

Selective Nanocrystal Synthesis and Calculated Electronic Structure of All Four Phases of Copper-Antimony-Sulfide

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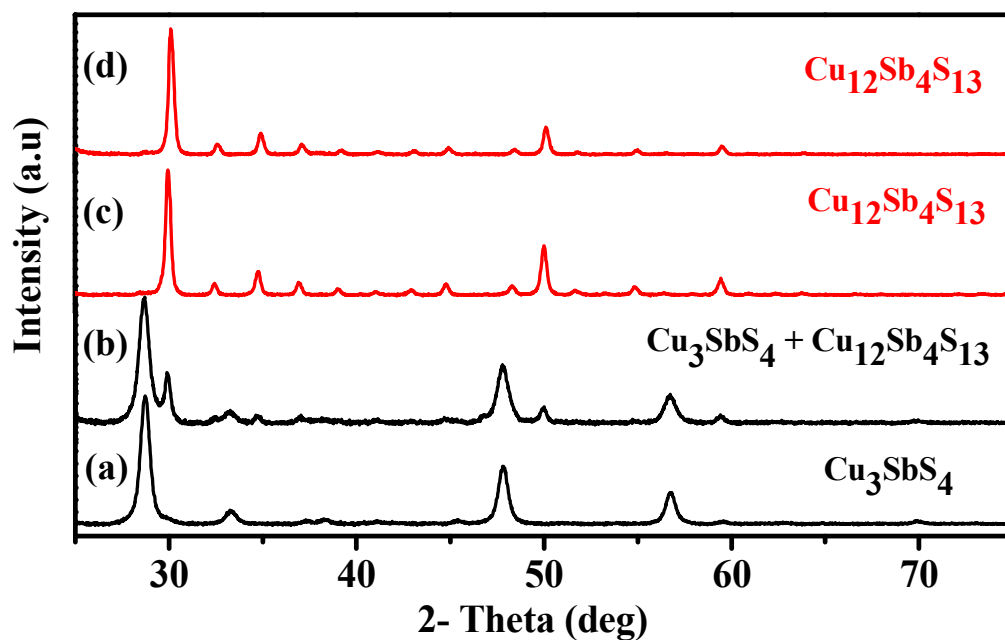


Figure S1. XRD patterns of nanocrystals synthesized using S/OLA with fixed $\text{Cu}(\text{acac})_2$: SbCl_3 ratio of 3:1 at reaction temperatures of (a) 190 °C, (b) 220 °C, (c) 250 °C and (d) 280 °C.

