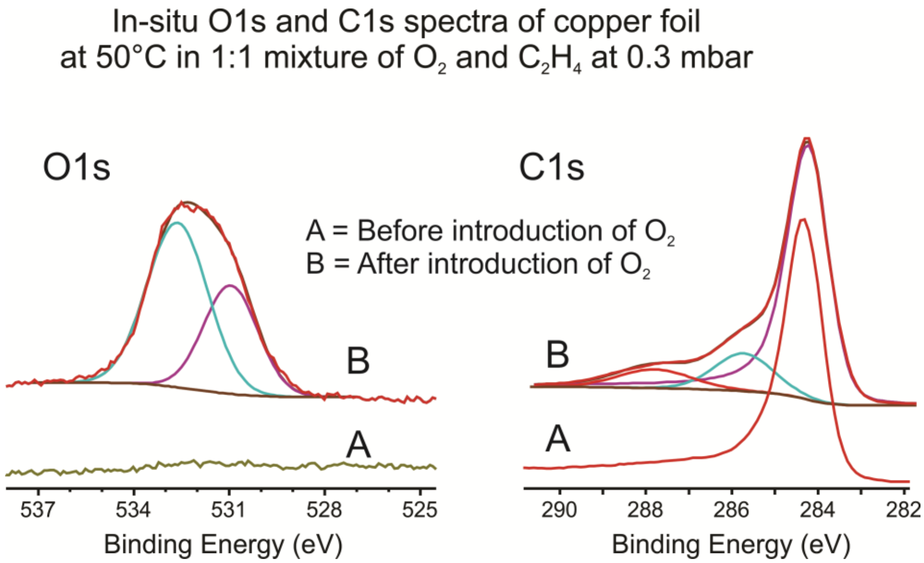
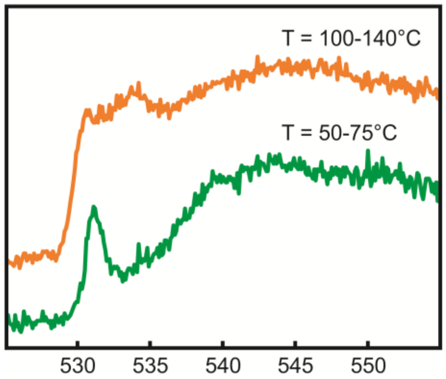
Supplementary Information

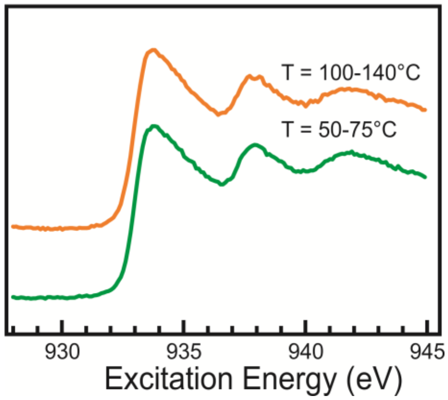


In-situ O1s and C1s spectra of copper foil at 50°C in 1:1 mixture of O_2 and C_2H_4 at 0.3 mbar

Figure S1 – O1s and C1s spectra measure from a Cu foil at 50°C in (A) 0.3 mbar of C_2H_4 and (B) 0.3 mbar of 1:1 O_2+C_2H_4



(a) O K-edge during oxidation



(b) Cu L_3-edge during oxidation

Figure S2 – O K-edge and Cu L_3-edge of a copper foil during a temperature ramp in a 1:1 mixture of O_2 and C_2H_4 at 0.5 mbar.

