Electronic Supplementary Material (ESI) for CrystEngComm


# Supporting Information

# Controlled synthesis of $CuInS_2$, $Cu_2SnS_3$ and $Cu_2ZnSnS_4$ nanostructures: insight into the universal phase-selectivity mechanism

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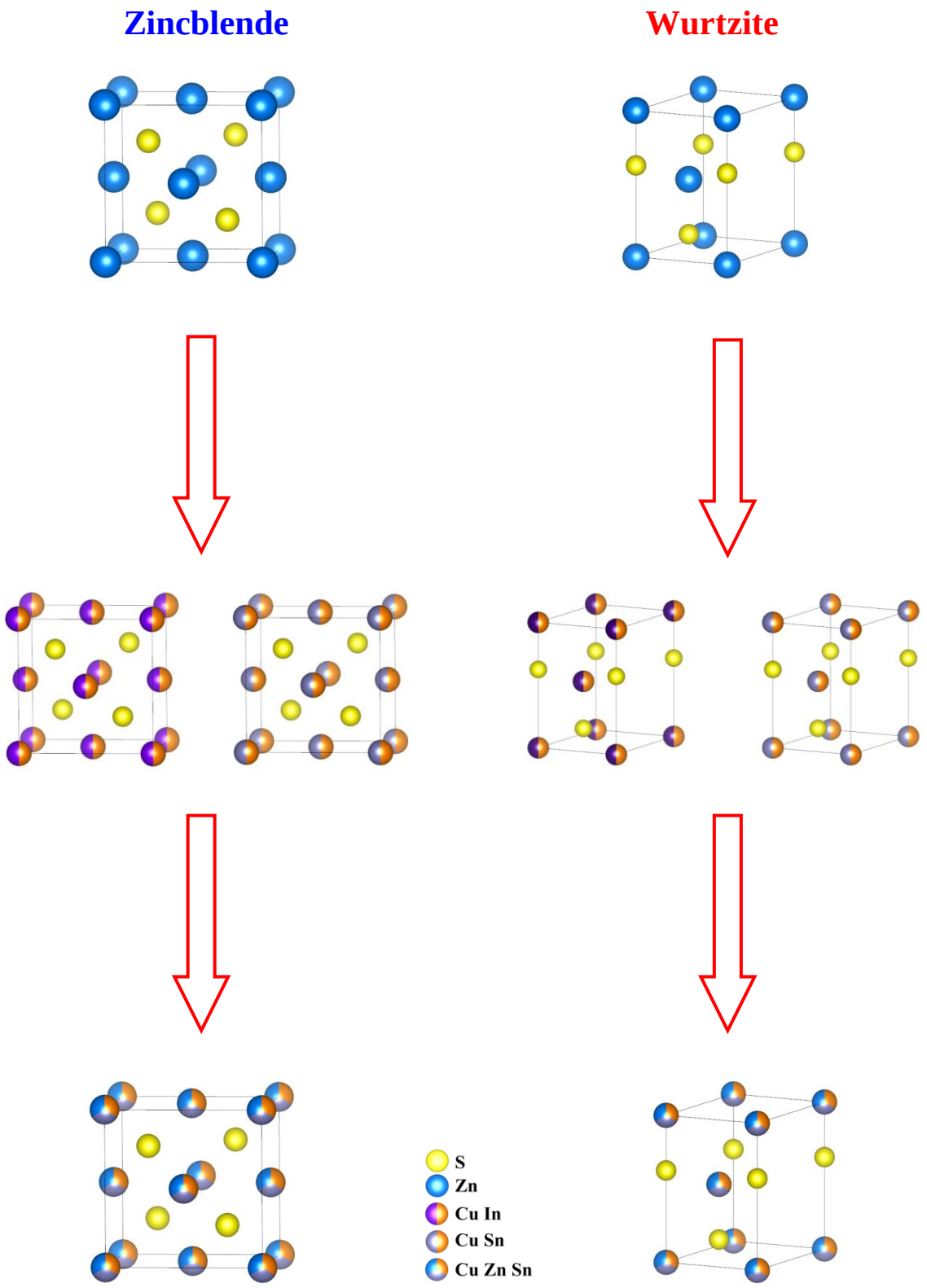


**Fig. S1** The unit cells and structure relations of ZnS, $CuInS_2$, $Cu_2SnS_3$ and $Cu_2ZnSnS_4$ with zincblende (left) and wurtzite (right) structures.

