Electronic Supplementary Materials

$Cu_{2-x}S$ nanocrystals synthesis: a chemical toolbox for controlling nanocrystal geometry, phase and plasmonic behavior

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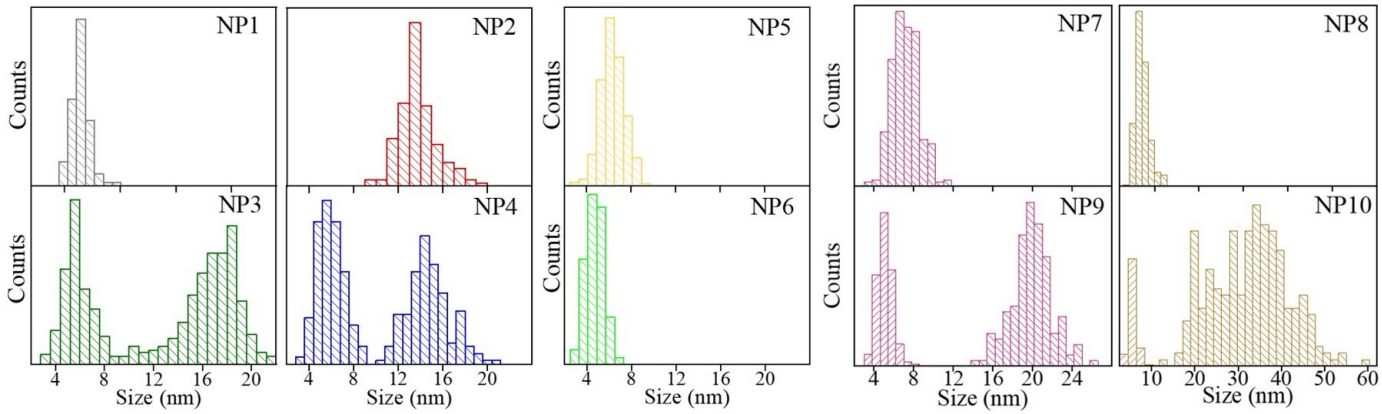
Sample	*CuCl: OA: Olam : ODE (mmol)*	*$CuCl_2$: OA : Olam : ODE (mmol)*	*$Cu(AcO)_2$: OA: Olam : ODE (mmol)*	*$Cu(AcA)_2$: OA: Olam : ODE (mmol)*	*S : OA: Olam : ODE (mmol)*
NP 1	0.5 : 5 : 10 : 20				0.5 : 4 : 0 : 4
NP 2		0.5 : 5 : 10 : 20			0.5 : 4 : 0 : 4
NP 3			0.5 : 5 : 10 : 20		0.5 : 4 : 4
NP 4				0.5 : 5 : 10 : 20	0.5 : 4 : 4
NP 5	0.5 : 0 : 10 : 20				0.5 : 0 : 4 : 4
NP 6		0.5 : 0: 10 : 20			0.5 : 0 : 4 : 4
NP 7	0.5 : 0 : 10 : 20				1 : 0: 8 : 8
NP 8	0.5 : 0 : 10 : 20				2.5 : 0 : 8 : 8
NP 9		0.5 : 0 : 10 : 20			1 : 0 : 8 : 8
NP 10		0.5 : 0 : 10 : 20			2.5 : 0 : 8 : 8

Table S1. Reaction mixture composition used for the synthesis of NP1-NP10 samples, according to a two-pots approach. Oleic Acid (OA), Oleyl amine (Olam), Octadecene (ODE), copper (II) acetylacetonate ($Cu(AcAc)_2$), copper (II) acetate ($Cu(AcO)_2$).



