

## Supporting information

### High-conductive Cu-substituted brownmillerite with emergent 3-dimensional oxygen vacancy channels

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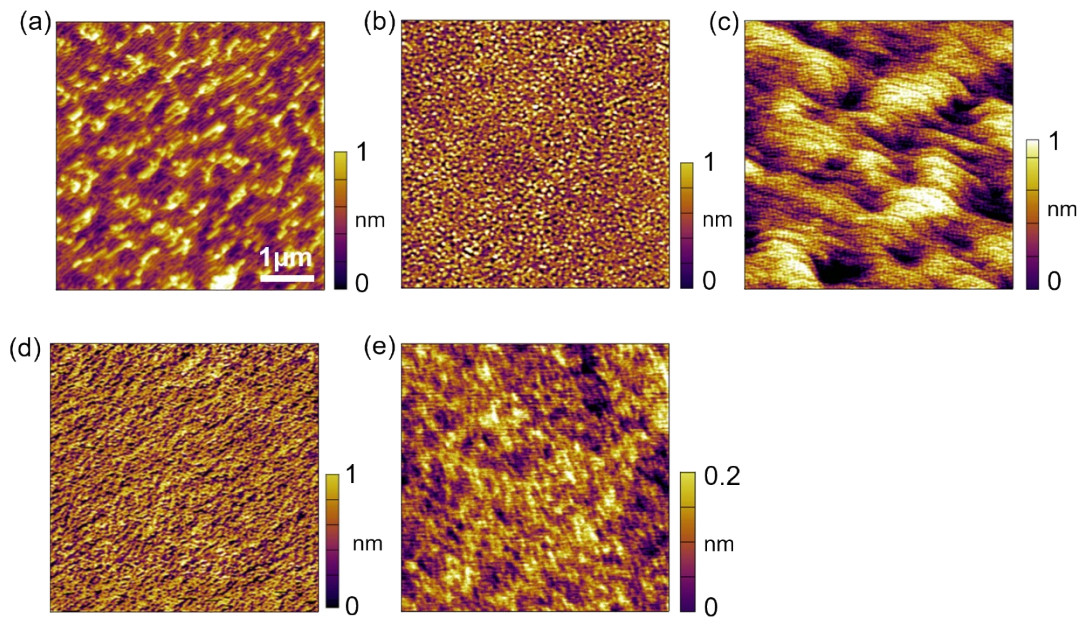
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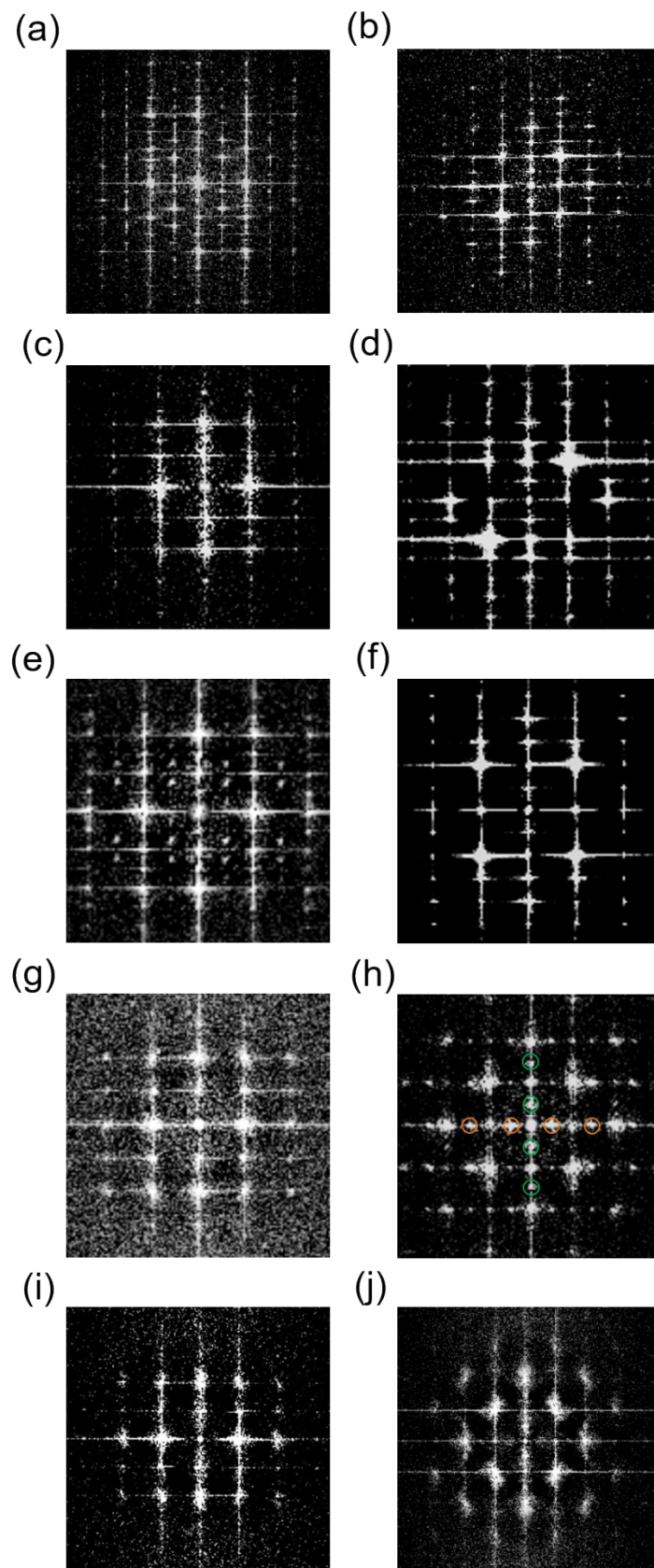
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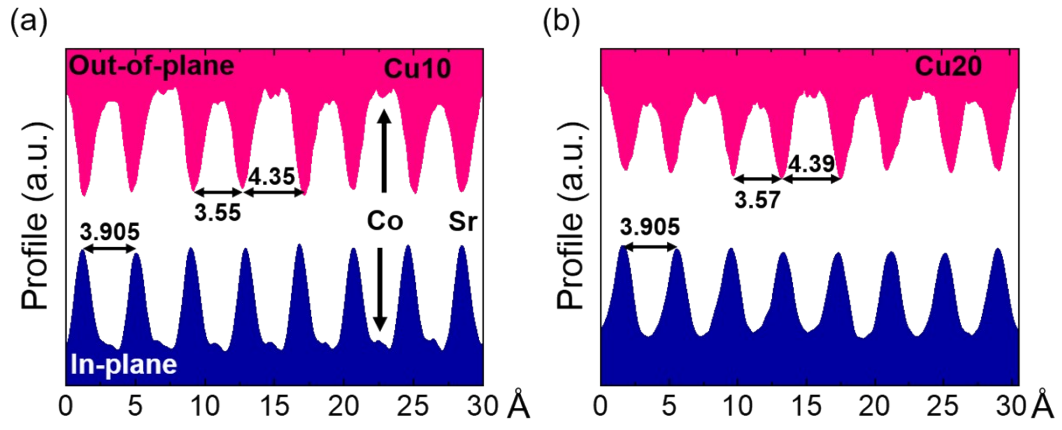
<sup>‡</sup>These authors contributed equally.



