

Supporting information for
Activating Lattice Oxygen of Single-layer ZnO
for Catalytic Oxidation Reaction

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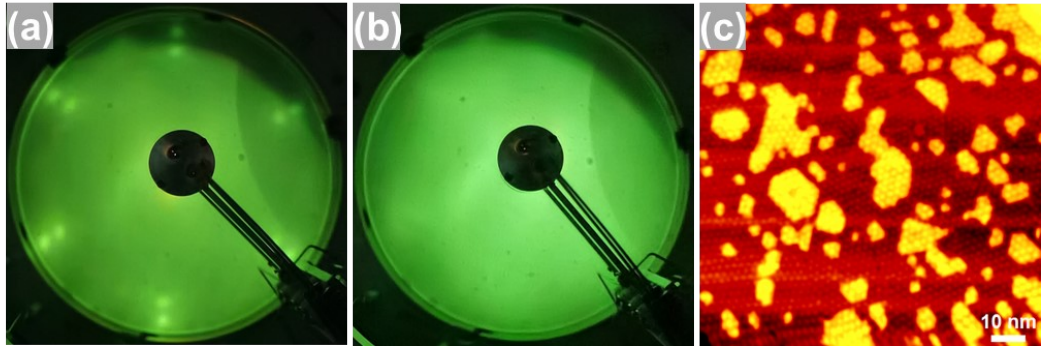


Fig. S1. (a) LEED pattern of pristine ZnO/Au(111) surface. (b) LEED pattern of ZnO/Au(111) after exposure to 1×10^{-6} mbar O_3 . (c) STM image of 1.2 monolayer (ML) ZnO/Au(111) surface. Electron energy (E_{kin}): (a) 10 eV; (b) 30 eV. Scanning parameter: (c) $I_t = 0.090$ nA, $V_s = 1.062$ V.

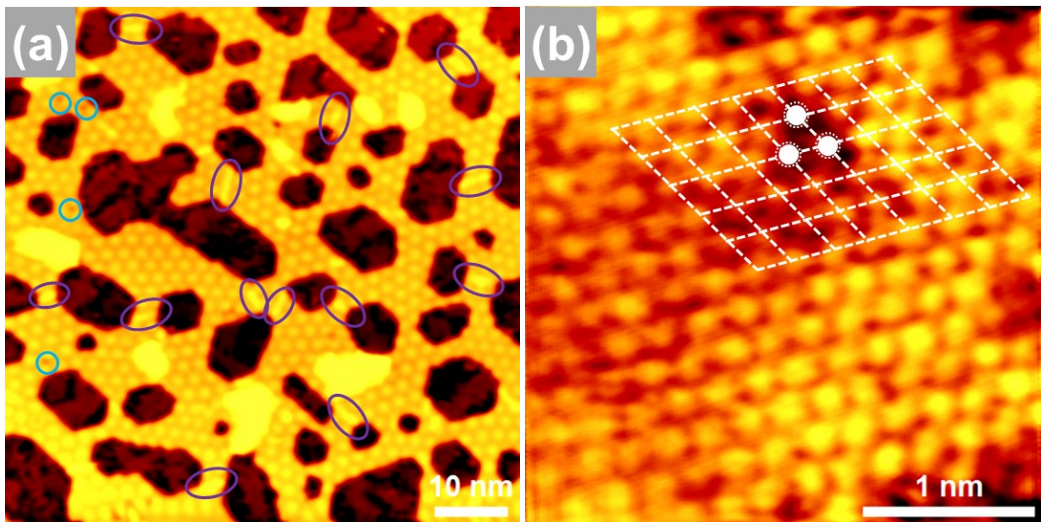


Fig. S2. (a) Large scale STM image of 0.6 ML ZnO/Au(111) surface with domain boundaries (purple circles) and defects (blue circles). (b) Atomic resolution STM image of ZnO/Au(111) surface with atomic defects, the white solid circles represent the missing atoms. Scanning parameters: (a) $I_t = 1.230$ nA, $V_s = 1.400$ V. (b) $I_t = 0.200$ nA, $V_s = 0.085$ V.

