Electronic Supplementary Material (ESI) for Nanoscale.

Electron-beam irradiation induced transformation of $Cu_2(OH)_3NO_3$ nanoflakes into nanocrystalline CuO

S.K. Padhi[a,*], S.N. Gottapu[c], M. Ghanashyam Krishna [a,b]

[a]School of Physics and Advanced Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad 500046, India

[b]Centre for Advanced Studies in Electronics Science and Technology, School of Physics, University of Hyderabad, Prof C R Rao Road, Hyderabad 500046, Telangana, India

[c]School of Chemistry, University of Hyderabad, Hyderabad 500046, India

[*] Corresponding Author Email:spadhee1@gmail.com

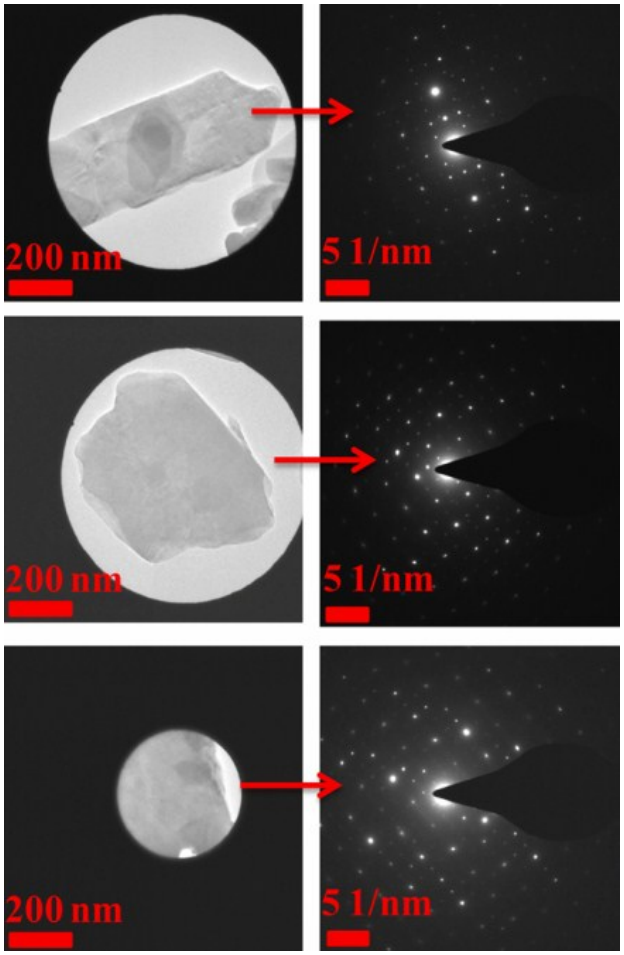

Fig. S1: SAED patterns recorded form individual CHN nanoflakes.

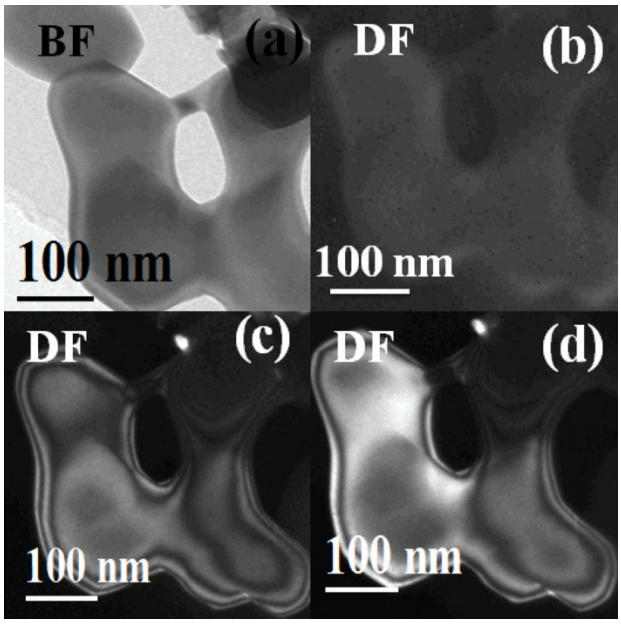

Fig. S2: (a) TEM BF and (b) TEM DF micrographs (gray appearance) of a nanoflake. Same flake with bright appearance can be seen in (c) and (d) micrographs with e-beam tilting. Reconfirms the step like edges (Figs. 1(a)-(b)) and single domain nature).

