

Supporting Information:

## Synthesis of Cu–Sb–S Nanocrystals: insight into the mechanism of composition and crystal phase selection

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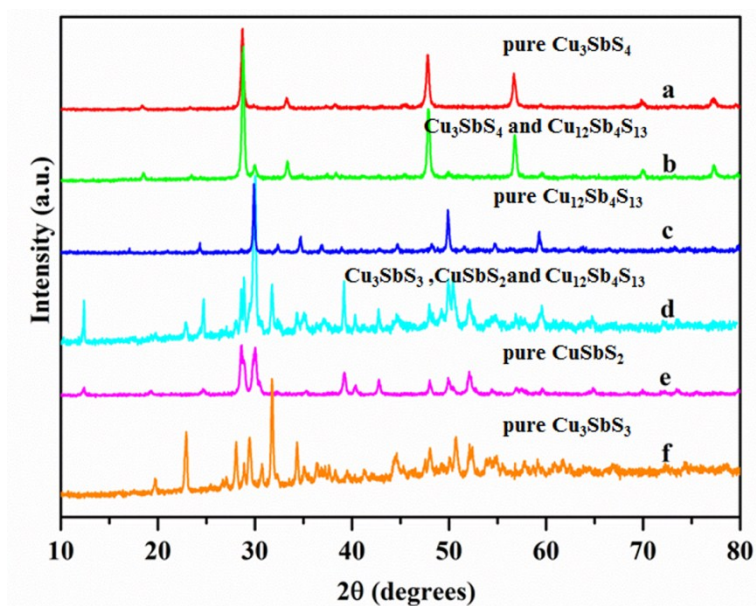


Figure S1. XRD patterns of nanocrystals synthesized using different amount of DDT (a) 3.6 mmol; (b) 4 mmol; (c) 5.5 mmol; (d) 6.5 mmol; (e) 20.5 mmol; (f) 25.6 mmol with fixed Cu (Ac)<sub>2</sub>: SbCl<sub>3</sub> ratio of 1:1 and reacted at 200 °C for 1h.

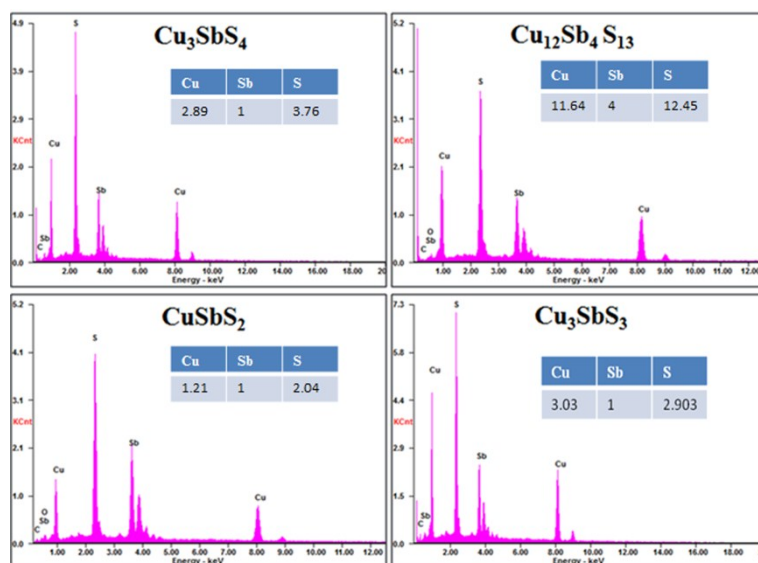


Figure S2. SEM-EDX spectra of Cu<sub>3</sub>SbS<sub>4</sub>, Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>, CuSbS<sub>2</sub> and Cu<sub>3</sub>SbS<sub>3</sub> nanocrystals

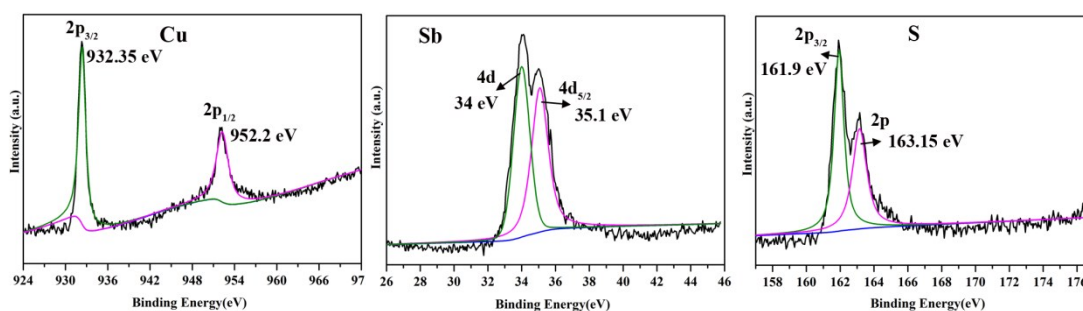


Figure S3. X-ray photoelectron spectra of as-prepared Cu<sub>3</sub>SbS<sub>4</sub> NCs.

