

Supporting Information

Effect of Water Vapor on Oxidation Processes of the Cu(111) Surface and Sub-Layer

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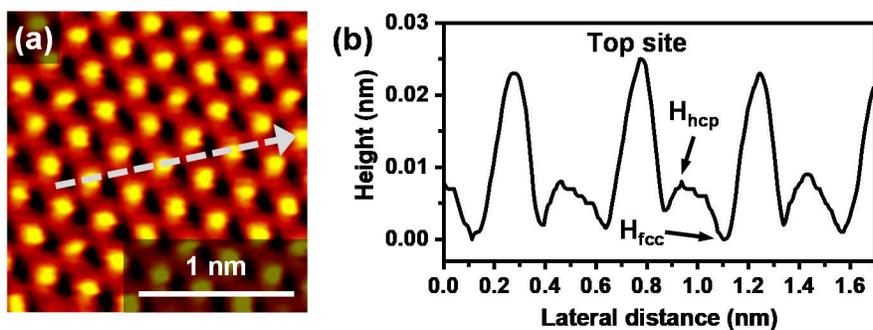


Figure S1. (a) Atomic-resolved NAP-STM image of the Cu(111) at UHV. (b) Representative height profile of the Cu(111) surface.

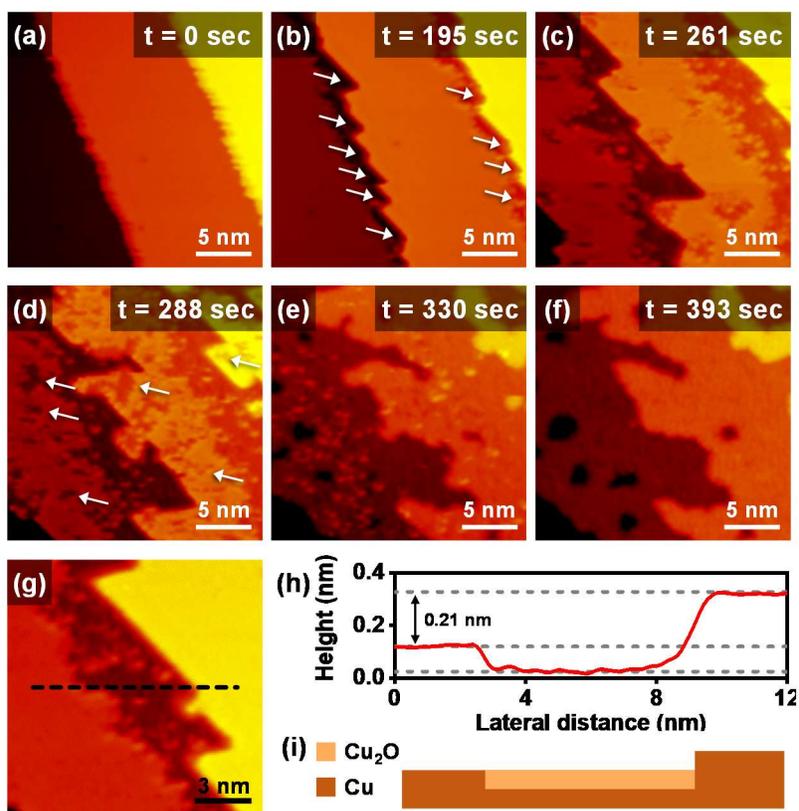


Figure S2. Time-lapse operando NAP-STM images of Cu(111) surface under 0.01 mbar of O_2 gas at (a) 0 sec, (b) 195 sec, (c) 261 sec, (d) 288 sec, (e) 330 sec, and (f) 393 sec ($V_s = 0.71 - 0.76$ V; $I_t = 0.13 - 0.15$ nA). (g) Enlarged NAP-STM image during the dry oxidation, (h) representative height profile of (g), and (i) schematic image of surface morphology corresponding with the height profile.