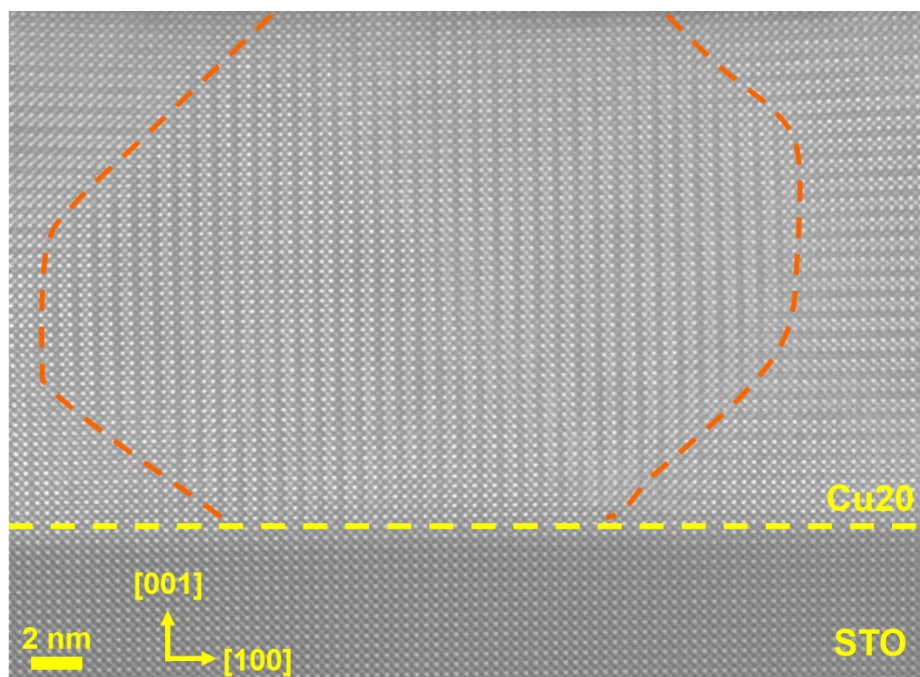
**Figure S1.** Surface topography of as-deposited (a) BM-SCO, (b) Cu10, (c) Cu20, (d) Cu33 and (e) Cu50.