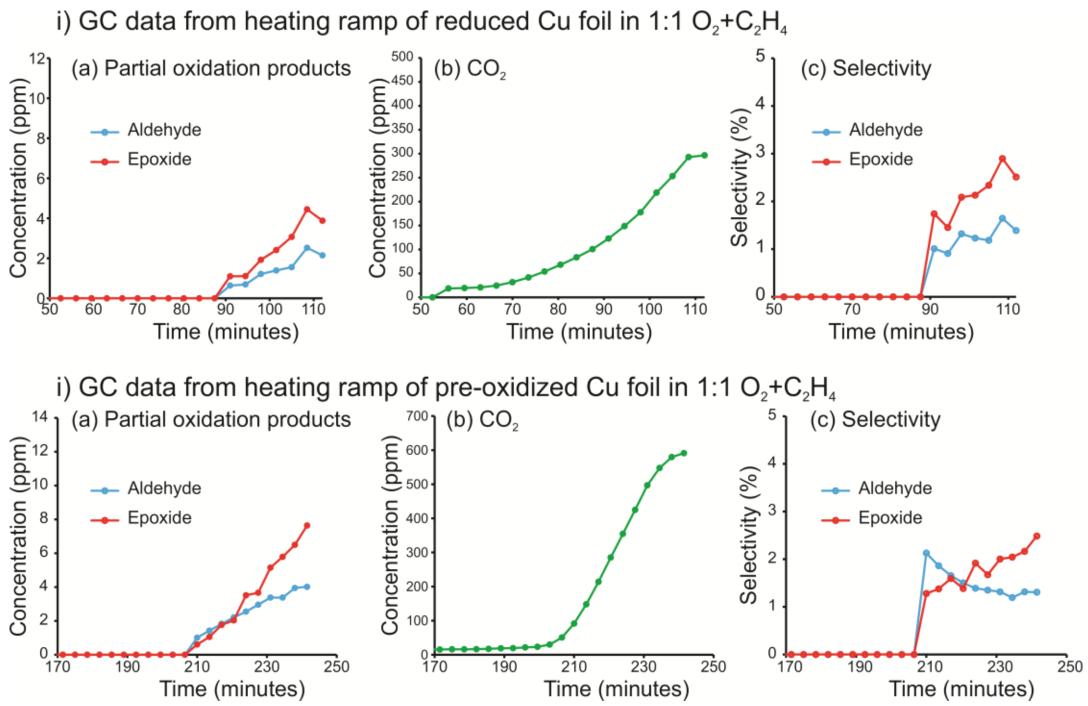


Figure S3 – GC data of copper foil during a heating ramp from 50°C to 400°C in a 1:1 mixture of O_2+C_2H_4 at 0.3 mbar, starting from i) a reduced metal foil and ii) a pre-oxidized foil. (a) ethylene oxide and ethyl aldehyde production, (b) CO_2 production and (c) ethylene oxide and ethyl aldehyde selectivity

