Supplementary Materials for

Plasmon-induced ultrafast charge transfer in single-particulate copper sulfide-zinc sulfide nanoheterostructures

Xueyi Guo,[ac] Sheng Liu,[ac] Weijia Wang,[*bc] Chongyao Li,[ac] Ying Yang,[ac] Qinghua Tian,[ac] and Yong Liu [bc]

[a.] *School of Metallurgy and Environment, Central South University, Changsha 410083, China*

[b.] *State Key Laboratory for Powder Metallurgy, Powder Metallurgy Research Institute, Central South University, Changsha 410083, China*

[c.] *Research Institute of Resource Recycling, Central South University, Changsha 410083, China*

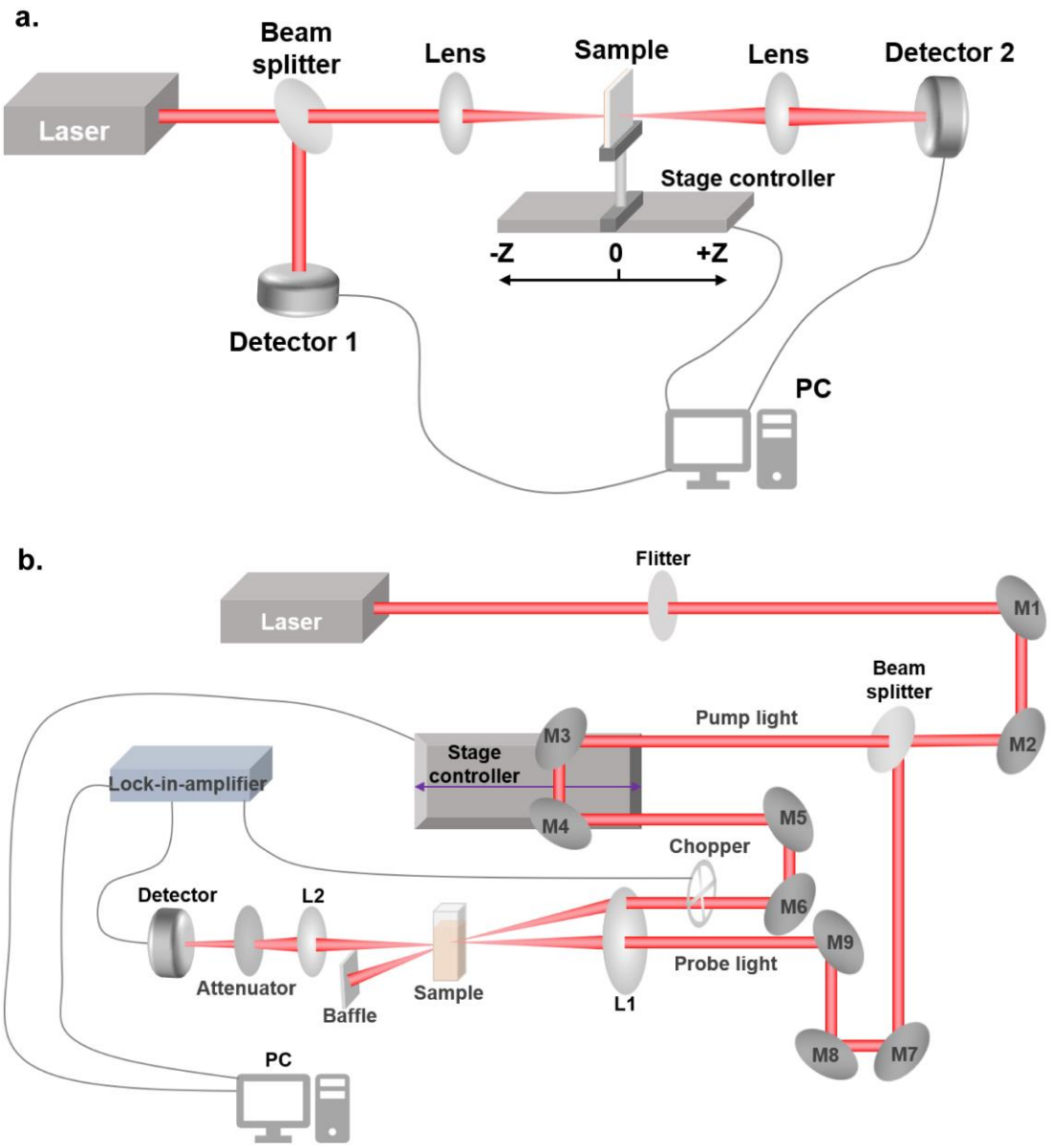
[*] Corresponding author at:

State Key Laboratory for Powder Metallurgy, Powder Metallurgy Research Institute, Central South University, Changsha 410083, China. E-mail address: wangweijia@csu.edu.cn (Weijia Wang).

