

Unraveling the Impurity Location and Binding in Heavily Doped Semiconductor Nanocrystals; the Case of Cu in InAs Nanocrystals

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Determination of Cu Impurity Concentration By Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) Measurements:

In order to estimate the number of Cu atoms per NC the doping reaction was terminated and the Cu-doped NCs were isolated via a solvent/anti-solvent precipitation, as reported in our previous work.ⁱ The NCs were then dissolved in concentrated nitric acid (HNO₃) and diluted with triply distilled water. The numbers of Cu atoms per NC were extrapolated based on a calibration curve of different ICP standards (Merck) and with

accordance to the estimated number of In and As atoms per NC, which was calculated assuming spherical shaped particles of known size. Table S1 shows the Cu doping levels as calculated in solution, i.e. the volume fraction of the dopant solution added to the NC dispersion, and the corresponding ICP results. The loading ratios obtained here correspond to those shown in our previous work^[i], where a yields of 10 - 25% were reported for NCs of 2.5 - 4nm in diameter.

Table S1: Estimation of impurity concentration for 5nm (diameter) InAs NCs doped with Cu.

Cu atoms/NC (in solution)	Cu atoms/NC (ICP-AES)
200	75
560	221
800	248
1600	497
2500	609

EXAFS Fitting of In and As K-Edges for As-Synthesized InAs NCs :

The structure of the as-synthesized InAs NCs was analyzed by fitting of both In and As K-edges using FEFF6 theory. Both In and As K-edge data were analyzed concurrently, by constraining the In-As bond length and disorder to be the same as seen from each edge. Figure S1 demonstrates good agreement between the experimental data, measured for the as-synthesized InAs NCs, (open symbols) and the theoretical fit (solid lines).

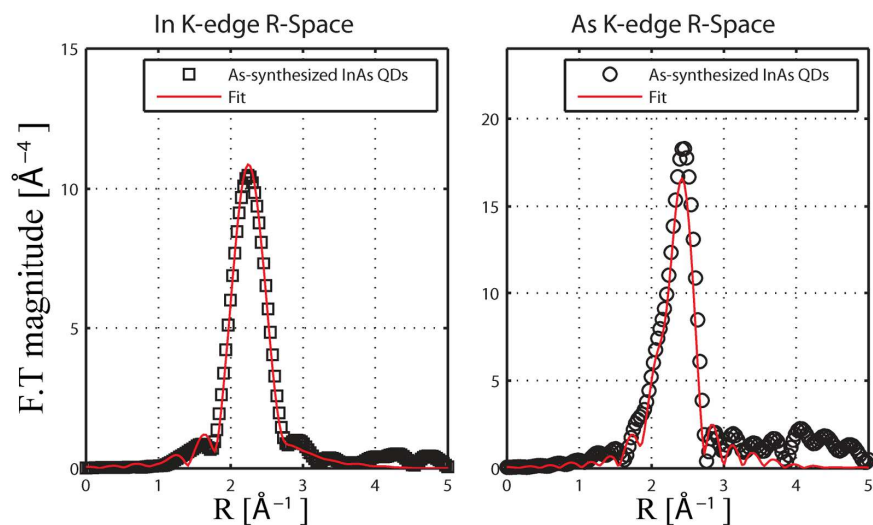


Figure S1: Fourier transform magnitudes of the In K-edge (left) and As K-edge (right) k3-weighted EXAFS data (open symbols) and theoretical fit (solid lines) of the as-synthesized 5nm InAs.

The resulting fit values for the In-As bond length (table S1) were found to be in good agreement to those reported in the literature for the zincblende InAs structure.ⁱⁱ

Table S2: Best fit results for the nearest neighbor distance obtained by In K-edge and As K-edge EXAFS analysis of the as-synthesized InAs QDs.