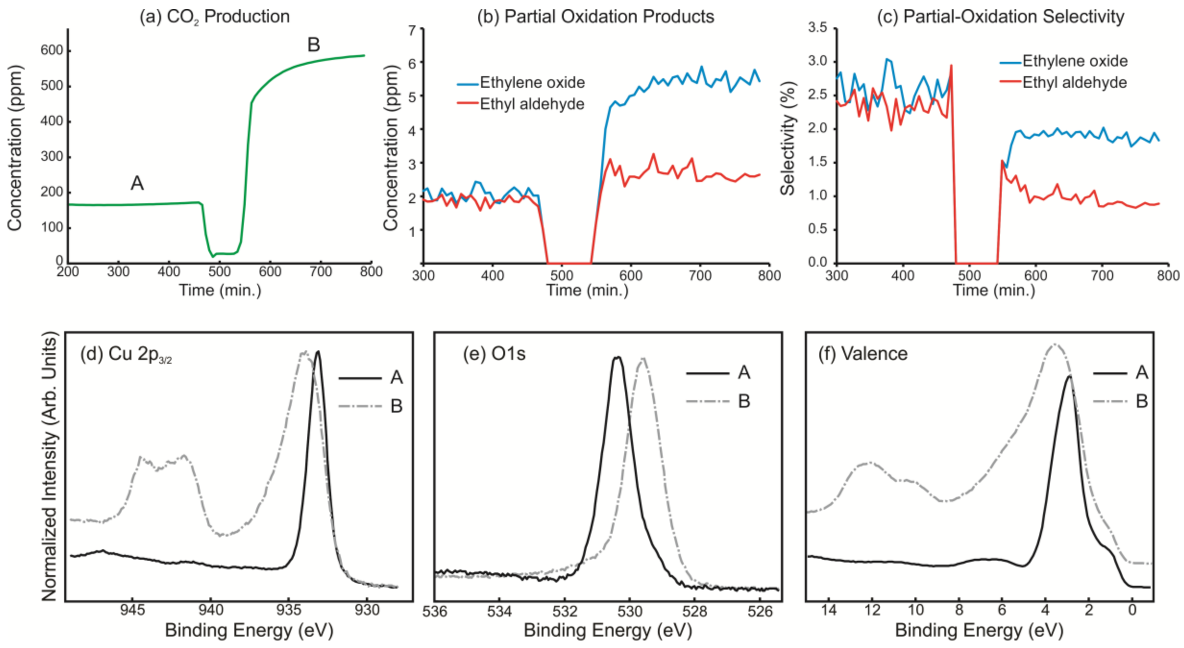


Figure S4 – GC data of (a) CO_2 production, (b) ethylene oxide and ethyl aldehyde production, and (c) ethylene oxide and ethyl aldehyde selectivity from an oxidized copper foil in a 2:1 mixture of O_2 and C_2H_4, at 0.3 mabr total pressure and at 350°C. The dip in activity from times ca. 450 to 550 minutes is due to a cooling/heating ramp. (d) $Cu2p_{3/2}$, (e) O1s and (f) valence spectra of the surface of the foil at time points labelled A and B in (a).