This PDF file includes:

- **Scheme S1**
- **Fig. S1 to S8**
- **Table S1 to S3**
- **References**

- **Supplementary Materials: Scheme S1.**



Scheme S1. (a) Z-scan experimental setup. (b)Pump-Probe experimental setup: M1-M9: Mirrors; L1-L2: Lens.

- **Supplementary Materials: Fig. S1.**

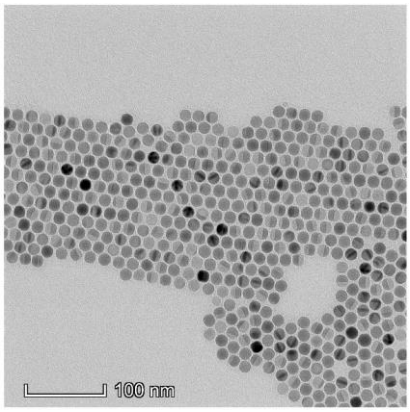


Fig. S1 Low magnification TEM images of $Cu_{1.94}S$-ZnS NHs.

- **Supplementary Materials: Fig. S2.**

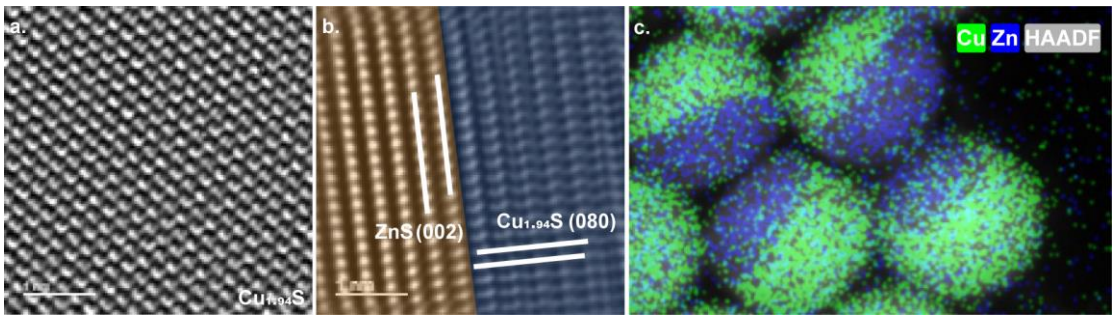


Fig. S2 Local enlarged HRTEM images of $Cu_{1.94}S$ NCs (a) and $Cu_{1.94}S$-ZnS NHs (b) after a fast Fourier transform (FFT) process using DigtalMicrograph software. (c) Merged image of EDS element maps and HAADF-STEM.

- **Supplementary Materials: Fig. S3**

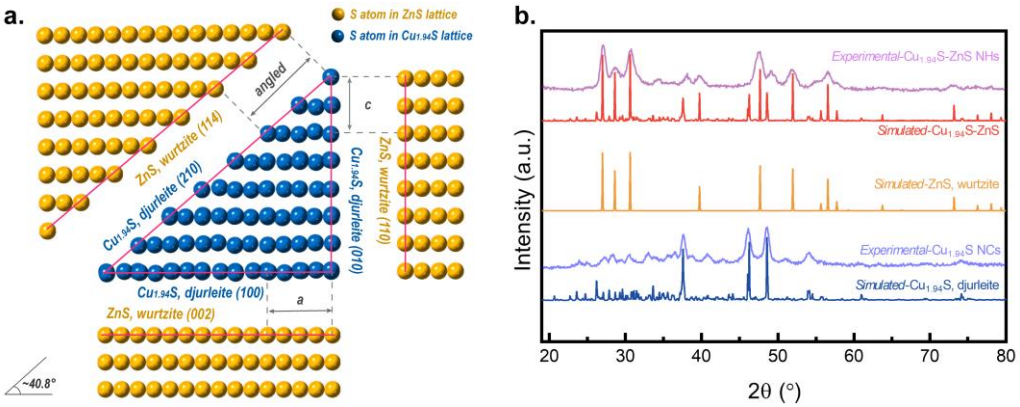


Fig. S3 (a) Idealized projections of the crystal planes of sulfur sublattice in wurtzite ZnS and djurleite $Cu_{1.94}S$. (b) Simulated XRD patterns of djurleite $Cu_{1.94}S$, wurtzite ZnS, and merged $Cu_{1.94}S$ (45%)-ZnS (55%). The crystallographic information files (CIFs) of standard djurleite $Cu_{1.94}S$ and wurtzite ZnS were acquired from the American

