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$_2$O layers on top of a three-atomic-layer Cu substrate. To be consistent with the (5 x 6) CSL Cu$_2$O-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$_2$O wetting layer growing atop has a lateral dimension of 5 Cu$_2$O 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$_2$O 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 $\Gamma$-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 $\sigma=0.2$. The optimized geometries for the Cu$_2$O/Cu structures are shown in Fig. s1.

![Fig. s1: Minimum-energy structures](image)

(a) (b) (c) (d)

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

$$E_{\text{int}} = E_{\text{tot}} - N_{\text{Cu}} E_{\text{Cu}} - N_{\text{Cu}_2\text{O}} E_{\text{Cu}_2\text{O}}$$

where $E_{\text{tot}}$ is the total system energy, $E_{\text{Cu}}$ is the energy of bulk Cu unit cell, and $E_{\text{Cu}_2\text{O}}$ is the energy of Cu$_2$O unit cell. $N_{\text{Cu}}$ is the number of the Cu unit cell in the system and $N_{\text{Cu}_2\text{O}}$ is the number of Cu$_2$O unit cell in the wetting layer. Using this notation, a positive value of $E_{\text{int}}$ indicates that the surface is thermodynamically unstable towards dissociation into bulk Cu and Cu$_2$O.
References: