Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

A General and Rapid Room-Temperature Synthesis Approach for Metal Sulphide Nanocrystals with Tunable Properties

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Section I. Reaction Kinetics

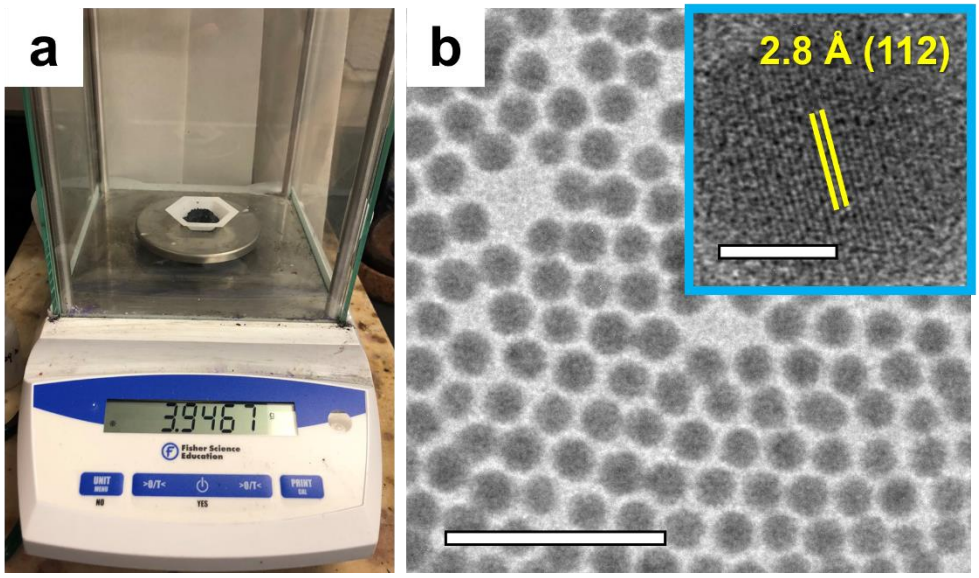

Figure S1. (a) Photograph of Ag_2S NP powders produced by large-scale synthesis in a single batch. Based on ICP-OES results, the yield of the product Ag_2S is 95.1% relative to the amount of Ag precursor provided. (b) TEM image of Ag_2S NPs from scaled up synthesis. The inset shows an HRTEM image of a single Ag_2S NP. The scale bars in the main panel and inset are 50 nm and 5 nm, respectively.

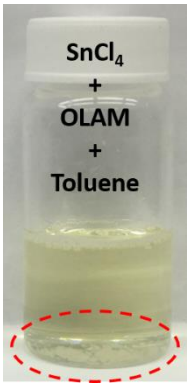

Figure S2. Photograph of the mixture after sonicating Sn^{4+} precursor with oleylamine.