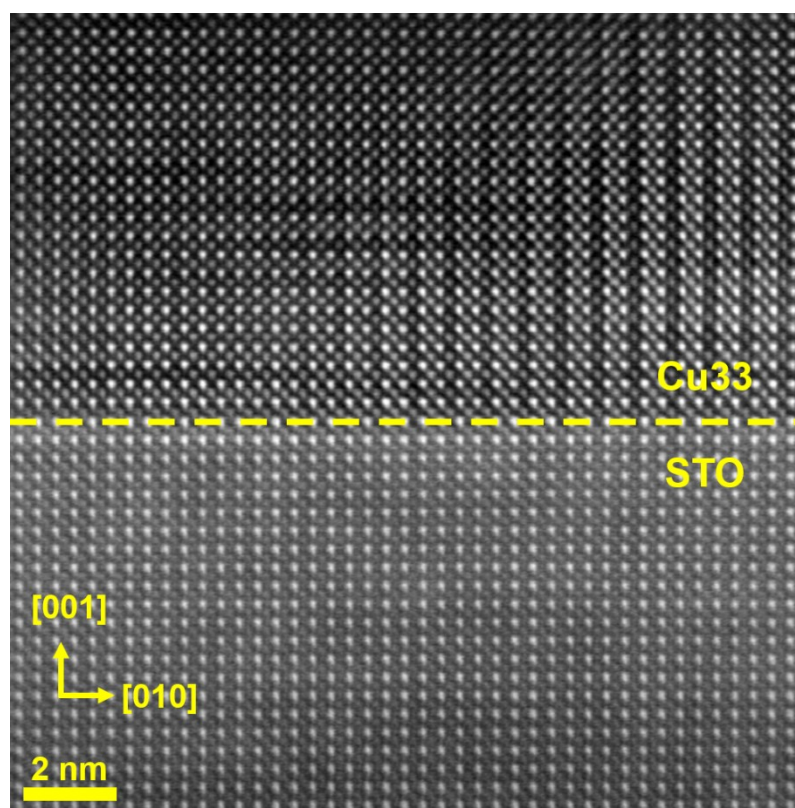
**Figure S2.** The fast Fourier transform (FFT) of the STEM images in **Figure 2a-j**.



