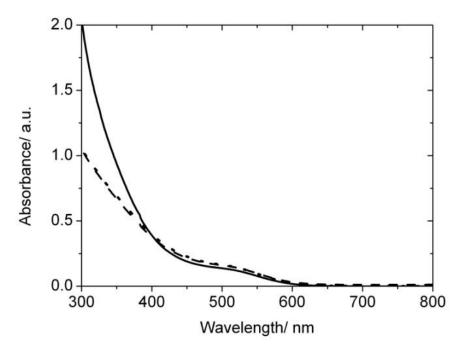# Determining the Concentration of CuInS$_2$ Quantum Dots from the Size Dependent Molar Extinction Coefficient

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Figure S1 shows the absorbance spectra for CIS-QDs as synthesized and after subsequent purification by centrifugation (see experimental section in the main text). The difference between the impure and purified solutions is significant between 300 nm and 400 nm. The decrease in absorption after cleaning suggests that impurities have been removed. Importantly, the difference in absorption after the first purification process and after the second purification is negligible, suggesting that just one step would be necessary to remove the majority of the organic excess material (thiol ligands) and unreacted precursors. However, all QD solutions were purified at least twice to ensure purity during AAS measurements.

Figure S1. Absorption spectra of a CIS QD solution before purification (solid line), after purification (dashed line) and after repeated purification (dotted line).

For QD sizing, a minimum of 100 CIS-QDs per solution were measured from TEM images using Gatan's Digital Micrograph. The resulting histogram was fitted to a Gaussian (Figure S2); the reported size of a solution could be taken as either the mean size of the 100 measured CIS-QDs, with the uncertainty being the standard deviation from the mean, or the centre of the normal distribution with the uncertainty being the full width half maximum (FWHM), both methods yielding identical results within experimental error.
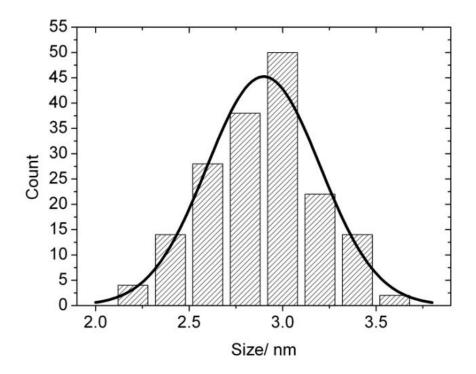
Figure S2. Size histogram for a CIS QD solution with mean diameter equal to 2.9 nm.
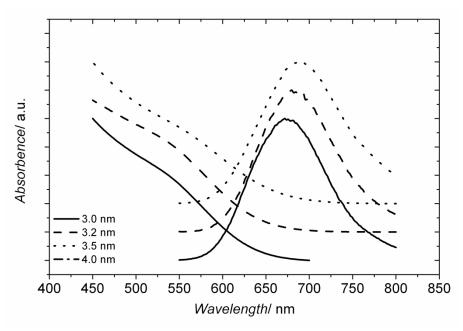

Figure S3: PL and absorption spectra for three CIS-QD dispersions of different sizes.

The centre of the PL spectral peak can be determined with straightforward fitting methods to good accuracy, however as can be seen in Figure S3, the first excitation peak position is more difficult to identify. In order to determine the first excitation peak wavelength, the second derivative of the absorption spectrum was taken and the location of the first excitation determined by the local minima (Figure 3 main text). When looking at the absorption curves alone, it is not possible to see a clear size dependent pattern, yet when the second derivatives are studied, a size dependent red shift can clearly be observed. The wavelength of the first excitonic transition determined through this method was plotted against the PL peak position of the same sample and a linear correlation was observed with gradient 1.21 ± 0.09 (Figure S4). This is indicative of a weakly size dependent Stokes shift.
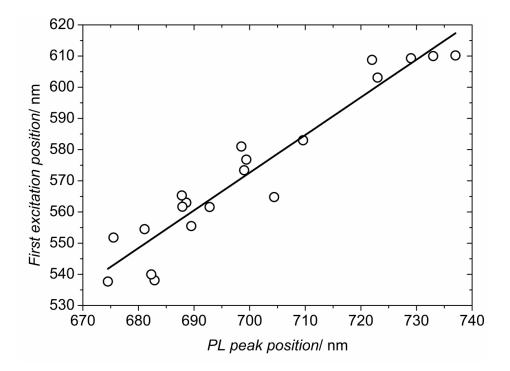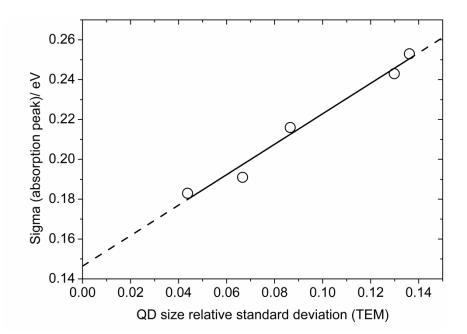
Figure S4. The first excitation position displays a linear relationship with the PL peak position.