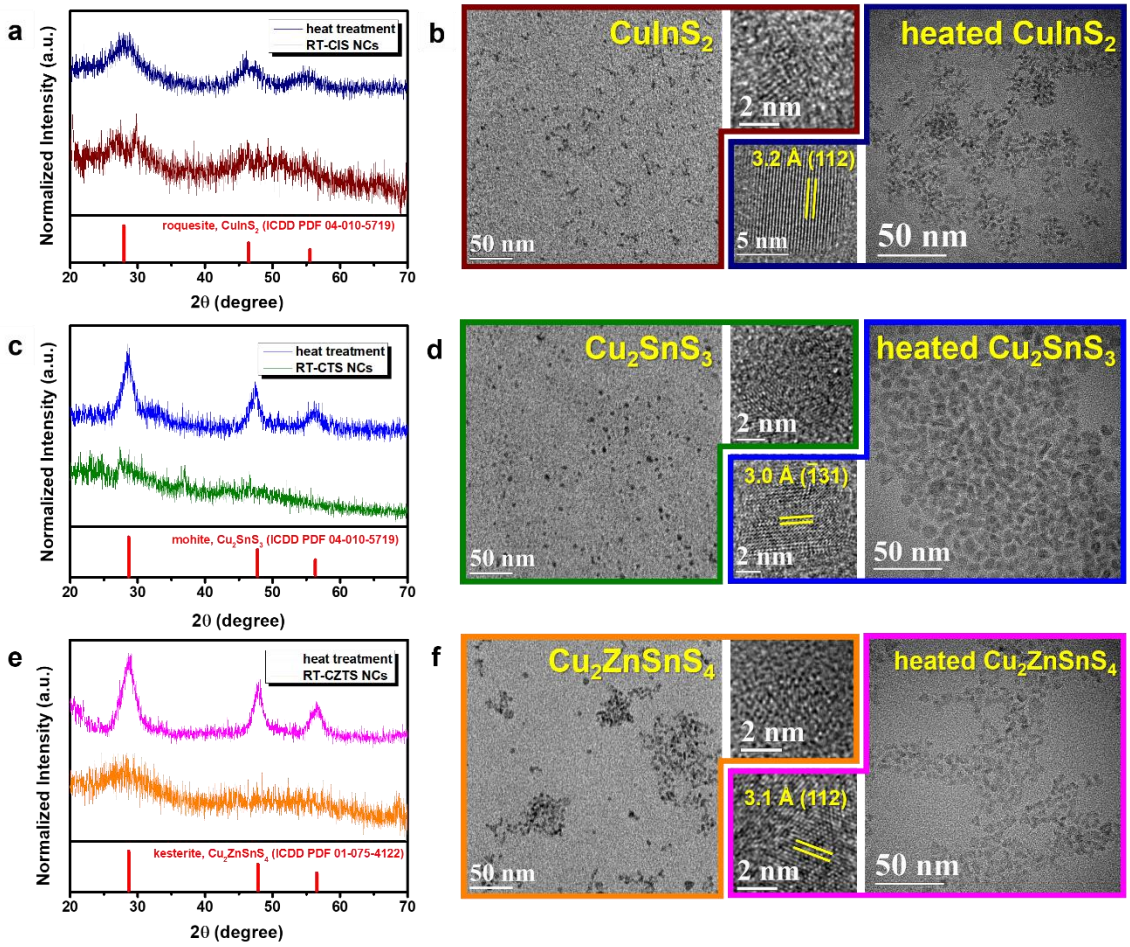

Figure S3. (a) XRD pattern, (b) TEM and HRTEM images of $CuInS_2$ NCs before and after heat treatment. (c) XRD pattern, (d) TEM and HRTEM images of Cu_2SnS3 NCs before and after heat treatment. (e) XRD pattern, (f) TEM and HRTEM images of Cu_2ZnSnS_4 NCs before and after heat treatment. The results indicate the overall size of ternary and quaternary metal sulfide NCs was increased, and the crystallinity of these NCs was greatly improved, upon post-synthetic heat treatment.

Section II. Morphology of Metal Sulphide NCs.