**Figure S3.** The  $d_{\text{Sr-Sr}}$  for (a) Cu10 and (b) Cu20 along in-plane and out-of-plane direction.

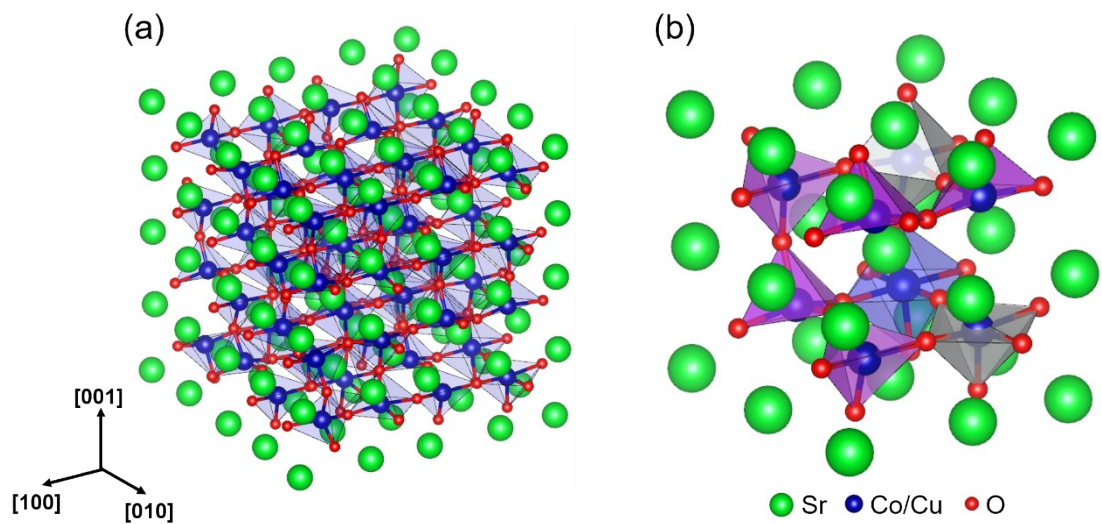


**Figure S4.** Cross-section of the Cu<sub>2</sub>O with both in-plane and out-of-plane arrangement of octahedra and tetrahedra layers.

