Supporting information

Interplay Between Surface Chemistry, Precursor Reactivity and Temperature Determines Outcome of ZnS Shelling Reactions on $CuInS_2$ Nanocrystals

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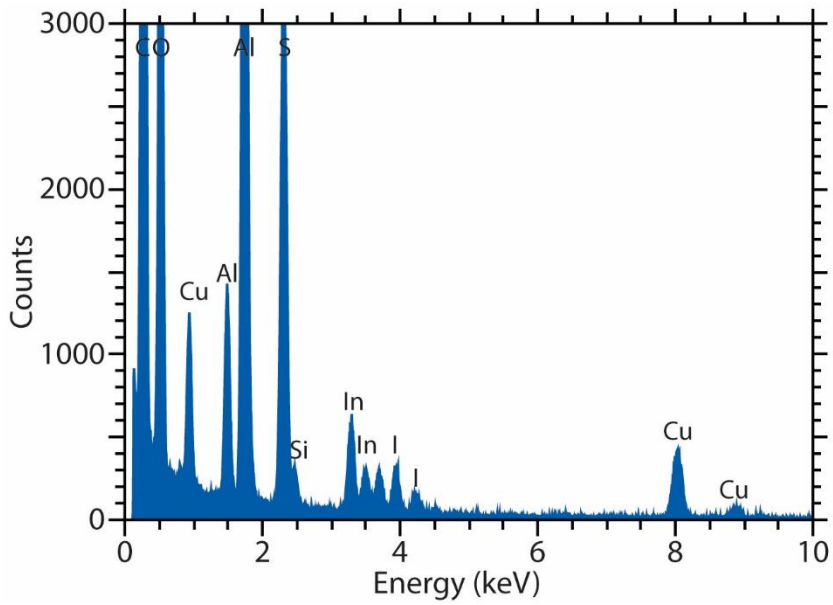

Figure S1. Representative EDS spectrum of unwashed CIS NCs with peak assignment. Aluminum originates from the TEM grids that were used.

Standard deviations of the Cu/In ratios determined by EDS, ICP and XPS.

Standard deviation in EDS. The Cu, In and Zn concentrations were determined by fitting the peaks corresponding to the K-lines. To determine the Cu/In ratio with EDS, the average Cu and In concentrations (C_{Cu} and C_{In}) of three measurements on the same grid were calculated (based on values a_{Cu}, b_{Cu}, c_{Cu}). Based on the fit, an uncertainty percentage was given for each value, yielding (after multiplication) a standard deviation for each concentration in each measurement (SD). The average concentrations and corresponding standard deviations are calculated as

$$C_{Cu} = \frac{a_{Cu} + b_{Cu} + c_{Cu}}{3}$$

$$SD_{Cu} = \frac{\sqrt{\left(SD_{a,Cu}{}^2 + SD_{b,Cu}{}^2 + SD_{c,Cu}{}^2\right)}}{3}$$

The Cu/In ratio (r) and corresponding standard deviation is given by

$$r = \frac{C_{Cu}}{C_{In}}$$

$$SD_{Cu/In} = r * \sqrt{\left(\left(\frac{SD_{Cu}}{C_{Cu}}\right)^2 + \left(\frac{SD_{In}}{C_{In}}\right)^2\right)}$$

Standard deviation in ICP. For each concentration in each measurement, an uncertainty percentage was given. Cu/In ratio and the corresponding standard deviation were calculated as explained above.

Standard deviation in XPS. A fitting uncertainty of 5% in the peak area was assumed and taken as the standard deviation for each concentration. The standard deviation in the Cu/In ratio was calculated as explained above.