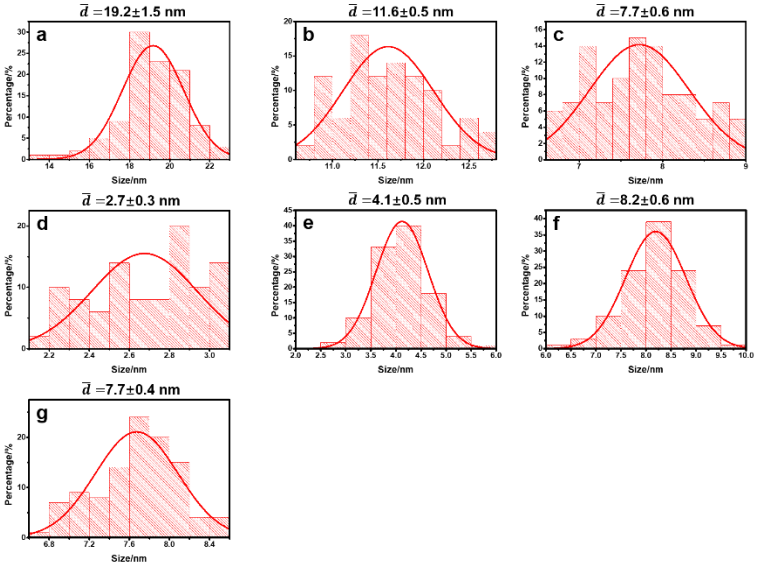

Figure S4. Size distribution for (a) CuS NPls, (b) CdS NCs. Size distribution for PbS NPls, (a) side length and (b) thickness. PbS NCs (f) before and (g) after AS-treatment. Diameters of hexagons are reported as mean ± one standard deviation, according their excircles.

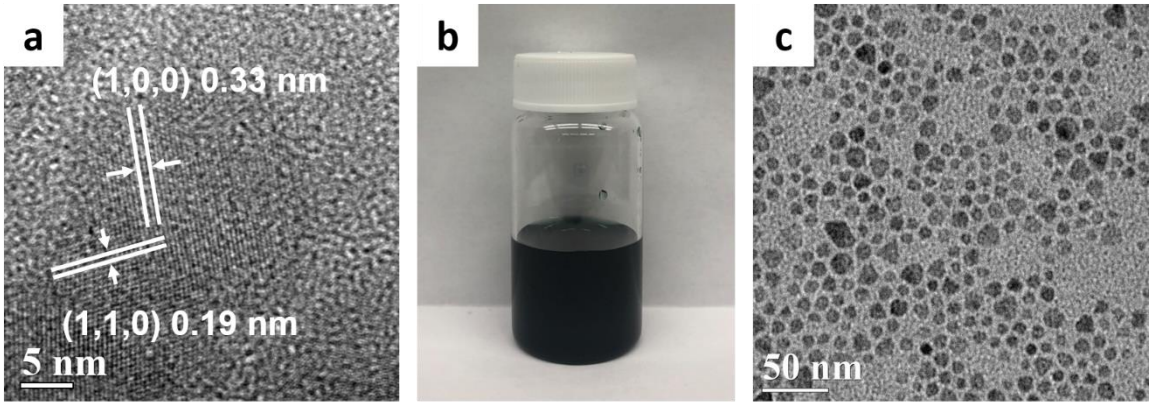

Figure S5. (a) HRTEM image of top view CuS NPls. (b) Photograph of Cu-OAm precursor produced using CuCl. The dark green color of the solution indicates formation of Cu(II) species. (c) TEM image of CuS NPls synthesized using CuCl.

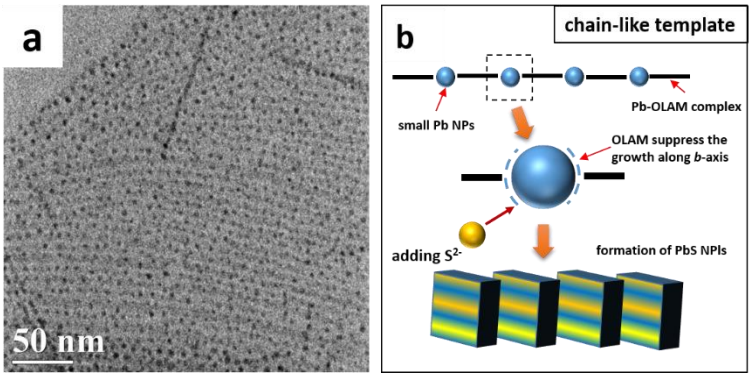

Figure S6. (a) TEM image of Pb-OLAM complex. (b) A schematic illustration of template-assistant growth of PbS NPls.

Section III. Crystal Phase and Optical Properties of MS NCs.

