Electronic supplementary information

A General Strategy for Synthesis of Quaternary Semiconductor Cu_2MSnS_4 ($M=Co^{2+}$, Fe^{2+}, Ni^{2+}, Mn^{2+}) Nanocrystals

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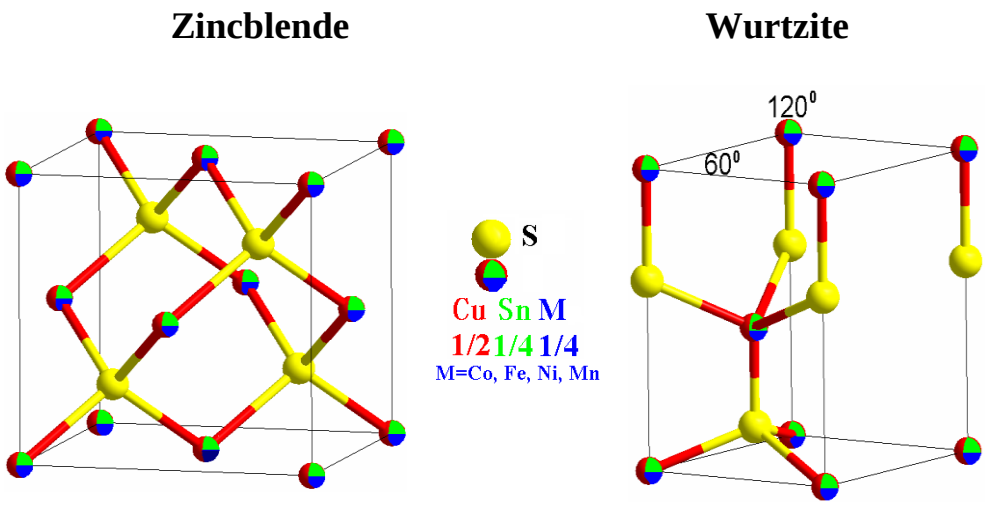

Figure S1. Unit cells of zincblende (left) and wurtzite (right) Cu_2MSnS_4 (M=Co, Fe, Ni, Mn).

Table S1. Comparison of experimental and simulated XRD peaks for zincblende Cu_2CoSnS_4.

hkl	Observed 2θ	Simulated 2θ	Δ2θ
111	28.656	28.676	-0.020
220	47.741	47.706	+0.035
311	56.555	56.613	-0.058

Crystal data

Formula Cu_2CoSnS_4

Crystal system Zincblende

Space group *F*-43 m (No. 216)

Unit cell dimensions $a = b = c = 5.3877$ Å

Atomic coordinates

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**
S	4c	1/4	1/4	1/4
Sn	4a	0	0	0
Co	4a	0	0	0
Cu	4a	0	0	0

Note that Cu^+, Co^{2+}, and Sn^{4+} ions occupy the same position, and the occupancy possibilities of Cu^+, Co^{2+}, and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

Table S2. Comparison of experimental and simulated XRD peaks for zincblende Cu_2FeSnS_4.

hkl	Observed 2θ	Simulated 2θ	Δ2θ
111	28.693	28.706	-0.013
220	47.769	47.759	+0.010
311	56.652	56.678	-0.026

Crystal data

Formula Cu_2FeSnS_4

Crystal system Zincblende

Space group *F*-43 m (No. 216)

Unit cell dimensions $a = b = c = 5.3821$ Å

Atomic coordinates

Atom	**Wyck.**	**x/a**	**y/b**	**z/c**
S	4c	1/4	1/4	1/4
Sn	4a	0	0	0
Fe	4a	0	0	0
Cu	4a	0	0	0

Note that Cu^+, Fe^{2+}, and Sn^{4+} ions occupy the same position, and the occupancy possibilities of Cu^+, Fe^{2+}, and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

Table S3. Comparison of experimental and simulated XRD peaks for wurtzite Cu_2NiSnS_4.

hkl	Observed 2θ	Simulated 2θ	Δ2θ
100	26.690	26.694	-0.004
002	28.123	28.071	+0.052
101	30.198	30.231	-0.033
102	39.143	39.124	+0.019
110	47.164	47.137	+0.027
103	51.050	51.043	+0.007
112	55.786	55.763	+0.023

