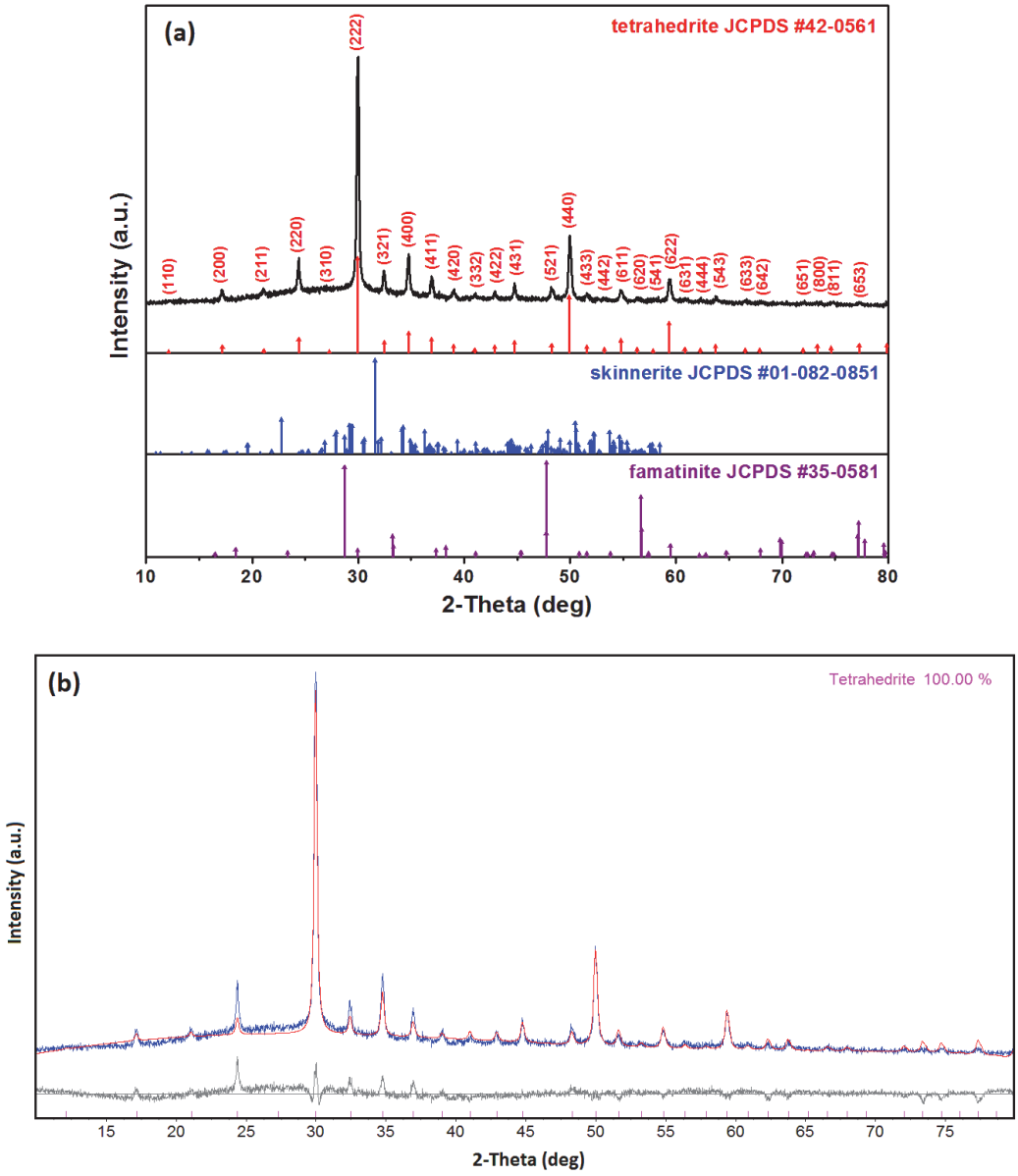

Fig. S3 (a) XRD pattern of the product obtained when the synthesis was carried out using a solvent mixture of 5 mL OM + 5 mL DDT. All the observed diffraction peaks can be indexed to tetrahedrite. No noticeable peaks from other Cu–Sb–S phases (e.g. skinnerite and famatinite) are seen. (b) Rietveld refinement of the experimental XRD pattern. Displayed are the observed (blue) and refined (red) patterns, the difference curve (grey), and the reflection positions of tetrahedrite (pink sticks at the bottom).