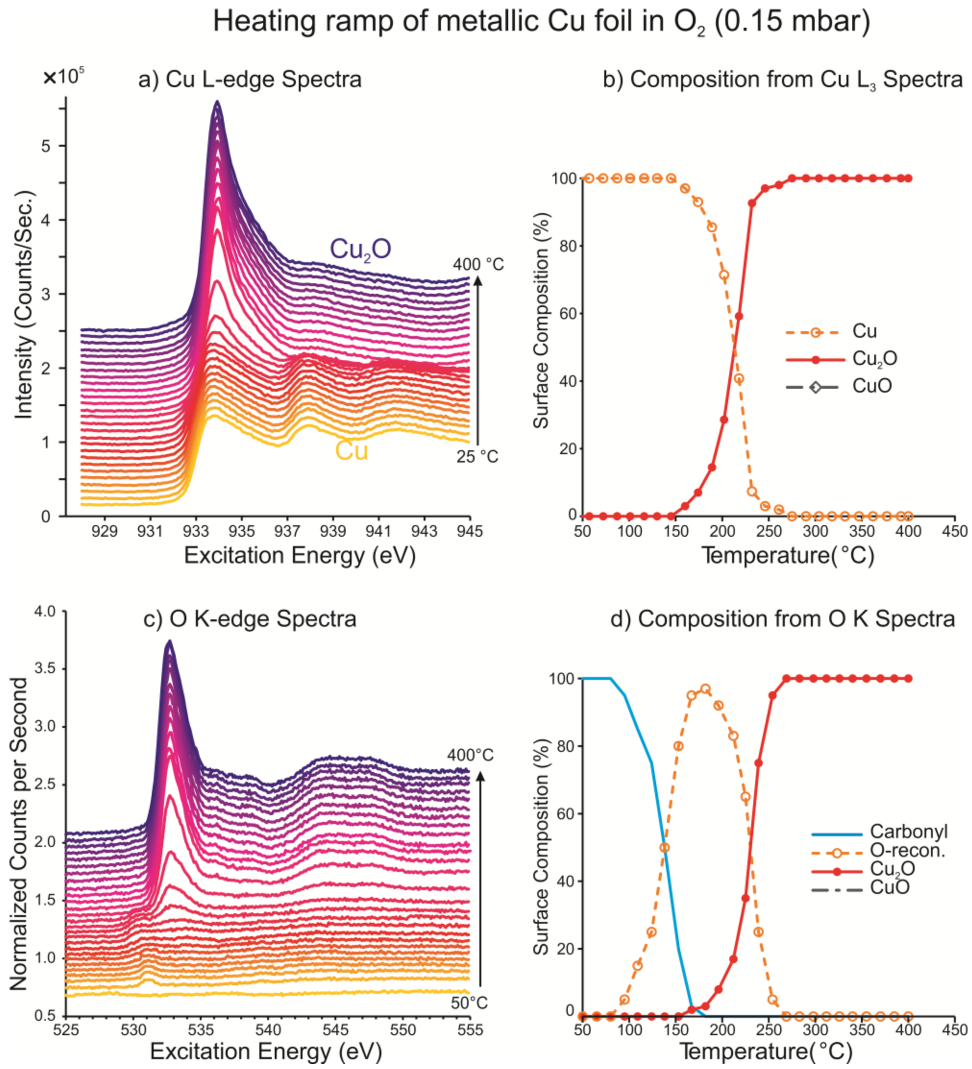
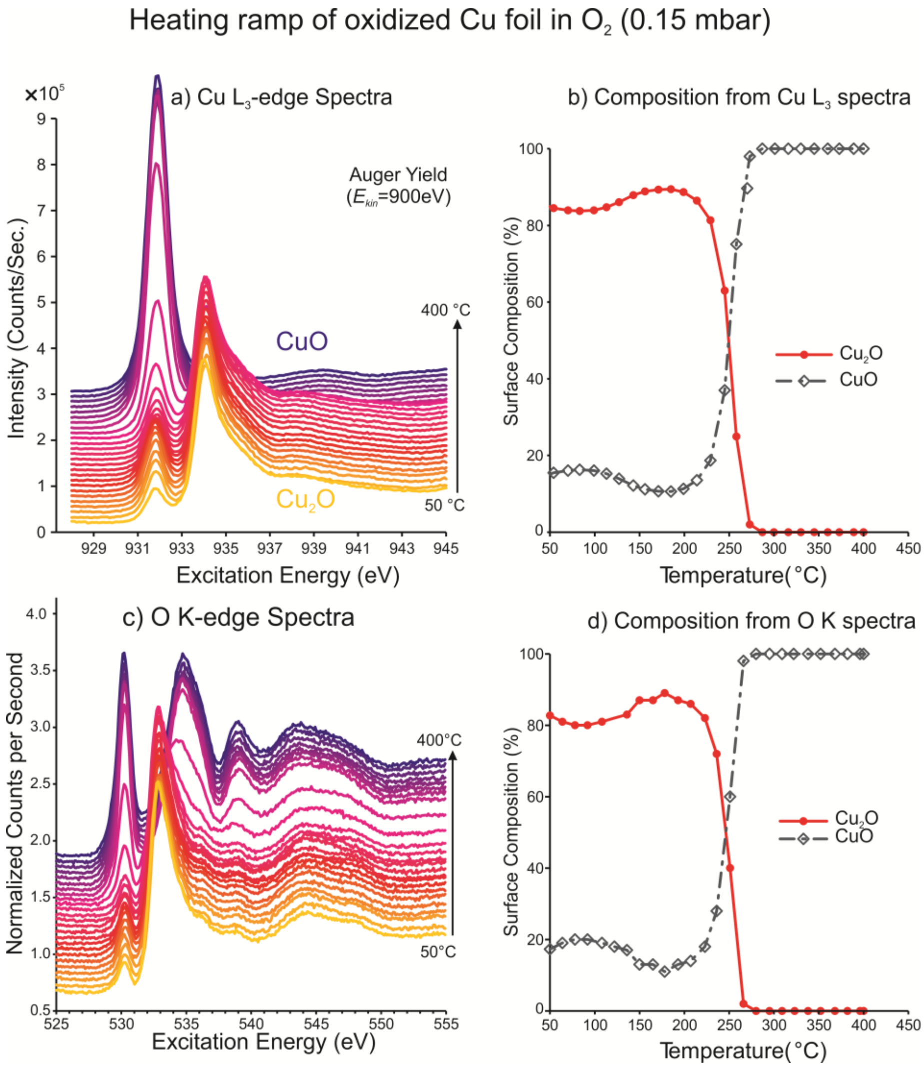


Figure S5 – (a) Cu L_3-edge spectra, (b) Cu L_3 fitting, (c) O K-edge spectra and (d) O K-edge fitting of a reduced copper foil during a heating ramp in 0.15 mbar O_2 (i.e. first heating ramp).