## Crystal data

| | | |
|---|---|---|
| Formula | $CuInS_2$ | |
| Crystal system | Zincblende | Wurtzite |
| Space group | *F*-43m (No. 216) | $P6_3mc$ (No. 186) |
| Unit cell dimensions | $a = b = c = 5.523(8)$ Å | $a = b = 3.897(5)$ Å, $c = 6.441(0)$ Å |

## Atomic coordinates

| Atom | Wyck. | x/a | y/b | z/c | Atom | Wyck. | x/a | y/b | z/c |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 4a | 0 | 0 | 0 | Cu | 2b | 1/3 | 2/3 | 0.3752 |
| In | 4a | 0 | 0 | 0 | In | 2b | 1/3 | 2/3 | 0.3752 |
| S | 4a | 1/4 | 1/4 | 1/4 | S | 2b | 1/3 | 2/3 | 0 |

As shown in Figure S1, the $Zn^{2+}$ sites in both zincblende and wurtzite ZnS can be replaced by a lower valence $Cu^{+}$ and a higher valence $In^{3+}$, giving $CuInS_2$ with remained crystal structures. Note that both Cu and In atoms occupy the same position and the both occupancy possibilities are 50%. Similarly, the $Zn^{2+}$ sites of ZnS can also be replaced by a $Cu^{+}$ and a $Sn^{3+}$, resulting zincblende and wurtzite $Cu_2SnS_3$ structures. Both Cu and Sn atoms occupy the same position and the occupancy possibilities of Cu and Sn are 2/3 and 1/3, respectively. Furthermore, when $Zn^{2+}$ sites in ZnS are replaced by $Cu^{+}$, $Zn^{2+}$ and $Sn^{4+}$, zincblende or wurtzite $Cu_2ZnSnS_4$ structures are obtained. In this case, Cu, Zn and Sn atoms occupy the same position, the occupancy possibilities of Cu, Zn and Sn are ½, 1/4 and 1/4, respectively.

