Electronic Supplementary Material (ESI) for Materials Advances.

Zinc oxide—copper model nanocatalysts for carbon dioxide hydrogenation: morphology and interface effects

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1.Zn LMM Auger spectra on ZnO/Cu(111) as a function of the Zn thickness

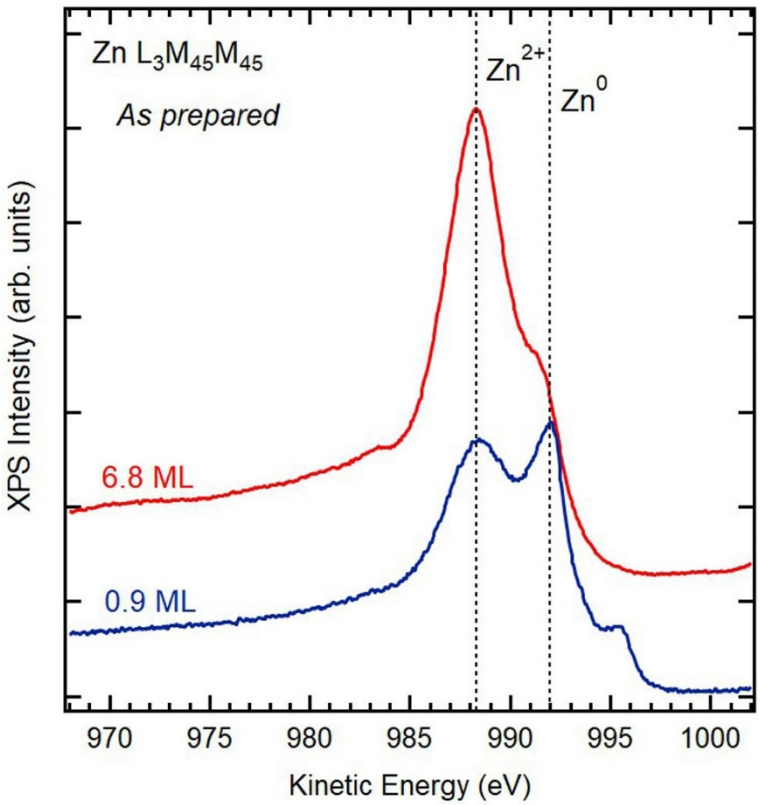

Figure S1. High resolution LMM Auger spectra of Zn acquired on ZnO/Cu(111) as a function of Zn thicknesses (0.9 ML and 6.8 ML) at room temperature as prepared (UHV) before exposure to the reactive gases.

2. Deconvolution of Zn 3p and Cu 3p core-level spectra acquired on ZnO/Cu(111) samples as a function of reactive gases (CO_2, H_2, and CO_2+H_2) exposures, Zn thickness and temperature