Crystal data

Formula Cu_2NiSnS_4

Crystal system Wurtzite

Space group $P6_3mc$ (No. 186)

Unit cell dimensions $a = b = 3.8530$ Å, $c = 6.3523$ Å

Atomic coordinates

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

Note that Cu^+, Ni^{2+}, and Sn^{4+} ions occupy the same position, and the occupancy possibilities of Cu^+, Ni^{2+}, and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

Table S4. Comparison of experimental and simulated XRD peaks for wurtzite Cu_2MnSnS_4.

hkl	Observed 2θ	Simulated 2θ	Δ2θ
100	26.941	26.945	-0.004
002	28.211	28.235	-0.024
101	30.488	30.492	-0.004
102	39.433	39.425	+0.008
110	47.622	47.598	+0.024
103	51.431	51.411	+0.020
112	56.264	55.266	-0.002

Crystal data

Formula Cu_2MnSnS_4

Crystal system Wurtzite

Space group $P6_3mc$ (No. 186)

Unit cell dimensions $a = b = 3.8178$ Å, $c = 6.3163$ Å

Atomic coordinates

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

Note that Cu^+, Mn^{2+}, and Sn^{4+} ions occupy the same position, and the occupancy possibilities of Cu^+, Mn^{2+}, and Sn^{4+} are 1/2, 1/4 and 1/4, respectively.

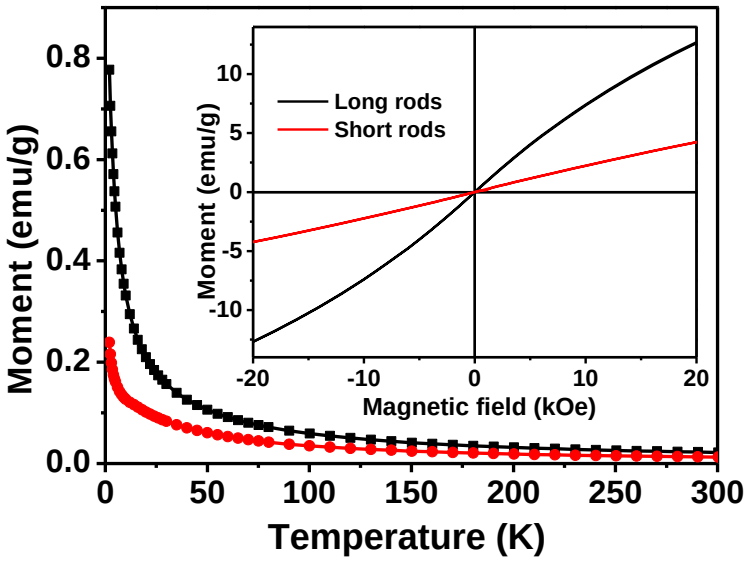

Figure S2. Temperature dependence of the magnetization for wurtzite Cu_2MnSnS_4 nanocrystals with different aspect ratios, measured in a magnetic field of 1000 Oe; Inset: The field dependence of the magnetization for the same samples at 2 K.