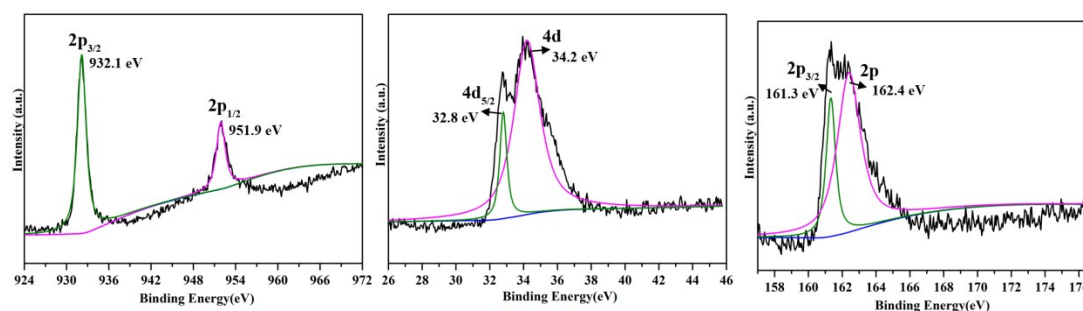


Figure S4. X-ray photoelectron spectra of as-prepared Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub> NCs.

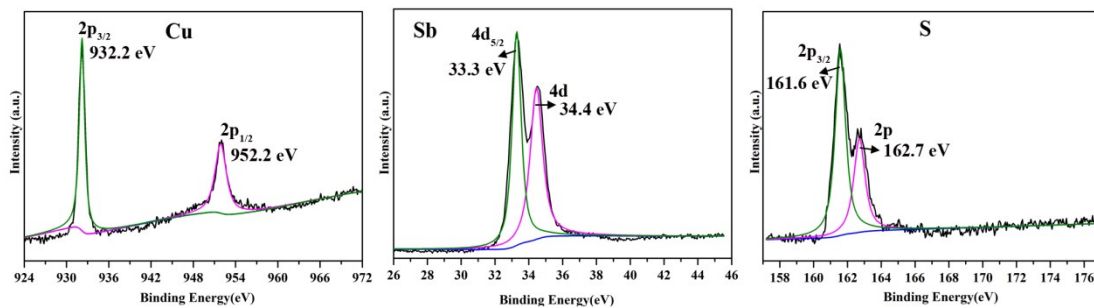


Figure S5. X-ray photoelectron spectra of as-prepared  $\text{CuSbS}_2$  NCs.

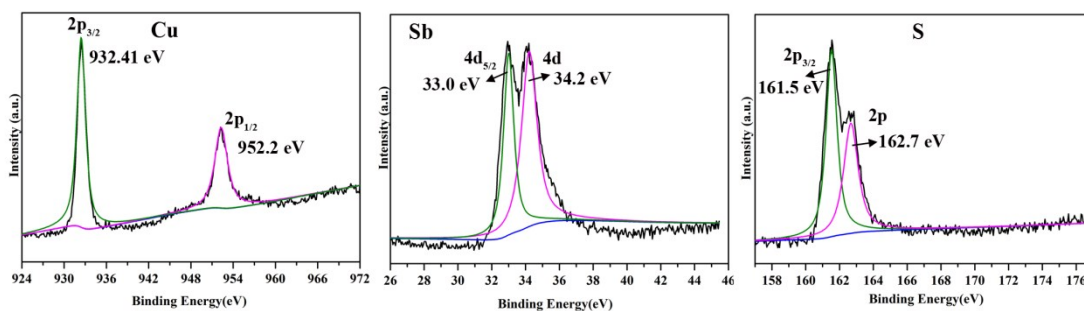


Figure S6. X-ray photoelectron spectra of as-prepared  $\text{Cu}_3\text{SbS}_3$  NCs.