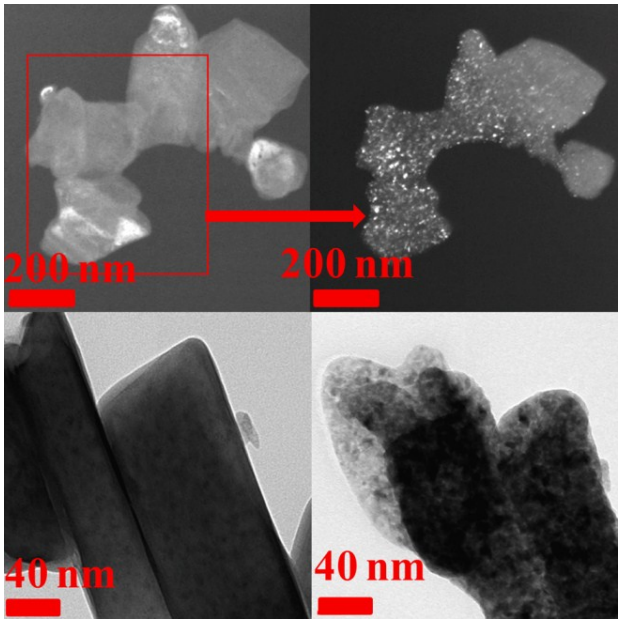

Fig. S3: Evolved fully grown structural (single domain to multi domain) and morphological features after 90 s of e-beam irradiation on two different shape CHN flakes.

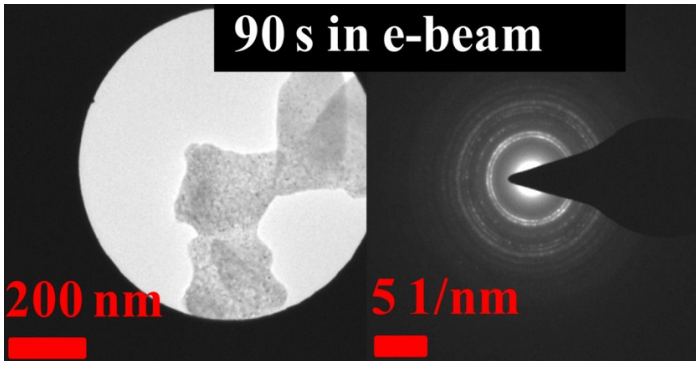

Fig. S4: SAED ring pattern after 90 s e-beam irradiation demonstrates fully grown nanocrystallites as the source of diffraction.

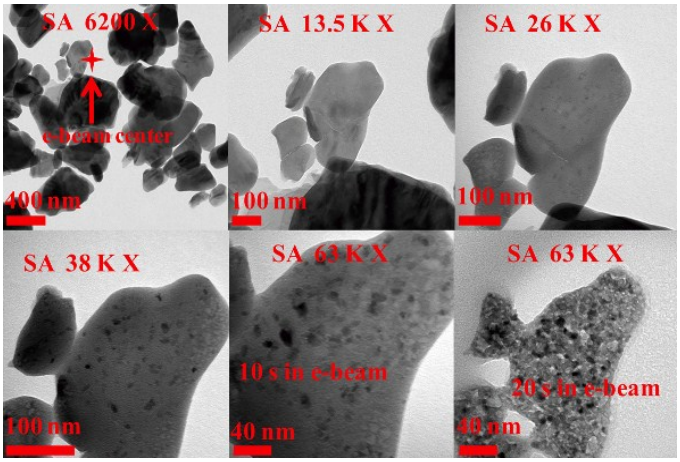

Fig. S5: TEM BF micrographs acquired with increasing magnification steps at 120 keV exposure.

These TEM BF micrographs recorded while operating at 120 keV, the gradual movement low magnification (LM) TEM BF to the high-resolution mode (LM→M→SA→Mh) demonstrate microstructural changes similar to 200 keV e-beam operation. The holding time is just 20 s for optimum crystal growth as 90 s at 200 keV exposure.

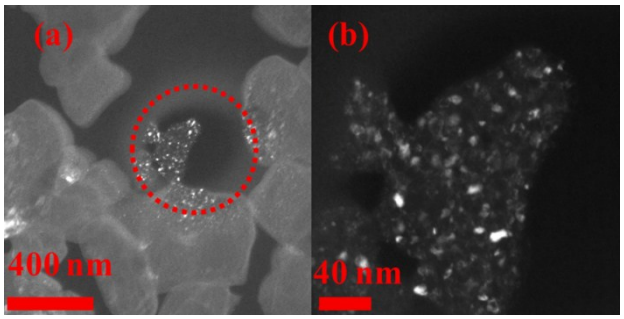

Fig. S6: TEM DF micrographs of (a) marked e-beam irradiated region, (b) well grown crystals after 20 s of e-beam exposure at 120 keV.