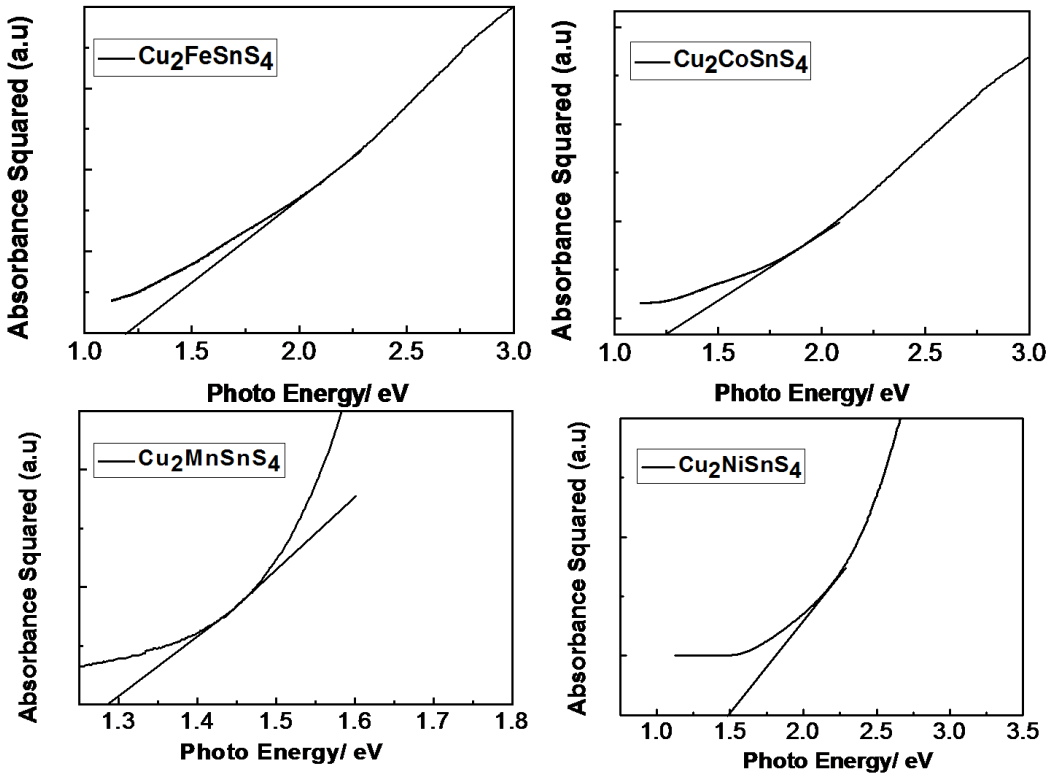

Figure S3. Plots of (abs^2) *vs hv* for the Cu_2MSnS_4 (M=Co, Fe, Ni, Mn) nanocrystals with the band gap