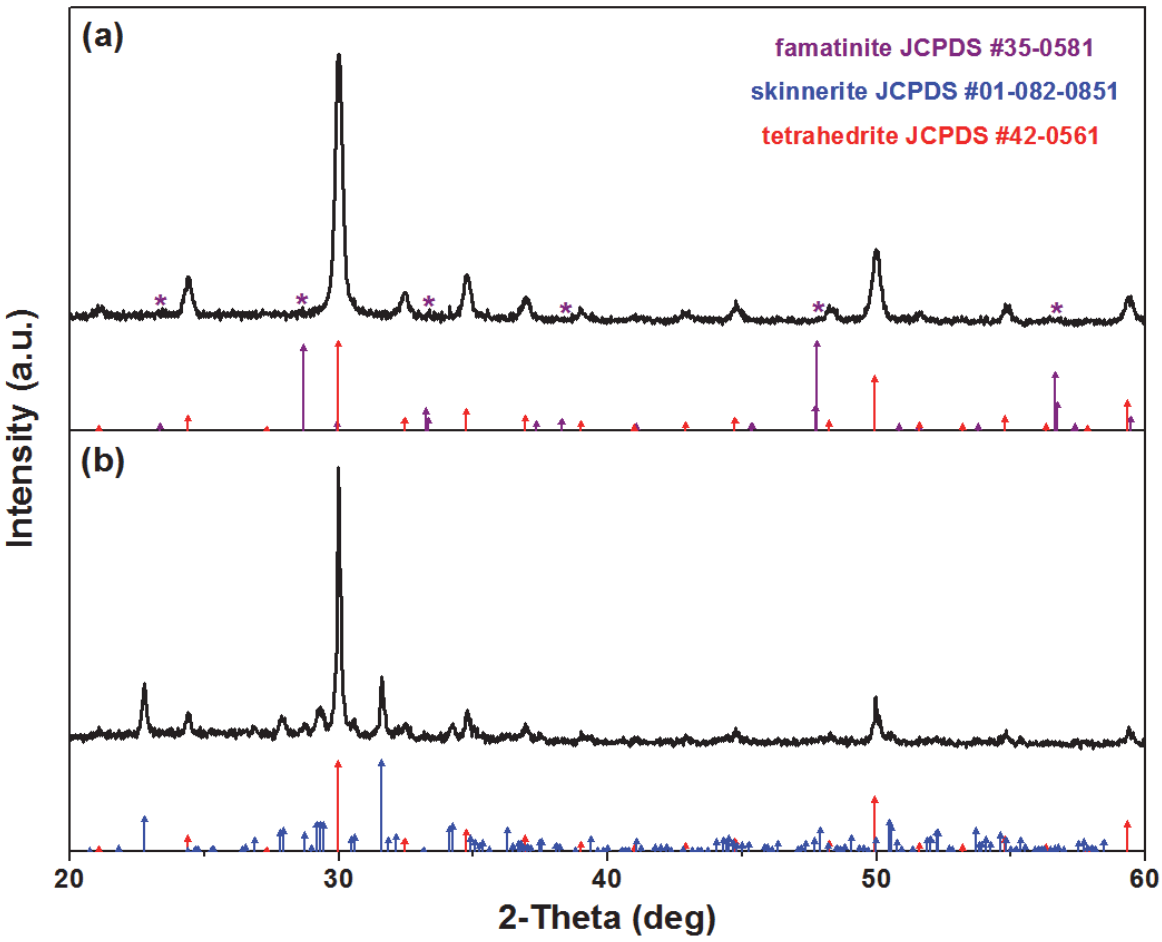

Fig. S4 XRD patterns of the products obtained when the synthesis was carried out using a solvent mixture of: (a) 7.5 mL OM + 2.5 mL DDT, and (b) 2.5 mL OM + 7.5 mL DDT. Note: Red lines are from standard JCPDS file [42-0561] for cubic $Cu_{12}Sb_4S_{13}$ (tetrahedrite). Blue lines are from standard JCPDS file [01-082-0851] for monoclinic Cu_3SbS_3 (skinnerite). Purple lines are from standard JCPDS file [35-0581] for tetragonal Cu_3SbS_4 (famatinite). Purple stars are used to mark the weak peaks attributed to Cu_3SbS_4.