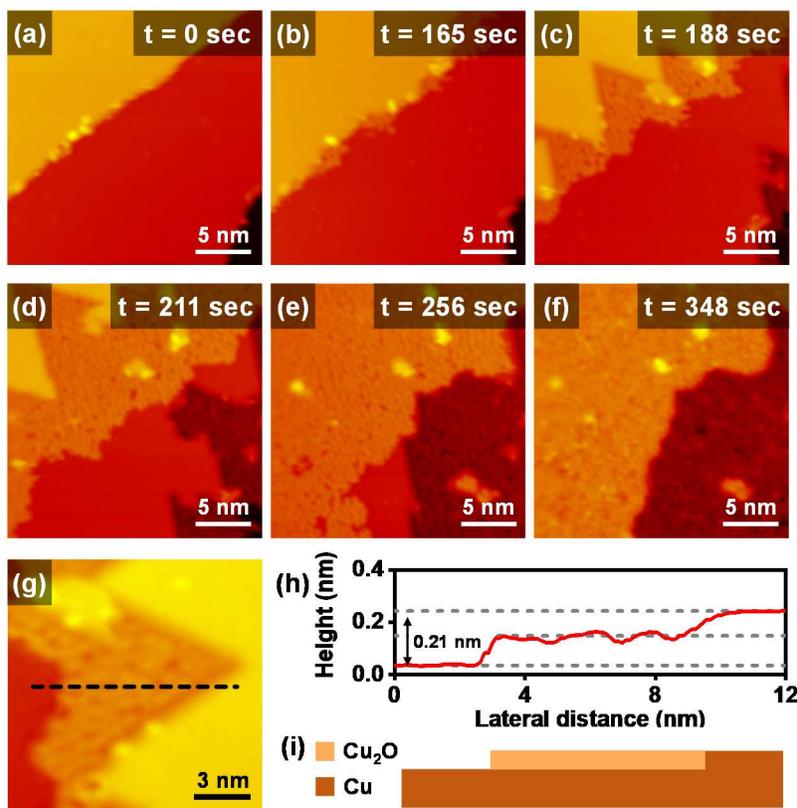


Figure S3. Time-lapse operando NAP-STM images of Cu(111) surface under 0.02 mbar of H₂O/O₂ gas mixture at (a) 0 sec, (b) 165 sec, (c) 188 sec, (d) 211 sec, (e) 256 sec, and (f) 348 sec ($V_s = 0.81 - 0.88$ V; $I_t = 0.12 - 0.14$ nA). (g) Enlarged NAP-STM image during the humid oxidation, (h) representative height profile of (g), and (i) schematic image of surface morphology corresponding with the height profile.

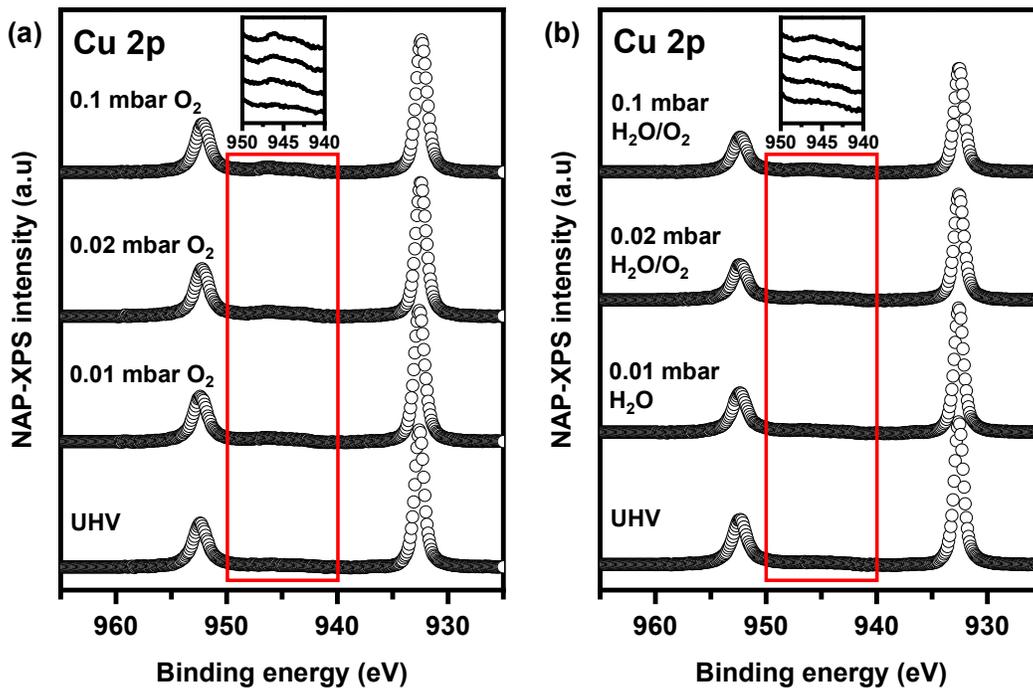


Figure S4. NAP-XPS operando core-level spectra for Cu 2p of Cu(111) at RT (a) under O₂ gas conditions and (b) 1:1 ratio H₂O/O₂ gas mixture conditions.