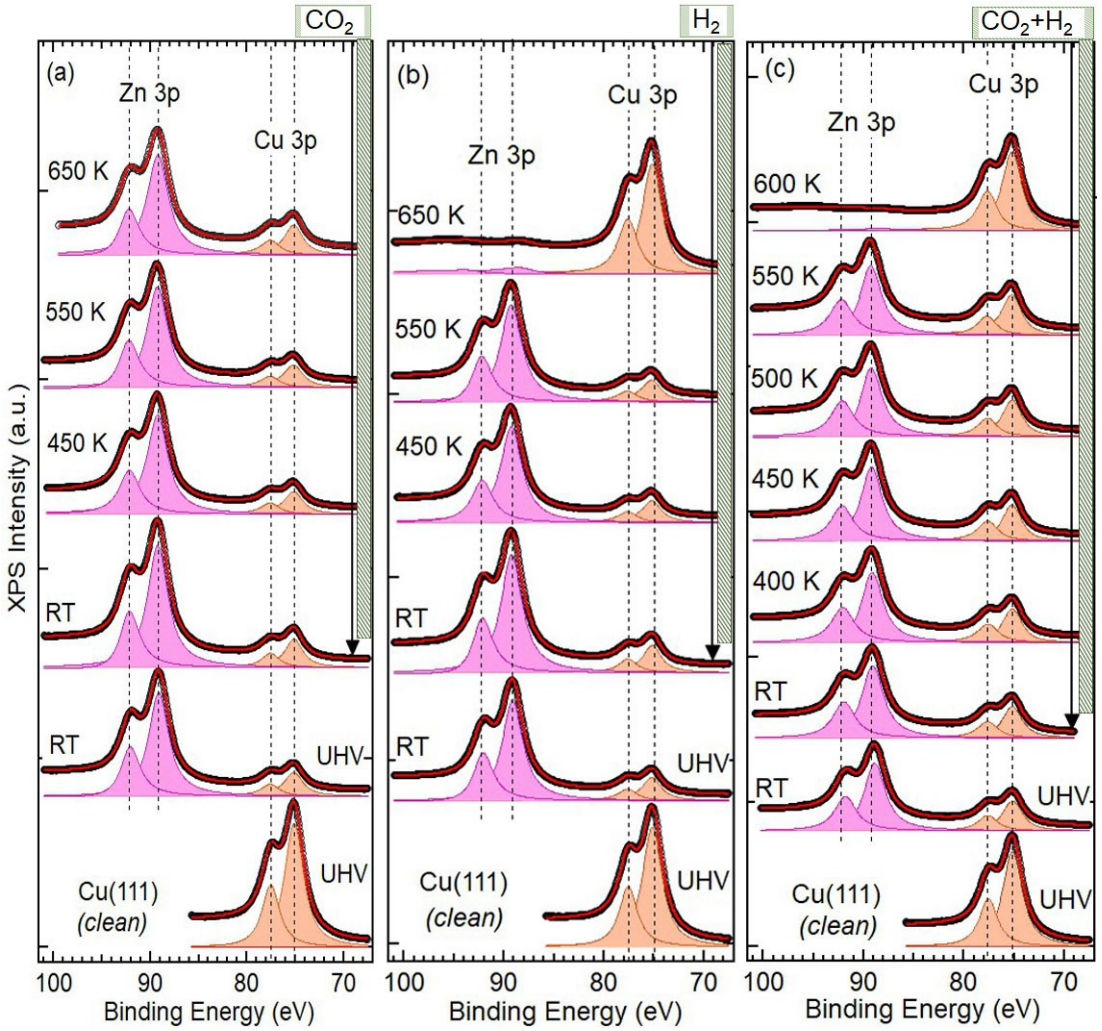

Figure S2. XPS Cu 3p and Zn 3p core level spectra of similar three ZnO ultrathin film samples with a thickness of 6.8 ML grown on the Cu(111) surface as a function of the temperature and gas exposures. (a) exposure to pure CO_2 at 5 mbar nominal pressure. (b) exposure to pure H_2 at 5 mbar nominal pressure. (c) exposure to the gas mixture (CO_2:H_2) at 5 mbar nominal pressure at a (1:3) ratio. The spectra labeled UHV were acquired on the samples as prepared before exposure to reactive gases. The spectra labeled Cu(111) (clean) were acquired on the clean Cu(111) surface prior to ZnO growth.

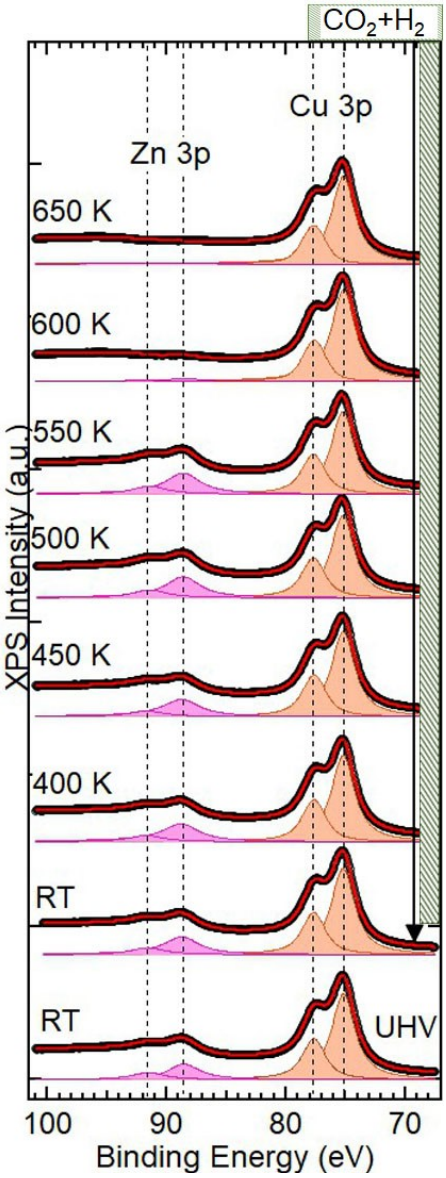

Figure S3. XPS Cu 3p and Zn 3p core level spectra of the ZnO ultrathin film sample with a thickness of 0.9 ML grown on the Cu(111) surface as a function of the temperature and gas exposures (CO_2:H_2) at 5 mbar nominal pressure at a (1:3) ratio. The spectrum labeled UHV was acquired on the sample as prepared before exposure to reactive gases.