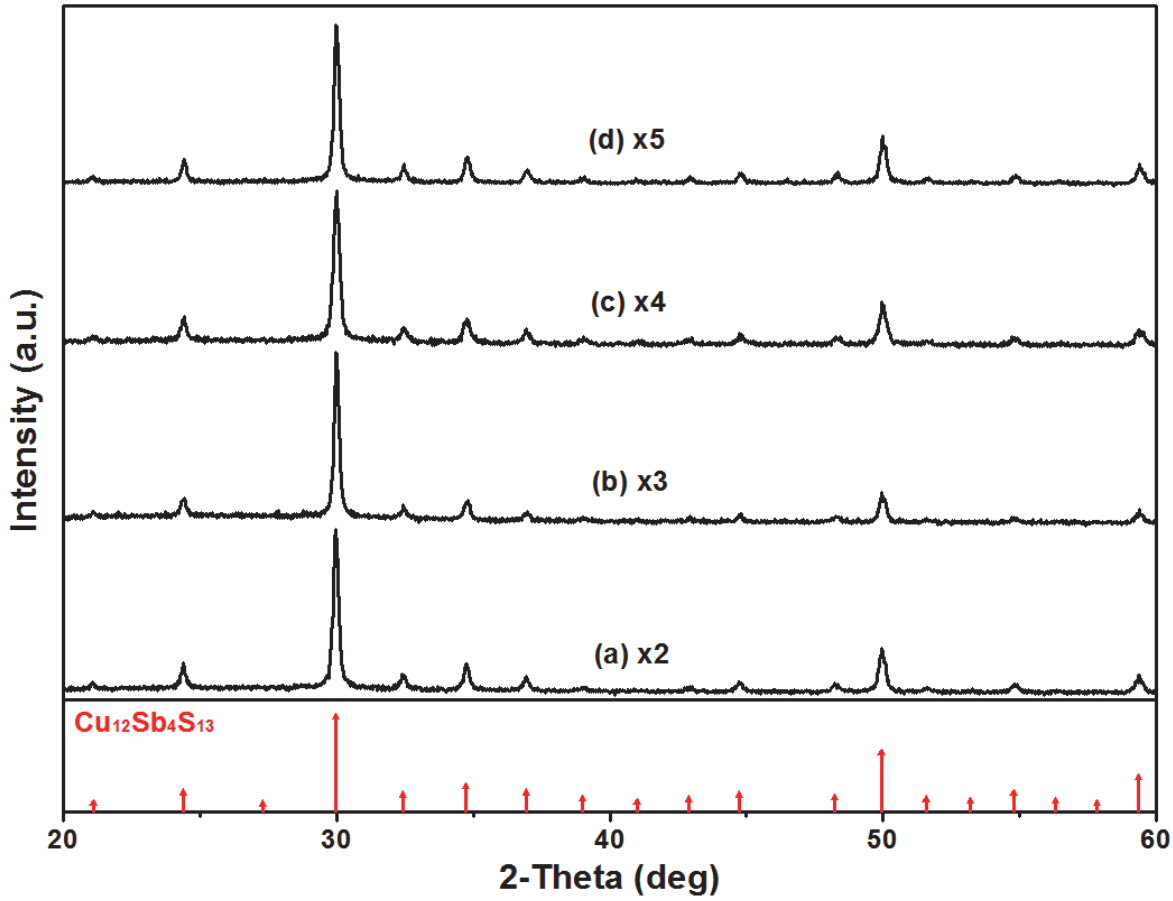

Fig. S5 XRD patterns of tetrahedrite samples prepared using 2, 3, 4 and 5 times of the original amount of precursors and solvents. The red stick pattern at the bottom is from standard JCPDS file [42-0561] for cubic-phase tetrahedrite.