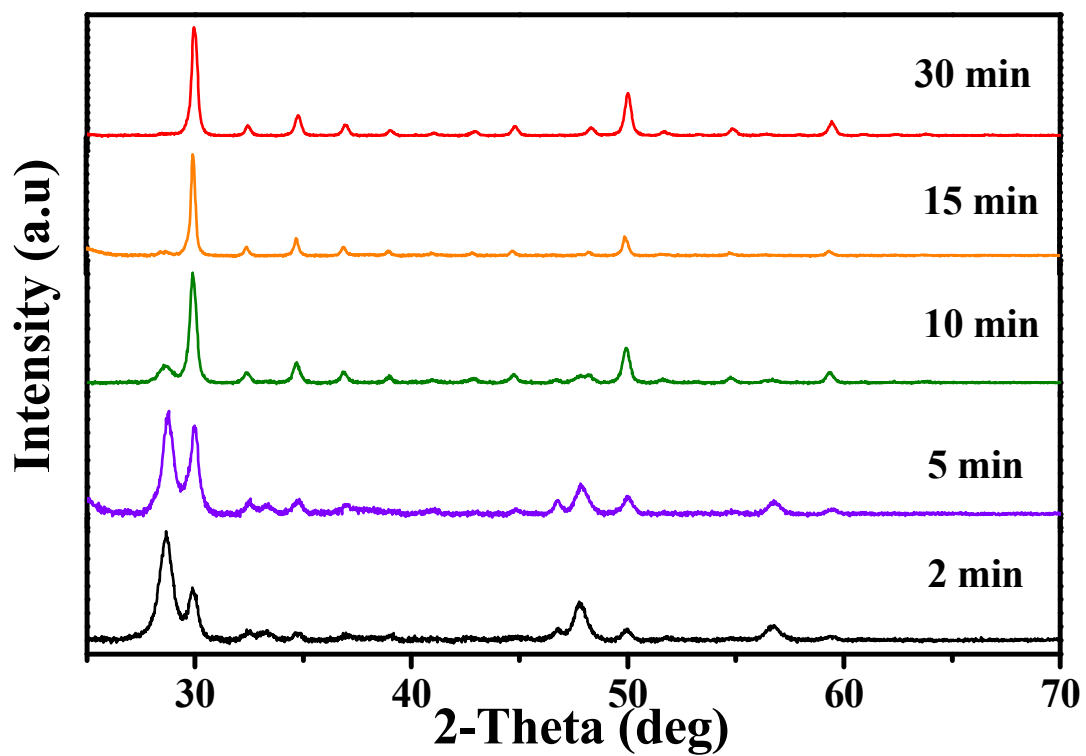


Figure S2. XRD patterns of nanocrystals synthesized using S/OLA with fixed $\text{Cu}(\text{acac})_2$: SbCl_3 ratio of 3:1 at reaction temperature of 250 °C for 2, 5, 10, 15 and 30 min.

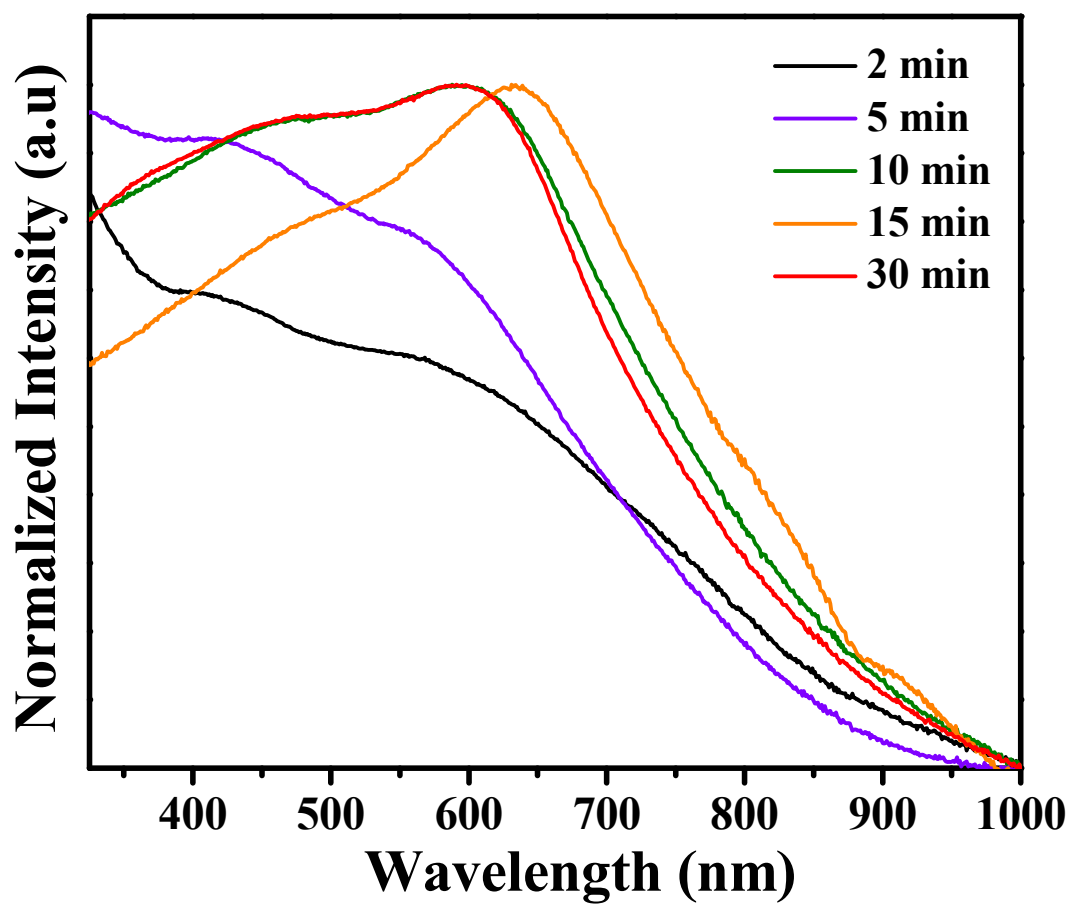


Figure S3. UV-Vis spectra of nanocrystals synthesized using S/OLA with fixed $\text{Cu}(\text{acac})_2$:
 SbCl_3 ratio of 3:1 at reaction temperature of 250 °C for 2, 5, 10, 15 and 30 min.