Heating ramp of oxidized Cu foil in O_2 (0.15 mbar)

a) Cu L_3-edge Spectra

b) Composition from Cu L_3 spectra

c) O K-edge Spectra

d) Composition from O K spectra

Figure S6 – (a) Cu L_3-edge spectra, (b) Cu L_3 fitting, (c) O K-edge spectra and (d) O K-edge fitting of a pre-oxidized copper foil during a heating ramp in 0.15 mbar O_2 (i.e. second heating ramp).

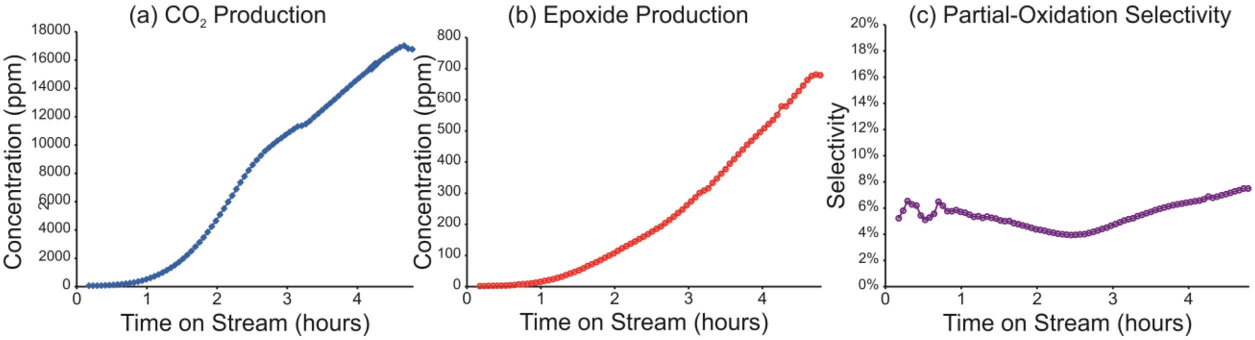


Figure S7 – Gas chromatography data from a silver foam in 1:1 O_2+C_2H_4 during a temperature ramp from 80°C to 380°C at 0.3 mbar.