Mineralogist Crystal Structure Database. **Djurleite $Cu_{1.94}S$:** Monoclinic, **a**=26.8970 Å, **b**=15.7450 Å, **c**=13.5650 Å, **β**=90.13°, $P2_{1/n}$.[1] **Wurtzite ZnS:** Hexagonal, **a**=3.8110 Å, **c**=6.2340 Å, $P6_{3mc}$.[2] The fractions of $Cu_{1.94}S$ and ZnS in the merged simulated XRD pattern were referenced from the XPS results of the real sample with appreciated adjustment. The crystallographic projections were generated using CrystalMaker ® software, and the simulated and merged XRD patterns were generated using CrystalDiffract ® software.

- **Supplementary Materials: Fig. S4.**

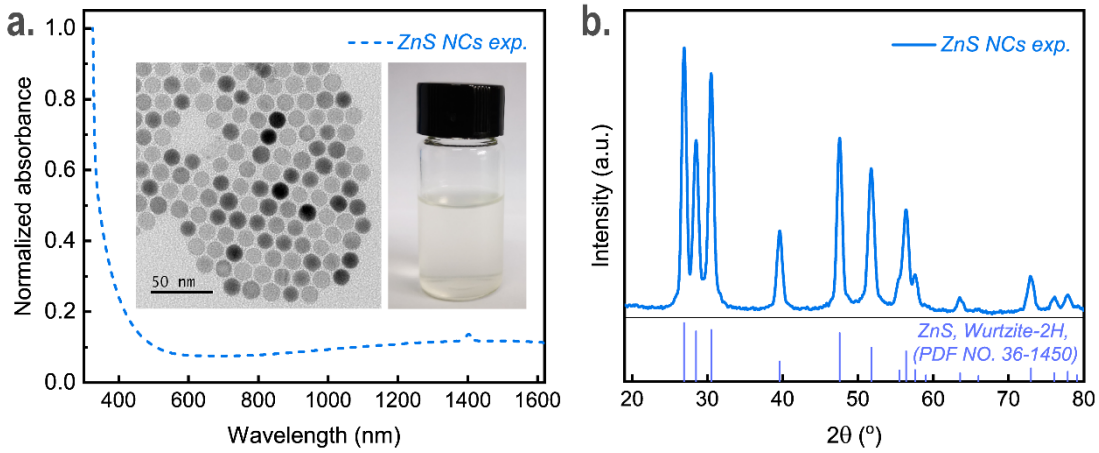


Fig. S4 Key characterization of ZnS NCs. (a) UV-vis-NIR absorption spectra and (b) XRD result. Inset: TEM image and digital photograph of ZnS NCs dispersed in NMP.

