Wurtzite Cu_2ZnSnS_4 Nanocrystals: A Novel Quaternary Semiconductor

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Electronic Supplementary Information

S1. Crystal structure

Crystal Data

Molecular formula	ZnS	Cu_2ZnSnS_4
Crystal system	Wurtzite	Wurtzite
Space group	$P6_3mc$	$P6_3mc$
Crystal parameter	a=b=3.8227 Å c=6.2607 Å	a=b=3.8387 Å c= 6.3388 Å

The cell structure of wurtzite Cu_2ZnSnS_4 (CZTS) was obtained by replacing Zn(II) with Cu(I), Zn(II) and Sn(IV) in wurtzite ZnS. Each sulfur ion equally coordinates with two Cu(I), one Zn(II) and one Sn(IV) nearby, which should obey the octet rule (8/4+6=8). Note that in this model metal cations randomly distribute in the fixed framework formed by sulfur anions, the XRD pattern of wurtzite CZTS would not change much from wurtzite ZnS. Moreover, the radius of Zn(II) (74 pm) and Sn(IV) (71 pm) are nearly the same, but Cu(I) (96 pm) is larger than the other two. Therefore, the parameter of the cell parameter would expand a little, resulting in the left shit of the diffraction peaks. Since we have not found any standard card of wurtzite CZTS in JCPDS database, we simulated XRD pattern for the wurtzite CZTS based on our proposed crystal structure (Fig. 1 insert). It could be found that difference between the simulated crystal lattice constants and experimental lattice constants is very minute (Table S1).

Table S1 Table comparing the calculated d-spacings with the experimental d-spacings.

h	k	l	Experimental 2θ / °	Experimental d-spacing / Å	Calculated d-spacing / Å
1	0	0	26.70	3.339	3.324
0	0	2	28.10	3.175	3.169
1	0	1	30.26	2.954	2.944
1	0	2	39.19	2.299	2.294
1	1	0	47.32	1.921	1.919
1	0	3	51.23	1.783	1.783

S2. Band-gap energy calculation

It is known that band gap energy (E_g) could be obtained by the following equation:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where A is a constant, α the absorption coefficient, and n equals to 1/2 for direct transition. The band gap value could be determined by the intercept of the fitted straight line of the linear part of the $(\alpha h\nu)^2$ versus (hν) plot.

We use Kubelka-Munk function (F(R∞)) to substitute α in estimating band gap energy. F(R∞) can be illustrated as absorption coefficient (α) divided by scattering coefficient (S):

$$F(R\infty) = \frac{\alpha}{S}$$

Then the correlation of $(\alpha h\nu)^2$ and (hν) could be transformed into $(F(R\infty)h\nu)^2$ vs. hν. Normally, the collected UV-vis spectra could be converted into F(R∞) as following:

$$F(R\infty) = \frac{(1 - R\infty)^2}{2R\infty}$$

In our calculation, the absorbance was used to instead R∞. In the final plot, Y-axis was set as the value of $[\frac{(1 - Abs)^2}{2Abs} h\nu]^2$ and X-axis was set as the value of $h\nu$. By fitting a straight line to the linear part of the plot, we estimated the band-gap energy of CZTS to be 1.4 eV from the crossing point of fitted line and X-axis.

S3. Composition Analysis

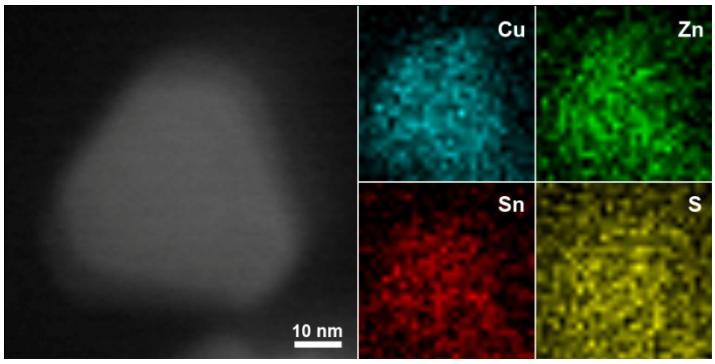
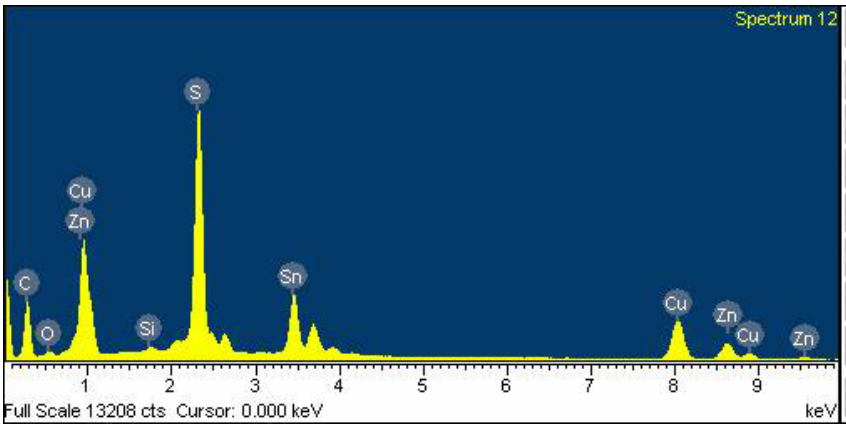


Fig. S1 HAADF STEM image of CZTS nanoplates prepared in DDT and OA, and corresponding EDS elemental mapping images.