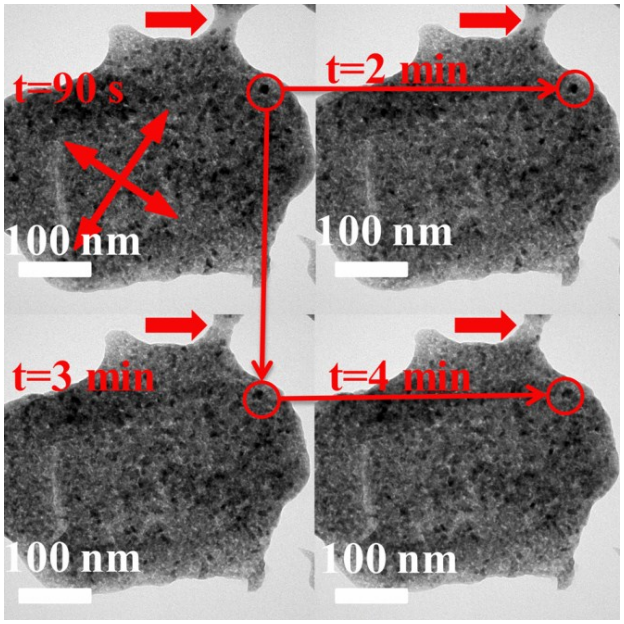

Fig. S7(a): TEM BF micrographs recorded after 90 s, 2 min, 3 min, and 4 min of e-beam exposure.

The TEM BF micrographs having longer exposure times (2 min, 3 min, and 4 min) does not show any further microstructural and morphological development or degradation. The marked arrow and circle highlight the intactness and no further growth or degradation of nanometric features even after longer exposure. A smaller flake above the larger can be distinguished from its step-like appearance even retains original physical morphology.

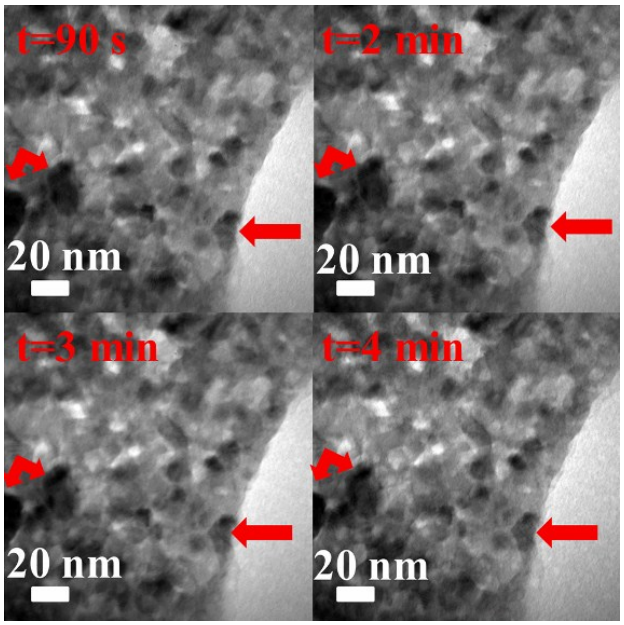

Fig. S7(b): TEM BF micrographs recorded at higher magnification after 90 s, 2 min, 3 min, and 4 min of e-beam exposure.

The TEM BF micrographs acquired at higher magnification with longer exposure times (2 min, 3 min, and 4 min) does not show any further nanoparticulate material nucleation, growth, and or parent matrix depletion. Thereby retaining grown particulate number density (number of dark contrast regions) as evolved after 90 s. The arrows in the presented micrographs depict the exact location of nanoparticulate mater, their shape, and subsequent neighbors after longer exposure.

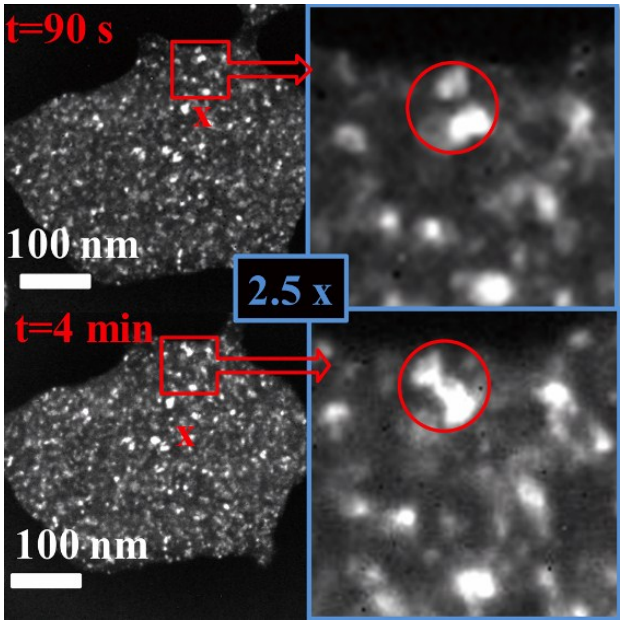

Fig. S7(c): TEM DF micrographs after 90 s and 4 min exposure.