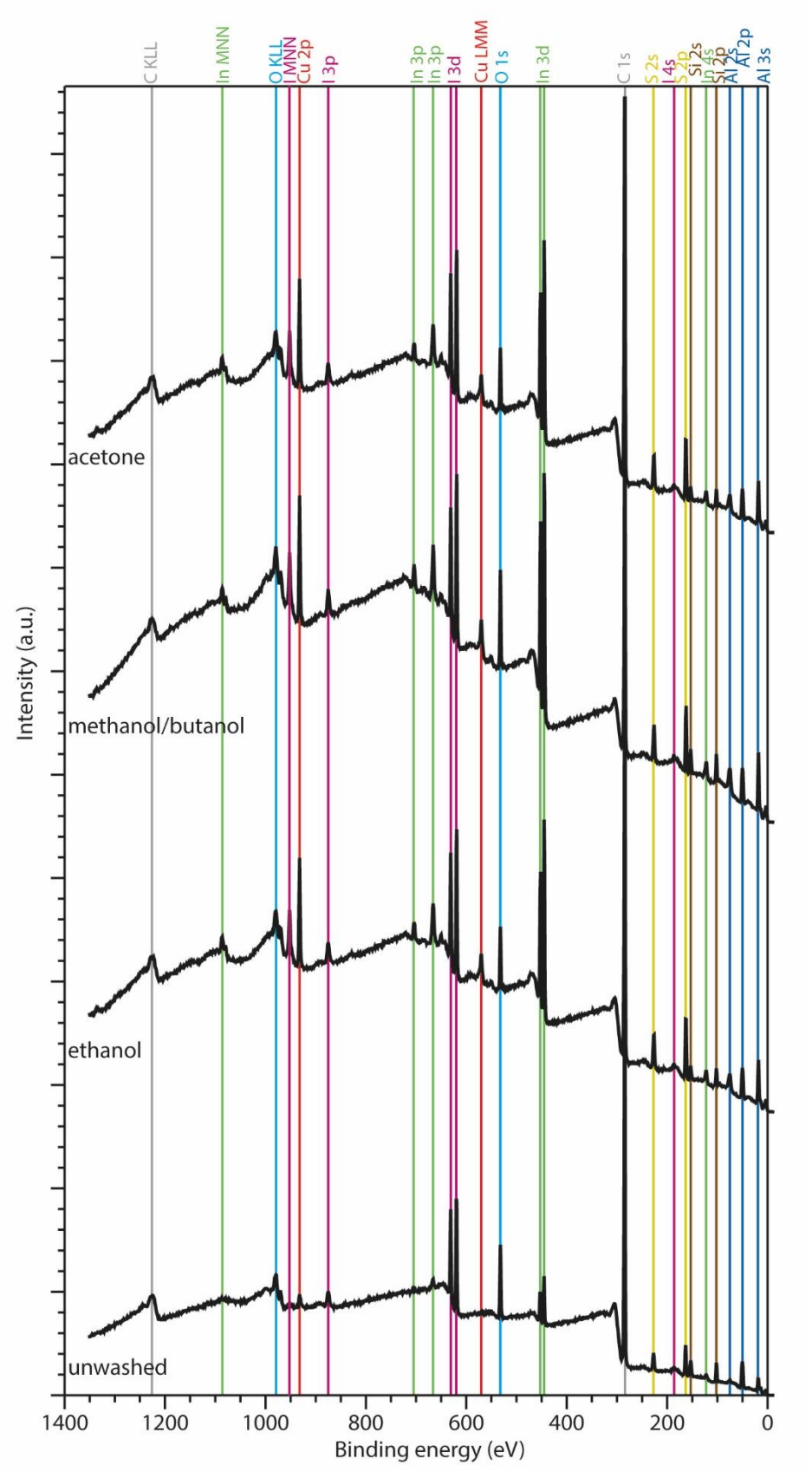

Figure S2. XPS survey spectra of the differently washed and unwashed CIS NC samples, with assignment of the observed peaks (top of panel).