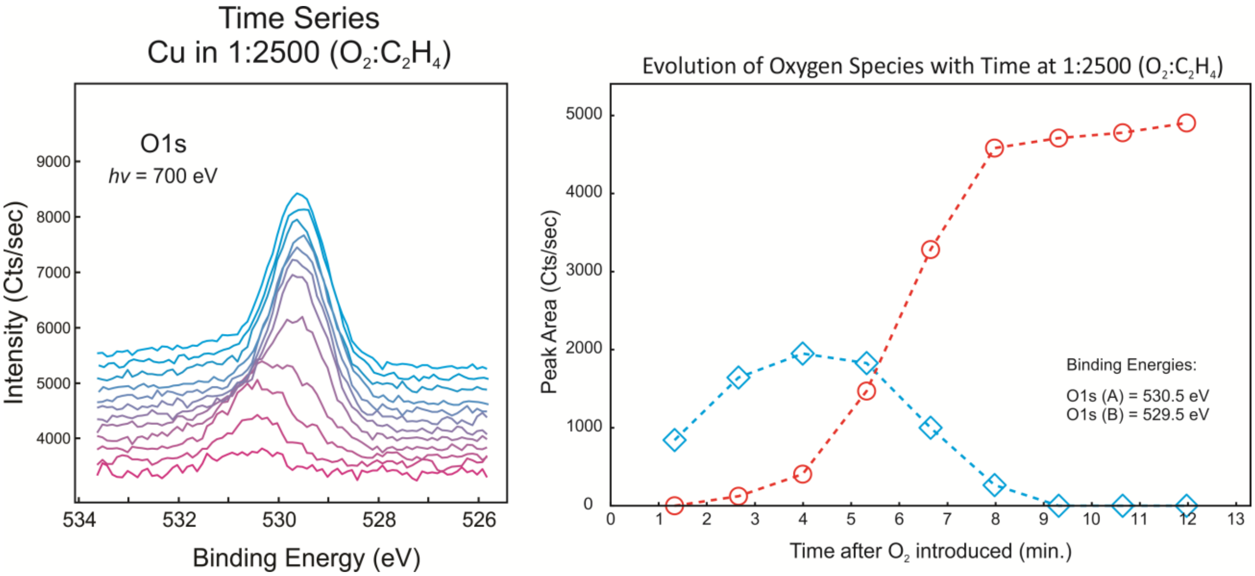


Figure S8 – (a) Time resolved O1s spectra of a reduced copper foil in a 1:2500 mixture of O_2:C_2H_4 at 350°C. (b) O1s peak composition versus time for the spectra in (a), using two peaks to fit the spectra, one at 530.5 eV and one at 529.5 eV.

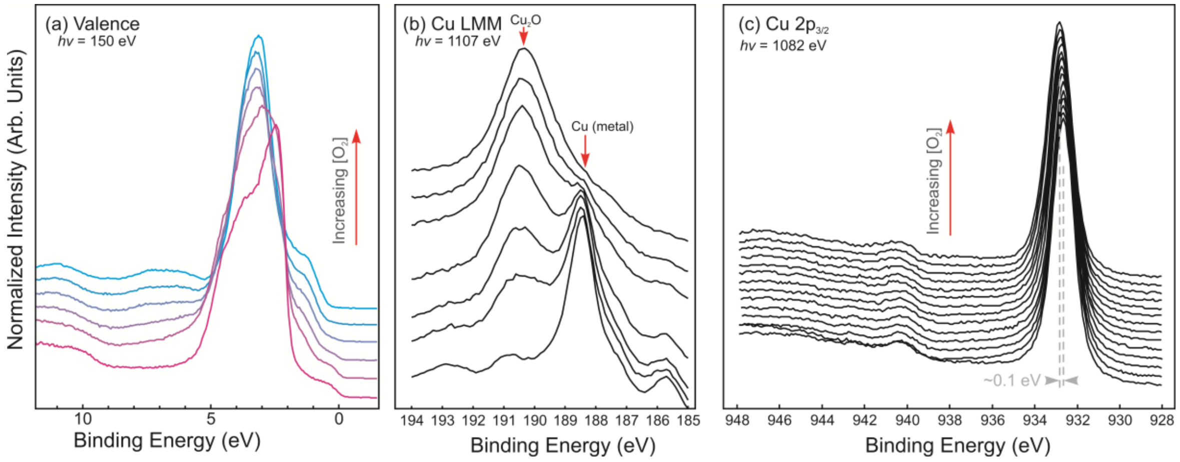


Figure S9 – (a) Valence spectra, (b) Cu LMM Auger spectra and (c) Cu $2p_{3/2}$ spectra of a reduced copper foil in a gas atmosphere (0.3 mbar) of O_2 and C_2H_4 ranging in composition from 1:2500 to 64:2500 (O_2:C_2H_4) at 350°C.