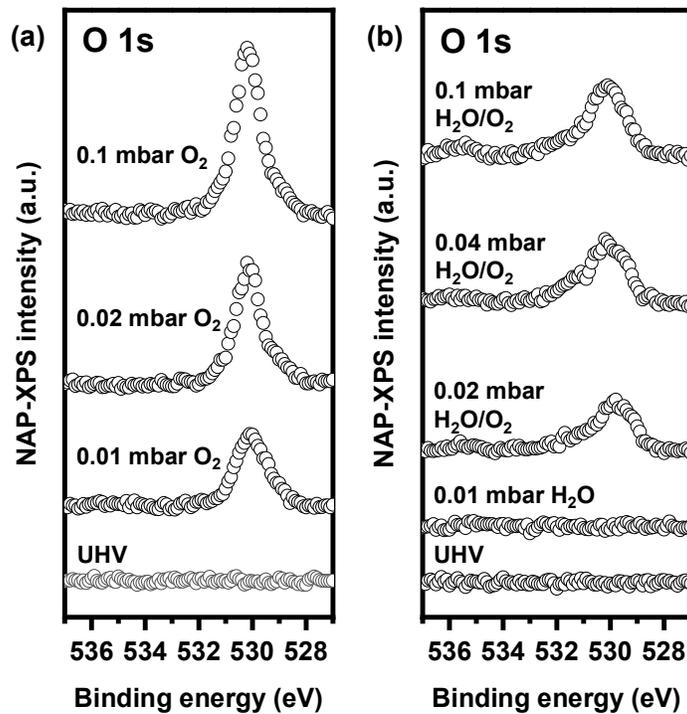


Figure S5. NAP-XPS operando core-level spectra for O 1s of Cu(111) at RT (a) under O₂ gas conditions and (b) 1:1 ratio H₂O/O₂ gas mixture conditions.

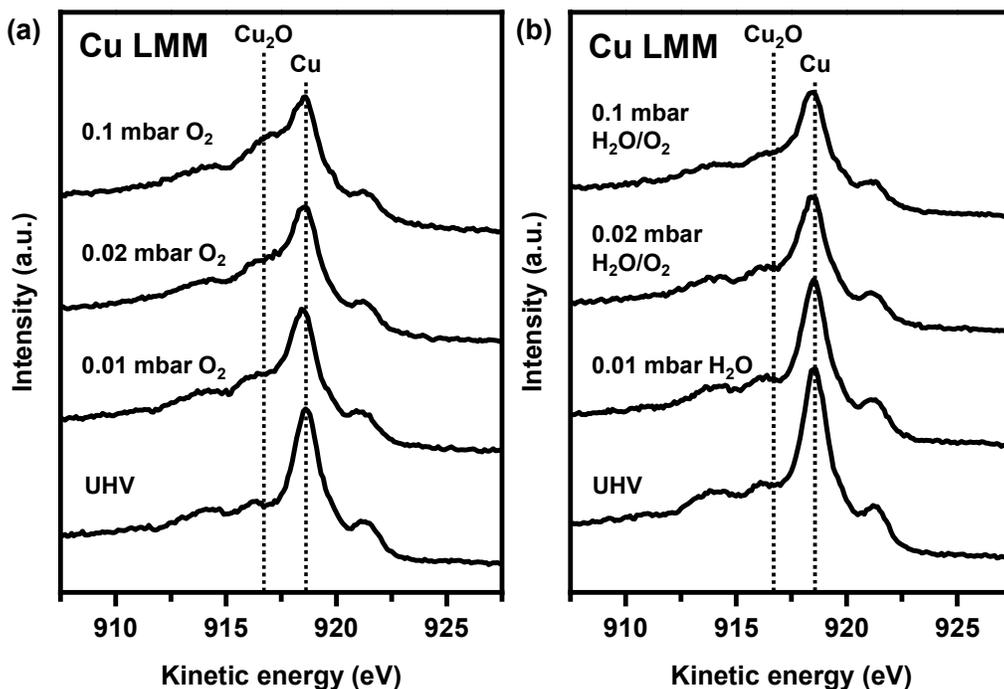


Figure S6. Operando XAES for Cu LMM of Cu(111) at RT (a) under O₂ gas conditions and (b) 1:1 ratio H₂O/O₂ gas mixture conditions.