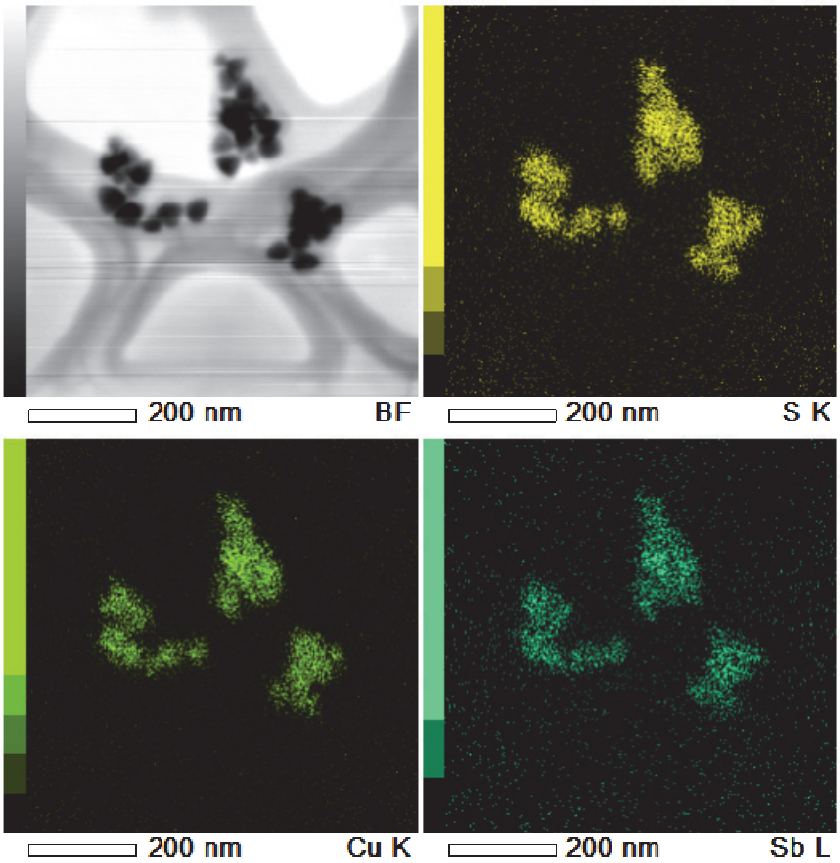

Fig. S6 STEM image (upper left) and the corresponding Cu, Sb and S elemental maps of the tetrahedrite nanostructures.