Parameter	Values obtained by fit
$\Delta E_0(\text{In-As})$ [eV]	4.0 ± 1.1
$\Delta E_0(\text{As-In})$ [eV]	3.7 ± 1.0
$r(\text{In-As})$ [Å]	2.612 ± 0.00
$\sigma^2(\text{In-As})$ [Å ²]	0.0050 ± 0.0005

Further Discussion on the Cu K-Edge EXAFS Fitting, Assuming an Interstitial Hexagonal Impurity Site:

Whereas the geometrical model of the interstitial hexagonal site dictates that each Cu atom would have exactly three In and three As nearest neighbors (Figure 3 of the manuscript), the best-fit results somewhat deviate from the expected values (Table 1 of the manuscript). These deviations, seen for both Cu-In and Cu-As contributions, may result from the assumption of the model, which considers the S_0^2 value of the Cu impurity to be the same as that of metallic Cu. However, given that the S_0^2 value is expected to be within the interval of 0.7 and 1.0 for most materials, the error in the coordination numbers should not exceed ca. 30%, i.e., the qualitative conclusions regarding the position of Cu in an interstitial hexagonal site remain valid. Furthermore, the Cu-In and Cu-As distances are not biased by this amplitude factor uncertainty (because they contribute to the phase of the EXAFS oscillations). Hence, they can be independently used for the validation of this model. In addition, the fits obtained using the other proposed models, e.g., attempts to fit the EXAFS data assuming an interstitial tetrahedral impurity site, resulted in poor quality fits and the numerical values obtained were not physically reasonable (e.g., the energy corrections were larger than 10 eV). Moreover, attempts to fit the EXAFS data using a combination of impurities occupying both substitutional and interstitial sites resulted in poorer quality fits compared to those obtained by the sole use of hexagonal sites.

Detailed Results of In and As K-Edge (XANES and EXAFS) Linear Combination Analysis:

Figures S2 (S3) show the As (In) K-edge linear combination fit results of both XANES and EXAFS spectra for all the measured doping levels, using the two end states of a pure InAs NC and a nearly saturated Cu doped InAs NC.

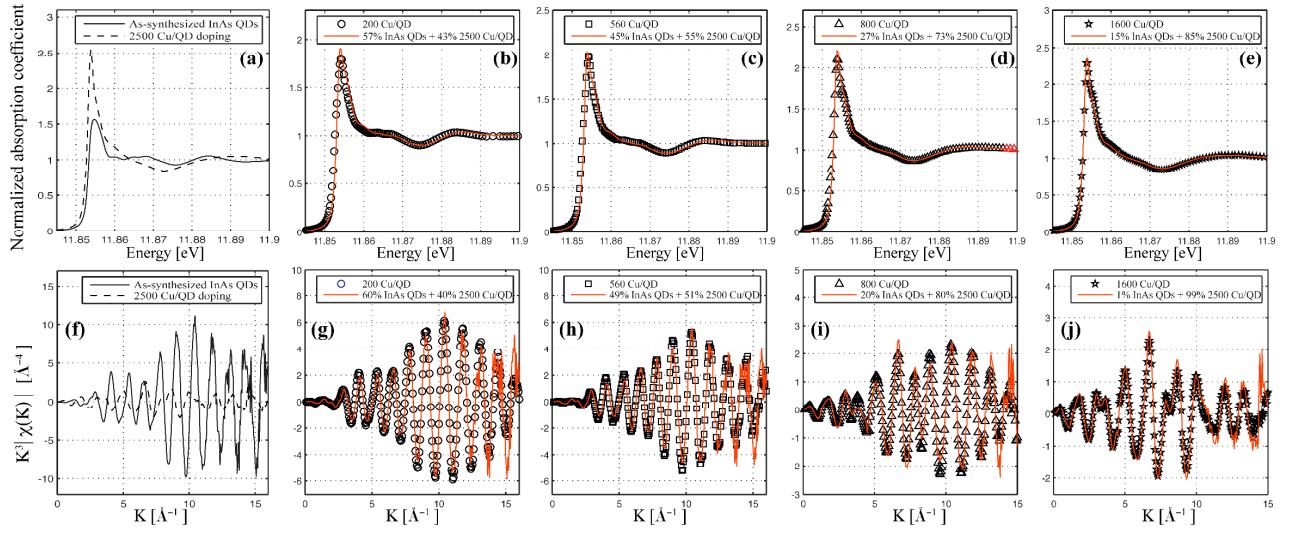


Figure S2: As K-edge XANES (a-e) and EXAFS (f-j) showing the linear combination analysis fit results for all intermediate Cu doping levels (b,g) 200, (c,h) 560, (d,i) 800, and (e,j) 1600 by use of the two end phases: (a,f solid line) the as synthesized InAs QDs and the (a,f dashed line) Cu 2500 doping level.