3. STM images of the pristine Cu(111) and Cu2O/Cu(111) surfaces

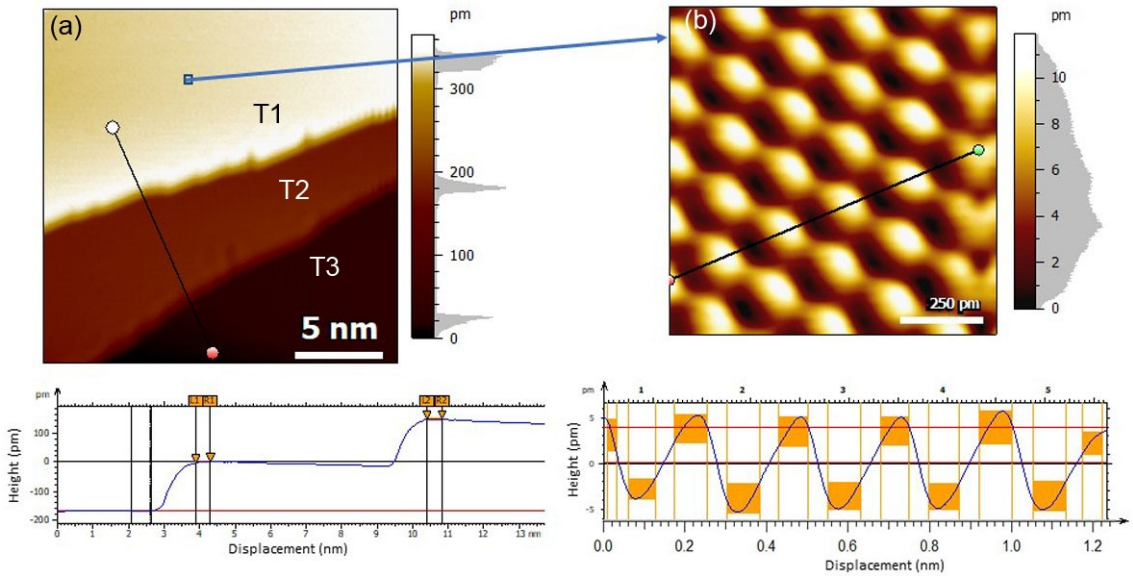

Figure S4. STM images of the clean Cu(111) surface after several cycles of argon ion sputtering (15 µA) and annealing at 723 K in UHV. (a) is a large-scale image featuring three terraces (T1, T2 and T3). The step height between two terraces is mono-atomic. (b) high resolution image featuring Cu atomic resolution.

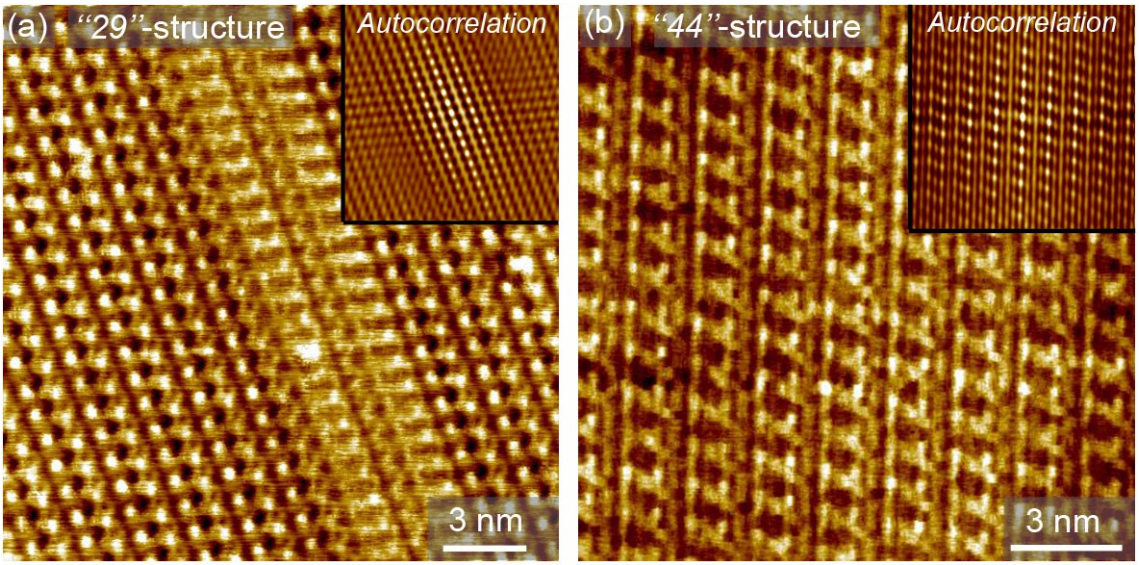

Figure S5. high resolution STM images obtained on the Cu_2O metal-oxide grown on a clean Cu(111) surface after exposure to O_2 and annealing. (a) displays atomic resolution of the "29-structure" corresponding to the ($\sqrt{73}R5.8° \times \sqrt{21}R10.9°$) adlayer. (a) displays atomic resolution of the "44-structure" corresponding to the ($\sqrt{13}R46.1° \times 7R21.8°$) adlayer. The Inserts are autocorrelation images reflecting the periodic signal corresponding to the atomic arrangement of the two Cu_2O structures.