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Facile One-Pot Synthesis of Copper Sulfide–Metal Chalcogenide Anisotropic Heteronanostructures in a Noncoordinating Solvent

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Supplementary Information

Experimental

Materials

Copper acetate (CuAc, 99.995%), zinc stearate (90%), potassium ethylxanthate (90%), zinc chloride (90%), 1-dodecanethiol (DDT, 97%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Zinc chloride (90%) was purchased from Riedel-deHaën AG (Seelze, Germany). Indium acetate (InAc, 99.98%) was purchased from Alfa-Aesar (Ward Hill, MA, USA). All organic solvents were purchased from EM Sciences. All chemicals were used directly without further purification. Zinc ethylxanthate was synthesized by a method similar to that used by Nair et al.[1]

Synthesis of Cu_2S nanocrystals and Cu_2S-CIS HNS rods

CuAc (0.6 mmol), DDT (10 mmol), and 5 mL of ODE were loaded into a reaction vessel equipped with a condenser and a thermometer with an attached Schlenk line. The mixture was degassed under vacuum, purged three times with argon, and heated to 40 °C for 1 h. The resulting solution was subsequently heated to 240 °C. After the solution was kept at the reaction temperature for the desired time, the heating source was removed and the solution was cooled to room temperature. The Cu_2S particles were precipitated by the addition of 30 mL of methanol followed by 20 min of centrifugation at 6000 rpm. The supernatant, which contained unreacted material, was discarded, and the remaining precipitate was then redispersed in hexanes. Methanol was again added, and the solution was centrifuged for 20 min. Cu_2S-CIS HNS rods were prepared by a similar procedure, except that an additional 0.2 mmol of InAc was introduced into the same reaction vessel.

Synthesis of Cu_2S-ZS and Cu_2S-CIZS HNS rods

The injection solution of the ZnS precursor was prepared by mixing 9 mL of zinc

stearate (0.267 M) in ODE and 3 mL of zinc ethylxanthate (0.1 M) in toluene containing 300 μL of dimethylformamide. CuAc (0.6 mmol), DDT (10 mmol), and 5 mL of ODE were loaded into a reaction vessel equipped with a condenser and a thermometer with an attached Schlenk line. The mixture was degassed under vacuum, purged three times with argon, and heated to 40 °C for 1 h. The resulting solution was subsequently heated to 240 °C. Without further separation or purification, ZnS precursors were added dropwise by means of a syringe pump (KD Scientific KDS100, USA) at a flow rate of 0.13 mL/min for the desired time once the temperature reached 240 °C. After the addition was complete, the reaction mixture was cooled to room temperature, followed by centrifugation at 6000 rpm for 20 min. The supernatant was then discarded. The precipitate was redispersed in chloroform under sonication and precipitated by the addition of methanol, followed by 20 min of centrifugation at 6000 rpm. The supernatant, which contained unreacted material, was discarded, and the remaining precipitate was then redispersed in hexanes. For Cu_2S-CIZS, HNS rods were prepared by a similar procedure, except that an additional 0.2 mmol of InAc was introduced into the same reaction vessel.

Sample Characterization

The nanocrystal solutions were dropped onto carbon-coated nickel grids by slowly evaporating the solvent in air at room temperature. The ultrastructure of the nanocrystals was examined and high-angle annular dark field (HAADF) scanning transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) experiments were performed by field-emission TEM on a Philips Tecnai G2 F20 microscope (Philips, Holland) operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) samples were prepared by depositing the nanocrystals on a Si(100) wafer; the XRD patterns were recorded at room temperature with a Bruker AXS D8 X-ray diffractometer using Cu Kα radiation in the θ-θ mode. The generator was operated at 40 kV and 40 mA; data were collected between 20° and 70° in 2θ with a step size of 0.1° and a counting time of 5 s per step. UV-vis–near infrared (NIR) absorption spectra were measured with a JASCO V-670 spectrometer. The simulated $CuInS_2$ powder XRD pattern was obtained by using the GSAS software package[2] with the EXPGUI interface[3] and Material Studio (Accelrys Software, Inc.).

