† ELECTRONIC SUPPLEMENTARY INFORMATION (ESI):

Tailored defect induced sharp excitonic emission from microcrystalline CuI and its *ab-initio* validation

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Instrumentation: Crystallinity and phase purity of the samples were examined by X-ray diffraction (XRD) using Cu Kα radiation (λ=1.5406 Å) (D8 Advanced, Bruker). The chemical state of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα X-ray source (hν = 1486.6 eV) and a hemispherical analyzer (SPECS, HSA 3500).The morphology of the synthesized samples was examined with field emission scanning electron microscope (FESEM Hitachi S-4800), while the crystalline structure of the individual samples was investigated with a high resolution transmission electron microscope (HRTEM JEOL JEM 2100). The UV-Vis absorption and photoluminescence spectra were taken on Shimadzu UV3600 spectrophotometer and Edinburgh, FLSP-920 luminescence spectrometer, respectively. Cathodoluminescence (CL) spectra of the samples were recorded by using Gatan Mono CL equipment attached to the FESEM using a beam accelerating voltage of 5 kV.

Computational details: Our first-principles calculations were performed by CASTEP code [1] which implements a supercell approach to density functional theory. Perdew–Burke–Ernzerhof (PBE) functional [2] within the generalized gradient approximation (GGA) was used to deal with exchange and correlation term. Vanderbilt ultrasoft pseudopotential [3] was used to represent the copper and iodine atoms and plane waves up to energy cut off 450 eV was used in the calculation. Brillouin zone integrations were performed within the Monkhorst Pack scheme [4] using 1×1×1 k-point mesh. For geometrical optimization, the system was allowed to fully relax using BFGS (Broyden-Fletcher-Goldfarb-Shanno) scheme [5] until the total energy converged to less than 2×10^{-5} eV/atom, the maximum force converged to lower than 0.05 eV/Å and the maximum displacement was 0.002 Ǻ. All calculations were performed in spin unrestricted manner.

To corroborate with the experimental results, two types of CuI structures were considered. For pure CuI system, a 2×2×2 supercell containing 32 Cu atoms and 32 I atoms was used while to investigate the effect of I vacancy (V_I), one I atom was removed from the optimized pure CuI structure to accommodate a 3.125% I vacancy. Prior to the properties calculation all systems were fully optimized in a spin unrestricted manner. A scissors operator of 2.174 eV was used for all electronic properties calculations to compensate for the inherent bandgap related problems associated with DFT.

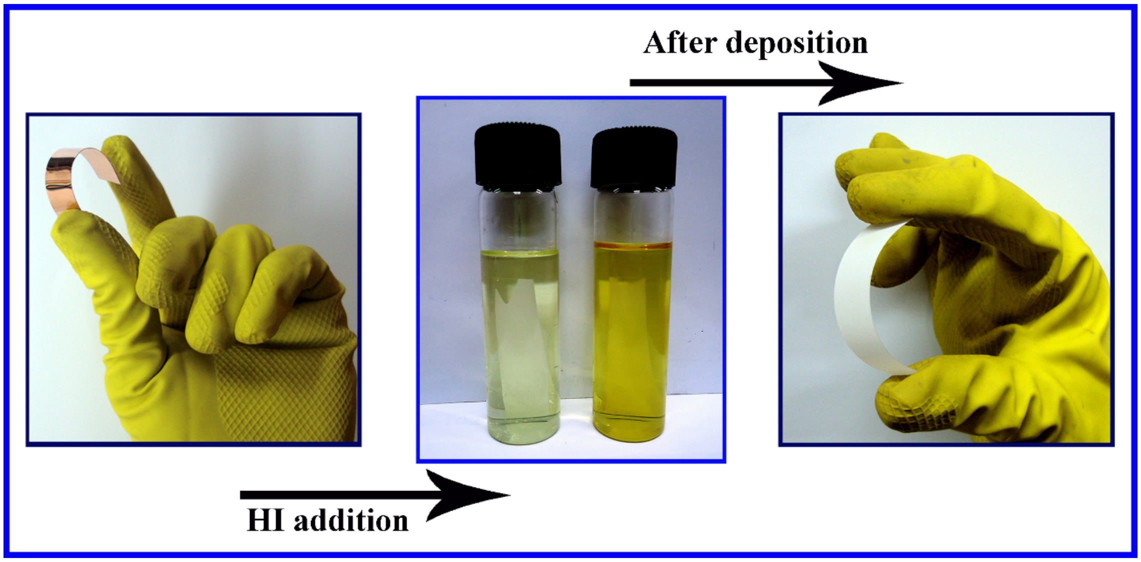

Figure S1: Cu deposited PETs were treated in HI medium under pH3 and pH1 condition. Even after complete replacement of Cu layers by CuI, the films fully retain their initial flexibility.