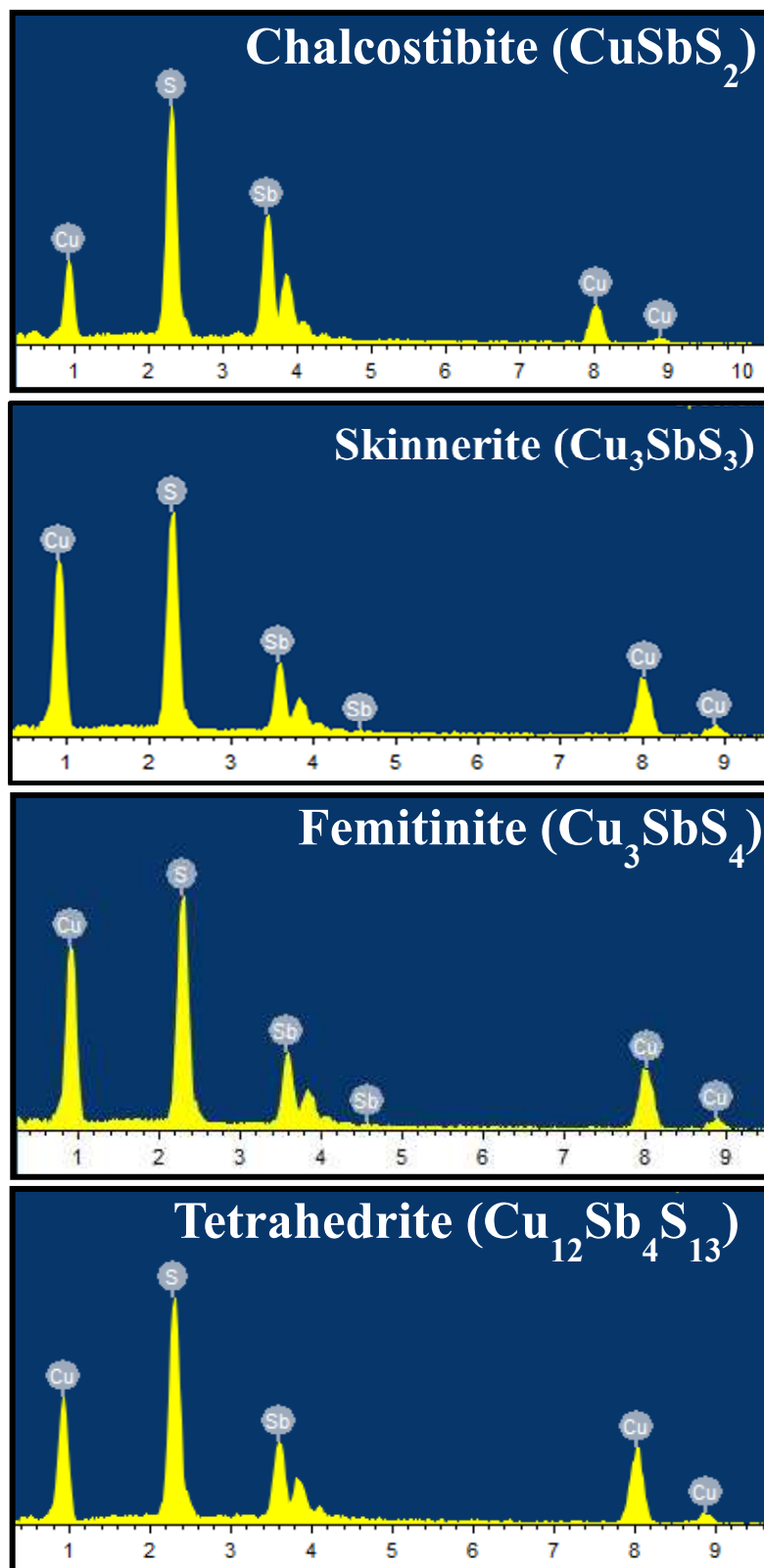


Figure S4. SEM-EDX spectra of CuSbS_2 , Cu_3SbS_3 , Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ nanocrystals.

Table S1. Elemental composition of Cu₃SbS₄, CuSbS₂, Cu₁₂Sb₄S₁₃ and Cu₃SbS₃ nanocrystals (from SEM-EDX).

Phase	Cu (%)	Sb (%)	S (%)	S/ (Cu+Sb)
CuSbS ₂	22.36	27.1	50.52	1.02
Cu ₃ SbS ₄	36.13	14.40	49.47	0.98
Cu ₁₂ Sb ₄ S ₁₃	40.12	14.91	44.95	0.82
Cu ₃ SbS ₃	41.6	14.6	43.8	0.78

Table S2. Elemental composition of CuSbS₂ nanocrystals synthesized at different temperatures using S/OLA.

Temperature	Cu (%)	Sb (%)	S (%)	S/ Cu+Sb
190	22.78	25.71	51.5	1.06
220	22.55	26.43	51.01	1.04
250	22.36	27.1	50.52	1.02
280	24.75	28.06	47.18	0.89
280*	26.68	26.63	46.68	0.88

(* synthesized using mixture of *l*-dodecanethiol and *t*-dodecanethiol)