Sample	*γ (Hz)/10^{14}*	*ω_{sp} (eV)*	*ω_p (eV)*	*N_h (cm^{-3})/10^{21}*	*$Cu_{2-x}S$*
NP 1	1.44	0.99	2.73	4.22	$Cu_{1.80}S$
NP 2	1.63	0.92	2.69	4.12	$Cu_{1.81}S$
NP 3	1.60	0.88	2.60	3.83	$Cu_{1.82}S$
NP 4	1.60	0.93	2.69	4.09	$Cu_{1.81}S$
NP 5	1.60	1.01	2.84	4.58	$Cu_{1.78}S$
NP 6	1.60	1.19	3.21	5.86	$Cu_{1.72}S$
NP 7	1.60	1.05	2.92	4.85	$Cu_{1.77}S$
NP 8	1.60	1.08	2.98	5.04	$Cu_{1.76}S$
NP 9	1.60	1.02	2.86	4.65	$Cu_{1.78}S$
NP 10	1.60	0.95	2.73	4.24	$Cu_{1.80}S$

Figure S1. Upper panels. Statistical analysis of the size distribution of the $Cu_{2-x}S$ NP1-NP10 samples as measured from the TEM micrographs reported in Figure 1 and Figure 4 in the main manuscript.
Table (bottom panel) of the $Cu_{2-x}S$ NP1- NP10 sample plasmonic properties: γ full width at half maximum of the localized surface plasmon band, ω_{sp} localized surface plasmon band position, ω_p bulk plasmon band, N_h, hole carrier density, and final stoichiometry of the as-synthesized nanoparticles as measured from the UV-Vis-NIR absorption spectra in Figure 3h and Figure 4e-f in the main manuscript and theoretically determined from the following equations adopting the Mie Theory

$$\omega_p = \sqrt{(\omega sp^2 + \gamma^2)(1 + 2\varepsilon_m)} \qquad N_h = \frac{\varepsilon_0 m_h \omega_p^2}{10^6 e^2}$$

$$Cu_{\%} = 50\frac{N_h P M_{Cu_2S}}{\rho N_A} \qquad Cu_{2-x} = \frac{100 - Cu_{\%}}{50}$$

where ε_m is the dielectric constant of the solvent, e is the electron charge, ε_0 is the free space permittivity, m_h is the hole effective mass (nearly $0.8m_0$), and ρ is Cu_2S density equal to ρ= 5.6 g/cm^3

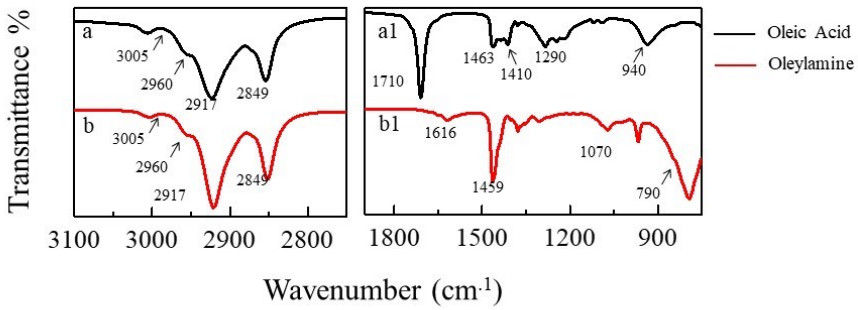


Figure S2. FTIR spectra in ATR mode of Oleic Acid (a, a1,black line) and Oleylamine (b, b1, red line)

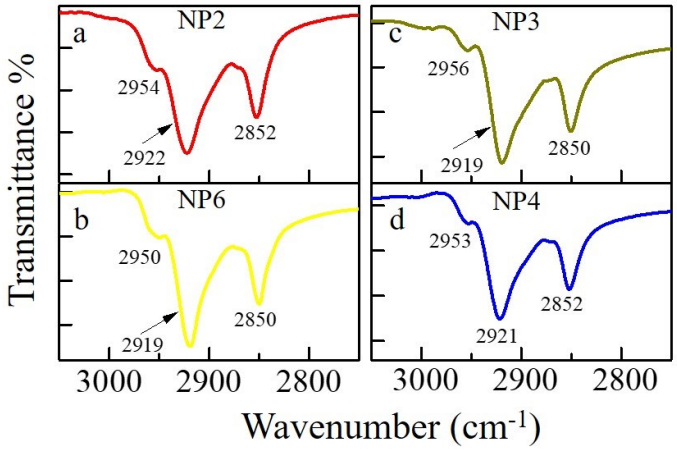
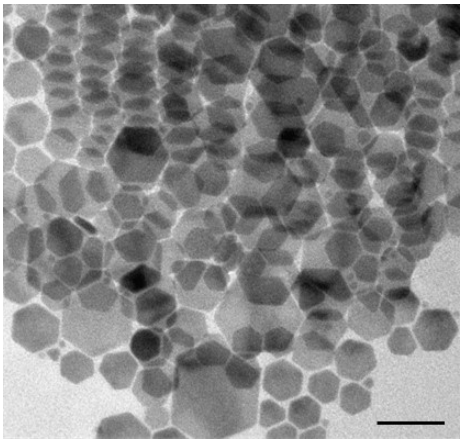