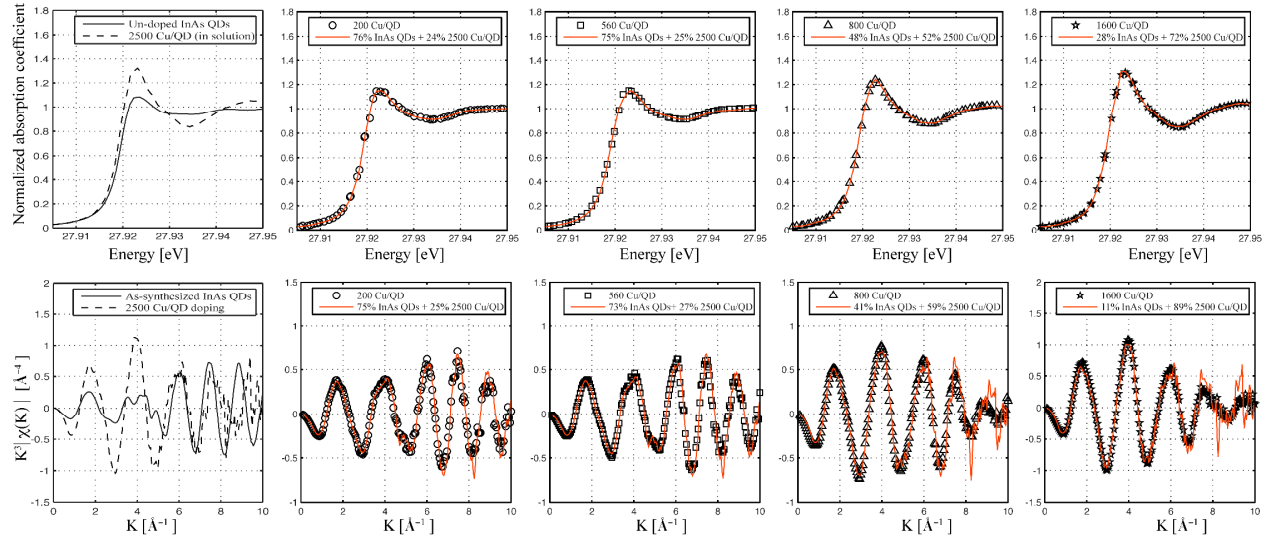


Figure S3: In K-edge XANES (a-e) and EXAFS (f-j) showing the linear combination analysis fit results for all intermediate Cu doping levels (b,g) 200, (c,h) 560, (d,i) 800, and (e,j) 1600 by use of the two end phases: (a,f solid line) the as synthesized InAs QDs and the (a,f dashed line) Cu 2500 doping level.

Nearly Saturated Doping Level – the Onset of Cu-Cu Interactions:

Table S3 presents the values obtained by fitting the EXAFS data measured for the 2500 Cu/NC doping level in solution. The fit was performed at the Cu K-edge using the revised structural model of two adjacent impurities in a single unit cell.

Table S3: Best fit results for the nearest neighbor distance obtained by Cu K-edge EXAFS analysis of the 2500 Cu/NC (in solution).