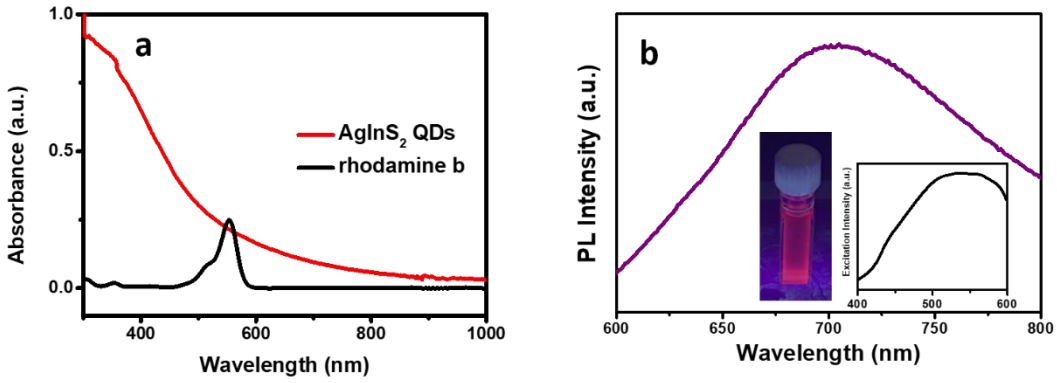

Figure S7. (a) The UV-vis absorbance spectrum of Rhodamine B (black curve) and $AgInS_2$ QDs (red curve). (b) Photoluminescence emission spectrum of $AgInS_2$ QDs excited at 491 nm, insets show a hexane dispersion of the sample under UV illumination, and the PL excitation spectrum of the $AgInS_2$ QDs for an emission wavelength of 700 nm. We measured the PL and absorbance spectrum using the same samples.

The QY was calculated in the usual manner.[1]

The relative quantum yield QY can be calculated as:

$$\mathrm{QY} = \Phi_{ref}\left(\frac{A_{ref}}{A}\right)\left(\frac{I}{I_{ref}}\right)\left(\frac{\eta}{\eta_{ref}}\right)^2$$

Φ_{ref} is the absolute fluorescence quantum yield of the reference sample, A is the absorbance at the excitation wavelength, I is the integrated photoluminescence intensity, η is the refractive index of the solvent. So, QY of $AgInS_2$ QDs yields to:

$$QY_{AgInS_2} = 31\%(\frac{0.10}{0.25})(\frac{2.33\times10^8}{1.52\times10^9})(\frac{1.379}{1.333})^2$$

Therefore,

$$QY_{AgInS_2} = 2.0\%$$

Section IV. Tuning Size and Properties of Metal Sulphide NCs

4.1. Synthesis details of integrated study for growth of Ag_2S NPs

The variables are listed in Figure 4e. When varying the reaction time, the amount of AS solution and Ag precursor are kept as 0.25 ml and 0.25 mmol, respectively. When varying amount of AS solution, the amount of Ag precursor and reaction time are kept as 0.25 mmol and 60 sec, respectively. When varying the amount of Ag precursor, the amount of AS solution and reaction time are kept as 0.25 ml and 60 sec, respectively.

4.2. Quantum Yield Estimation of CdS QDs.

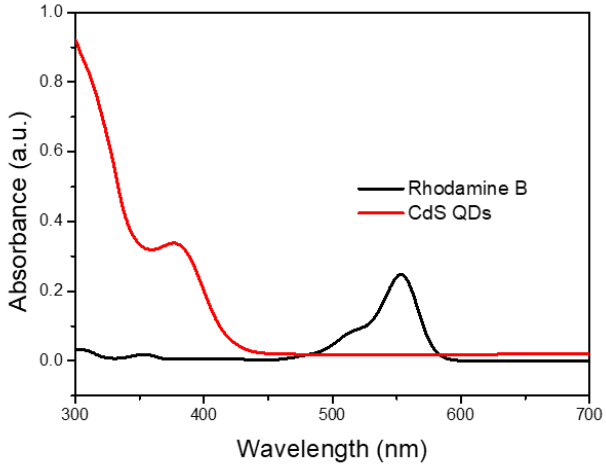

Figure S8. The UV-vis spectrum of Rhodamine B (black curve) and CdS QDs (red curve). We measure the PL and absorbance spectrum using the same samples.