Figure S3. FTIR spectra in ATR mode (3050 - 2750 cm^{-1}range) of (a) NP2, (b) NP6 (c) NP3, (d) NP 4. See Table S1 for reaction mixture composition.

Vibrational modes	NP2	NP3	NP4	NP6	Olam	OA
νCH (-CH=CH-)					3006	3006
ν_{AS} CH_3	2954	2956	2953	2950	2960	2960
ν_{AS} CH_2	2922	2919	2921	2919	2917	2917
ν_S CH_2	2852	2850	2852	2850	2849	2849
ν C=O	1736	1734	1736	1730		1710
ν C=C ν_{AS} NH_3^+	1648	1650	1648	1650	1653	1653
δNH_2 (scissoring)				1624	1616	
ν_{AS} $-(CO)^-_2$	1550	1553				
δ_S CH_2 and $\delta a_S CH_3$	1461	1460	1461	1461	1459	1459
ν_S $-(CO)^-_2$	1403	1408		1404		
δ_S CH_3	1371	1367	1371	1371	1379	1379
ν C-O	1257	1260	1256			1246
Wagging CH_2	1185	1174		1185		
ν C-C-O	1100	1080		1113	1145	1090
δC-N	1056			1056	1070	
δ=C-H out of plane	1013	1018		1013		

Table S2. Table with the assessments of all the characteristic vibration modes as detected from the FTIR-ATR spectra reported in Figure 3a-d in the main manuscript. Oleic Acid (OA), Oleyl amine (Olam).



S4. TEM micrograph of $Cu_{2-x}S$ NP9 sample after 40 minutes of reaction. Scale bar 50 nm