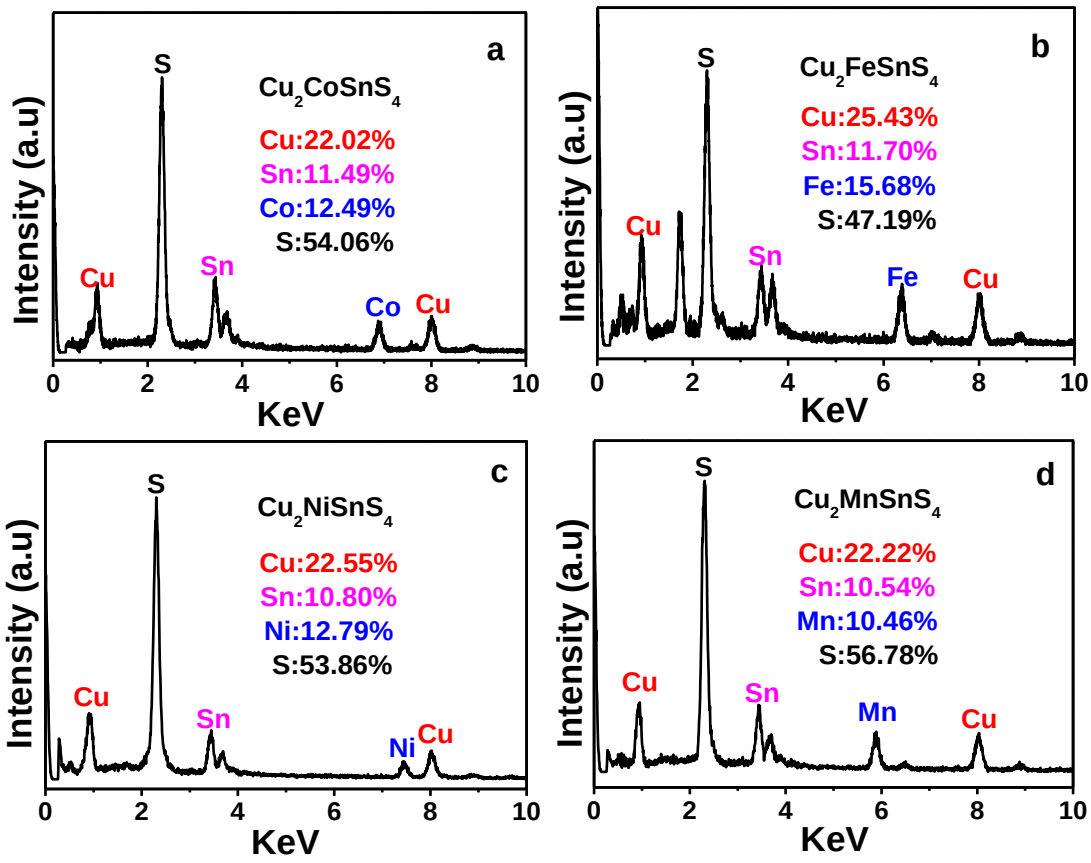

Figure S4. EDS spectra and chemical compositions (atomic percent) of zincblende and wurtzite Cu_2MSnS_4 (M=Co, Fe, Ni, Mn) nanocrystals.