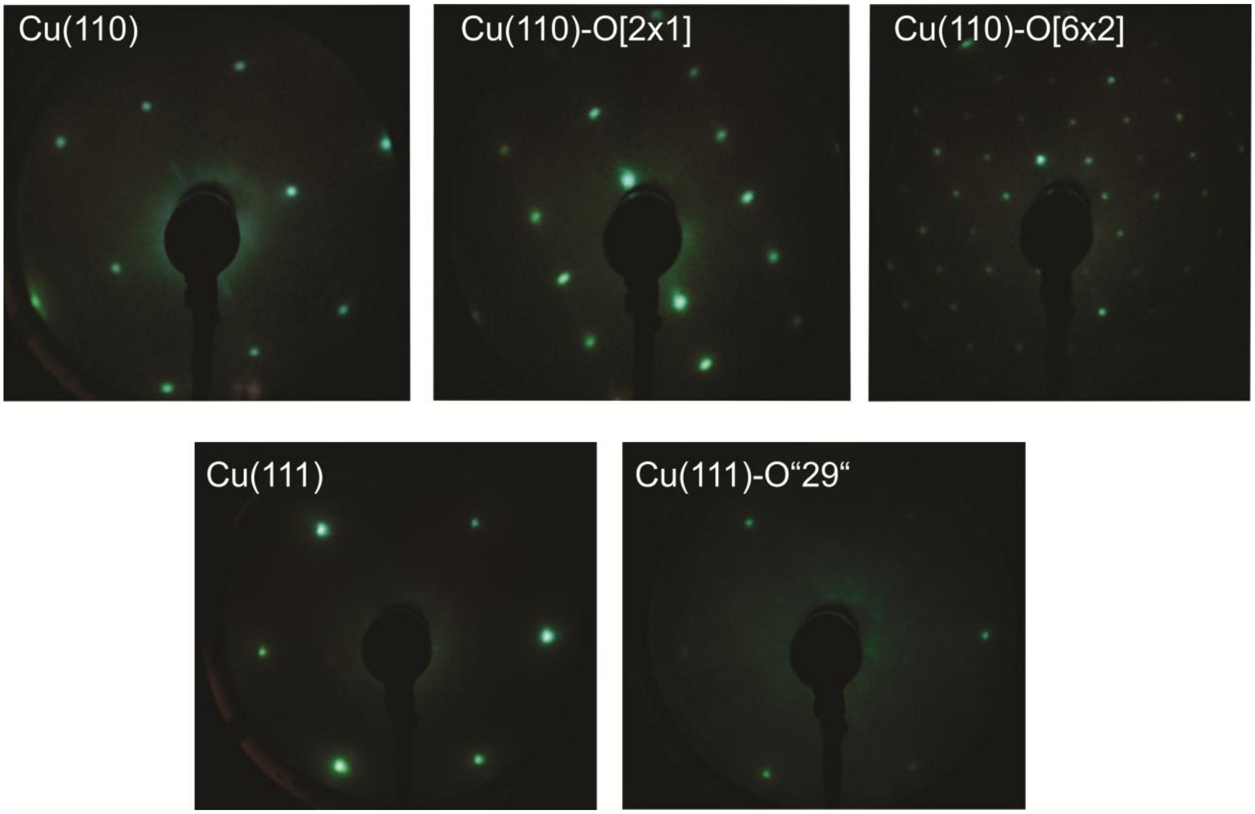
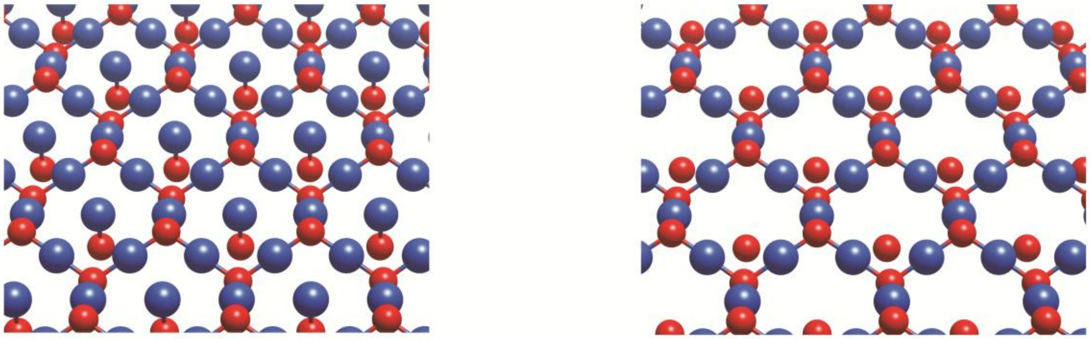
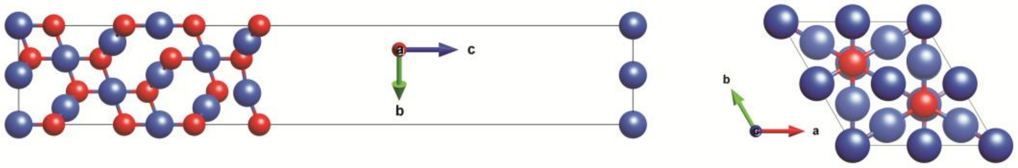


Figure S10 – LEED patterns of clean and O-terminated copper single crystals.