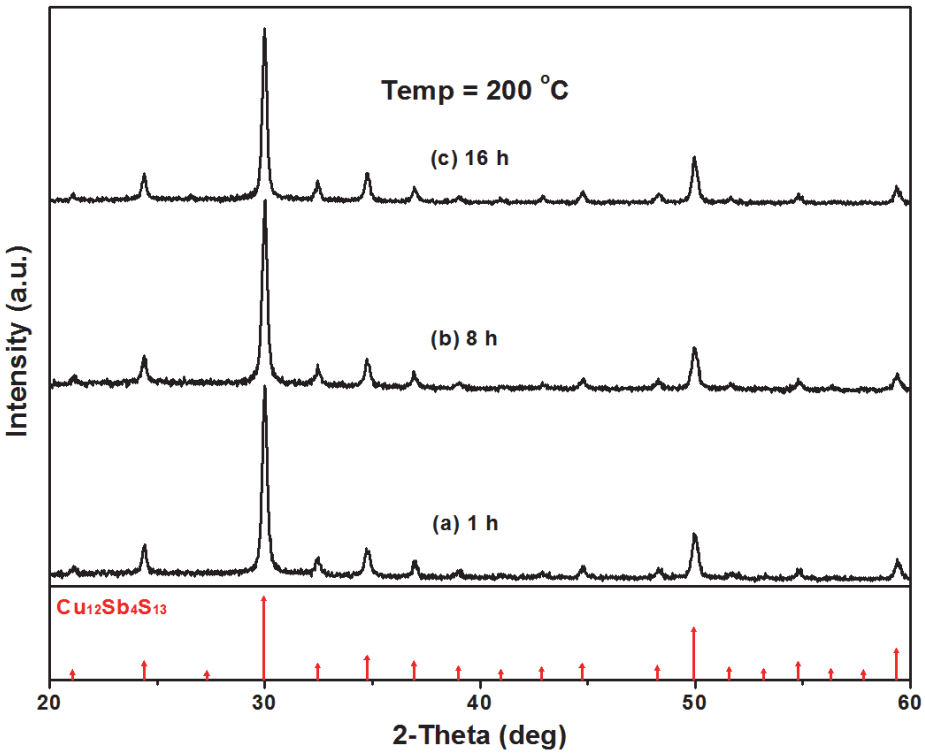

Fig. S7 XRD patterns of the nanostructures obtained when the solvothermal synthesis was performed at 200 °C for (a) 1 h, (b) 8 h, and (c) 16 h. Red stick pattern at the bottom is from standard JCPDS file [42-0561] for cubic $Cu_{12}Sb_4S_{13}$ (tetrahedrite).

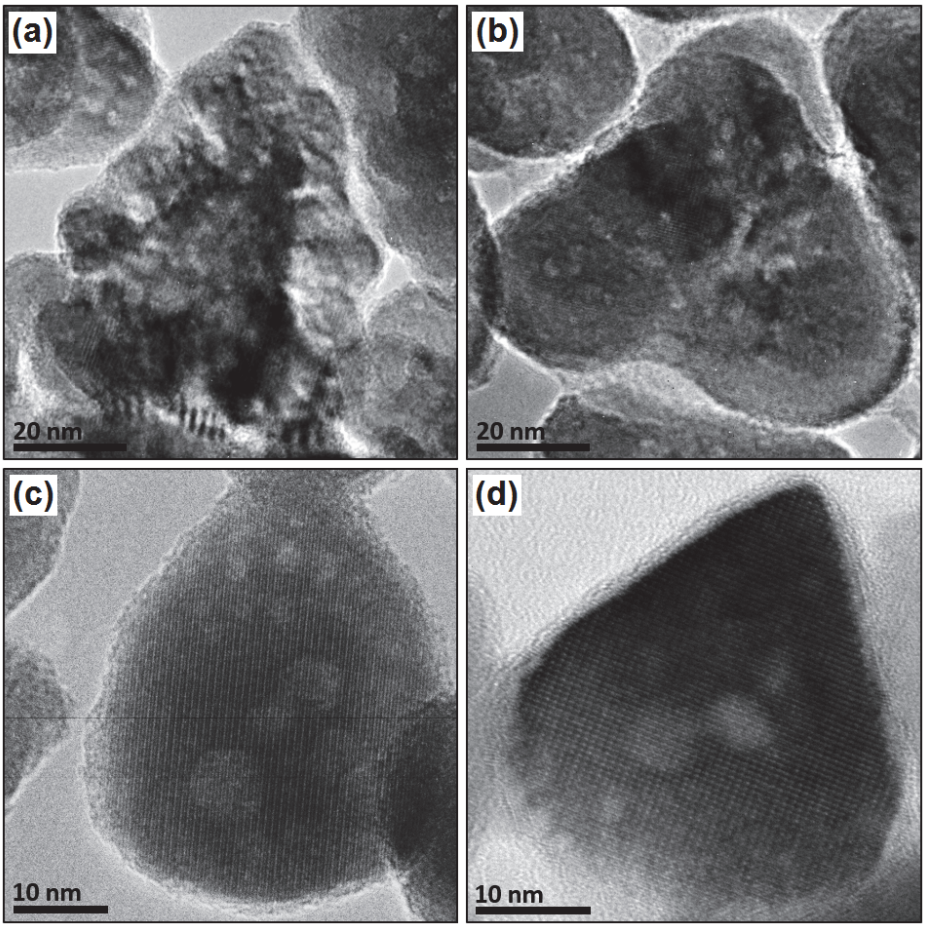

Fig. S8 Higher-resolution TEM images of the tetrahedrite nanotetrahedrons produced when the synthesis was performed at (a) 80, (b) 120, (c) 160, and (d) 200 °C for 16 h.