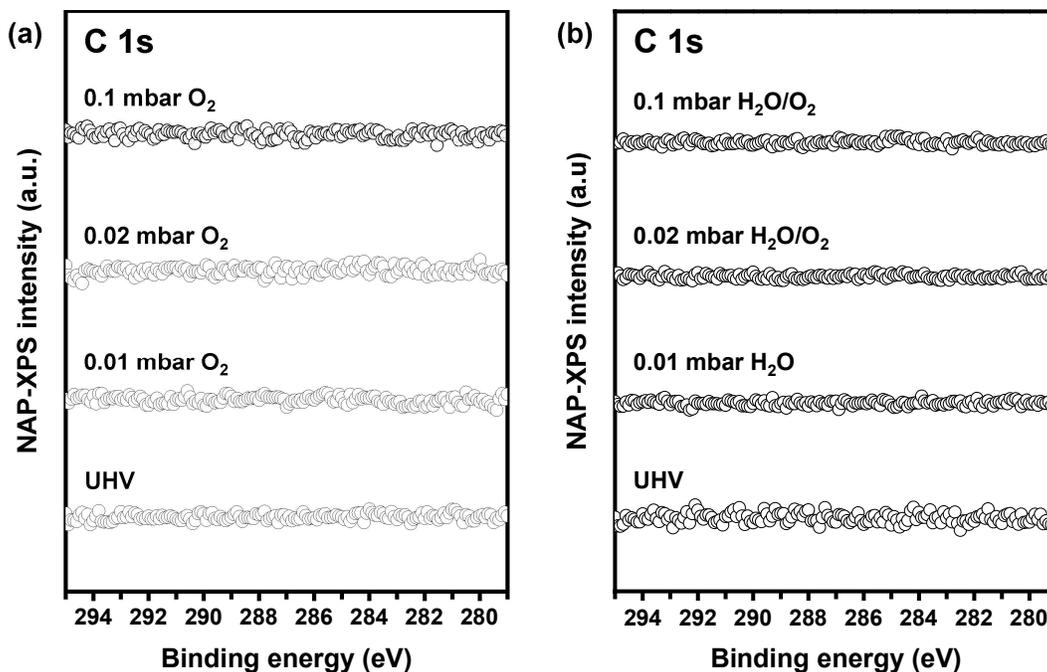


Figure S7. NAP-XPS operando core-level spectra for C 1s of Cu(111) at RT (a) under O₂ gas conditions and (b) 1:1 ratio H₂O/O₂ gas mixture conditions.

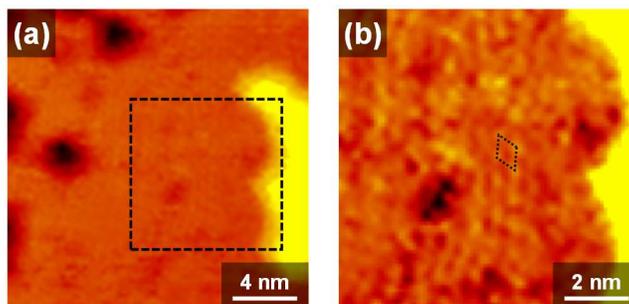


Figure S8. (a) A NAP-STM image of O/Cu(111) at RT under 0.03 mbar of O₂ gas and (b) an enlarged NAP-STM image of the dashed square region ($V_s = 0.59$ V; $I_t = 0.12$ nA).