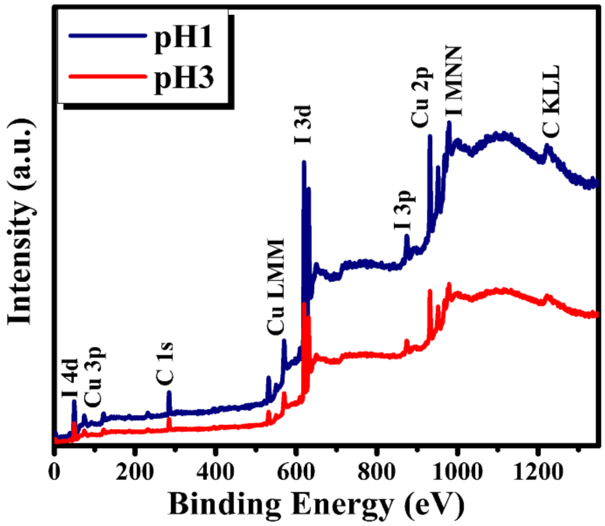

Figure S2: Survey spectra of both the thin films obtained from XPS evidently shows the full indexing of all the peaks which strongly discards any possibility of having impurity species.

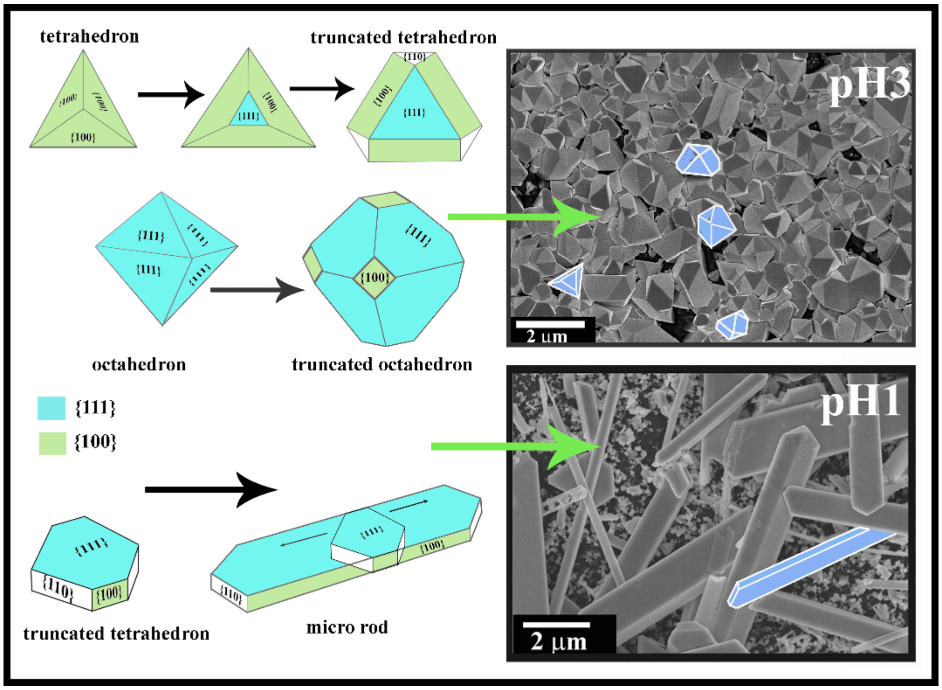

Figure S3: Schematic growth mechanism of the CuI films grown under different concentration of HI.

The slow addition of hydroiodic acid (HI) in water dissociates them into Hydronium ion (H_3O^+) and I^- (as stated in the manuscript). They at first react with bare copper metal and make copper electro positive. In this run, the Cu^+ ions take over I^- ion and start forming CuI nuclei. As the solubility of CuI in water is very poor ~ 4.3 X 10^{-4} g/L, as a result, it comes out as thin film all over the substrate's surface. Furthermore, CuI exists in zinc blende structure and in this structure, the minimum energy configuration supports truncated tetrahedron as one of the stable structure. So at pH1, as the growth rate is faster, this truncated tetrahedron served as a building block and in progression they side wise adjoined in oriented attachment process and form rod like microstructure. Whereas, at pH3, the reaction takes longer time to form the thin film. In this condition, these truncated tetrahedrons reform and stabilize into truncated octahedron shape by minimizing their surface energy of the exposed faces. As a result, pH3 thin film shows mixed structures of polyhedron, spread all over its surfaces.