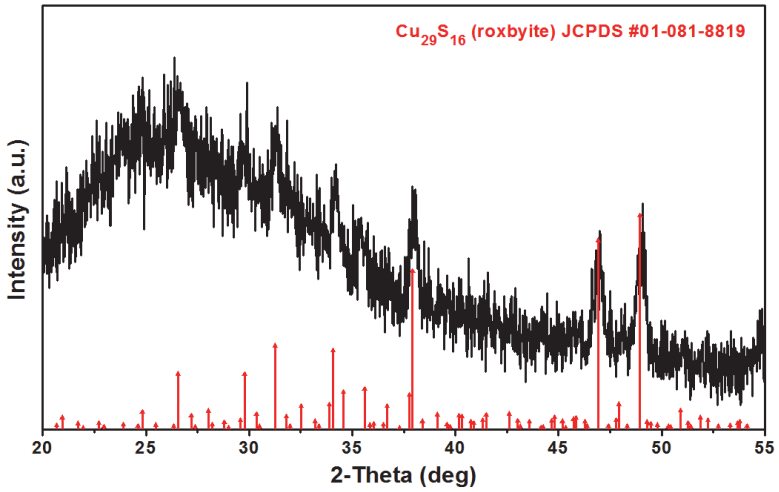

Fig. S9 XRD pattern of the solid obtained when 0.3 mmol $Cu(dedtc)_2$ was solvothermally heated without the Sb precursor at 80 °C in 5 mL OM + 5 mL DDT.

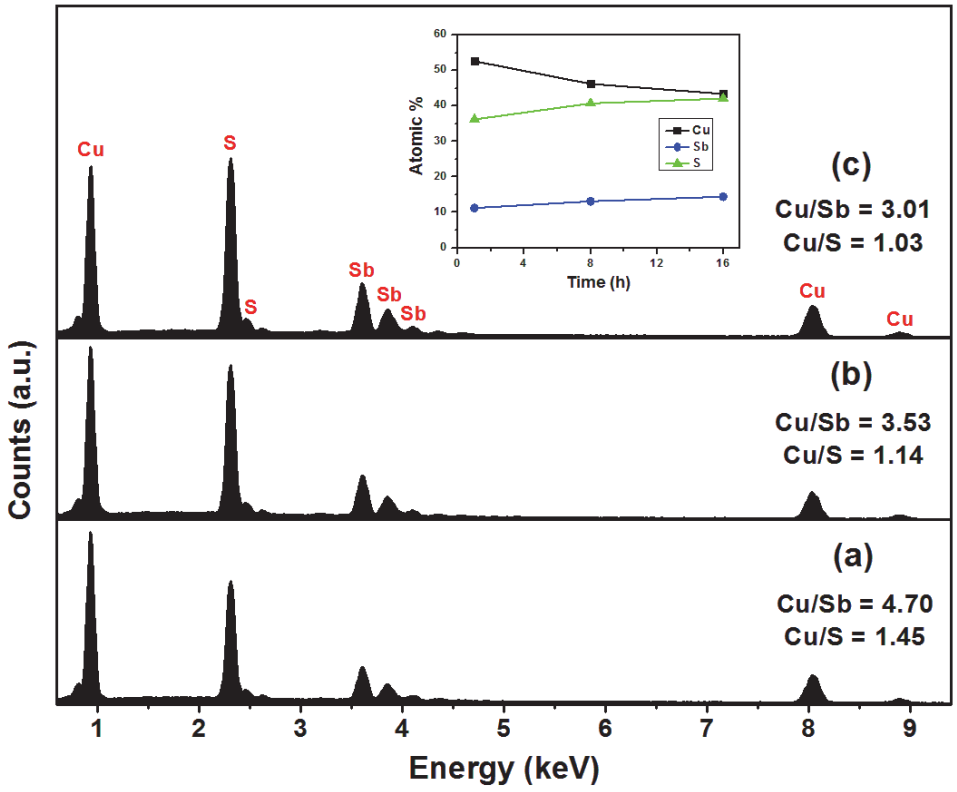

Fig. S10 EDX spectra of the nanostructures obtained when synthesis was performed at 80 °C for (a) 1 h, (b) 8 h, and (c) 16 h. Inset shows the atomic percentage as a function of time.