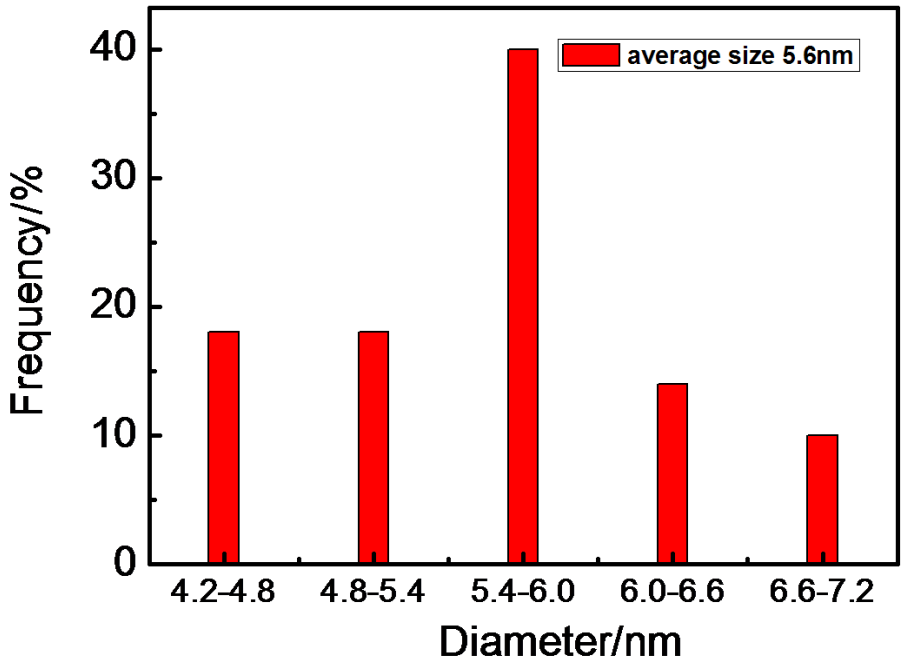

Figure S5. Size distribution of Cu_2FeSnS_4 nanocrystals

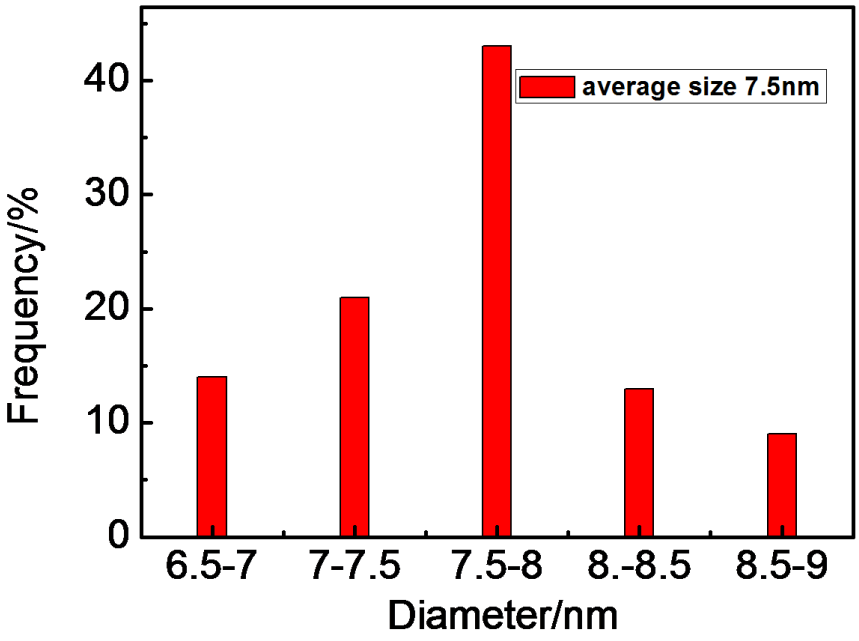

Figure S6. Size distribution of Cu_2CoSnS_4 nanocrystals

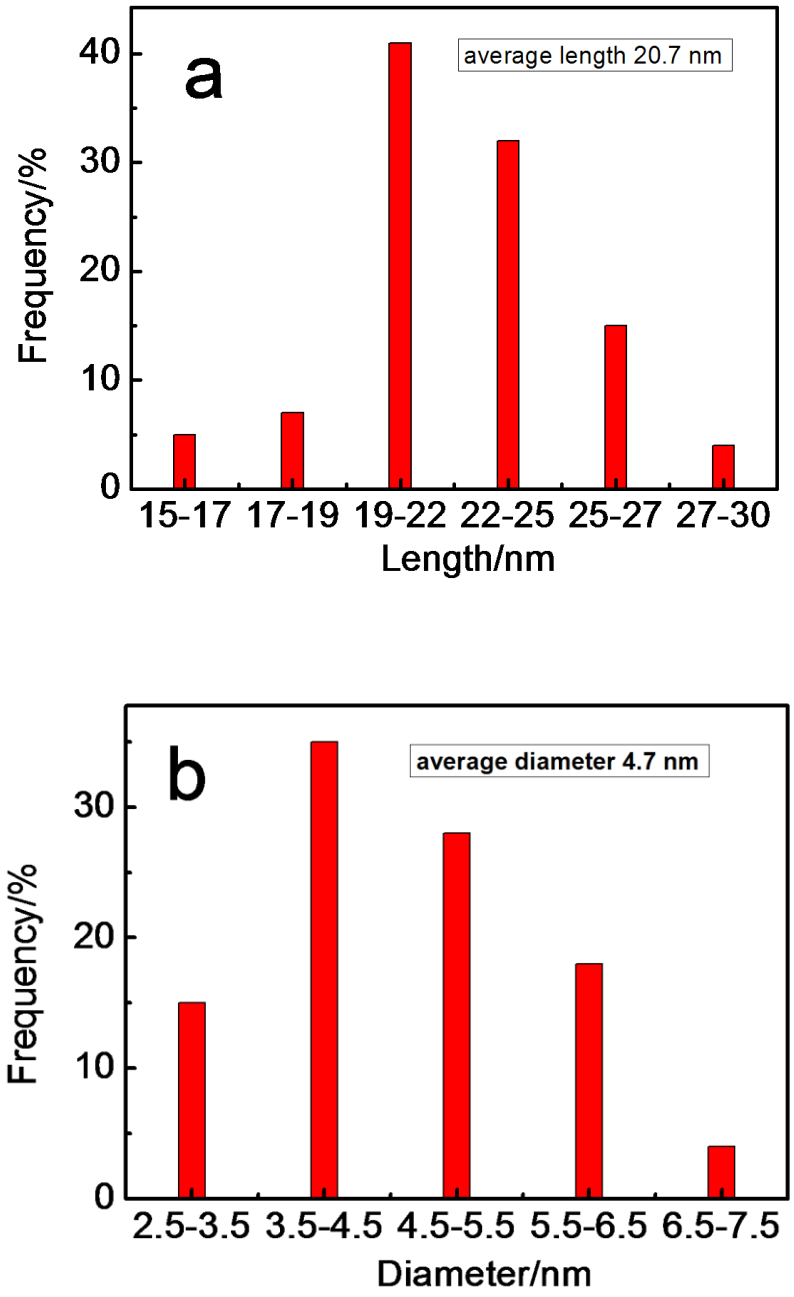

Figure S7. Size distribution of Cu_2MnSnS_4 nanorods with an aspect ratio of 4.4 (a: length distribution; b: diameter distribution).