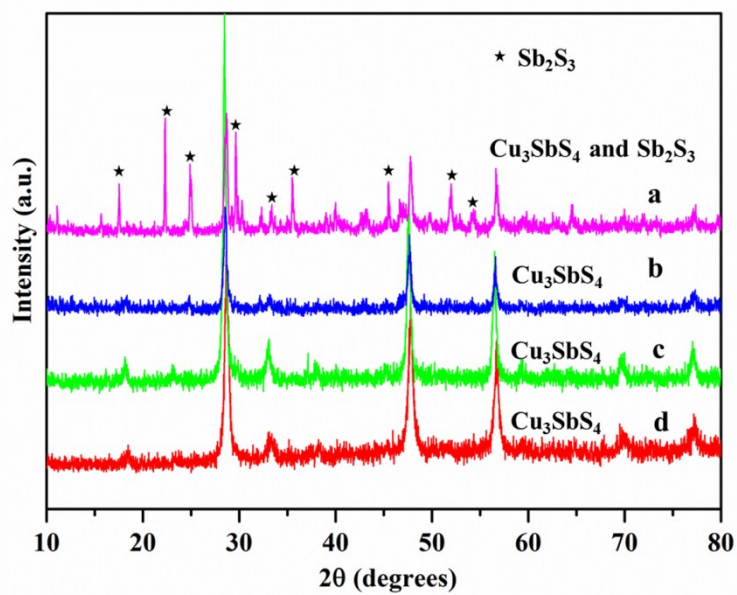


Figure S7. XRD patterns of nanocrystals synthesized with different  $\text{Cu}(\text{Ac})_2:\text{SbCl}_3$  ratio. (a) 1:3; (b) 1:2; (c) 1:1; (d) 1:0.3.

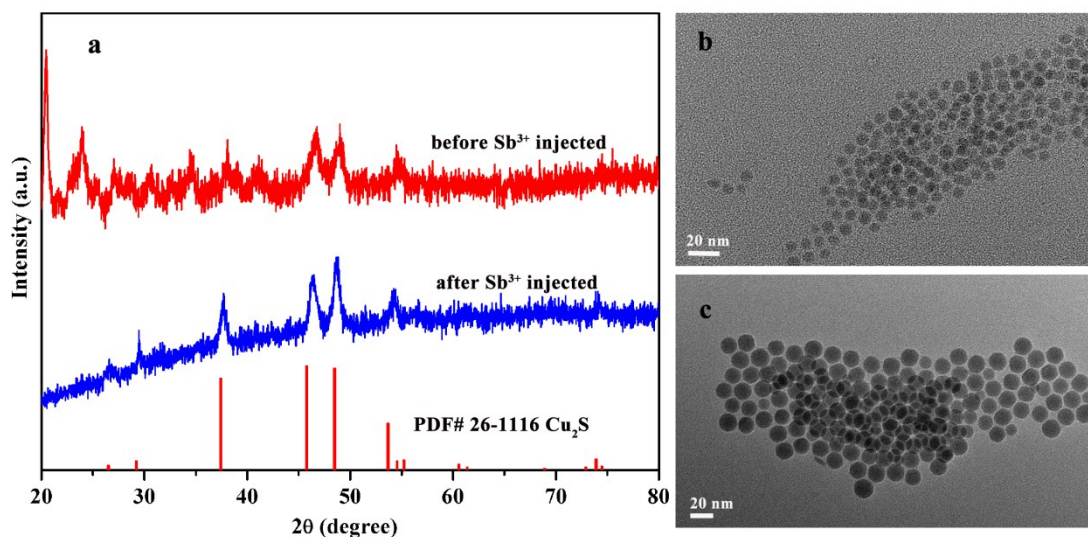


Figure S8. (a) XRD patterns of as-prepared  $\text{Cu}_2\text{S}$  nanocrystals before and after  $\text{Sb}^{3+}$  injection. (b) TEM image of  $\text{Cu}_2\text{S}$  seeds before  $\text{Sb}^{3+}$  injection. (c) TEM image of  $\text{Cu}_2\text{S}$  nanocrystals after  $\text{Sb}^{3+}$  injection.

