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A DFT study of adsorption of imidazole, triazole, and tetrazole on oxidized copper surfaces: $Cu_2O(111)$ and $Cu_2O(111)$-w/o-Cu^{CUS}†

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Supporting Information

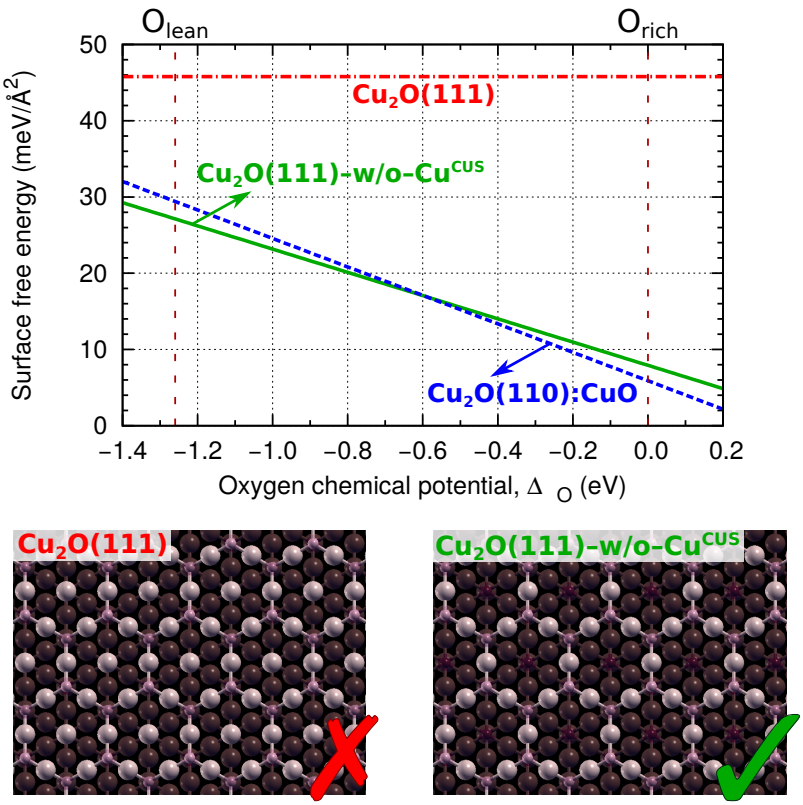

Fig. S1 Top: calculated surface free energies for stoichiometric $Cu_2O(111)$ and non-stoichiometric $Cu_2O(111)$-w/o-Cu^{CUS} and $Cu_2O(110)$:CuO surfaces as a function of oxygen chemical potential. The two non-stoichiometric surfaces are considerably more stable than the $Cu_2O(111)$. Current results are in good agreement with those published previously by Soon et al.[1] Bottom: top view of $Cu_2O(111)$ and $Cu_2O(111)$-w/o-Cu^{CUS} surfaces; the surface O–Cu–O trilayer is emphasized with pale color.

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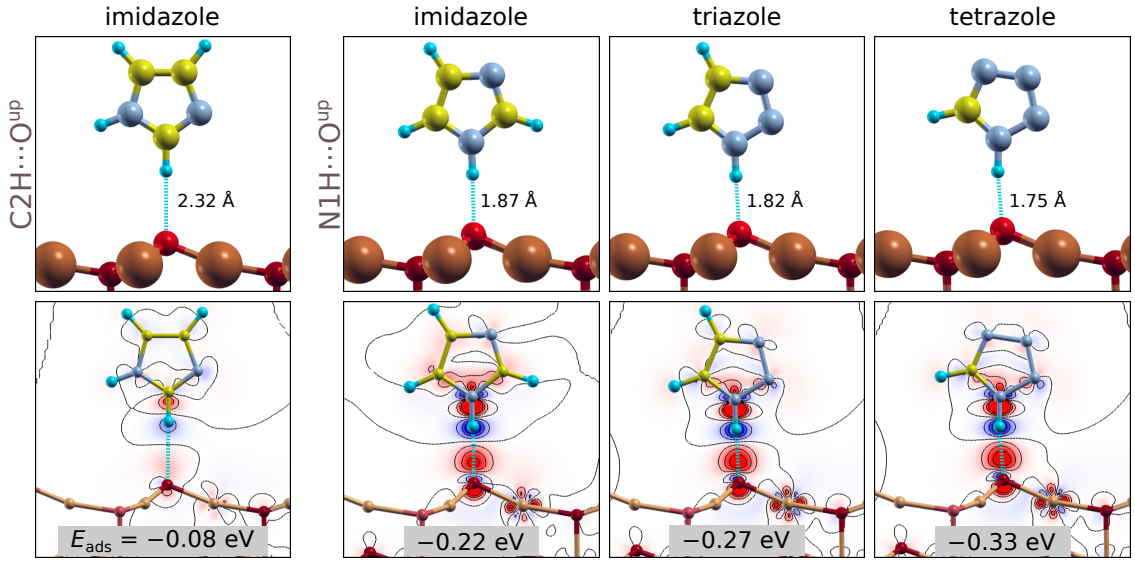