According the calculation for QY of $AgInS_2$ QDs, QY of CdS QDs yields to:

$$QY_{cds} = 31\%(\frac{0.10}{0.27})(\frac{5.90 \times 10^8}{1.52 \times 10^9})(\frac{1.379}{1.333})^2$$

Therefore,

$$QY_{cds} = 4.8\%$$

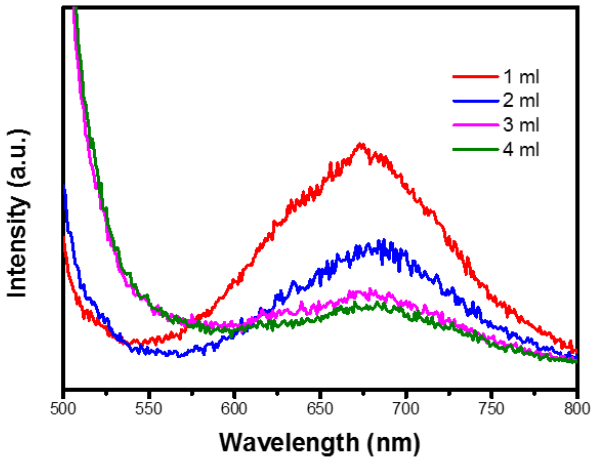

Figure S9. PL spectrum of CdS QDs synthesized using excess AS solution from 1 mL to 4 mL.

4.3. Additional TEM images of PbS and SnS NCs.

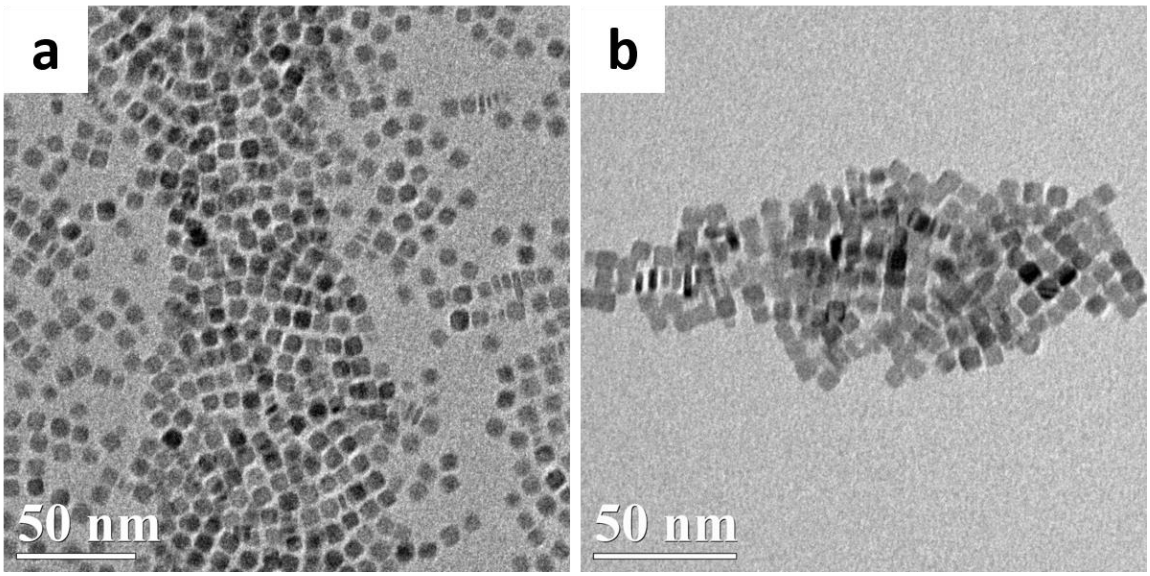

Figure S10. (a) TEM image of PbS NPls synthesized using 0.1 mmol of $PbCl_2$ and 0.1 mL of AS. (b) PbS NPls after 0.25 mL AS solution treatment.