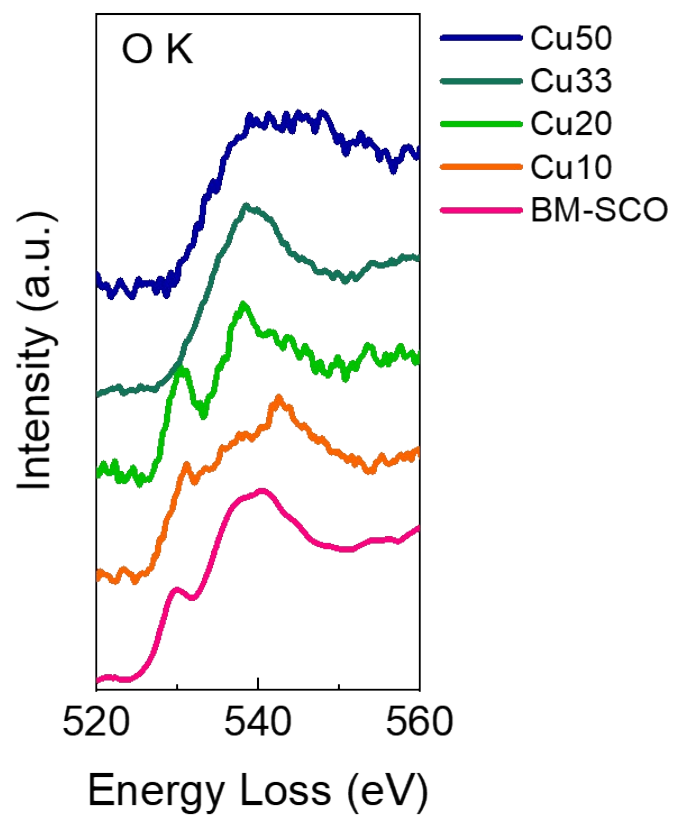


**Figure S5.** Cross-section of (010) plane of Cu33.



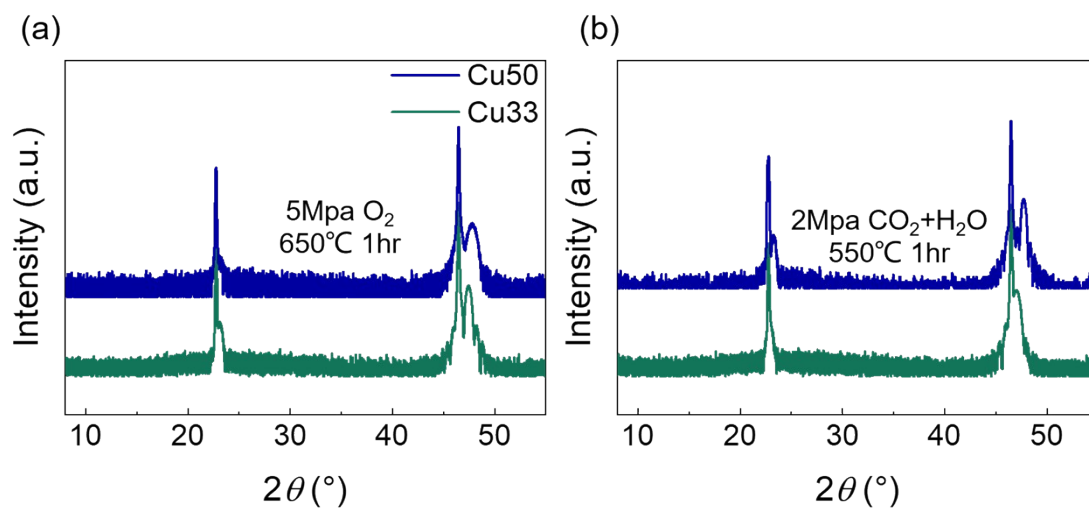


**Figure S6.** (a) Atomic structure for the novel 3D  $V_O^{\bullet\bullet}$  structure of Cu<sub>33</sub>; (b) shows the magnified view of the structure, which is one-eighth the size of that in (a).

