Supplementary Information

Stoichiometry-Controllable Optical Defects in $Cu_xIn_{2-x}S_y$ Quantum Dots for Energy Harvesting

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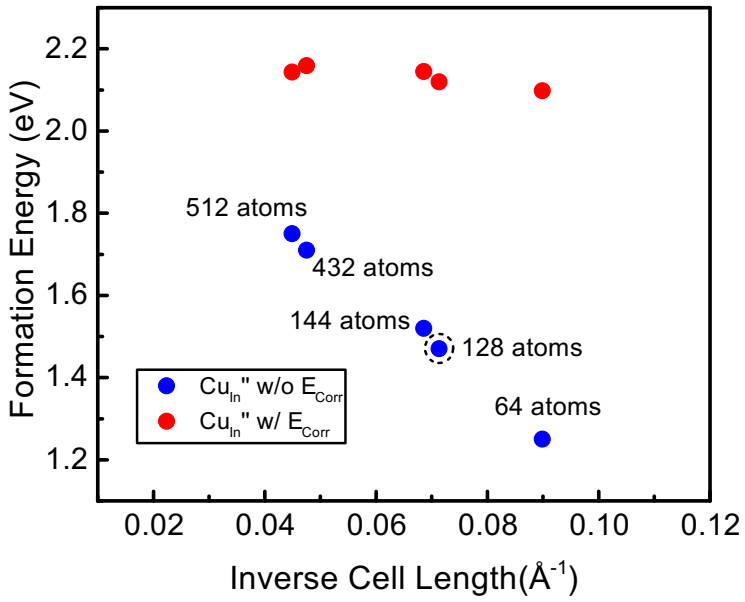
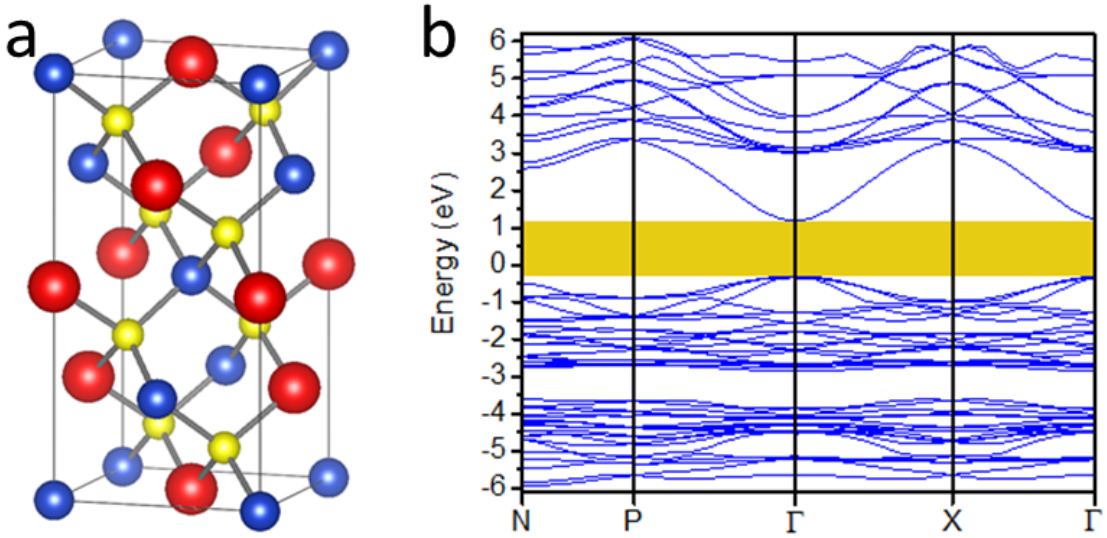


Fig. S1. Effect of supercell size on the formation energy of charged Cu_{In}'' defects with and without FNV correction. The results and analysis presented throughout the main text are for the 128 atom supercell (marked with a dashed black circle).



