

Supporting Information Available

Alloyed $(\text{ZnS})_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ and $(\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ Nanocrystals with Arbitrary Composition and **Broad** Tunable Band Gaps

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Experimental Section

I. Chemicals

CuCl, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, sulfur powder (99.999%), carbon disulfide (CS_2 , 99.9%), *n*-dibutylamine (99%), oleylamine (OM, 80~90%), *n*-Dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), and tetrachloromethane (HPLC) were purchased from Aladdin Inc. Oleic acid (OA, 90%) and tri-*n*-octylphosphine oxide (TOPO, 90%) were obtained from Sigma-Aldrich. SnCl_2 was purchased from Alfa Aesar. All chemicals were used as received.

II. Preparation of two types of sulfur precursors

a) 1.0 M S/OM solution was prepared by dissolving 0.64 g (20.0 mmol) of sulfur powder in 20.0 mL of oleylamine at 120 °C.

b) 1.0 M dibutyldithiocarbamic acid/ODE (DBDCA/ODE) solution was prepared by dropping 1.52 g (20.0 mmol) of CS_2 and 2.6 g (20.0 mmol) of dibutylamine in 10.0 mL of ODE at room temperature. Subsequently, the solution was diluted to 20.0 mL

with ODE. DBDCA (HS_2CNBu_2) was synthesized by the reaction of dibutylamine and CS_2 according to the literature.¹

III. Synthesis of zincblende Cu_2SnS_3 and alloyed $(\text{ZnS})_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ and $(\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ nanocrystals

In a typical synthesis, 20.0 mg (0.2 mmol) of CuCl , 19.0 mg (0.1 mmol) of SnCl_2 , and 10.0 mL of oleylamine were added to a 50 mL three-neck flask and the reaction mixture was heated to 130 °C. The inside of the flask was degassed by a vacuum pump for 10 min and argon gas was charged from the balloon. This procedure was repeated three times to remove the oxygen and water. Then, the temperature was increased to 240 °C, and 1.0 mL of S/OM solution was swiftly injected into the flask under magnetic stirring. After 60 min, the crude solution was cooled to 60 °C and then precipitated with 30 mL of ethanol and further isolated by centrifugation and decantation. The purified nanocrystals were re-dispersed in toluene for TEM and XRD measurements without any size sorting. The same procedure as above was applied to synthesize alloyed $(\text{ZnS})_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ and $(\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ nanocrystals by changing stoichiometric ratios between CuCl , SnCl_2 , ZnCl_2 , and InCl_3 precursors. Detailed synthetic conditions were listed in Table S1.

IV. Synthesis of wurtzite Cu_2SnS_3 nanocrystals

Wurtzite Cu_2SnS_3 nanocrystals were synthesized by using more reactive sulfur precursor (DBDCA) and stronger capping agents (OA, DDT and TOPO). The effects of the sulfur precursors and the capping agents on the Cu_2SnS_3 structures will be

published elsewhere. 34.0 mg (0.2 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 19.0 mg (0.1 mmol) of SnCl_2 , 0.2 mL of oleylamine, 2.0 mL of OA, 0.5 g of TOPO, and 5.0 mL ODE were placed in a 50 mL three-neck flask and the reaction mixture was heated to 210 °C under argon atmosphere. Next, 1.0 mL of DDT was injected into the flask by a syringe. When the temperature was returned to 210 °C, 1.0 mL of DBDCA/ODE solution was swiftly injected into the flask under magnetic stirring, and the reaction temperature was maintained at 210 °C for 20 min.

V. Characterization

The powder XRD patterns were recorded using a Bruker D8 FOCUS X-ray diffractometer. The simulated Cu_2SnS_3 powder XRD patterns were obtained by using Diamond 3.0 and CCDC Mercury 1.4.2 programs. The lattice mismatch was calculated via the following function: $\delta = 2|(a_2 - a_1)/(a_2 + a_1)| * 100\%$, where a is a -axis lattice constant. UV-Vis-NIR absorption spectra were measured by Shimadzu UV-3600. Low resolution TEM (LR-TEM) images and selected area electron diffraction (SAED) were taken on a JEOL-1011 electron microscope with an accelerating voltage of 100 kV. High resolution TEM (HR-TEM) images were taken on a FEI Tecnai G2 F20 with an accelerating voltage of 200 kV. Energy Disperse Spectroscopy (EDS) spectra were obtained by using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. X-ray photoelectron spectra (XPS) were measured with VG ESCALAB MK (VG Company, UK) at room temperature by using a Mg $K\alpha$ X-ray source ($h\nu = 1253.6$ eV) at 14 kV and 20 mA.