Crystal data

Molecular Formula	ZnS	Cu_2S	$CuInS_2$
Crystal system	Wurtzite	Hexagonal chalcocite	Wurtzite
Space group	$P6_3mc$	$P6_3mmc$	$P6_3mc$
Crystal parameters	$a = b = 3.824$ Å, $c = 6.257$ Å	$a = b = 3.89$ Å, $c = 6.88$ Å	$a = b = 3.906$ Å, $c = 6.425$ Å

Atomic coordinates

Wurtzite ZnS

	Wyck.	x/a	y/b	z/c
Zn	2b	1/2	1/2	1/2
S	2b	1/2	1/2	1/2

Hexagonal chalcocite Cu_2S

	Wyck.	x/a	y/b	z/c
Cu′	2b	0	0	1/4
Cu′′	4f	1/3	2/3	0.578
Cu′′′	6g	0	1/2	0
S′	2c	0	0	0
S′′	2c	1/3	2/3	1/4

Wurtzite $CuInS_2$

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

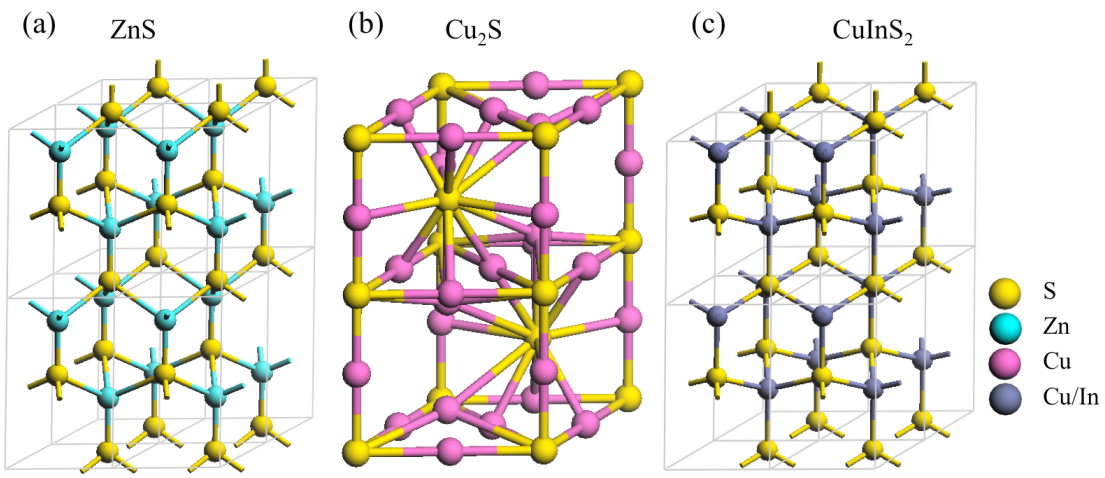

Fig. S1. Crystal structures of (a) wurtzite ZnS, (b) hexagonal chalcocite Cu_2S, and (c) wurtzite $CuInS_2$. Cu_2S has two molecules per cell, in which the sulfur atoms are arranged in nearly perfect hexagonal closest packing.[4] The wurtzite of $CuInS_2$ can be considered as being derived from the wurtzite structure of ZnS (space group, $P6_3mc$), in which Zn^{2+} cations are replaced by Cu^+ and In^{3+}, respectively. Cu^+ and In^{3+} are

randomly distributed in the Zn^{2+} positions, and the sulfur positions are maintained in the unit cells of wurtzite ZnS.[5]