The TEM DF micrographs acquired at 90 s, and 4 min were shown below. Both can be seen filled with nanometric grown crystals of merely same particle number density and are observed to be of the same size when compared. The TEM DF micrographs are in congruence with TEM BF micrographs, justifying overall CHN morphology, grown nanoparticulate mater intactness, and parent matrix depletion. A closer look at the zoomed section of both micrographs highlights the possibility of coalescence of adjacent crystals with longer exposure times. Therefore, grain coalescence leading to grain growth cannot be ruled out. The marked circular region in the 90 s zoomed region with two independent crystals can be seen to undergo coalescence after 4 min of e-beam exposure.

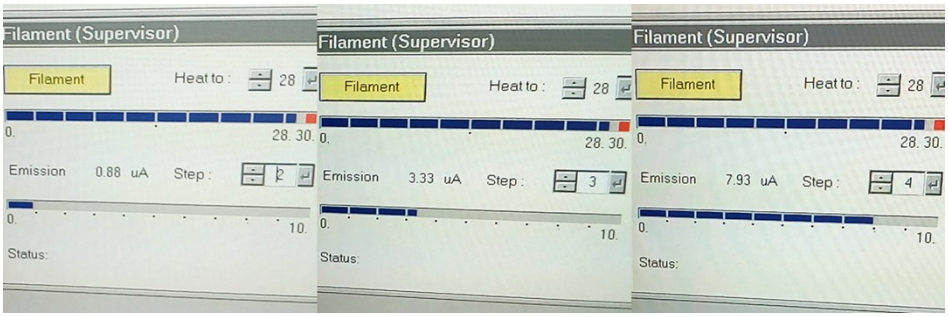

Fig. S8: Filament Supervisor with emission current steps.

The hydrated CHN samples are susceptible to damage under the e-beam irradiation conditions normally used for high-resolution imaging. The most preferable way to mitigate such problem is to use low e-beam emission current (TEM User Interface Filament Supervisor tip emission current steps). The emission (snapshot from TEM console screen) displayed below in Fig. S8. Step-2 filament emission current was used for the present irradiation studies. The CHN flakes micrographs with step-4 filament emission were shown in Fig. S9. Individual flakes outer periphery can be seen has a lighter contrast grown strip extending about ~30-35 nm and can be attributed to fluid outflow from hydrated CHN nanomaterials. An elongated CHN flake was exposed to e-beam at one of its end with step-4 beam emission for 10 s is shown in fig. S9 (a). This micrograph depicts the morphology variation away from the beam center. Adjacent to beam center particle expulsion, swelling, then bubbling along with grown particulate region (II), and finally only bubble formed region (I) can be seen.

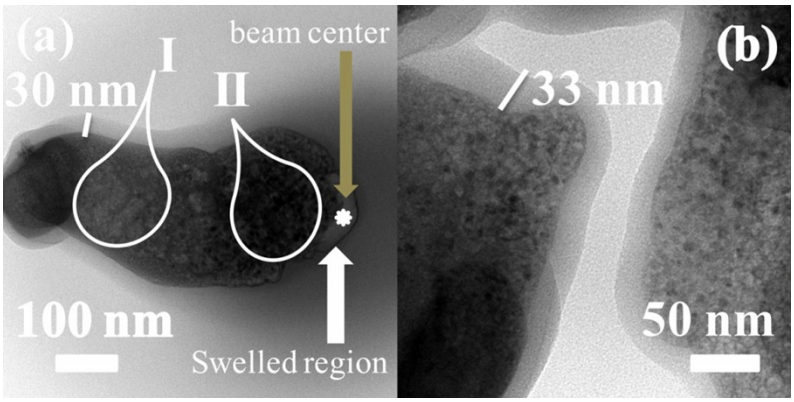

Fig. S9: Morphology of the CHN flakes exposed at step-4 filament emission. (a) CHN flake having e-beam center and exposed for 10 s, (b) CHN surfaces just approached in high-resolution mode, beam was stopped using beam stopper and imaged in TEM BF mode.