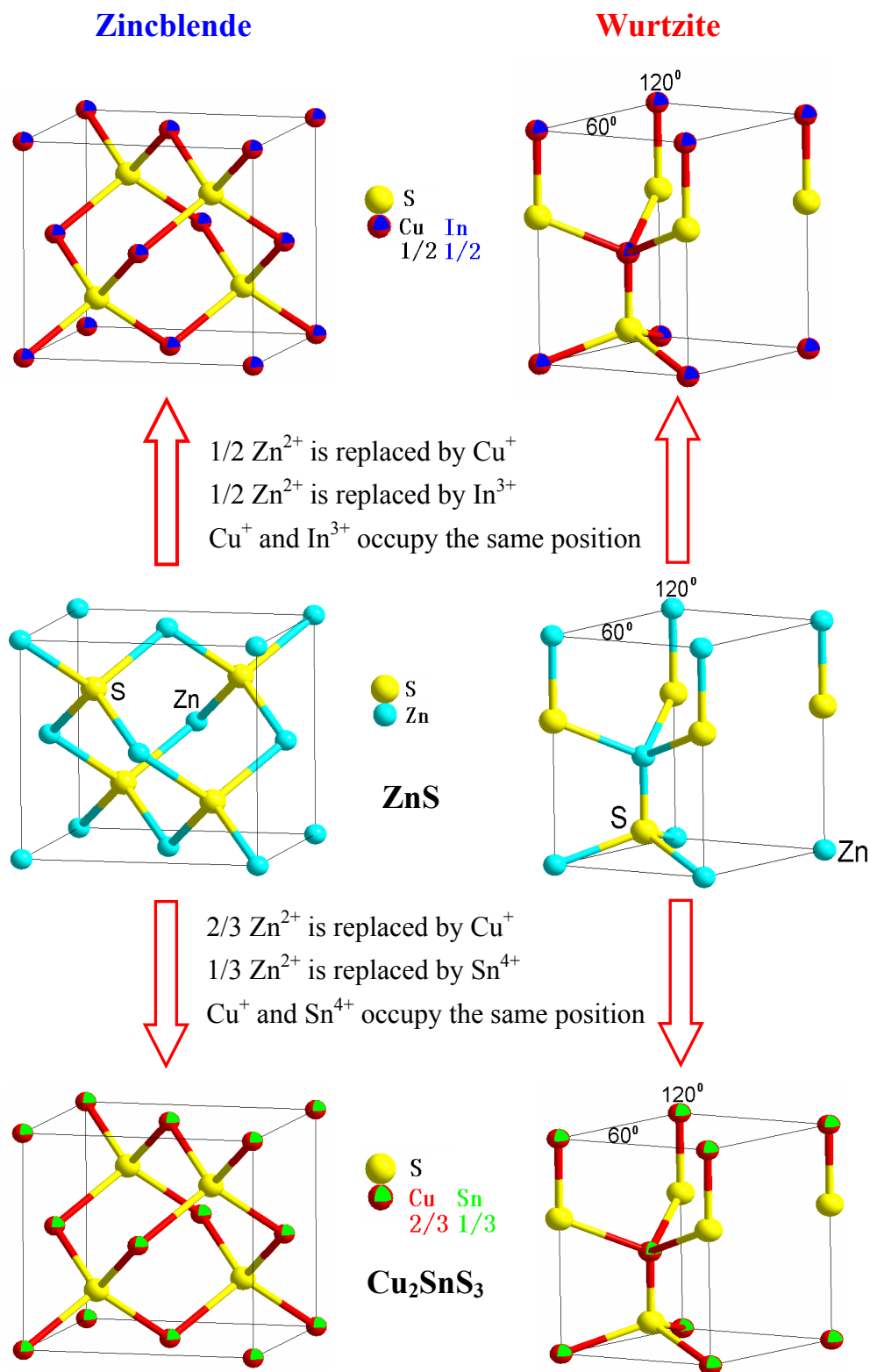


Figure S1. The unit cells and structure relations of ZnS, CuInS₂, and Cu₂SnS₃ with zincblende (left) and wurtzite (right) structures.