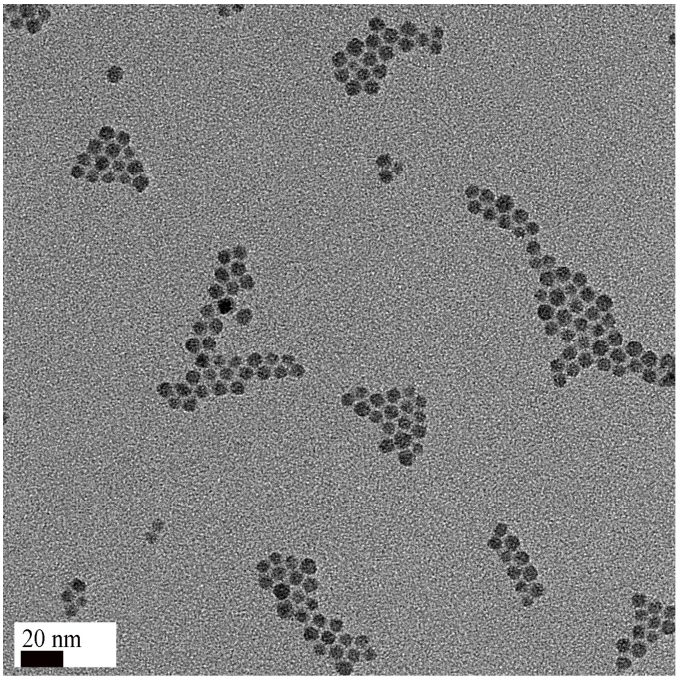

Fig. S2. Representative low-magnification TEM images of Cu_2S samples prepared at 240 °C for 30 min.

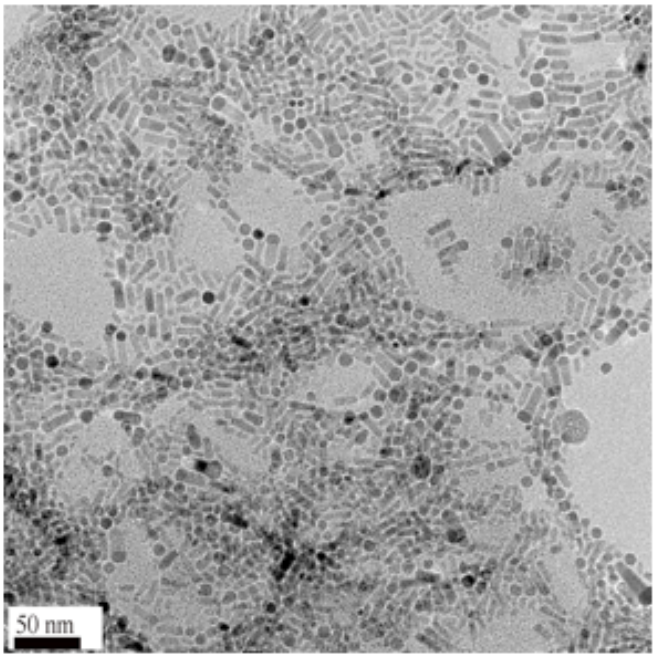

Fig. S3. Representative low-magnification TEM images of Cu_2S-ZS HNS dots and rods obtained using single injections of ZnS precursors (4 mL).

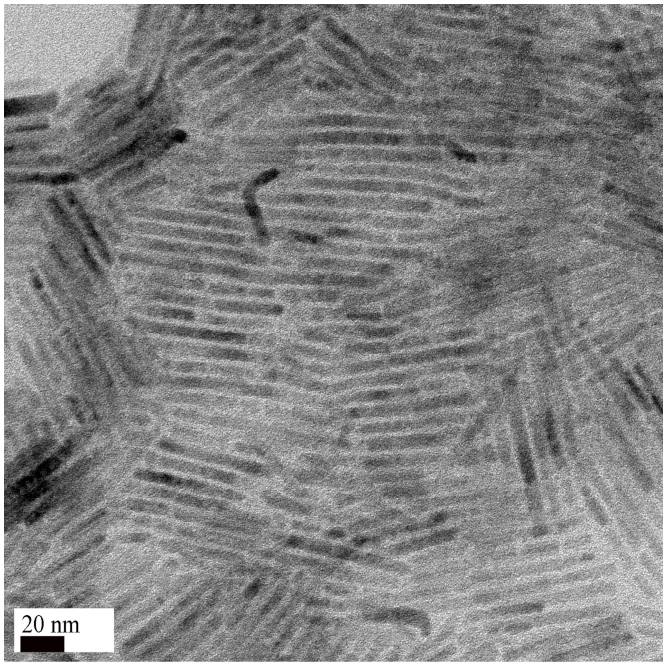

Fig. S4. TEM images of Cu_2S-ZS HNS rods with aspect ratio of 6 prepared at 240 °C by injecting ZnS precursors into Cu_2S solution for (c) 60 min.