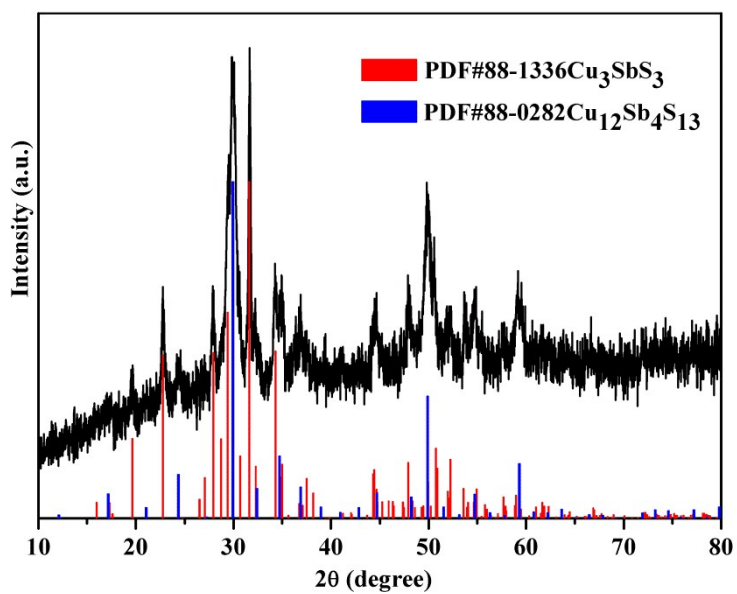


Figure S9. XRD pattern of nanocrystals synthesized with  $\text{Cu}_7\text{S}_4$  and  $\text{Sb}_2\text{S}_3$  as seeds and heated at  $200\text{ }^\circ\text{C}$  for 1h.

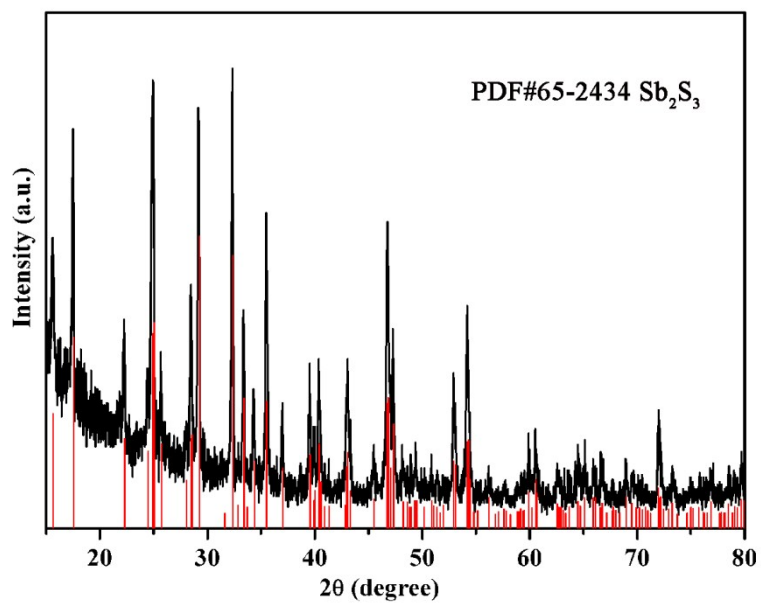


Figure S10. XRD pattern of  $\text{Sb}_2\text{S}_3$  nanocrystals.

