Electronic Supplementary Information

A Facile Synthetic Approach for Copper Iron Sulfide Nanocrystals with Enhanced Thermoelectric Performance

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EXPERIMENTAL DETAILS

All chemicals are used with no further purification. Oleic acid (OA, 90.0%), n-Dodecanethiol (DT, ≥ 98.0%), Iron (III) chloride anhydrous (≥97.0%) and Sodium diethyldithiocarbamate trihydrate ($NaS_2CN(C_2H_5)_2$, ≥99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd; Copper (II) chloride ($CuCl_2$, ≥99.0%), Toluene (≥99.5%), Acetone (≥99.5%) and Methanol (≥99.5%) were purchased from Beijing Chemical Works; bulk chalcopyrite was purchased from ALFA AESAR and ground with agate ball mill for measurements. All syntheses are performed under N_2 flow using a standard Schlenk Line.

0.085 g $CuCl_2$ and 0.081 g $FeCl_3$ are added into a mixture of 12 ml OA and 18 ml DT in a 100 ml round-bottom flask. Heat the flask at 140 ºC with a magnetic stirring bar under N_2 until reactants are fully dissolved, followed by an injection of 6 ml 0.2 M $NaS_2CN(C_2H_5)_2$ in DT suspension. Quickly raise temperature to 180 ºC and react for 15 min. To terminate the reaction, quench the reaction by immersing the flask in a cold water bath. The reaction is then washed with toluene/methanol pair for 2 times and toluene/acetone pair for 1 time to remove any impurity. For thermoelectric measurements, both the $CuFeS_2$ nanoparticles and bulk chalcopyrite samples are hot-pressed at 300 ºC under the pressure of 500 MPa, and then polished with sand paper to proper shapes for each measurement.

Powder X-ray diffraction (XRD) patterns are recorded on a Rigaku Ultra IV X-ray diffractometer with graphite-filtered Cu Kα radiation, at 40 kV and 30 mA over the range of 15-85 º (2θ) at a scanning rate of 2 º/min. Scanning electron microscope (SEM) images are observed by using JSM-6700F

electron microscope. Transmission electron microscope (TEM) images and high-resolution transmission electron microscopic (HRTEM) images are observed by using FEI TECNAI G2 S-Twin with a field emission gun operating at 200 kV. UV-vis spectra are obtained from Ultra IV X-ray diffractometer (Hitachi High-Technologies Corporation). Thermal conductivity is characterized based on the Netzsch LFA427 laser technique. Electrical conductivity and Seebeck coefficient are measured by a ZEM-3 apparatus (ULVAC-RIKO, Inc.). Hall effect is measured in Van der Pauw configuration by a Hall analyzer (Lakeshore 7707) at room temperature. EDX spectra are obtained by using JEOL JSM-6300 at 5kV.

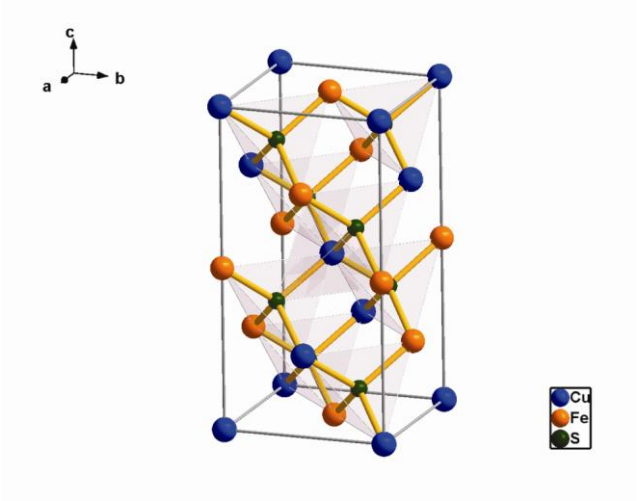

Fig. S1 Three-dimensional illustration of unit cell for chalcopyrite $CuFeS_2$.

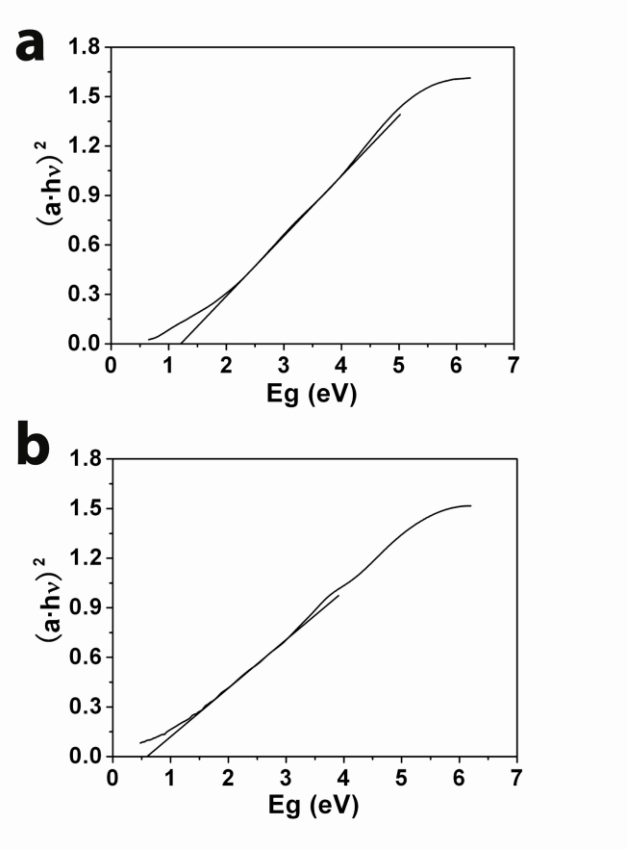

Fig. S2 Plot of $(a \cdot h\nu)^2$ versus photon energy. (a) $(a \cdot h\nu)^2$ -Eg spectrum of $CuFeS_2$ nanoparticles. Extrapolation of the linear region shows a band gap of 1.20 eV. (b) $(a \cdot h\nu)^2$ -Eg spectrum of bulk chalcopyrite powders. Extrapolation of the linear region shows a band gap of 0.59 eV.