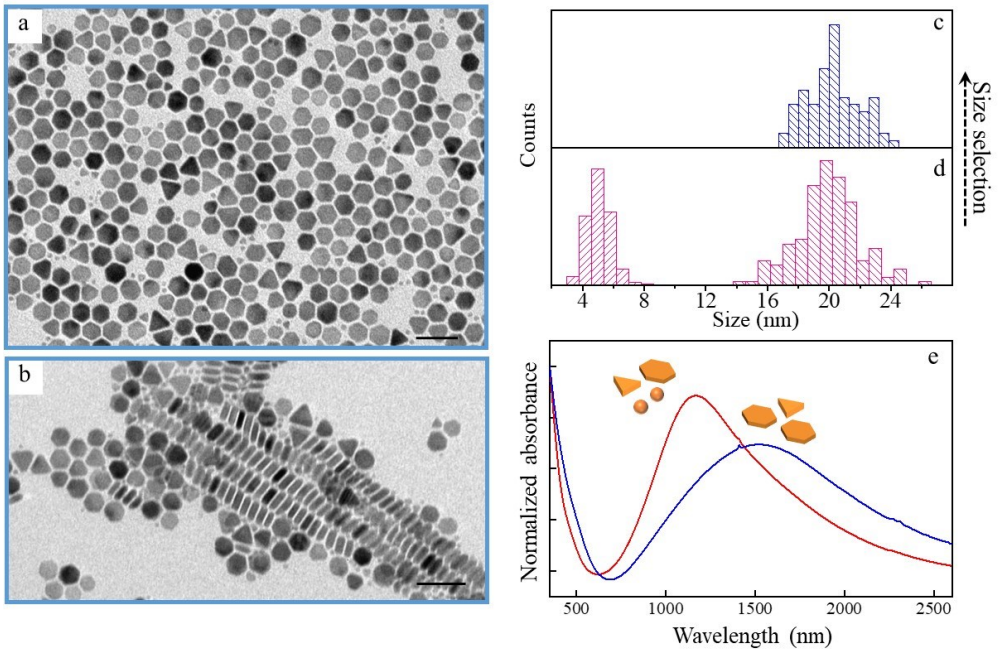


Figure S5. Size selective precipitation of NP9 by purposely adding ethanol in volumetric ration with reaction mixture of 6:1. TEM micrographs of the size selected sample (a, b, scale bar 50nm) showing monodispersed hexagonal and triangular nanoplates (NPLs). Statistical analysis (c, d) and UV-Vis-NIR absorbance spectra (e) of $Cu_{2-x}S$ NP9 sample before (d, e red line) and after (c, e blue line) size selection.

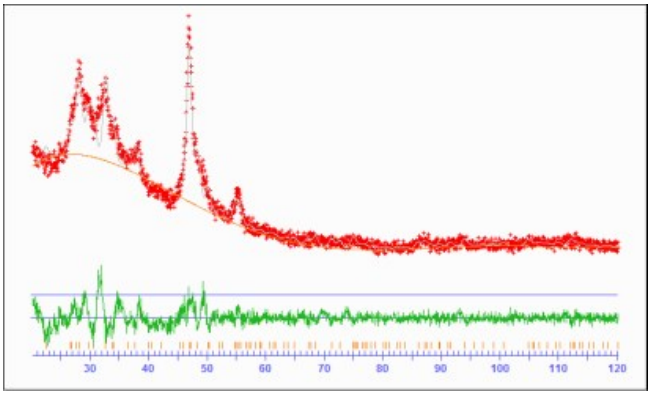


Figure S6. Rietveld fit of the XRD pattern collected on the NP1 sample (black line in Figure 3 of main test)

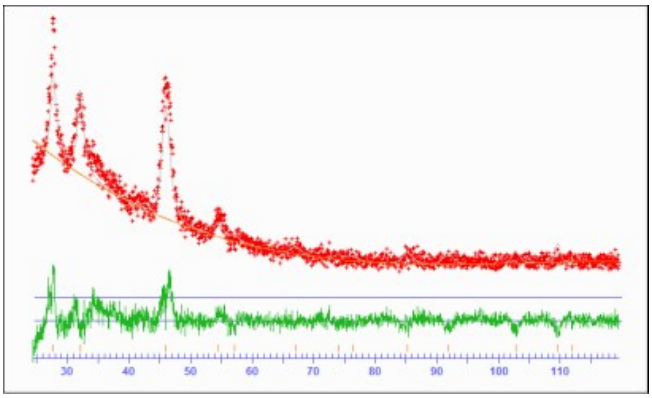


Figure S7. Rietveld fit of the XRD pattern collected on the NP4 sample (blue line in Figure 3 of main test)

Sample	*CuCl: Olam : ODE (mmol)*	*$CuCl_2$: Olam : ODE (mmol)*	*tDT (mmol)*	*DBDS (mmol*
NP 11	0.5 : 10 : 20		8	
NP 12		0.5 : 10 : 20	8	
NP 13		0.5: 10: 20		8