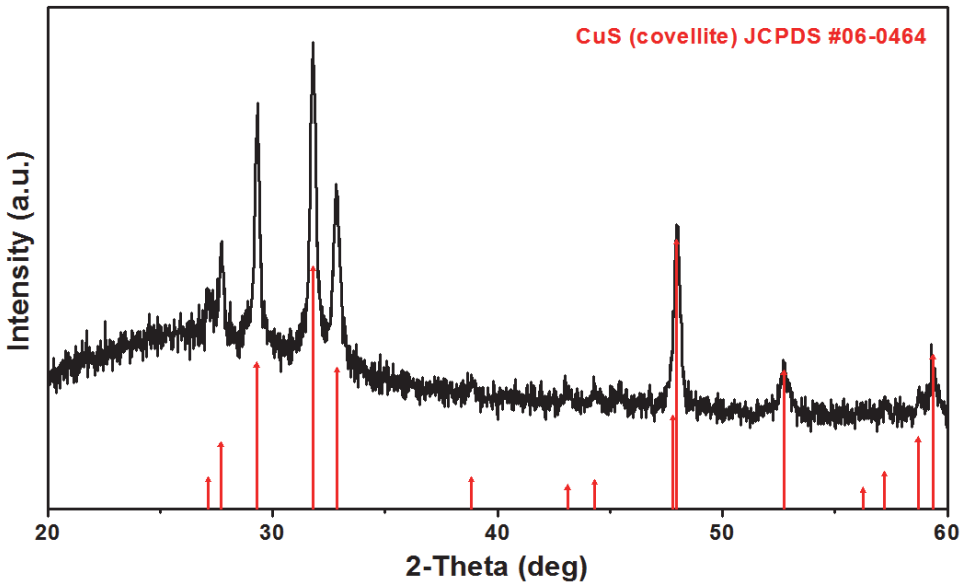

Fig. S11 XRD pattern of the product obtained when 0.3 mmol $Cu(dedtc)_2$ was solvothermally heated without the Sb precursor in 10 mL OM.