- **Supplementary Materials: Fig. S5.**

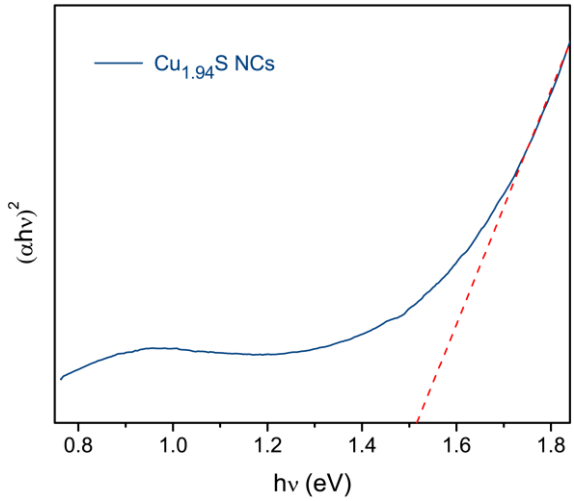


Fig. S5 $(\alpha h\upsilon)^2$-hυ curve of the $Cu_{1.94}S$ NCs

- **Supplementary Materials: Fig. S6.**

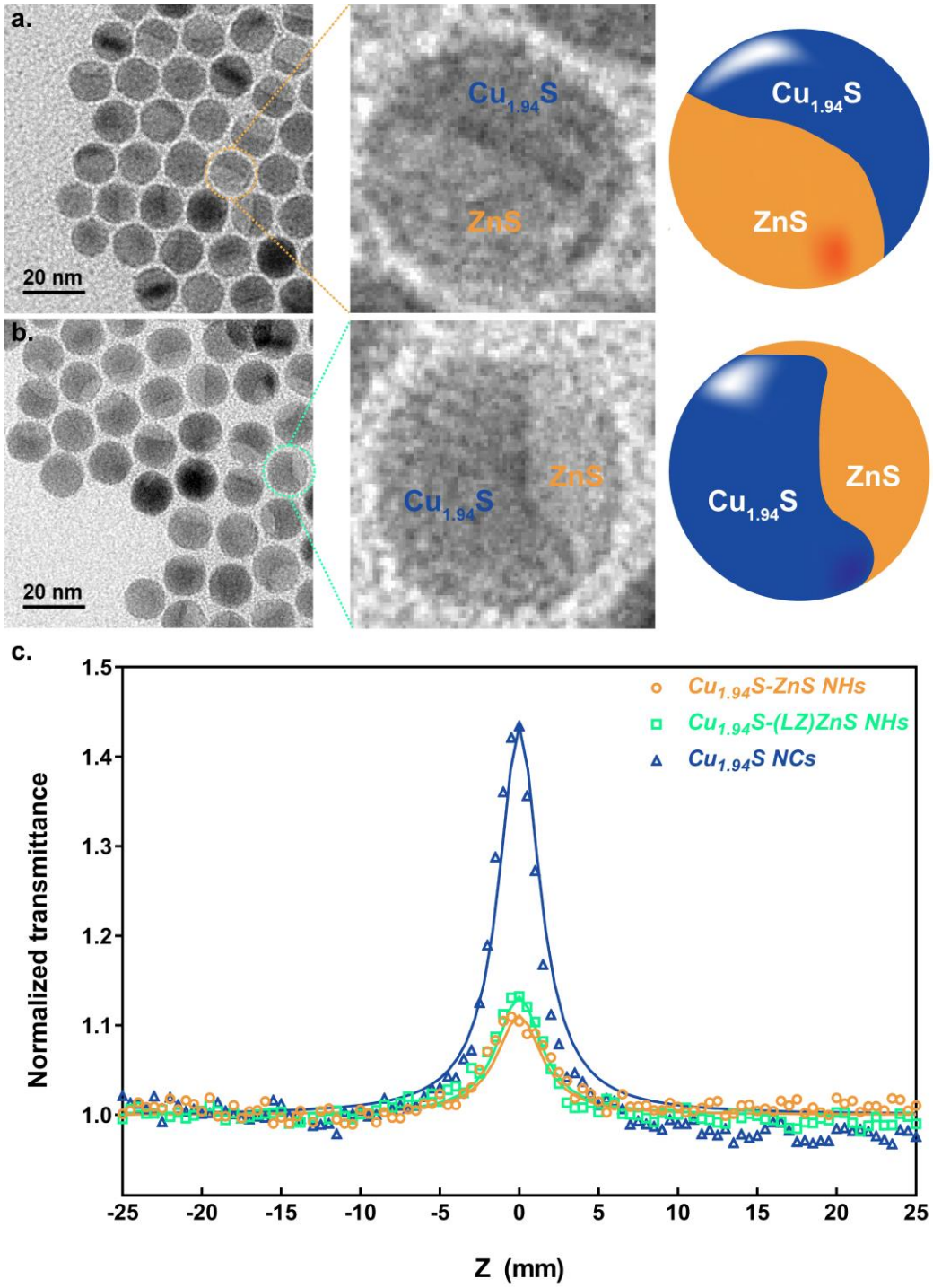


Fig. S6 TEM images of $Cu_{1.94}S$-ZnS NHs (a) and $Cu_{1.94}S$-(LZ)ZnS NHs (b). (c) Open-aperture Z-scan results of different samples at 1500 nm with identical input intensity.