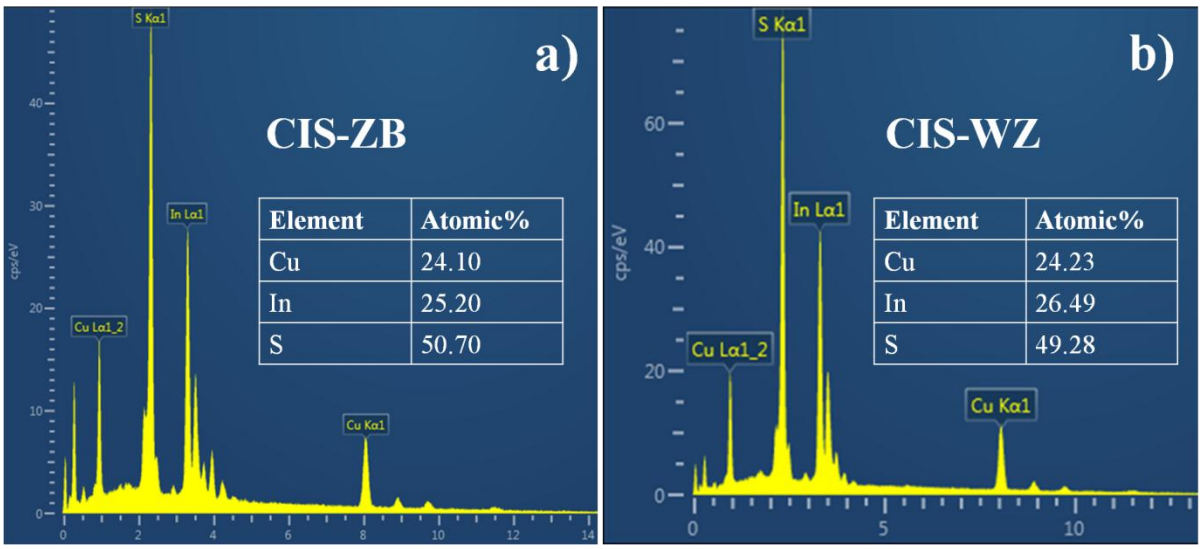


**Fig. S2** EDS spectra of $CuInS_2$ nanocrystals with (a) zincblende and (b) wurtzite structures, respectively.

**Table S1** Influence of capping agents variable on the structure of $CuInS_2$ nanocrystals.

| CIS samples | OLA | ODE | TOPO | OA | Crystal Structures |
|---|---|---|---|---|---|
| A | - | 4.0 mL | - | - | ZB |
| B | 0.5 mL | 3.5 mL | - | - | ZB |
| C | 2.0 mL | 2.0 mL | - | - | ZB + WZ |
| D | 3.5 mL | 0.5 mL | - | - | WZ |
| E | 4.0 mL | - | - | - | WZ |
| F | - | - | - | 4.0 mL | ZB |
| G | - | - | 4.0 g | - | WZ |
| H (hot-injection) | 4.0 mL | - | - | - | ZB |

ZB stands for zincblende structure; WZ stands for wurtzite structure.