Element	Weight%	Atomic%
C K	40.82	74.41
O K	2.03	2.78
Si K	0.30	0.24
S K	16.10	10.99
Cu K	17.20	5.93
Zn K	8.77	2.94
Sn L	14.78	2.73
Totals	100.00	

Fig. S2 Spectrum of the Energy Dispersive X-ray Spectroscopy of CZTS nanocrystals and its quantitative analysis.

The sample using in investigating the quantitative composition of wurtzite CZTS was prepared by dropping the concentrated dispersion of CZTS nanocrystals onto the silicon substrate. From the data in Fig. S2, we could find the Cu/Zn/Sn/S composition of the nanocrystals is 5.93:2.94:2.73:10.99, which is close to 2:1:1:4.

S4. Measurement of the Conductivity

To test the conductivity of wurtzite CZTS, we at first compressed the dried CZTS powder into tablets under the pressure of 10 Mpa. The resistivity data of the CZTS tablets were calculated from the I-V curve taken by linear sweep voltammetry on CH Instrument 660D electrochemical analyzer. From Table S2, we could observe that the conductivity of wurtzite CZTS nanoprisms was much better than CZTS nanoplates.

Table S2 The resistivity of CZTS tablets

sample	synthesis condition	diameter of tablet/cm	thickness of tablet/cm	resistivity/Ω·m
CZTS1	3mL DDT + 2mL OAm	0.62	0.29	0.838
CZTS2	1mL DDT + 4mL OA	0.62	0.14	5.740

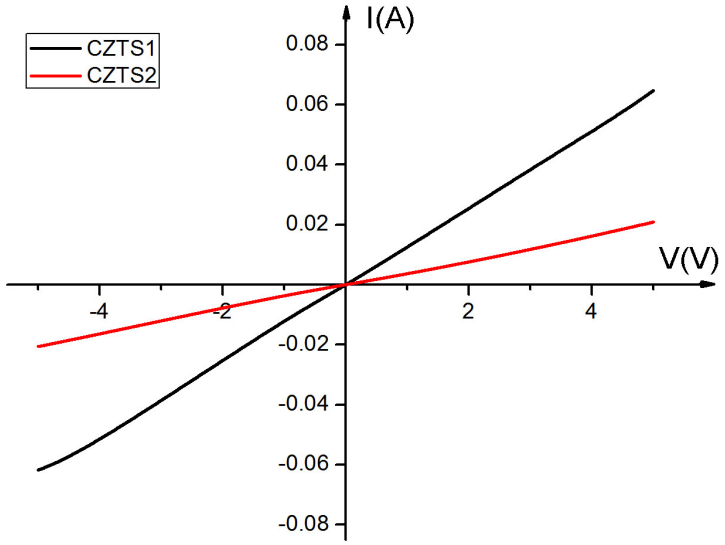


Fig. S3 The current-potential curves of CZTS tablets.

S5. Film Fabrication of CZTS nanocrystals

Films of CZTS nanocrystals was fabricated by dropping 100 μL of tetrachloroethylene dispersion with nanocrystal concentration of ~6.5 mg/mL onto 10 × 20 mm Mo-coated soda-lime glass substrates. The film was then dried overnight in the open air. To improve the conductivity of CZTS films, a post annealing treatment was conducted. The CZTS coated substrates were kept in the furnace at 350 °C for 60 min under Ar flow. The heating rate of the furnace was kept <2 °C/min to reduce generation of cracks.

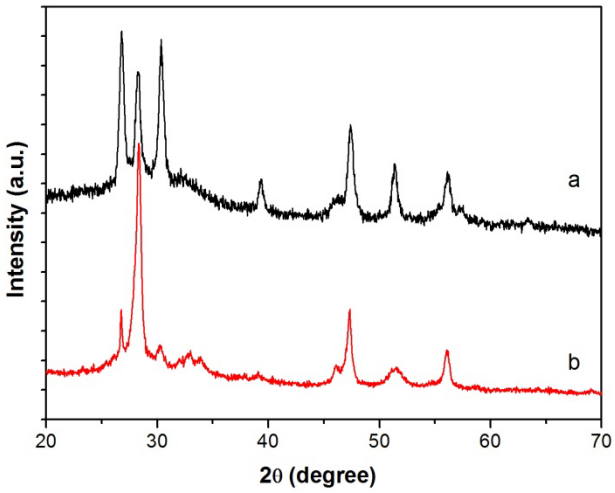


Fig. S4 XRD patterns of CZTS nanoparticles after annealing (a) nanoprisms prepared in DDT and OAm, (b) nanodiscks prepared in DDT and OA.

Comparing XRD patterns of the CZTS films before (Fig. 1) and after annealing (Fig. S4), we can hardly notice any tremendous change in the shape of diffraction peaks, indicating that anneal process did not produce by-products other than wurtzite CZTS or change the crystalline form. Therefore, the enhancement of electrical conductivity of CZTS nanocrystals may stem from two sources: improvement of the crystallinity and elimination of non-conducting surfactants.