- **Supplementary Materials: Fig. S7.**

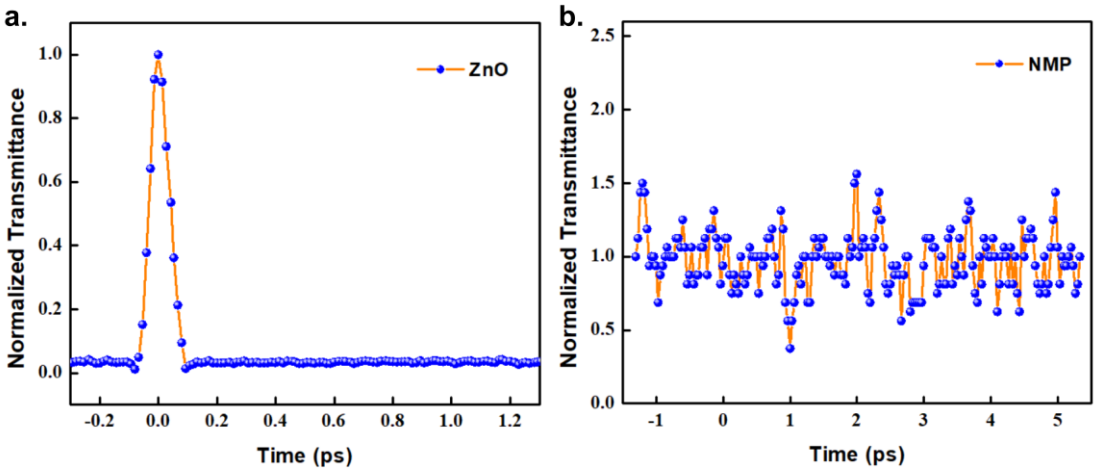


Fig. S7 Pump-probe results for the standard sample (a) and solvent (b).

- **Supplementary Materials: Fig. S8.**

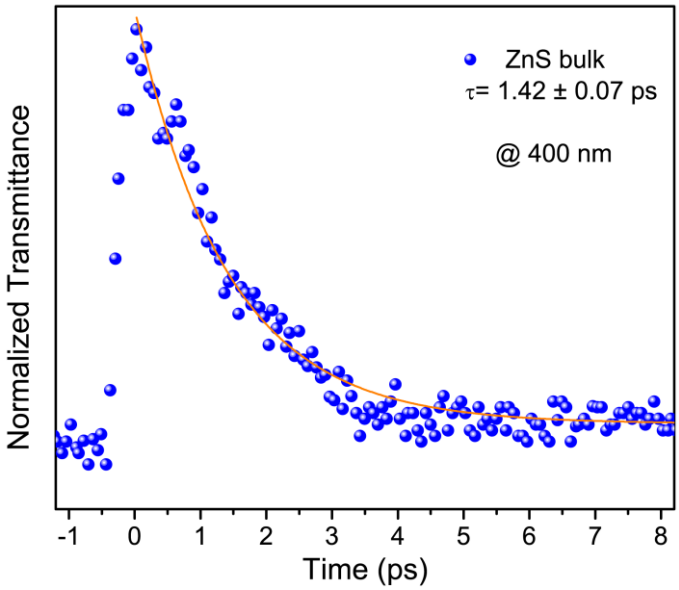


Fig. S8 Pump-probe signals of bulk ZnS.

- **Supplementary Materials: Table S1.**

Table S1. Lattice parameters of djurleite $Cu_{1.94}S$, roxbyite $Cu_{1.8}S$, and digenite $Cu_{1.8}S$

Lattice parameters	**$Cu_{1.94}S$, *djurleite*** [1]	**$Cu_{1.8}S$, *roxbyite*** [3]	**$Cu_{1.8}S$, *digenite*** [4]
a (Å)	26.8970	13.4090	5.5820
b (Å)	15.7450	13.4051	5.5820
c (Å)	13.5650	15.4852	5.5820
α (°)	90.000	90.022	90.000
β (°)	90.130	90.021	90.000
γ (°)	90.000	90.020	90.000
Spacegroup	$P\,2_{1/n}$	$P\,\bar{1}$	$F\,m\,\bar{3}m$

- **Supplementary Materials: Table S2.**

Table S2. The lattice parameters and mismatches in sulfur spacing for the djurleite $Cu_{1.94}S$-wurtzite ZnS system in possible interfacial directions