Crystal	a (Å)	c (Å)	E_g (eV)
$CuInS_2$	5.54 (5.52)	11.20 (11.12)	1.47 (1.55)

Fig. S2 DFT calculation on a bulk CIS unit-cell: (a) shows the optimized cell, while (b) represents the electronic structure. The band gap in (b) is marked in yellow. The table below shows the optimized lattice parameters, and the calculated band gap using HSE06. In all cases, experimental values are represented in parentheses.

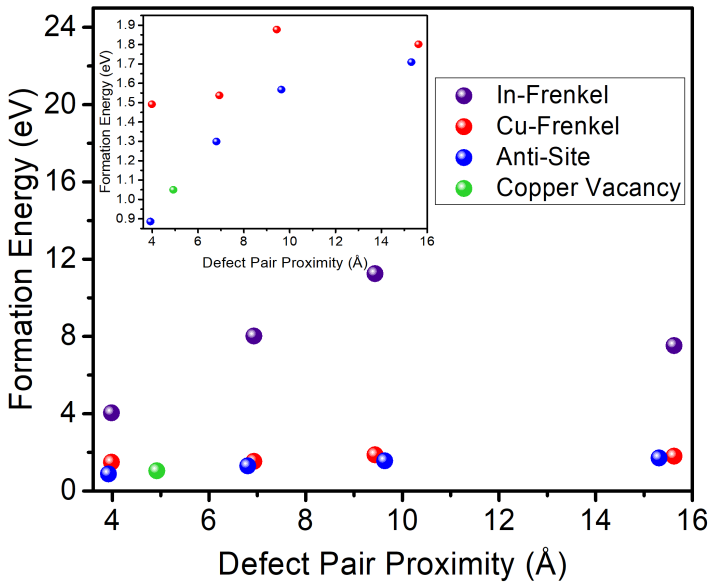


Fig. S3 DFT calculated formation energies of defect pairs at different separation distances. The inset zooms into the lower formation energy Cu defect portion of the calculations. The chemical potential ($-\Delta\mu_{Cu}$) and Fermi-level (E_F) versus the valence band used for the copper vacancy calculation is 0 here.

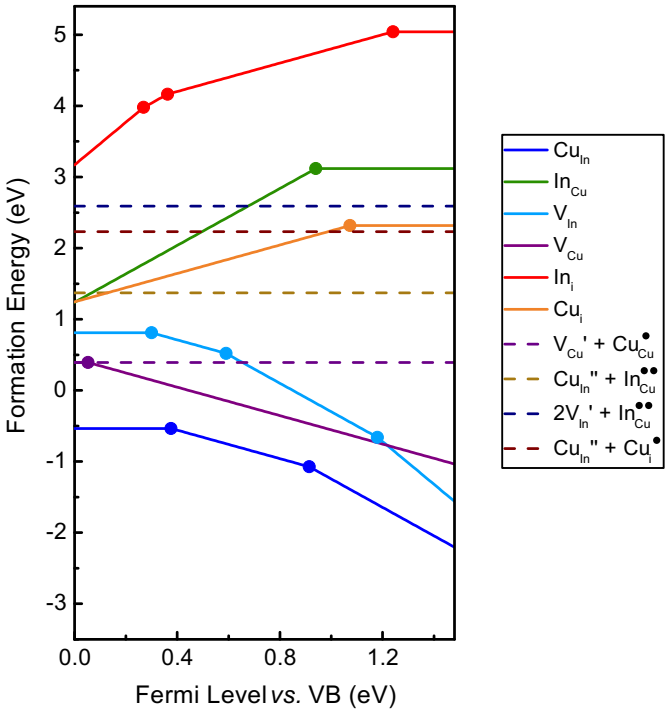


Fig. S4 DFT calculated formation energies and charge transition levels for defects in Cu-rich CIS.