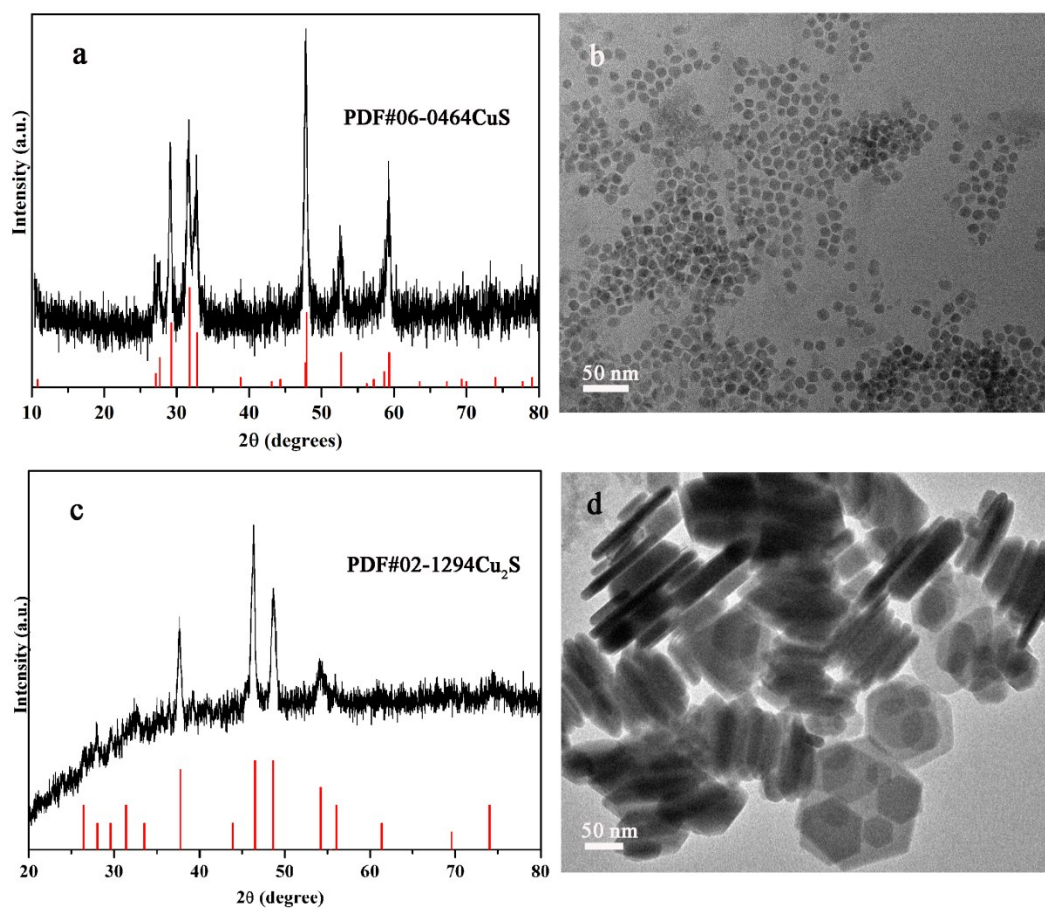


Figure S11. XRD and TEM images of  $\text{Cu}_{2-x}\text{S}$  nanocrystals with different reactivity of sulfur precursors: heating at (a,b) 150 °C; (c,d) 200 °C for 20 min. Both of the reactions were carried out at 200 °C for 1h with 1mL DDT.

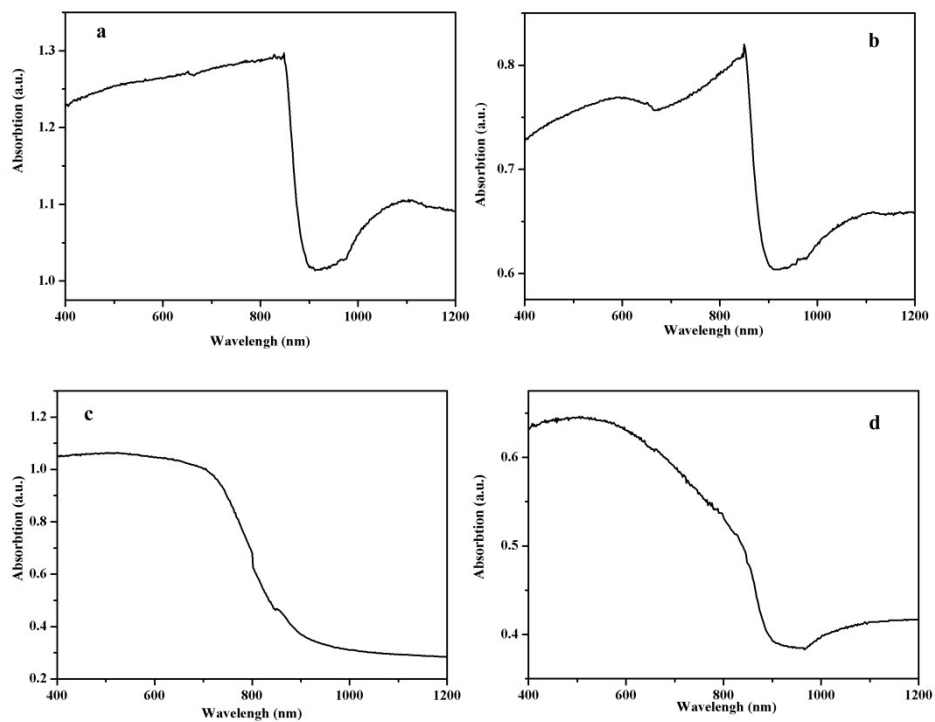


Figure S12. UV-vis-NIR absorption spectroscopy of as-prepared (a)  $\text{Cu}_3\text{SbS}_4$ , (b)  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , (c)  $\text{CuSbS}_2$ , and (d)  $\text{Cu}_3\text{SbS}_3$  nanocrystals.