Fig. S2 Top panels display the optimized structures of imidazole, triazole, and tetrazole bonded to O^{up} site on $Cu_2O(111)$-w/o-Cu^{CUS} via the *top-down* hydrogen bond. Left panel shows the C2H$\cdots$$O^{up}$ bonding of imidazole, whereas the three panels on the right display the N1H$\cdots$$O^{up}$ bonding of each molecule. Bottom panels display the electron charge density difference, $\Delta\rho(\mathbf{r})$, of these structures; seven contours are drawn in linear scale from -0.006 to $+0.006$ e/a_0^3 and electron charge flows from blue to red regions. A larger charge redistribution of the N1H$\cdots$$O^{up}$ bonds compared to the C2H$\cdots$$O^{up}$ bond clearly indicates that the former bonds are stronger than the latter bond, which is consistent with the respective shorter bond distances as well as stronger interaction energies, which are also stated.

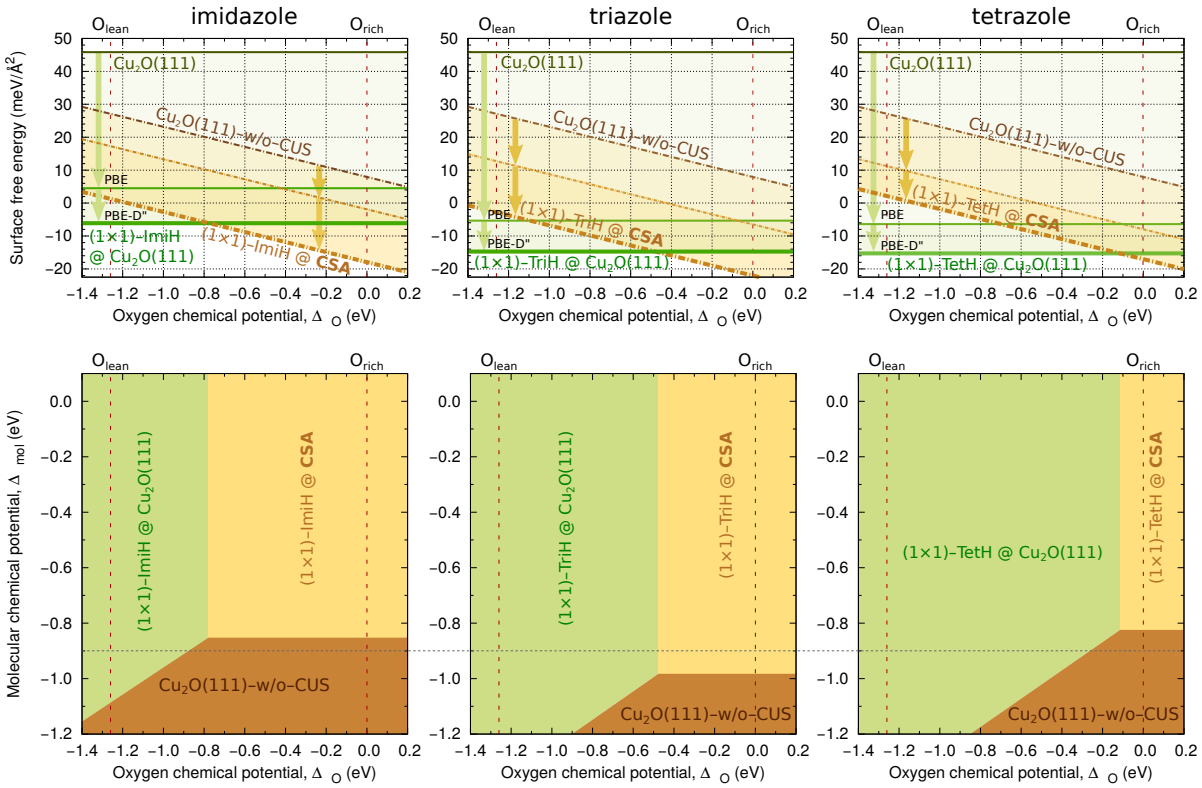

Fig. S3 Adsorption phase diagrams of imidazole (left), triazole (middle), and tetrazole (right) on considered Cu_2O surfaces as calculated by the PBE-D" functional. Top row: surface free energies, γ_{surf}, of $Cu_2O(111)$ and $Cu_2O(111)$-w/o-Cu^{CUS} and their stabilization due to high coverage molecular adsorption. For a given surface the upper γ_{surf} line corresponds to a bare surface and the middle and bottom lines to a molecularly covered surface, *i.e.*, middle line corresponds to PBE and bottom line to PBE-D" calculated stabilization; this stabilization is also indicated by two consecutive vertical arrows (the bottom one represents the stabilization due to dispersion correction). Bottom row: two dimensional phase diagrams as a function of molecular and oxygen chemical potentials. Beware that $\Delta\mu_{mol}$ range is expanded downward with respect to the Fig. 5 in the manuscript (thin dashed line indicates the lower bound of $\Delta\mu_{mol}$ range in Fig. 5).

References

1 A. Soon, M. Todorova, B. Delley and C. Stampfl, *Phys. Rev. B*, 2007, **75**, 125420.