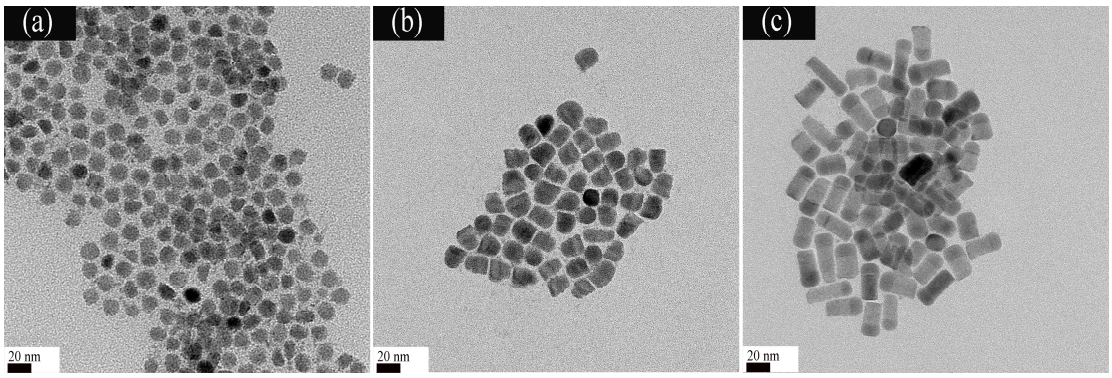

Fig. S5. Representative low-magnification TEM images of as-prepared Cu_2S-CIS HNS dots and rods obtained at 240 °C for different intervals: (a) 0 min, (b) 10 min, and (c) 30 min.

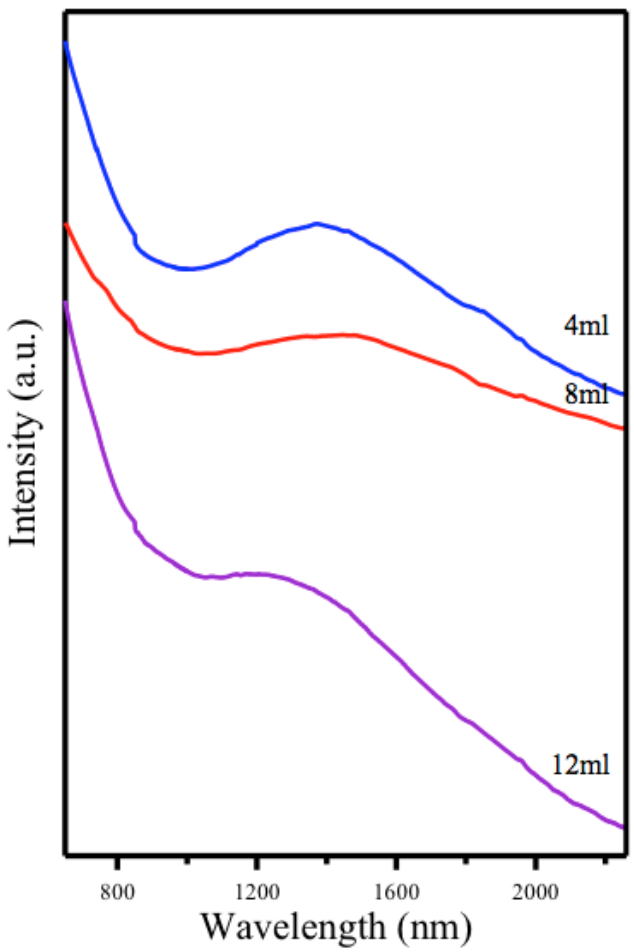

Fig. S6. Vis-NIR absorbance spectrum of Cu_2S-CIZS HNS rods prepared by adding 4, 8, and 12 mL of ZnS precursors.

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