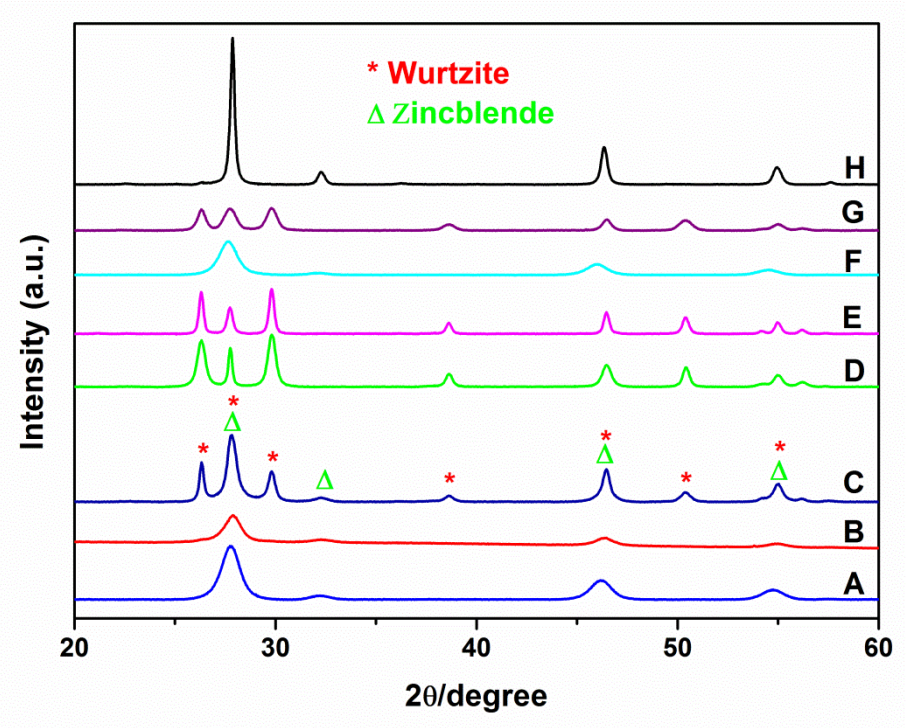


**Fig. S3** XRD patterns of $CuInS_2$ samples A-H prepared in various reaction conditions listed in Table S1.

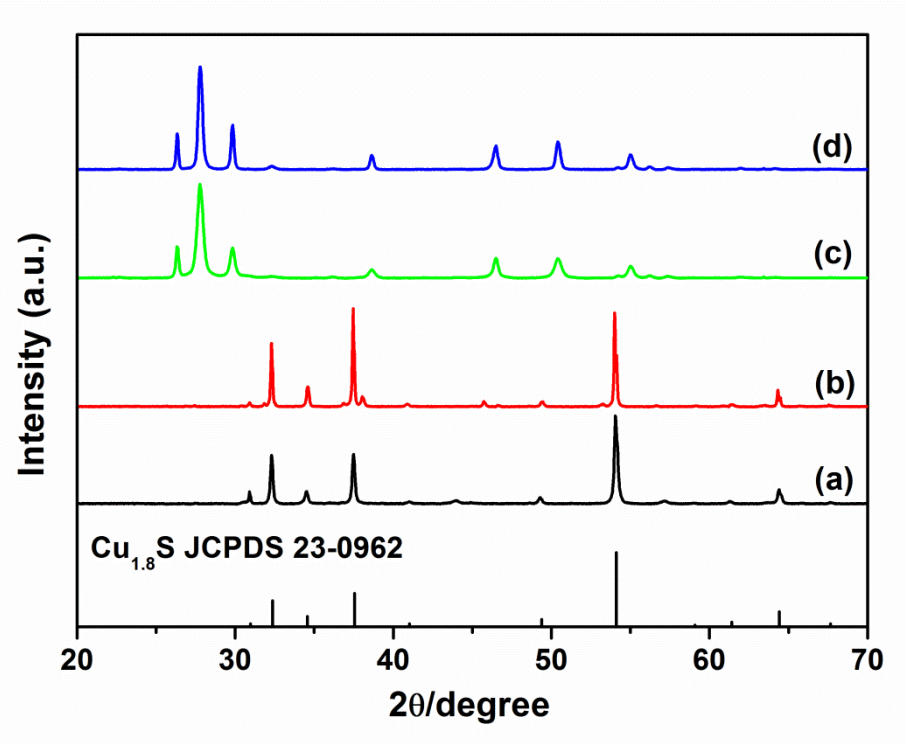


**Fig. S4** XRD patterns of $Cu_{1.8}S$ nanocrystals prepared by the reaction of $CuCl_2$ in (a) ODE and (b) OLA. XRD patterns of CIS nanocrystals synthesized by ion exchange between indium acetate and $Cu_{1.8}S$ nanocrystals in (c) ODE and (d) OLA.