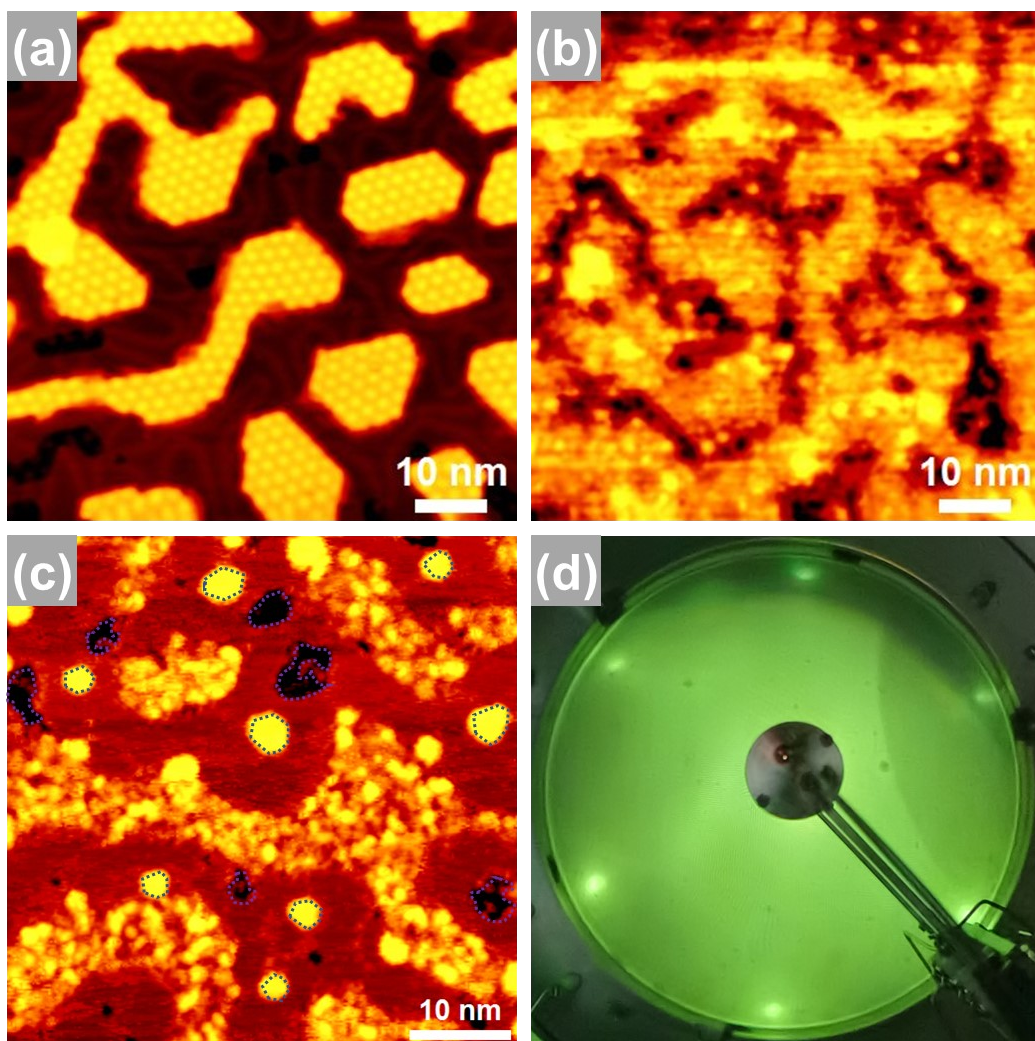


Fig. S3. STM images of the (a) 0.4 ML ZnO/ Au(111) and that after exposure to (b) 1×10^{-6} mbar O_3 and subsequent to (c) 1×10^{-6} mbar CO at room temperature (RT). (b) LEED pattern of ZnO/Au(111) after exposure to 1×10^{-6} mbar O_3 for 5 min followed by 1×10^{-6} mbar CO for 10 min. Scanning parameter: (a) $I_t = 0.100$ nA, $V_s = 1.201$ V. (b) $I_t = 0.410$ nA, $V_s = 1.317$ V. (c) $I_t = 0.080$ nA, $V_s = 2.926$ V. Electron energy (E_{kin}): (b) 30 eV.