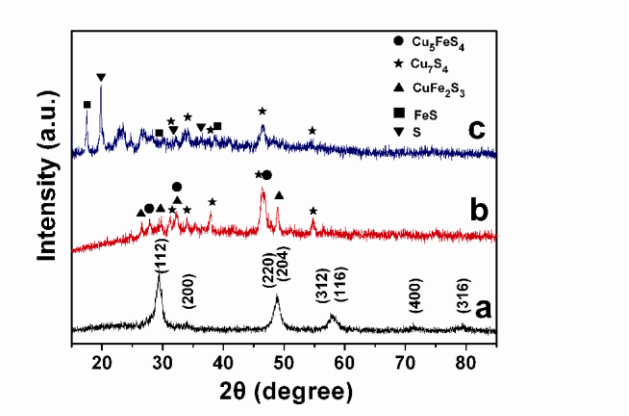

Fig. S3 XRD patterns of samples synthesized with different reactant ratios, indicating that dodecanethiol and sodium diethyldithiocarbamate are both necessary for $CuFeS_2$ nanoparticles synthesis. (a) as-synthesized $CuFeS_2$ nanoparticles. (b) sample with no dodecanethiol added during synthesis, indicating a mixture of Cu_5FeS_4, $CuFe_2S_3$ and Cu_7S_4. (c) sample with no sodium diethyldithiocarbamate added during synthesis, indicating a mixture of Cu_7S_4, FeS and S and some unclear component.

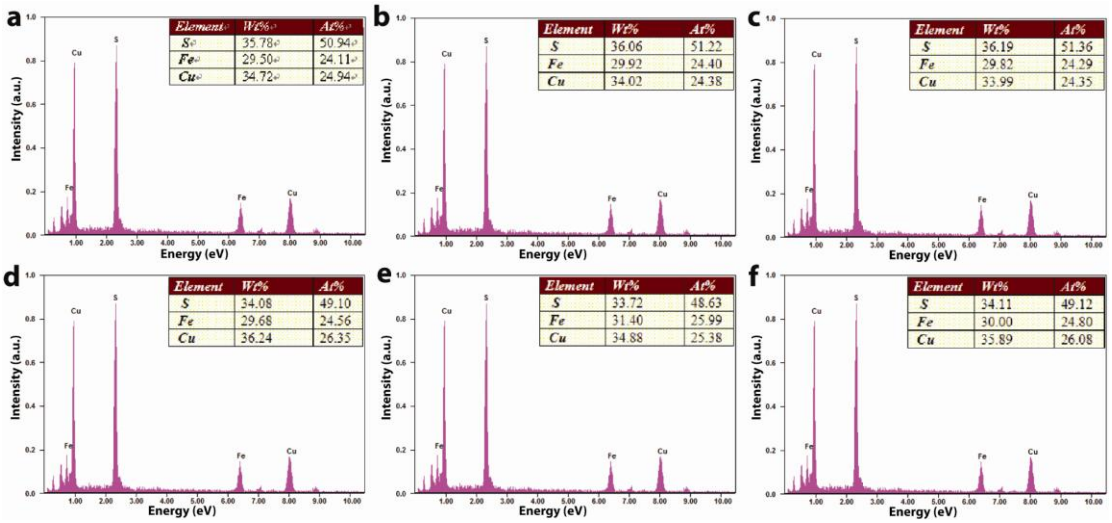

Fig. S4 EDX spectra of $CuFeS_2$ nanoparticles. (a-c) EDX spectra of the as-synthesized $CuFeS_2$ nanoparticles. (d-f) EDX spectra of $CuFeS_2$ nanoparticles after thermoelectric measurements.

Table S1. EDX analysis of $CuFeS_2$ nanoparticles before and after thermoelectric measurements. (a) EDX analysis of as-synthesized $CuFeS_2$ nanoparticles with a formula of $CuFe_{0.99}S_{2.08}$. (b) EDX analysis of $CuFeS_2$ nanoparticles after thermoelectric measurements with a formula of $CuFe_{0.97}S_{1.89}$.

Element	At% (a)	Cu : Fe : S (a)	At% (b)	Cu : Fe : S (b)
Cu	24.56	1	25.93	1
Fe	24.27	0.99	25.12	0.97
S	51.17	2.08	48.95	1.89
Total	**100**		**100**	

Table S2. Hall effect measurement of bulk chalcopyrite and $CuFeS_2$ nanoparticles, indicating a p-type conduction.

Sample	Resistivity (Ohm · cm)	type	Carrier Concentration (cm^{-3})	Hall Mobility ($cm^2 \cdot V^{-1} \cdot s^{-1}$)
Bulk $CuFeS_2$	0.06864	p	5.3931×10^{19}	1.6907
$CuFeS_2$ nanoparticles	1.215	p	1.5167×10^{18}	0.70352

Table S3. Comparison of measured transport data to literature values at 300 K.

	Electrical Conductivity ($S \cdot m^{-1}$)	Thermal Conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
As-synthesized nanoparticles	87.4	0.284
Bulk $CuFeS_2$	1302.8	5.087
S1		9
S2	700-1000 (natural samples) 25-90 (synthetic samples)	
S3	2000	
S4		7.992

References

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