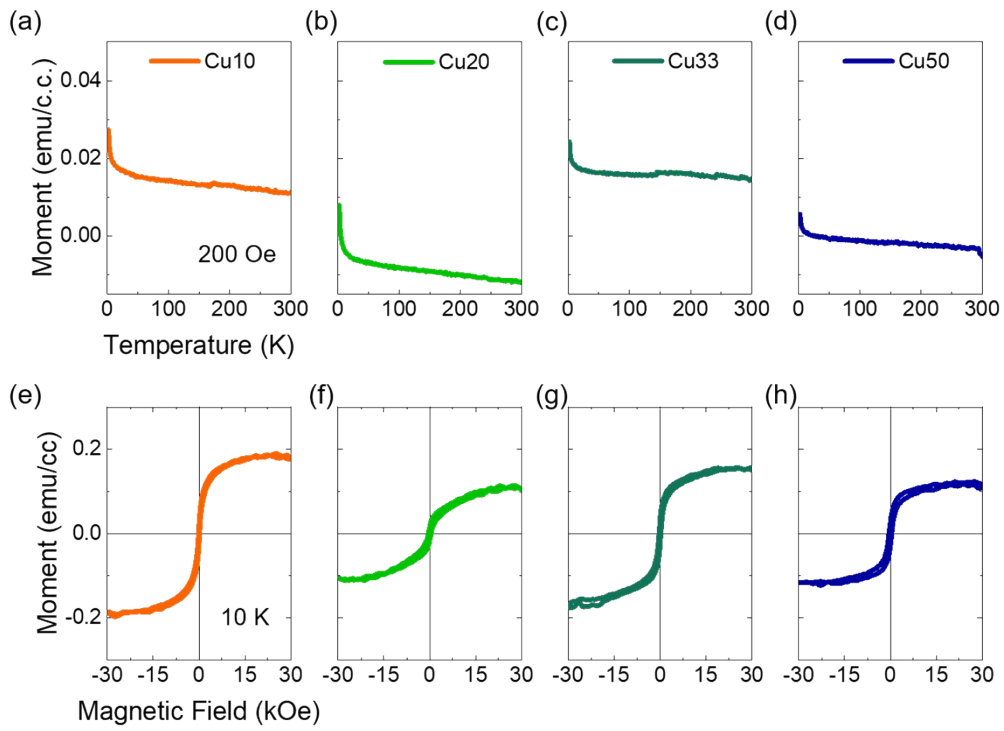


**Figure S7.** Electron energy-loss spectra (EELS) of the O *K*-edges for Cu-doped SCOs. The pink line presenting the data of BM-SCO was quoted from the work of B. Cui, et al.<sup>1</sup>

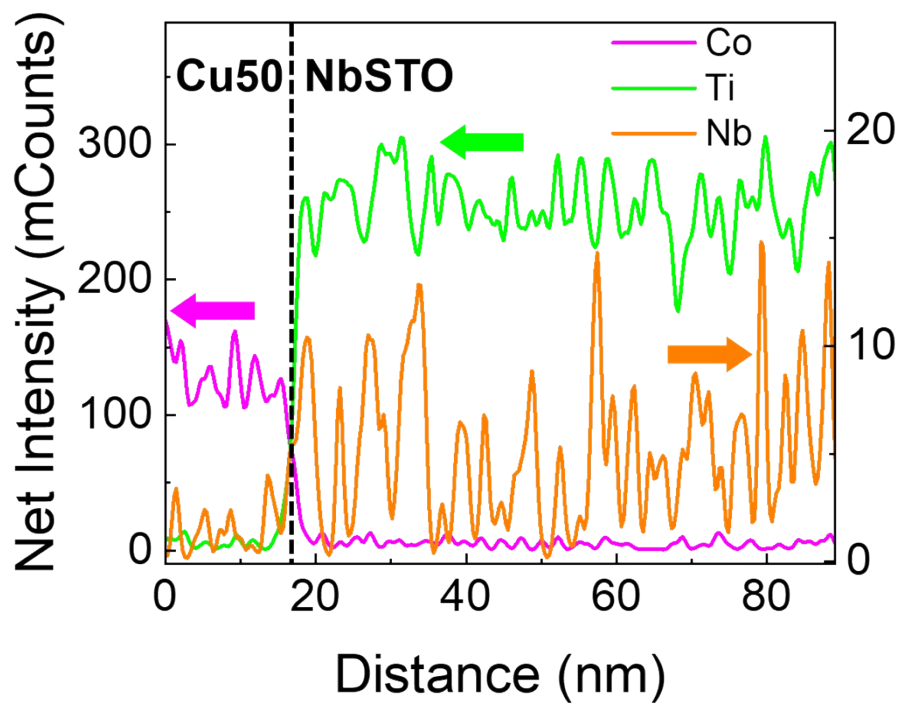




**Figure S8.**  $\theta$ - $2\theta$  scans for Cu33 and Cu50 after annealing under (a) high oxygen and (b) water vapor pressure atmosphere for 1hr.



**Figure S9.**  $M-T$  curves of (a) Cu10, (b) Cu20, (c) Cu33, and (d) Cu50 with the magnetic field of 200 Oe; the corresponding  $M-H$  loops measured at 10 K are shown in (e), (f), (g), and (h), respectively.



**Figure S10.** EDS intensity of Co, Ti and Nb across the film/substrate interface.

## References

1. B. Cui, P. Werner, T. Ma, X. Zhong, Z. Wang, J. M. Taylor, Y. Zhuang and S. S. P. Parkin, *Nat. Commun.*, 2018, **9**, 3055.