Surface morphology of dry oxidized Cu(111) in the same position

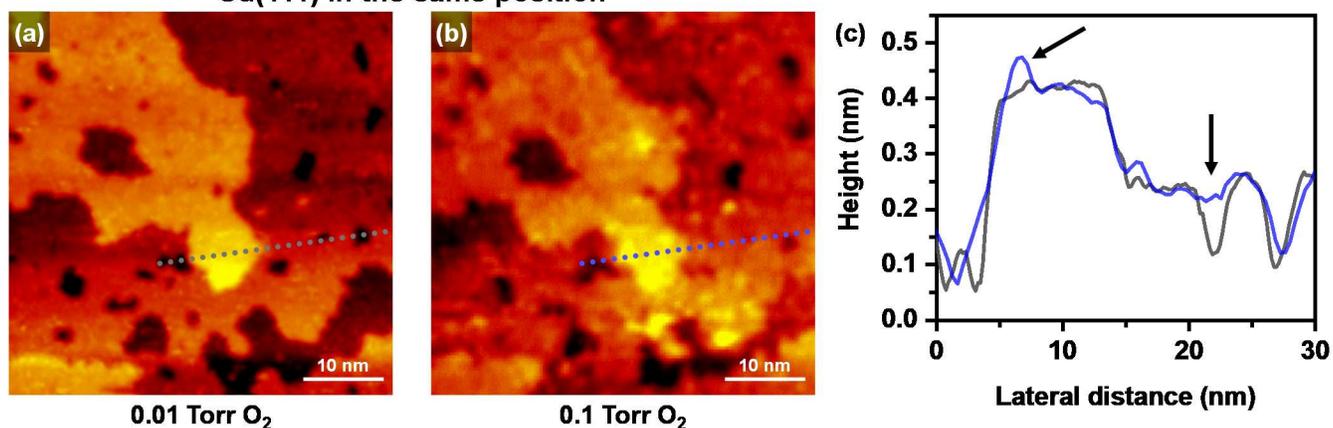


Figure S9. NAP-STM images of dry oxidized Cu(111) at same position and RT under (a) 0.01 mbar of O₂ gas ($V_s = 0.65$ V; $I_t = 0.15$ nA) and (b) 0.1 mbar of O₂ gas ($V_s = 0.63$ V; $I_t = 0.16$ nA). (c) Representative height profile for the dashed lines in (a) and (b).

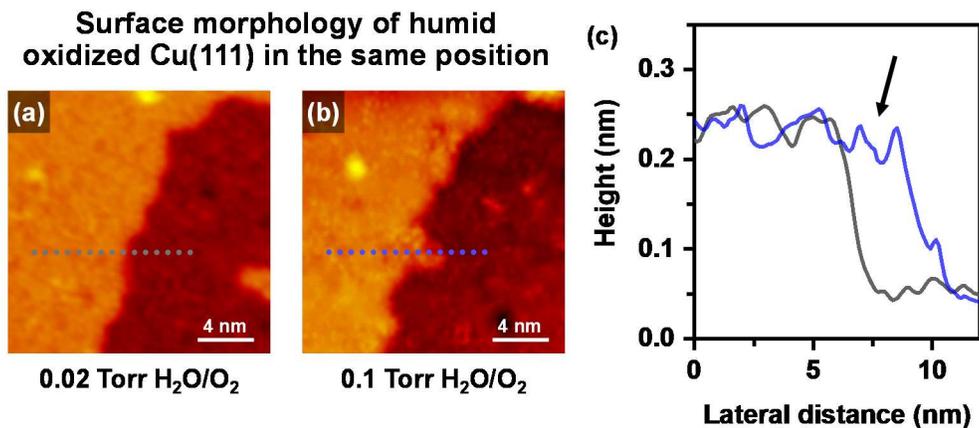


Figure S10. NAP-STM images of humid oxidized Cu(111) at same position and RT under (a) 0.02 mbar of $\text{H}_2\text{O}/\text{O}_2$ gas mixture ($V_s = 0.88$ V; $I_t = 0.14$ nA) and (b) 0.1 mbar of $\text{H}_2\text{O}/\text{O}_2$ gas ($V_s = 0.86$ V; $I_t = 0.14$ nA). (c) Representative height profile for the dashed lines in (a) and (b).

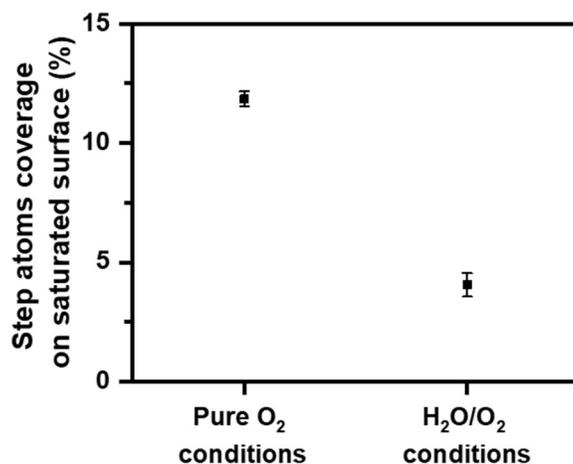


Figure S11. Coverages of step atoms on saturated Cu(111) surface under different oxidation conditions, which are acquired by NAP-STM images. In pure O_2 conditions, the pressure ranges from 0.01 mbar to 0.1 mbar of O_2 gas are included to calculate the step atoms coverages. Similarly, in $\text{H}_2\text{O}/\text{O}_2$ conditions, the pressure ranges from 0.02 mbar to 0.2 mbar of $\text{H}_2\text{O}/\text{O}_2$ (1:1) gas mixture are included to calculate the step atom coverages.