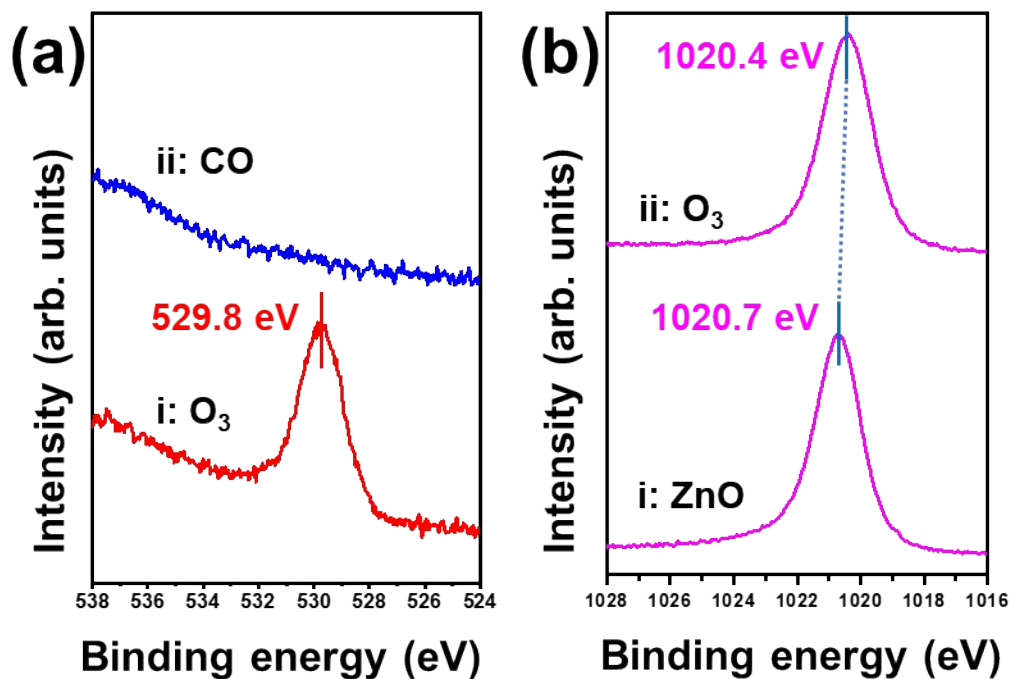


Fig. S4. (a) XPS O 1s spectra for Au(111) single crystal after exposure to 1×10^{-6} mbar O₃ and subsequently to 1×10^{-6} mbar CO at RT. (b) XPS Zn 2p_{3/2} spectra from 1.2 ML ZnO/Au(111) surfaces before and after exposure to 1×10^{-6} mbar O₃.

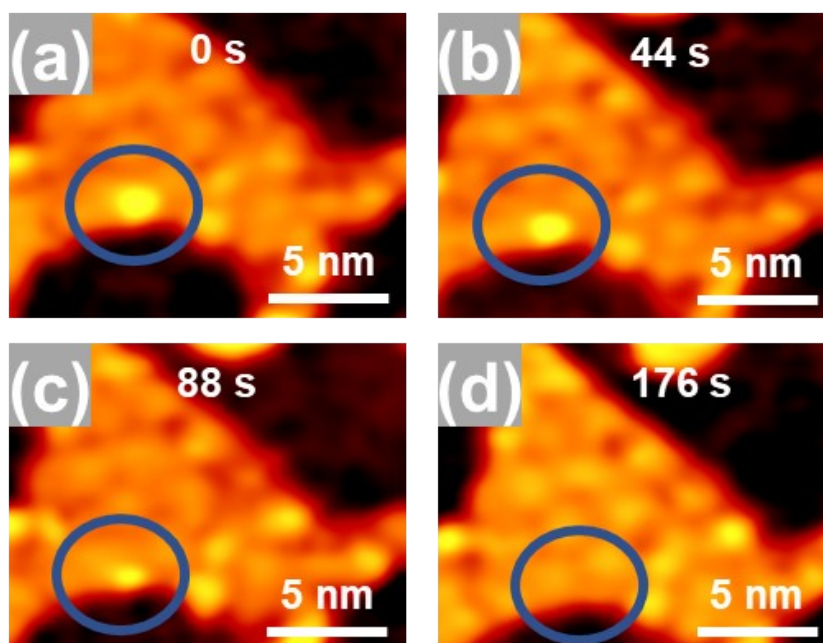


Fig. S5. (a) - (d) Sequential in situ STM images of the 0.4 ML ZnO/O/Au(111) surface after exposure to $\sim 1 \times 10^{-3}$ mbar CO at 300 K. The bright area marked by blue circles indicates the location of intercalated oxygen and disappears after exposure to CO for 176 s. The reaction time is labeled on the top of the STM image. Scanning parameter: (a) - (d) $I_t = 0.530$ nA, $V_s = 2.152$ V.