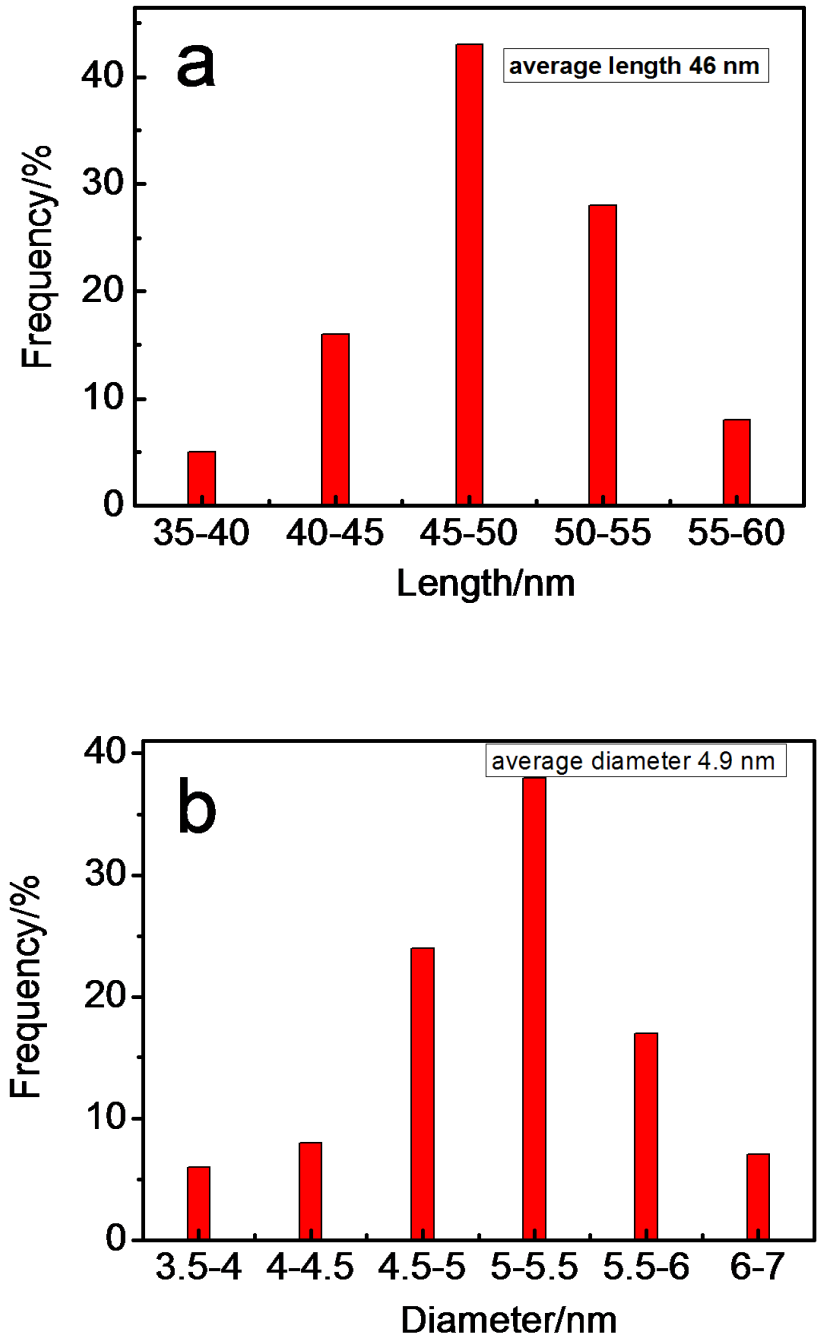

Figure S8. Size distribution of Cu_2MnSnS_4 nanorods with an aspect ratio of 9.4 (a: length distribution; b: diameter distribution).