Lattice parameters	**$Cu_{1.94}S$, *djurleite***	**ZnS, *wurtzite***	**Lattice mismatch, %**
a (Å)	3.877	3.811	***~1.70***
c (Å)	6.716	6.234	***~7.17***
Angled (Å)	10.193	*9.847*	***~3.39***
c/a ratio	1.732	~1.636	/

- **Supplementary Materials: Table S3.**

Table S3. Peak identifications of XPS from survey spectra*

Samples	BE (eV)	Elements	Attributions	Spectral Lines
$Cu_{1.94}S$ NCs	75.19	Cu	$Cu_{1.94}S$	***3p***
$Cu_{1.94}S$ NCs	122.19	Cu	$Cu_{1.94}S$	***3s***
$Cu_{1.94}S$ NCs	162.19	S	$Cu_{1.94}S$	***2p***
$Cu_{1.94}S$ NCs	225.19	S	$Cu_{1.94}S$	***2s***
$Cu_{1.94}S$ NCs	285.19	C	Organics	***1s***
$Cu_{1.94}S$ NCs	549.19	Cu	$Cu_{1.94}S$	***Auger***
$Cu_{1.94}S$ NCs	569.19	Cu	$Cu_{1.94}S$	***Auger***
$Cu_{1.94}S$ NCs	648.19	Cu	$Cu_{1.94}S$	***Auger***
$Cu_{1.94}S$ NCs	932.19	Cu	$Cu_{1.94}S$	$2p_{3/2}$
$Cu_{1.94}S$ NCs	951.19	Cu	$Cu_{1.94}S$	$2p_{1/2}$
$Cu_{1.94}S$-ZnS NHs	10.19	Zn	ZnS	***3d***
$Cu_{1.94}S$-ZnS NHs	75.19	Cu	$Cu_{1.94}S$	***3p***
$Cu_{1.94}S$-ZnS NHs	89.19	Zn	ZnS	***3p***
$Cu_{1.94}S$-ZnS NHs	122.19	Cu	$Cu_{1.94}S$	***3s***
$Cu_{1.94}S$-ZnS NHs	139.19	Zn	ZnS	***3s***
$Cu_{1.94}S$-ZnS NHs	162.19	S	$Cu_{1.94}S$/ZnS	***2p***
$Cu_{1.94}S$-ZnS NHs	226.19	S	$Cu_{1.94}S$/ZnS	***2s***
$Cu_{1.94}S$-ZnS NHs	285.19	C	Organics	***1s***
$Cu_{1.94}S$-ZnS NHs	472.19	Zn	ZnS	***Auger***
$Cu_{1.94}S$-ZnS NHs	495.19	Zn	ZnS	***Auger***
$Cu_{1.94}S$-ZnS NHs	531.19	O	Environment	***1s***
$Cu_{1.94}S$-ZnS NHs	570.19	Cu	$Cu_{1.94}S$	***Auger***
$Cu_{1.94}S$-ZnS NHs	932.19	Cu	$Cu_{1.94}S$	$2p_{3/2}$
$Cu_{1.94}S$-ZnS NHs	951.19	Cu	$Cu_{1.94}S$	$2p_{1/2}$
$Cu_{1.94}S$-ZnS NHs	1021.19	Zn	ZnS	$2p_{3/2}$
$Cu_{1.94}S$-ZnS NHs	1044.19	Zn	ZnS	$2p_{1/2}$

* The BE peaks in survey spectra are directly read from the original data and may be slightly different from the corresponding BE peaks in high-resolution spectra. This is caused by the scanning accuracy induced deviation. The scanning increment for survey spectra was 1.0 eV/point, and the increment for high-resolution spectra was 0.05 eV/point.

References

(1) Evans, H. T. The crystal structures of low chalcocite and djurleite. *Zeitschrift fur Kristallographie* **1979,** *150,* 299-320.

(2) Wyckoff, R. W. G. Wurtzite structure. *Crystal Structures*, Second edition **1963**, *1,* 85-237.

(3) Mumme, W. G.,; Gable, R. W.; Petricek, V. The crystal structure of roxbyite, $Cu_{58}S_{32}$. *The Canadian Mineralogist* **2012**, *50*, 423-430.

(4) Yamamoto, K.; Kashida, S. X-ray study of the average structures of Cu_2Se and $Cu_{1.8}S$ in the room temperature and the high temperature phases. Journal of Solid State Chemistry **1991**, *93*, 202-211.