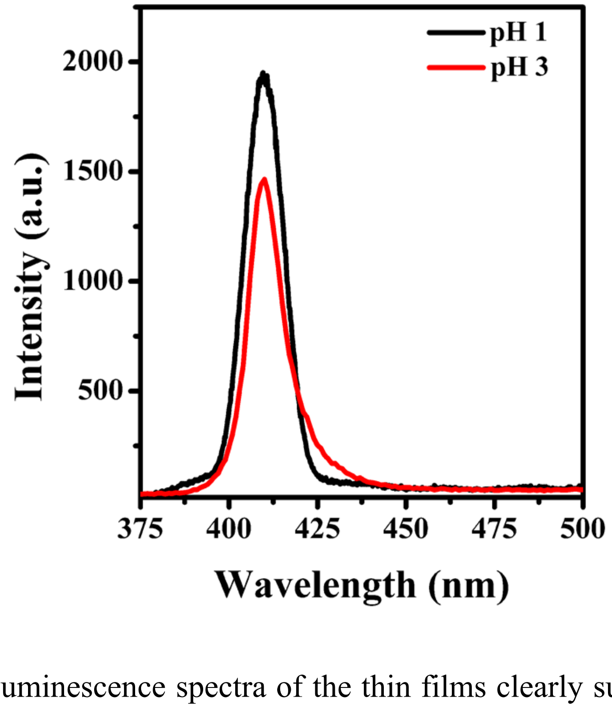

Figure S4: Cathodoluminescence spectra of the thin films clearly support the room temperature PL spectra.

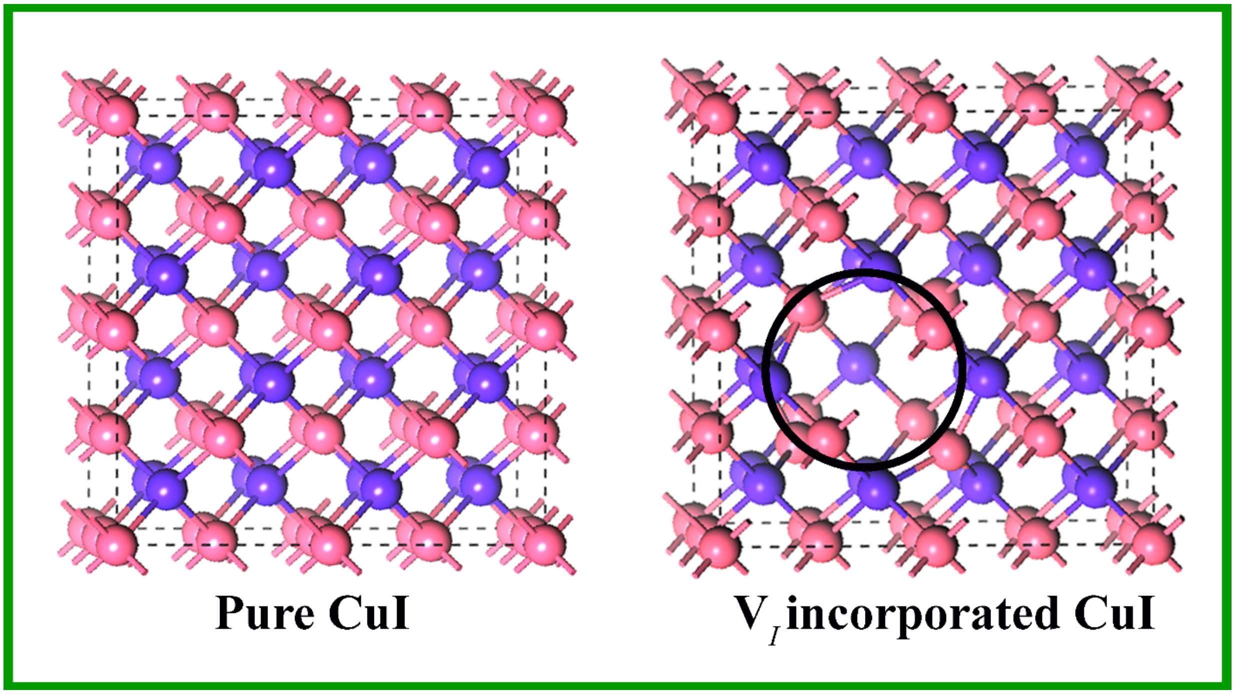

Figure S5: Demonstration of two 2×2×2 supercell structures containing 32 Cu atoms and 32 I atoms for the pure CuI while to investigate the effect of I vacancy (V_I), one I atom was removed from the optimized pure structure as indicated by the circle.

REFERENCES:

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