The DFT calculations are performed using the Vienna ab-initio simulation package (VASP) [1–4] with the PW91 generalized gradient approximation (GGA) [5] and projector augmented wave (PAW) potentials [6,7]. Our previous works have confirmed that a cutoff energy of 380 eV is sufficient to give a well converged system energy [8,9]. We model the growth of wetting Cu_2O layers on top of a three-atomic-layer Cu substrate. To be consistent with the (5 ×6) CSL Cu_2O-Cu interface model, the Cu substrate is modeled by a periodically repeated slab with a lateral dimension of 6 Cu lattice constants, whereas the Cu_2O wetting layer growing atop has a lateral dimension of 5 Cu_2O lattice constants. The bottom layer of the Cu substrate is kept fixed throughout the relaxation. In the surface normal direction, successive slabs are separated by a vacuum region of at least 11 Å. We used slabs with 1, 2, 3 and 4 Cu_2O wetting layers. For the largest system we had 416 Cu atoms and 100 O atoms. Considering the large number of atoms, we sampled the Brillouin zone only at the Γ-point for all slabs to have consistent results. This should be adequate because we use a larger surface super cell. Electron smearing is carried out following the Methfessel-Paxton technique [10] with N=1 and σ=0.2. The optimized geometries for the Cu_2O/Cu structures are shown in Fig. s1.

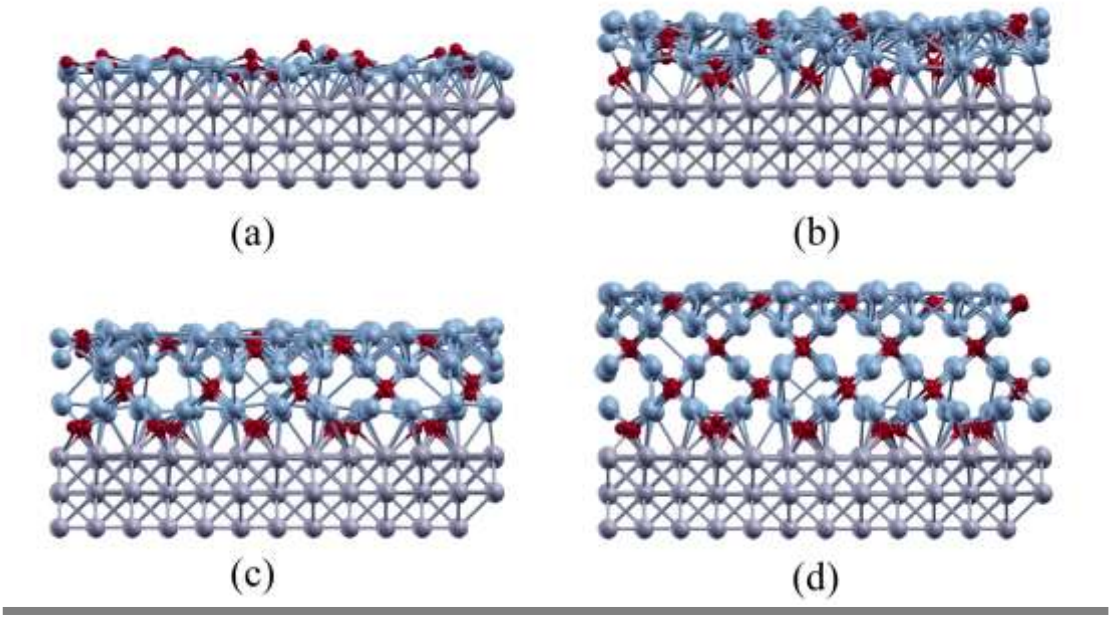

Fig. s1: Minimum-energy structures for (a) one-atomic-layer thick Cu_2O wetting layer, (b) two-atomic-layer thick Cu_2O wetting layer, (c) three-atomic-layer thick Cu_2O wetting layer and (d) four-atomic-layer thick Cu_2O wetting layer. Gray balls depict the Cu atom in the substrate, blue balls the Cu atoms in Cu_2O wetting layer and red balls oxygen atoms.

The interface energy E_{int} is calculated using the following equation

$$E_{int} = E_{tot} - N_{Cu}E_{Cu} - N_{Cu_2O}E_{Cu_2O}$$

where E_{tot} is the total system energy, E_{Cu} is the energy of bulk Cu unit cell, and E_{Cu_2O} is the energy of Cu_2O unit cell. N_{Cu} is the number of the Cu unit cell in the system and N_{Cu_2O} is the number of Cu_2O unit cell in the wetting layer. Using this notation, a positive value of E_{int} indicates that the surface is thermodynamically unstable towards dissociation into bulk Cu and Cu_2O.

References:

[1] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[2] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[3] G. Kresse, J. Furthmüller, Comput. Mat. Sci. 6 (1996) 15.
[4] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[5] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[6] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[7] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[8] G. Zhou, L. Luo, L. Li, J. Ciston, E. Stach, J.C. Yang, Phys. Rev. Lett. 109 (2012) 235502.
[9] L. Li, G. Zhou, Surf. Sci. 615 (2013) 57.
[10] M. Methfessel, A. Paxton, Phys. Rev. B 40 (1989) 3616.