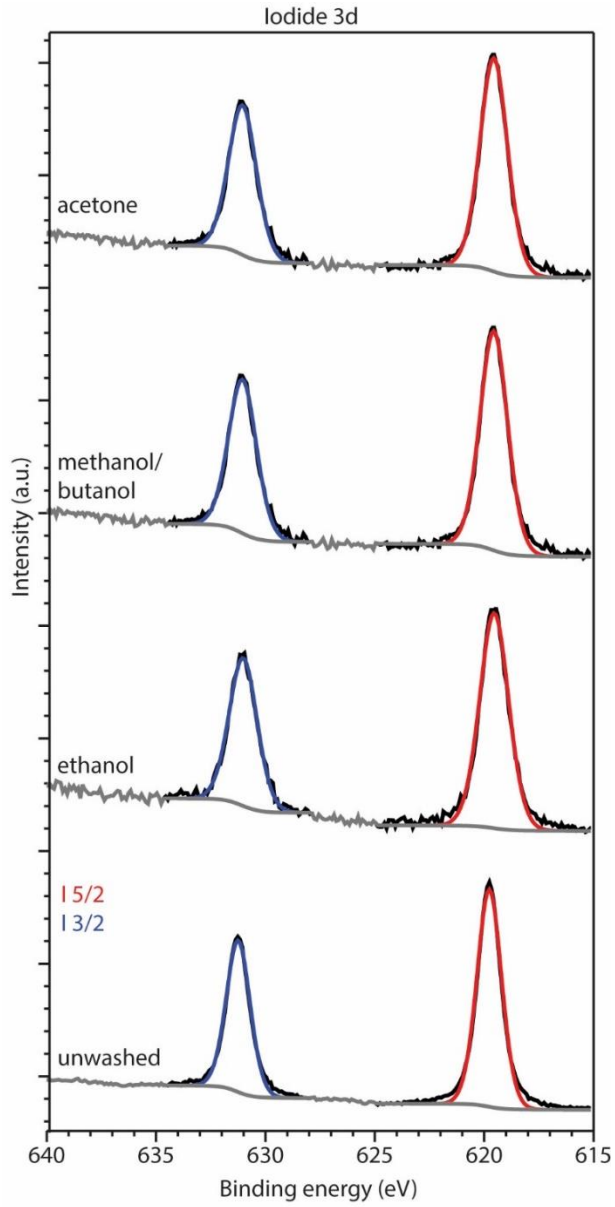

Figure S3. High resolution Iodide 3d XPS spectra of the differently washed and unwashed CIS NC samples. The colored lines are fits to the measured peaks, with the grey line as the background.

Estimate of the expected minimum carbon content on CIS NCs

Gromova *et al.* [1] determined a DDT coverage on CIS nanocrystals of 3.6 DDT molecules/nm^2. If a tetrahedral shape is assumed for the CIS NCs investigated in this work (they are in fact trigonal pyramidal, see figures 3 and 7 in the main text) with an edge length of 2.5 nm, a surface area of 10.8 nm^2 and a volume of 1.8×10^{-21} cm^3 are obtained. This surface area yields 40 DDT molecules/NC and thus 40×12= 480 C atoms per NC. PDF reference card 00-027-0159 gives a density of 4.7 g/cm^3 for chalcopyrite CIS, yielding a total of 82 atoms per NC. The expected Carbon content for a perfectly washed sample would thus be 480/(480+82)×100 = 85%.