Crystal data

Formula	Cu ₂ SnS ₃	
Crystal system	Zincblende	Wurtzite
Space group	<i>F</i> -43 <i>m</i> (No. 216)	<i>P</i> 63 <i>mc</i> (No. 186)
Unit cell dimensions	$a = b = c = 5.428(8) \text{ \AA}$	$a = b = 3.815(1) \text{ \AA}, c = 6.265(7) \text{ \AA}$

Atomic coordinates

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

Notice that both Cu and Sn atoms occupy the same position, and the occupancy possibilities of Cu and Sn are 2/3 and 1/3, respectively.

Table S1. Synthetic conditions of zincblende Cu₂SnS₃ as well as alloyed (ZnS)_x(Cu₂SnS₃)_{1-x} and (CuInS₂)_x(Cu₂SnS₃)_{1-x} nanocrystals.

Formula	Temp. (°C)	Time (min)	Ligand+Solvent
ZnS	280	60	10 mL OM
(ZnS) _x (Cu ₂ SnS ₃) _{1-x}	200-240	60	10 mL OM
Cu ₂ SnS ₃	240	60	10 mL OM
(CuInS ₂) _{1/5} (Cu ₂ SnS ₃) _{4/5}	200-240	60	10 mL OM
CuInS ₂	200	30	10 mL OM

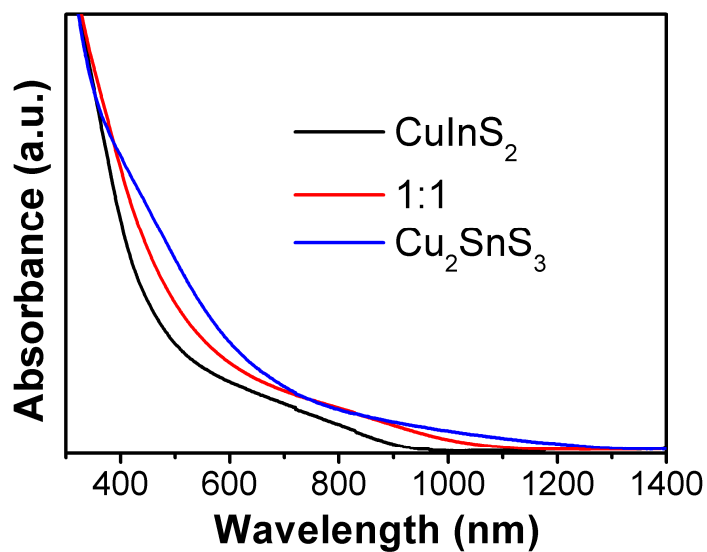


Figure S2. UV-Vis-NIR absorption spectra of CuInS_2 , $(\text{CuInS}_2)_{1/2}(\text{Cu}_2\text{SnS}_3)_{1/2}$, and Cu_2SnS_3 nanocrystals in tetrachloromethane.

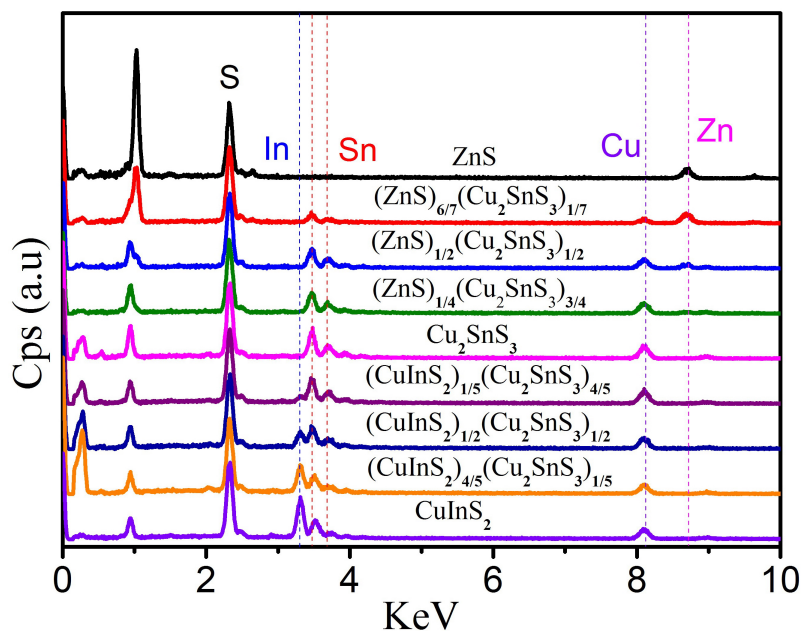


Figure S3. EDS spectra of alloyed $(\text{ZnS})_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ and $(\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ nanocrystals with a zincblende structure.