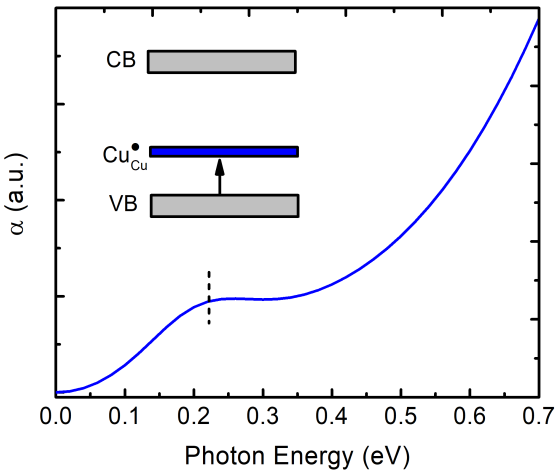


Fig. S5. Predicted IR transition from the excitation of a VB electron into the Cu^{2+} defect hole.

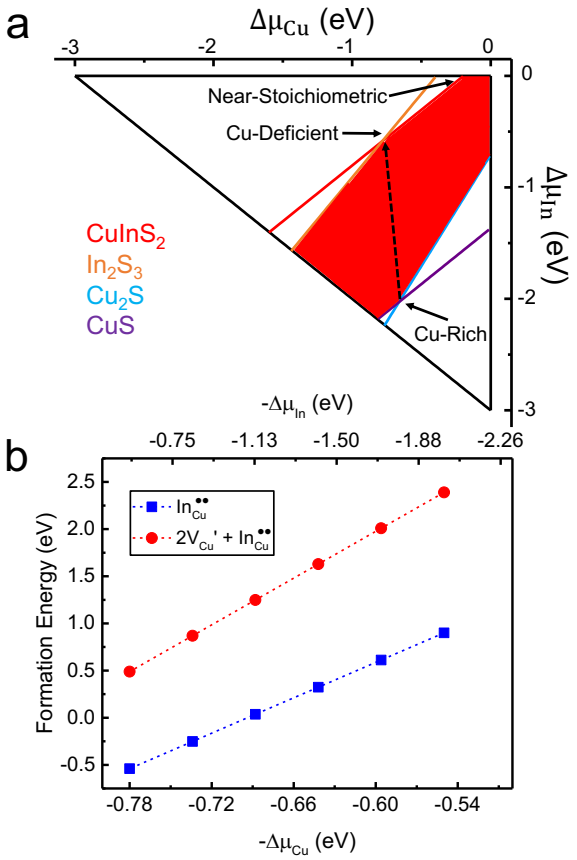


Fig. S6. Effect of Cu-deficiency on the formation of non-emissive defect phases in relationship to emissive defects. (a) The stability region for CIS (red shading) as a function of chemical potential. (b) Formation energy of electron trapping $In_{Cu}^{\bullet\bullet}$ and non-emissive defect phase $2V_{Cu}' + In_{Cu}^{\bullet\bullet}$ in comparison with emissive $V_{Cu}' + Cu_{Cu}^{\bullet}$ defects ($\Delta E_{Form} = E_{V_{Cu} + Cu_{Cu}} - E_{\alpha}$, where $\alpha = In_{Cu}^{\bullet\bullet}$ or $2V_{Cu}' + In_{Cu}^{\bullet\bullet}$). The chemical potential values used are marked in (a) using a dashed black arrow. For $In_{Cu}^{\bullet\bullet}$ defects, we use the low E_F (p-type, VB+0.026 eV) conditions described in the main text.

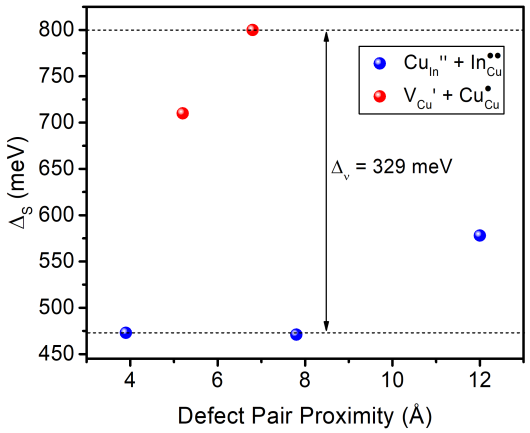


Fig. S7 Effect of defect position on Cu defect energy relative to the VB in CIS QDs, which can vary by ~330 meV.