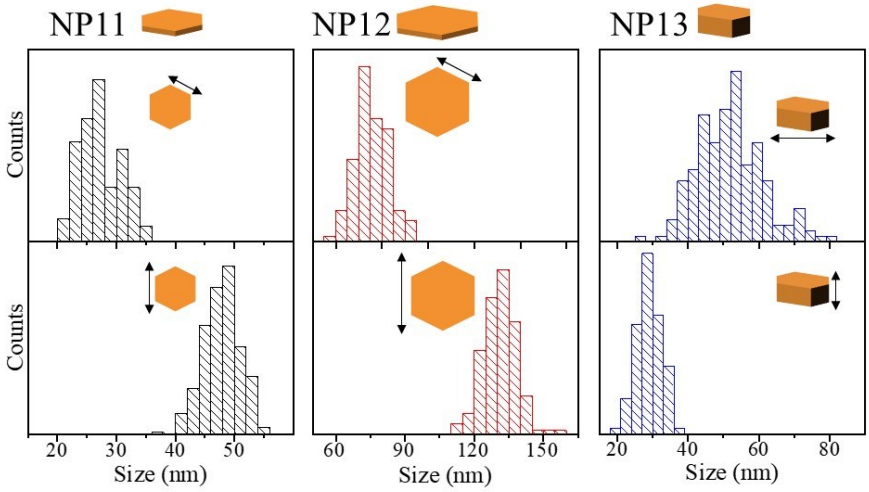
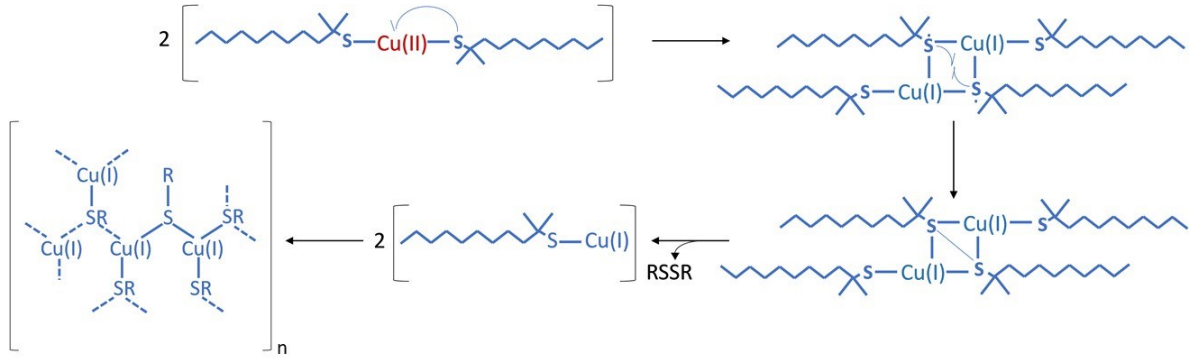


Figure S8. Upper table. Reaction mixture composition used for the synthesis of NP11-NP13 samples according to the one-pot approach (Oleyl amine (Olam), Octadecene (ODE), tert-dodecanthiol(tDT), dibuthyldisulfide (DBDS))
Bottom panel. Statistical analysis of TEM micrographs reported in Figure 5 in the main manuscript. Edge length and average size of 27 nm ($\sigma_{\%}$=16%) and 48 nm ($\sigma_{\%}$=7%) for NP11, 76 nm ($\sigma_{\%}$=10%) and 131 nm ($\sigma_{\%}$=6%), for NP12 prepared with $CuCl_2$, and lateral size of 52 nm ($\sigma_{\%}$=18%) and thickness of 29 nm ($\sigma_{\%}$=12%) for NP13.



Scheme S1. Proposed mechanism for the tert-dodecanthiol induced reduction of Cu(II) to Cu(I). Scheme adapted from reference 65 [Kreitman, G.Y., et al., *Reaction Mechanisms of Metals with Hydrogen Sulfide and Thiols in Model Wine. Part 1: Copper-Catalyzed Oxidation.* Journal of Agricultural and Food Chemistry, 2016. **64**(20): p. 4095-4104]

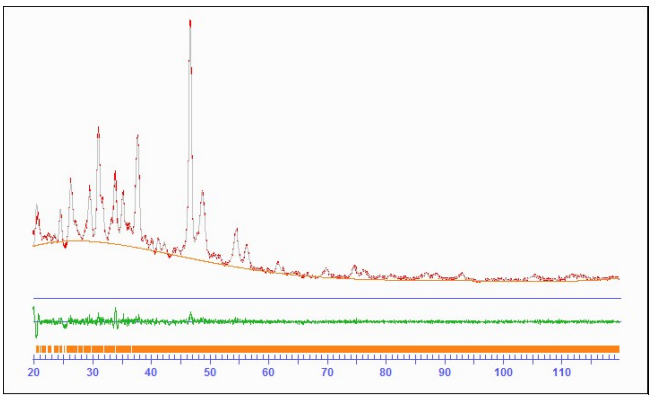


Figure S9. Rietveld fit of the XRD pattern collected on the NP12 sample (red line in Figure 5 of main test)