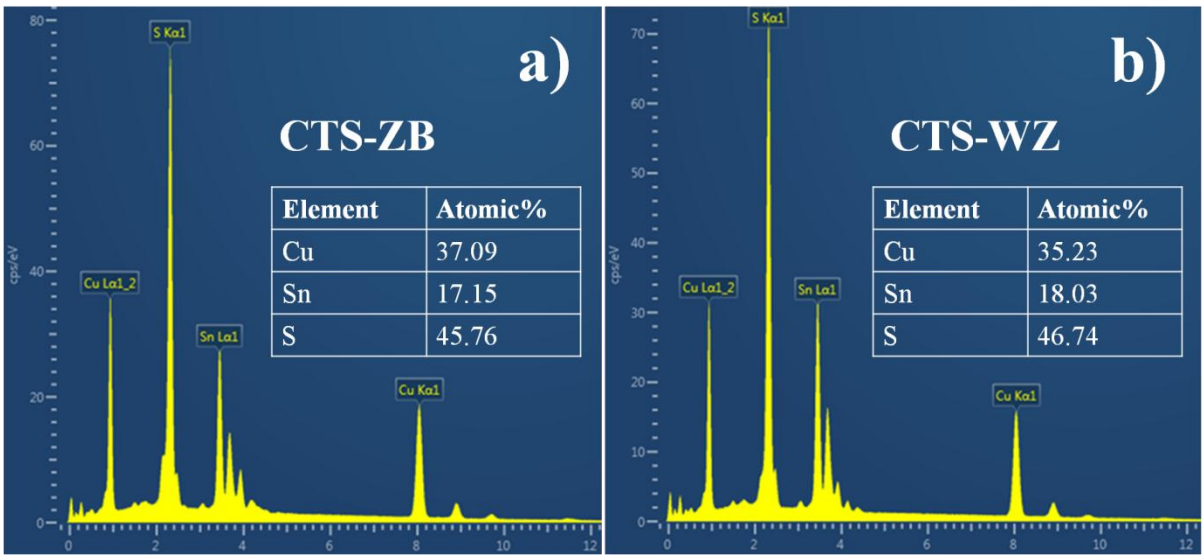


**Fig. S5** EDS spectra of $Cu_2SnS_3$ nanocrystals with (a) zincblende and (b) wurtzite structures, respectively.

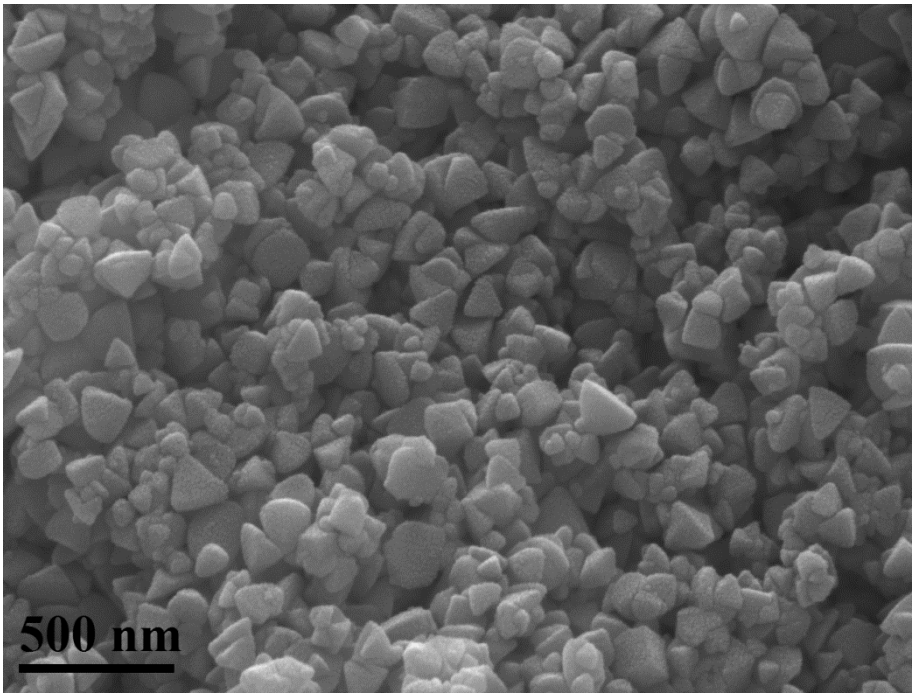


**Fig. S6** FE-SEM image of zincblende $Cu_2SnS_3$ nanocrystals.

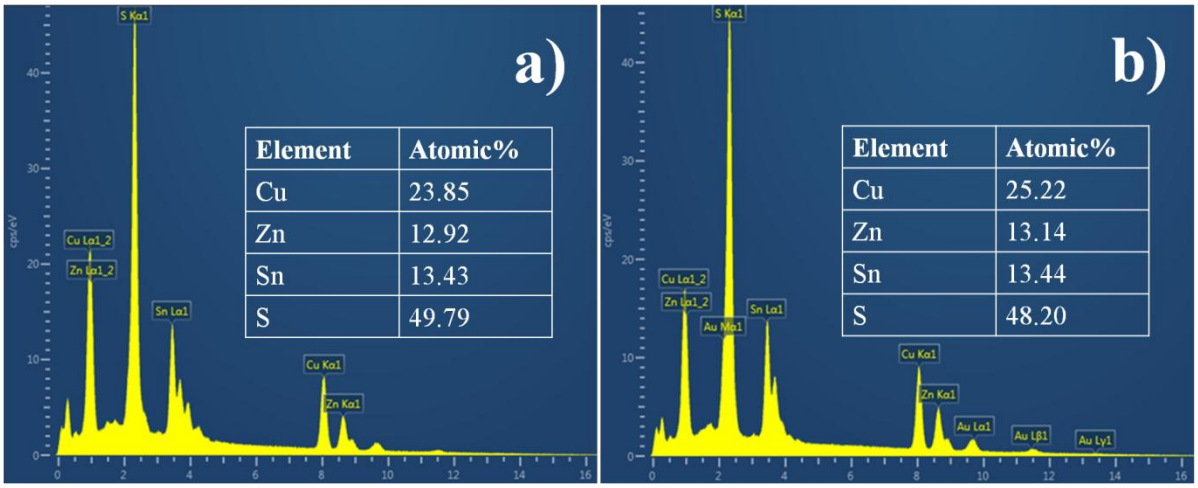


**Fig. S7** EDS spectra of $Cu_2ZnSnS_4$ nanocrystals with (a) zincblende and (b) wurtzite structures, respectively.