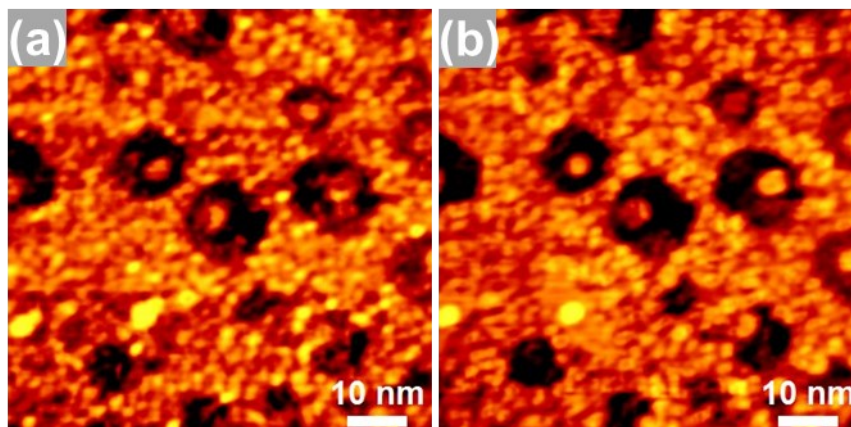


Fig. S6. In situ STM images of 0.6 ML ZnO/O/Au(111) (a) before and (b) after exposure to 72.6 mbar H₂. Scanning parameter: (a) - (b) $I_t = 0.070$ nA, $V_s = 0.969$ V.

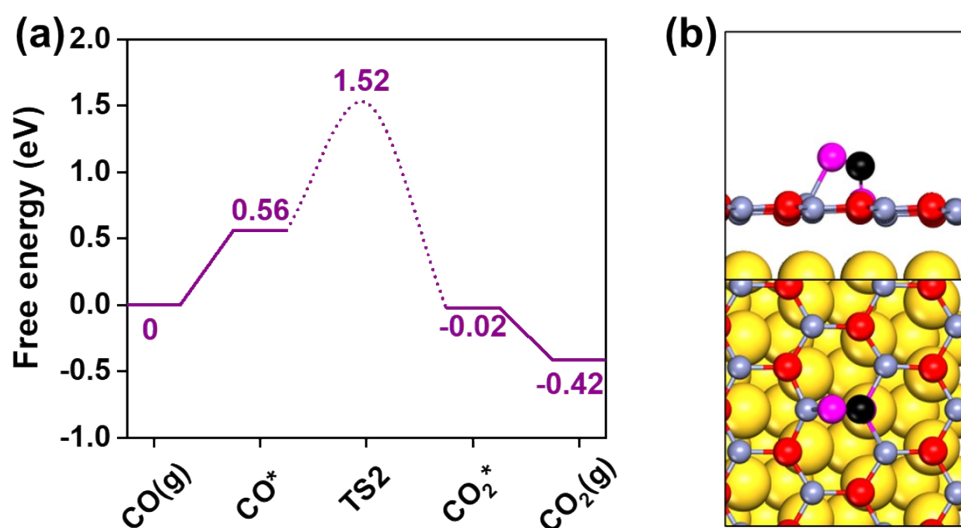


Fig. S7. COOX over ZnO/Au(111) surface. (a) Free energy diagram of the COOX process through CO reacting with surface O in ZnO/Au(111). Values are the relative energy levels of each state. (b) Configurations of the transition state (side and top views) corresponding to TS2 in (a). C: black; O: red and pink; Zn: gray; Au: yellow.

Table S1. The zero-point energy (ZPE), integrated heat capacity (δH), entropy correction ($T\Delta S$), and total Gibbs free energy correction ($G-E_{\text{elec}}$) at 298 K for the gaseous molecules. (unit: eV)

Gaseous molecules	ZPE	δH	$T\Delta S$	$G-E_{\text{elec}}$
CO	0.13	0.00	0.61	-0.92
CO ₂	0.31	0.00	0.66	-1.12

Note that the partial pressures of gaseous CO and CO₂ are 3.2×10^{-5} and 1.0×10^{-10} mbar in our experiments, respectively.

Table S2. The zero-point energy (ZPE), integrated heat capacity (δH), entropy correction ($T\Delta S$), and total Gibbs free energy correction ($G-E_{\text{elec}}$) at 298 K for the adsorbates. (unit: eV)

Adsorbates	ZPE	δH	$T\Delta S$	$G-E_{\text{elec}}$
O*	0.07	0.03	0.04	0.06
O*+CO*	0.24	0.13	0.29	0.08
CO ₂ ‡ (TS2)	0.25	0.09	0.16	0.18
CO ₂ *	0.29	0.09	0.17	0.21