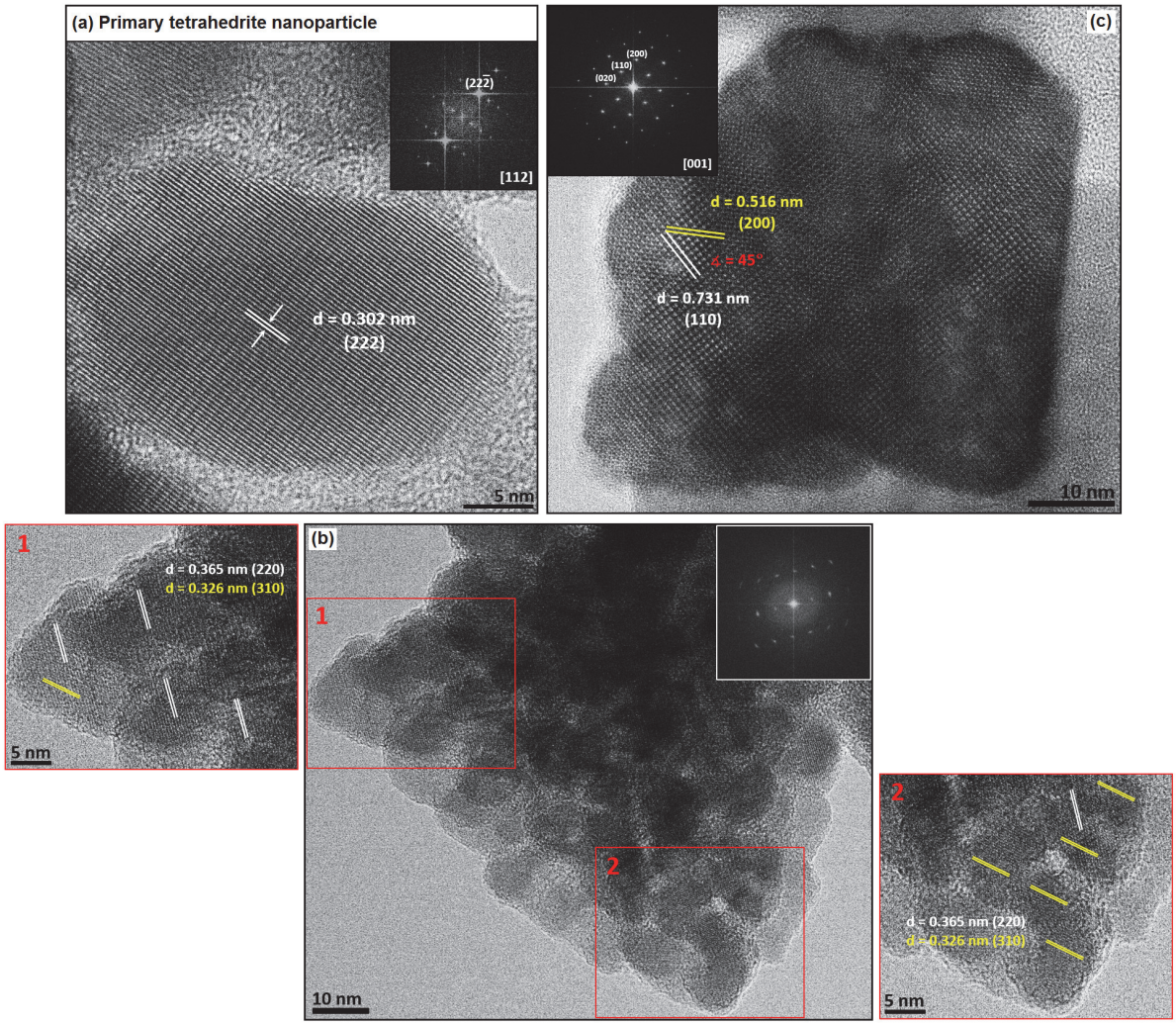

Fig. S12 (a) HRTEM image and corresponding FFT pattern (inset) of a primary tetrahedrite nanoparticle. (b) HRTEM image and corresponding FFT pattern (inset) of a grape-like tetrahedrite cluster obtained after heating for 4 h at 80 °C. Enlarged images of boxed areas 1 and 2 are shown beside the image. (c) HRTEM image and corresponding FFT pattern (inset) of a representative nanotetrahedron obtained after heating for 16 h at 80 °C.

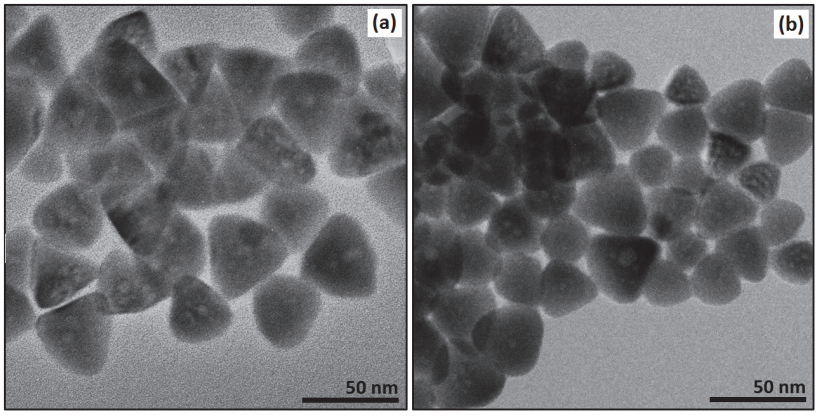

Fig. S13 TEM images of tetrahedrite nanostructures obtained when the solvothermal synthesis was performed at 200 °C for (a) 1 h and (b) 32 h.