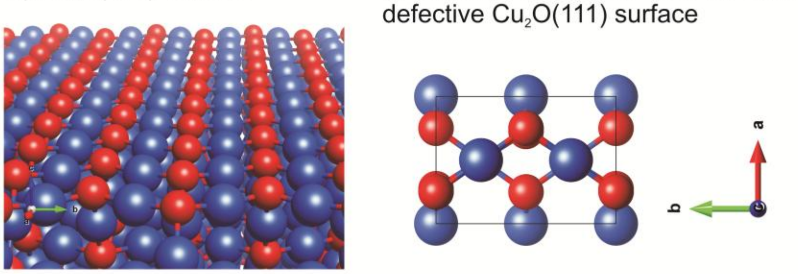
a) First three layers of perfect $Cu_2O(111)$ surface

b) First three layers of defective $Cu_2O(111)$ surface



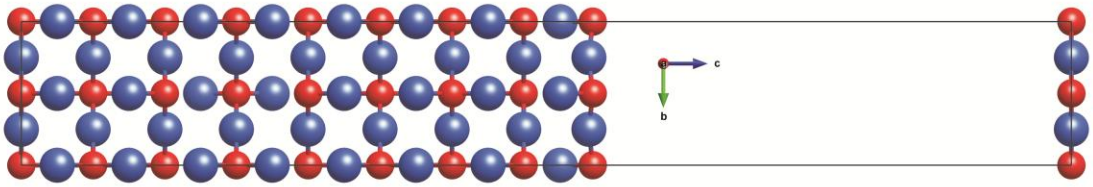
c) Side view of unit cell used for calculations of defective $Cu_2O(111)$ surface

d) Top view of unit cell used for calculations of defective $Cu_2O(111)$ surface

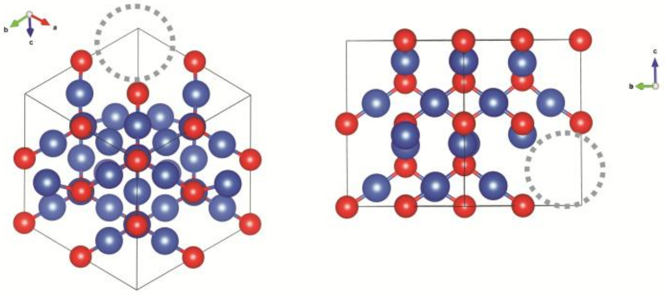


e) $Cu_2O(110)$ surface

g) Top view of unit cell used for calculations of defective $Cu_2O(111)$ surface

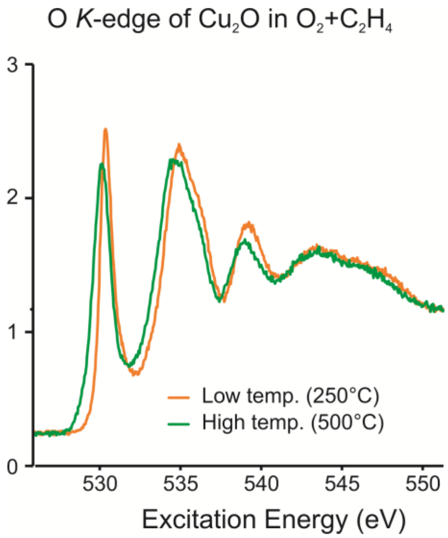


f) Side view of unit cell used for calculations of defective $Cu_2O(111)$ surface



h) Two views of unit cell used for calculations of bulk stoichiometric vacancy in $Cu_2O(111)$. Vacancy highlighted with dashed circle

Figure S11



O K-edge of Cu_2O in O_2+C_2H_4
3
2
1
0
530
535
540
545
550
Excitation Energy (eV)
Low temp. (250°C)
High temp. (500°C)

Figure S12