Table S2. EDS results (atomic percent) of zincblende $(\text{ZnS})_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ and $(\text{CuInS}_2)_x(\text{Cu}_2\text{SnS}_3)_{1-x}$ nanocrystals as well as wurtzite Cu_2SnS_3 nanocrystals.

Formula ^a	Zn%	Cu%	Sn%	In%	S%
^b ZnS	49.86	----	----	----	50.14
^b $(\text{ZnS})_{6/7}(\text{Cu}_2\text{SnS}_3)_{1/7}$	29.69	12.92	5.38	----	52.01
^b $(\text{ZnS})_{1/2}(\text{Cu}_2\text{SnS}_3)_{1/2}$	10.62	24.98	11.48	----	52.93
^b $(\text{ZnS})_{1/4}(\text{Cu}_2\text{SnS}_3)_{3/4}$	5.09	31.86	15.12	----	47.94
^b Cu_2SnS_3	----	32.90	16.90	----	50.20
^b $(\text{CuInS}_2)_{1/5}(\text{Cu}_2\text{SnS}_3)_{4/5}$	----	31.18	13.34	3.34	52.14
^b $(\text{CuInS}_2)_{1/2}(\text{Cu}_2\text{SnS}_3)_{1/2}$	----	31.09	9.68	9.04	50.19
^b $(\text{CuInS}_2)_{4/5}(\text{Cu}_2\text{SnS}_3)_{1/5}$	----	25.59	4.43	17.15	52.84
^b CuInS_2	----	23.62	----	24.31	52.07
^c Cu_2SnS_3	----	34.68	15.20	----	50.12

^a calculated by the ratio of co-precursors used

^b Zincblende phase

^c Wurtzite phase

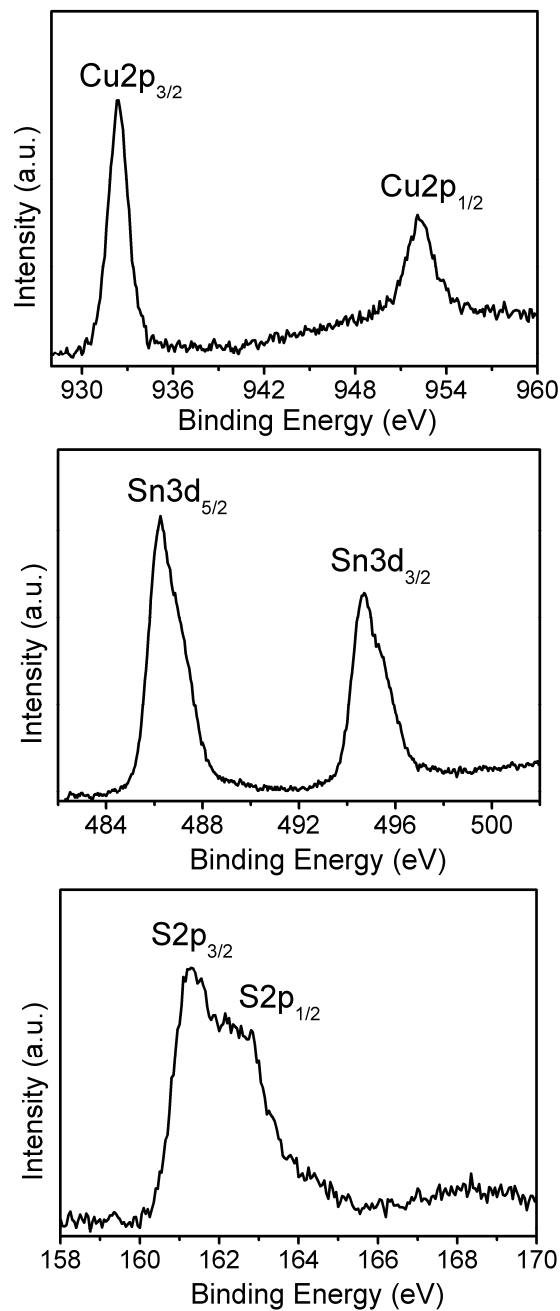


Figure S4. XPS spectra of oleylamine-capped Cu_2SnS_3 nanocrystals. (Top) $\text{Cu}2p$; (middle) $\text{Sn}3d$; (bottom) $\text{S}2p$.

Reference:

1. R. Nomura, S. Inazawa, K. Kanaya, H. Matsuda, *Appl. Organomet. Chem.* **1989**, *3*, 195.