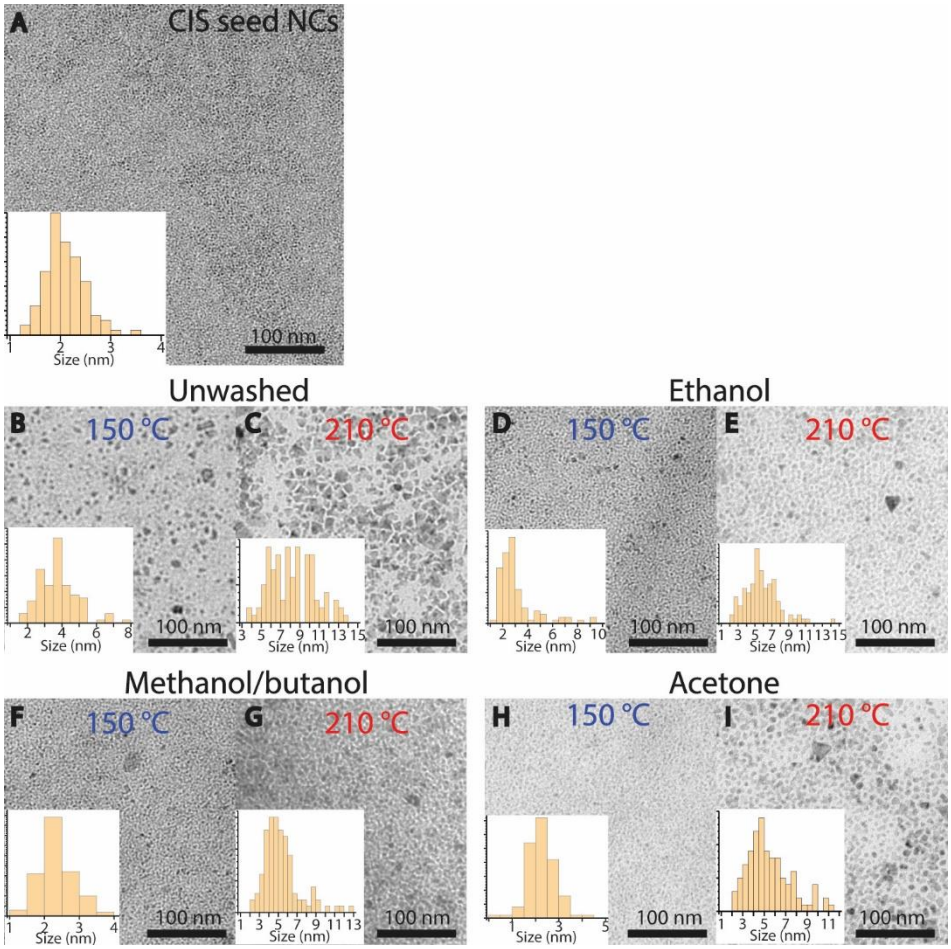

Figure S4. Overview TEM images of **(A)** CIS NCs used as seeds after different washing procedures and **(B-I)** product NCs obtained after reacting differently washed CIS seed NCs ((B,C) unwashed, (D,E) ethanol washed, (F,G) methanol/butanol washed, (H,I) acetone washed) with ZnI_2 and elemental sulfur at two different temperatures: 150 °C (B, D, F, H) or 210 °C (C, E ,G, I). The insets show the size histograms.

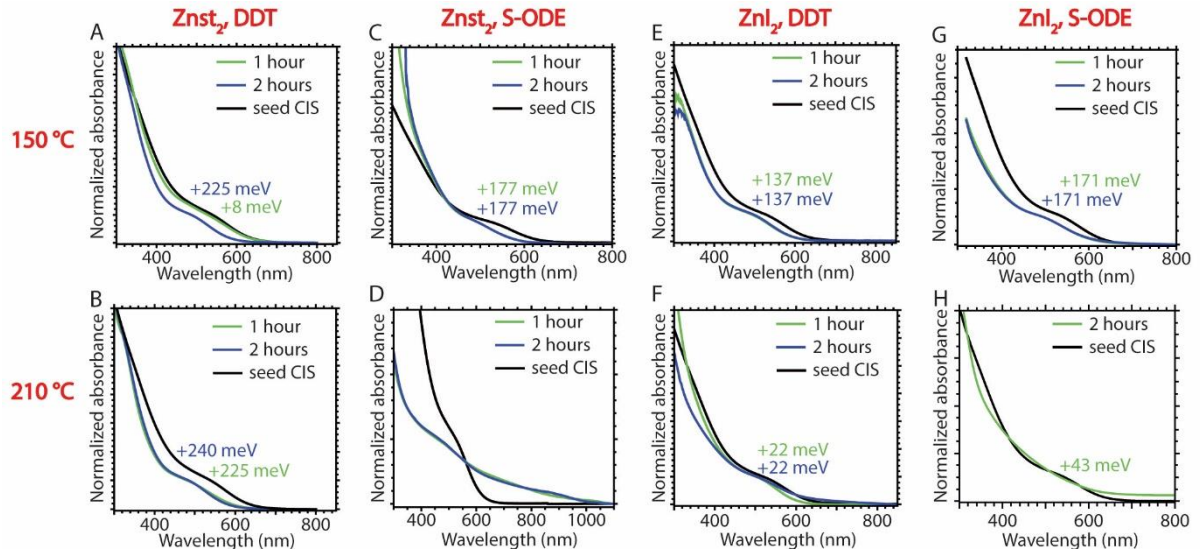

Figure S5. Absorption spectra of CIS seed NCs washed with a methanol/butanol mixture and product NCs after reaction with zinc stearate and DDT (**A, B**), zinc stearate and elemental sulfur (**C, D**), zinc iodide and DDT (**E, F**) and zinc iodide and elemental sulfur (**G, H**). The top row shows spectra of product NCs obtained at 150 °C, while the bottom row show the spectra for products of reactions at 210 °C. The absorption spectra of the CIS NCs used as seeds is included in all cases. The blue-shift in the absorption spectra of the product NCs compared to the seed NCs is indicated.