Before the value of the absorption at E_1 is used in the Beer-Lambert law to determine $\varepsilon(E_1)$, it must be calibrated to account for the standard deviation Δd of the QD sample size distribution (Equation 2 in the main text). Figure S5 shows the standard deviation of the first absorption peak σ_m (determined by fitting a Gaussian curve to the absorption spectrum) plotted against the relative size distribution $\Delta d/d$ of the sample as measured by TEM. A purely monodisperse QD solution would have an infinitely narrow size distribution and therefore a value of Δd equal to zero. Therefore, the expected standard deviation of the first absorption peak for a perfectly monodisperse sample, σ_0, will be where the linear fit in Figure S5 intercepts the y-axis. This is determined to be 0.146 ± 0.006 for the QD samples used in this study. The gradient was determined to be 0.76 ± 0.06.

Figure S5: The standard deviation of the first absorption peak plotted against the relative standard deviation of the QD size for five samples used in this study. The linear fit is extrapolated to the y-axis to determine the expected absorption peak width for a monodisperse sample.

In the main text Figure 6 demonstrates the validity of taking a value for the 'effective' core size of a CIS/ZnS QD and treating it as a CIS core-only QD when determining a value for the molar extinction coefficient. The effective QD diameter of each solution obtained by this method was compared to an experimentally determined core diameter and was found to be identical within experimental error (Table S1).
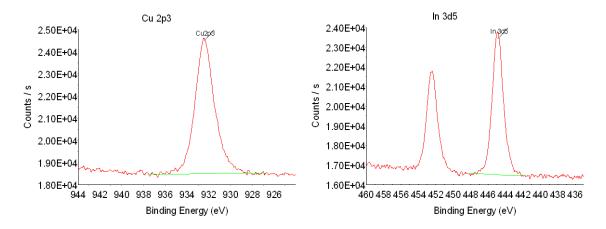
Table S1: A comparison between the estimated core diameter through the use of Equation S1 (or Equation 1 from the main text) and the experimentally determined core diameter.

Solution	PL peak position [± 1 nm]	'Effective' [a] core diammeter [D, nm]	Measured [b] core diameter [± 0.2 nm]	Total TEM measured QD diameter [± 0.2 nm]
A:CIS	671 ±1	3.0	3.0	3.0
A:CIS/ZnS	639 ±1	2.6	2.5	3.0
B: CIS	683 ±1	3.2	3.3	3.3
B:CIS/ZnS	638 ±1	2.6	2.4	3.4

[a] From PL measurements and Equation S1
[b] From TEM and AAS

The Cu:Zn ratio of solutions A:CIS/ZnS and B:CIS/ZnS was determined by AAS measurements, and this value was used in conjunction with the mean diameter of the entire CIS/ZnS-QD as determined from TEM to calculate the core diameter. In order to confirm the validity of this method, the Cu:In ratio was investigated with XPS after a known stoichiometric CIS-QD sample was passivated with ZnS.

Figure S6: Cu 2p3 and In 3d5 XPS spectra. The ratio of atomic percentages of In:Cu was determined to be 1:1.034, demonstrating that the CIS region of the CIS/ZnS-QDs remains stoichiometric after formation of a ZnS layer.