Parameter	Values obtained by fit
$\Delta E_0(\text{Cu-As})$ [eV]	7.8 ± 0.3
$\Delta E_0(\text{Cu-In})$ [eV]	-7.9 ± 0.3
$N(\text{Cu-As})$	3.8 ± 0.5
$N(\text{Cu-In})$	1.9 ± 0.1
$r(\text{Cu-As})$ [Å]	2.542 ± 0.008
$r(\text{Cu-In})$ [Å]	2.466 ± 0.009
$\sigma^2(\text{Cu-As})$ [Å ⁻²]	0.005 ± 0.001
$\sigma^2(\text{Cu-In})$ [Å ⁻²]	0.001 ± 0.001
$\Delta E_0(\text{Cu-Cu})$ [eV]	7.0 ± 0.8
$\sigma^2(\text{Cu-Cu})$ [Å ⁻²]	0.0056 ± 0.0003
$N(\text{Cu-Cu})$	2.0 ± 0.2
$r(\text{Cu-Cu})$ [Å]	2.450 ± 0.005

To further establish the occurrence of Cu-Cu interactions and validate the proposed model XRD patterns were collected. The diffractograms (Figure 8 of the manuscript) revealed a broadening around the zincblende (111) peak, which was accounted by the presence of Cu impurities in the interstitial hexagonal sites. The simulation of the theta-2theta pattern was performed using a Powder-Cell crystallography software package. The theoretical XRD spectra of the doped InAs NCs were obtained by manually modifying the structure of a pure InAs zincblende structure, adding Cu impurities within the interstitial

hexagonal sites of the unit-cell (Figure 3d-f of the manuscript). To account for Cu-Cu interactions we considered that a single unit-cell could populate 1, 2, 3, and 4 impurities at adjacent hexagonal sites (Figure 7c-d of the manuscript shows a representative structure with two impurities occupying adjacent hexagonal sites). The theoretical diffractograms of the reconstructed Cu doped InAs NCs (Figure 8 of the manuscript, red bars) reveal new diffraction peaks appearing at $2\theta=33.2^\circ$, $2\theta=36.5^\circ$ and at $2\theta=45^\circ$, $2\theta=47.6^\circ$. These added features are consistent with the observed changes in the experimental XRD data, corroborating the proposed model for the nearly saturated NC. Plotting the XRD spectra for a different number of Cu impurities in a unit-cell (positioned at adjacent hexagonal sites) yields identical peak positions and affects only the intensity of these peaks, increasing with the number of impurities per unit-cell (Figure S3). We note that XRD data measured for the doping with 1600 Cu atoms/NC in solution showed negligible changes compared to the XRD spectrum of the undoped sample. This signifies a transformation from non-interacting to interacting Cu impurities occurring between the 1600 and 2500 doping levels.

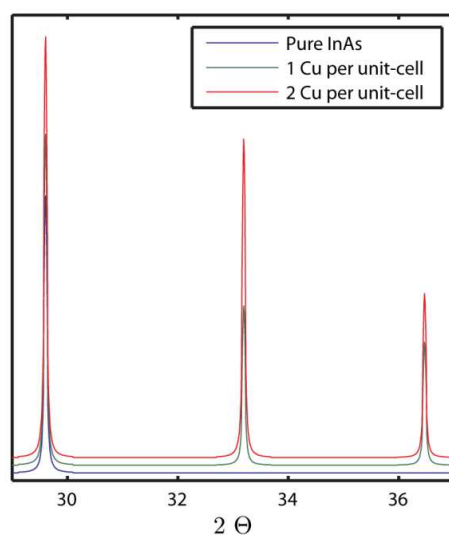


Figure S4: Theoretical XRD spectra of pure InAs (blue) and doping the InAs unit cell with a single (green) and two (red) Cu impurities positioned in hexagonal sites.

ⁱ Mocatta, D.; Cohen, G.; Schattner, J.; Millo, O.; Rabani, E.; Banin, U., Heavily Doped Semiconductor Nanocrystal Quantum Dots. *Science* **2011**, 332, 77-81.

ⁱⁱ Guzelian, A. A.; Banin, U.; Kadavanich, A. V.; Peng, X.; Alivisatos, A. P., Colloidal Chemical Synthesis and Characterization of InAs Nanocrystal Quantum Dots. *Applied Physics Letters* **1996**, 69, 1432-1434