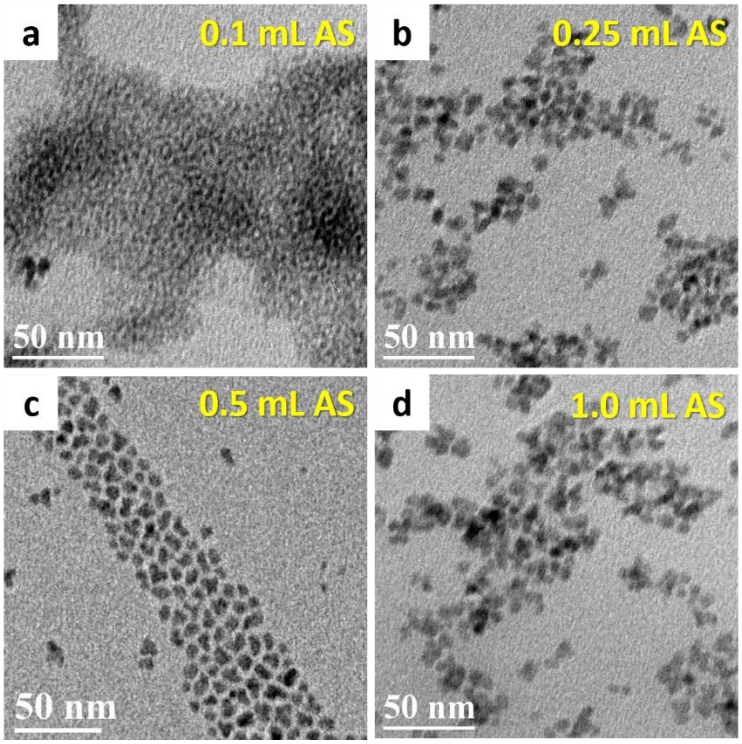

Figure S11. TEM images of SnS NCs prepared using different amount of AS solution.

Section V. Full synthesis parameters of MS NCs

Table 1. Parameters for Synthesis of All Metal Sulphide NCs.

Metal sulphide	Cation precursor amount (mmol)	AS solution amount (ml)	Reaction time (sec)	AS solution adding manner
CuS	0.25	0.75	60	0.25 ml×3 times with interval of 1 min
Ag_2S NPs	0.25	0.25	60	
small Ag_2S	0.25	0.01	10	
CdS NCs	0.5	0.5	60	
CdS QDs	0.1	0.01-0.2	10	
SnS	0.5	0.5	60	
PbS	0.1	0.1	60	
$AgInS_2$	0.25/0.25	0.25	60	
$CuInS_2$	0.25/0.5	0.05	60	dropwise
Cu_2SnS_3	0.5/1	0.2	60	dropwise
Cu_2ZnSnS_4	0.25/1/0.5	0.06	60	dropwise

Table 2. EDS Results of All Mentioned Metal Sulphide NPls (unit/%).

NCs	References	Cation			Sulphur
CuS	Fig. 2a	48.6			51.4
Ag_2S	Fig. 2b	85.8			14.2
small Ag_2S	Fig. 4a	87.2			12.8
CdS NCs	Fig. 2c	52.6			47.4
CdS QDs	Fig. 5c	47.9			52.1
PbS	Fig. 2f	48.1			51.9
SnS	Fig. 2d	56.8			43.2
$AgInS_2$	Fig. 2e	21.0		24.6	54.4
$CuInS_2$ (raw)	Fig. S2b	22.1		25.1	52.8
Cu_2SnS_3 (raw)	Fig. S2d	30.0		15.8	54.2
Cu_2ZnSnS_4 (raw)	Fig. S2f	22.7	14.6	8.9	53.8
$CuInS_2$ (annealed)	Fig. S2b	23.2		25.7	51.1
Cu_2SnS_3 (annealed)	Fig. S2d	33.2		14.0	52.8
Cu_2ZnSnS_4 (annealed)	Fig. S2f	23.8	15.1	10.3	50.8

Reference.

1. Zhou, J.; Liu, Q.; Feng, W.; Sun, Y.; Li, F., Chem Rev 2015, 115, 395-465.