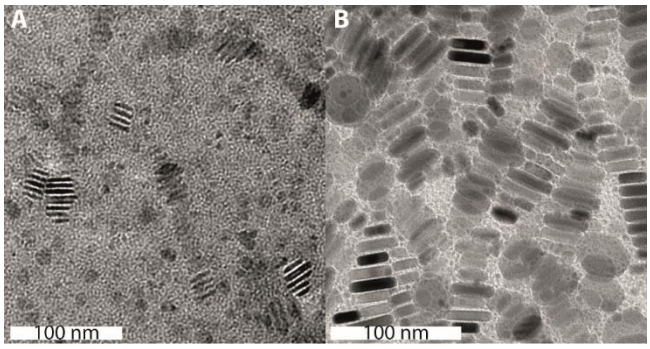

Figure S6. TEM images of product NCs obtained after reaction of seed CIS NCs (washed with methanol/butanol) with zinc stearate and elemental sulfur in the presence of oleylamine at **(A)** 150 °C or **(B)** 210 °C.

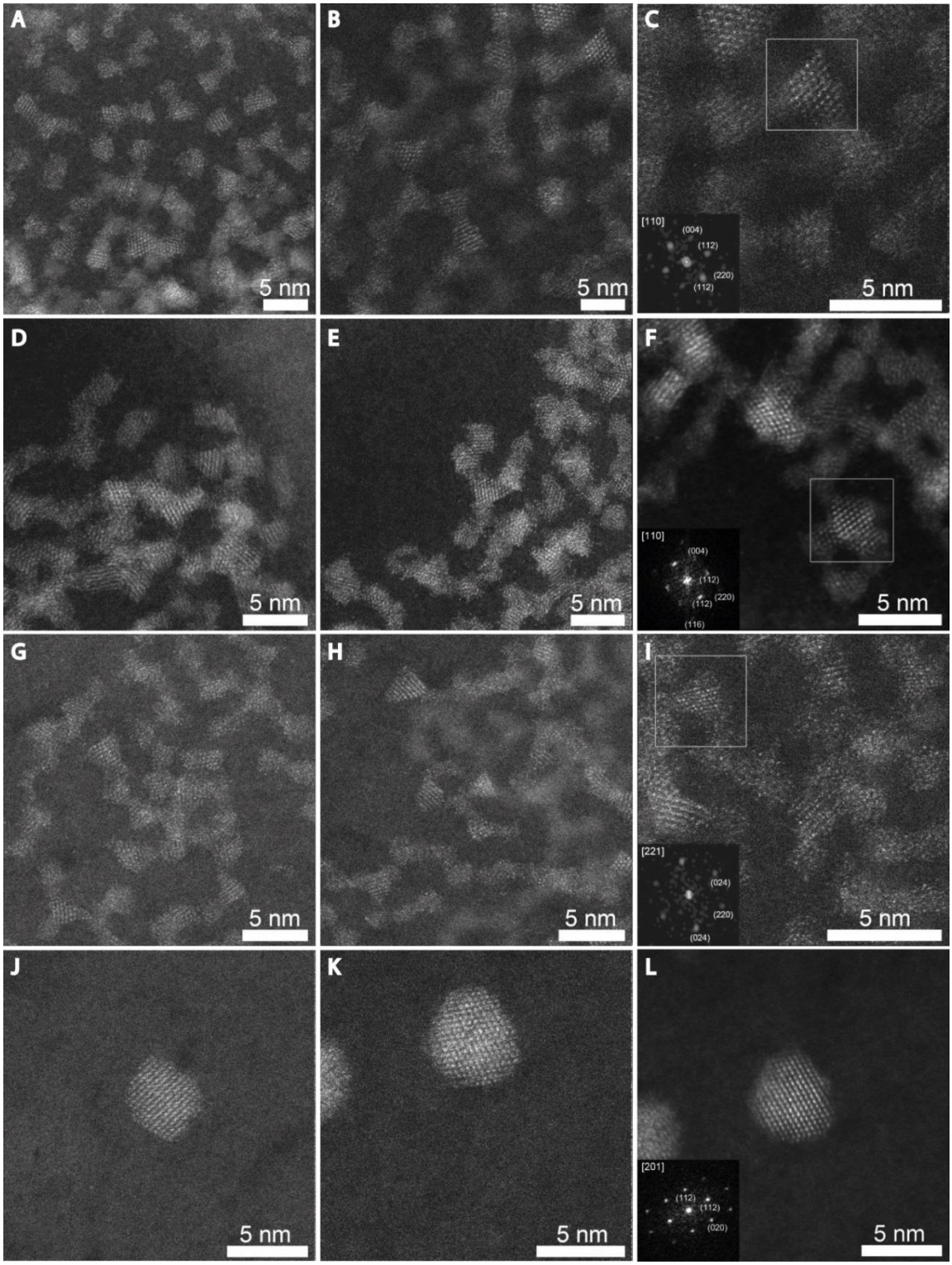

Figure S7. HR HAADF-STEM images of **(A-C)** (ethanol washed) CIS NCs that were used as seeds in a shelling reaction at 150 °C, yielding alloy NCs as products **(D-F)**. **(G-I)** (ethanol washed) CIS NCs that were used as seeds in a shelling reaction at 210 °C, yielding core/shell NCs as products (**J-L**) (see the main text for details). The insets show the FTs of the images, which can be indexed based on the CIS chalcopyrite structure for both the seed and the product NCs.

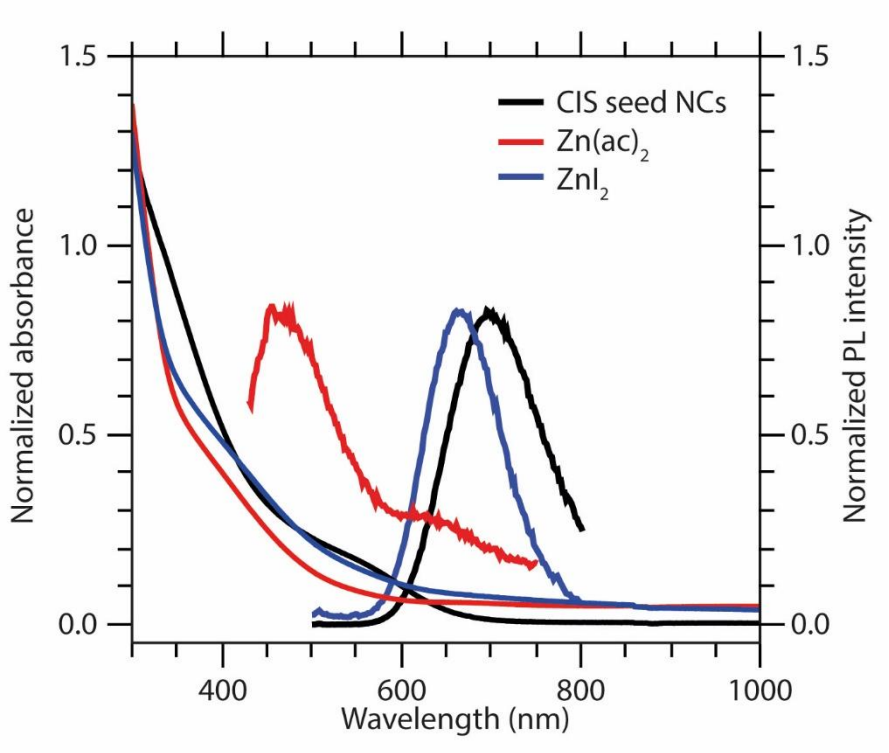

Figure S8. Absorption and PL spectra of CIS seed NCs (black lines) and product NCs obtained after reaction with ZnI_2 (blue) or Zn-acetate (red) at 210 °C. In both cases S-ODE was used as sulfur precursor and OLAM was added as ligand. The CIS seed NCs were washed with methanol/butanol prior to use. Both absorption and PL spectra are blue shifted with respected to the CIS seed NCs. The two emission peaks observed in the red spectrum are ascribed to CIS-ZnS alloy NCs (weak peak at 650 nm) and a metal complex formed in-situ (stronger peak at ~450 nm).

References

1. Gromova, M.; Lefrancois, A.; Vaure, L.; Agnese, F.; Aldakov, D.; Maurice, A.; Djurado, D.; Lebrun, C.; de Geyer, A.; Schulli, T. U.; *et al.* Growth Mechanism and Surface State of $CuInS_2$ Nanocrystals Synthesized with Dodecanethiol. *J. Am. Chem. Soc.* **2017**, *139*, 15748–15759.