Supporting information for

Revealing the surface chemistry for CO_2 hydrogenation on Cu/CeO_{2-x} using near-ambient pressure X-ray photoelectron spectroscopy

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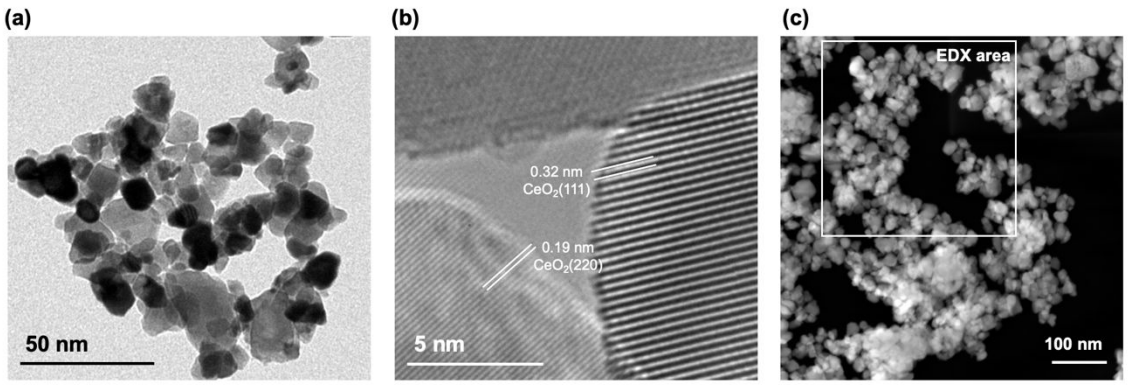


Figure S1 Representative (a) TEM, (b) HRTEM, (c) HAADF-STEM images of the Cu/CeO_{2-x} catalyst. The area for EDX element map is shown in (c).

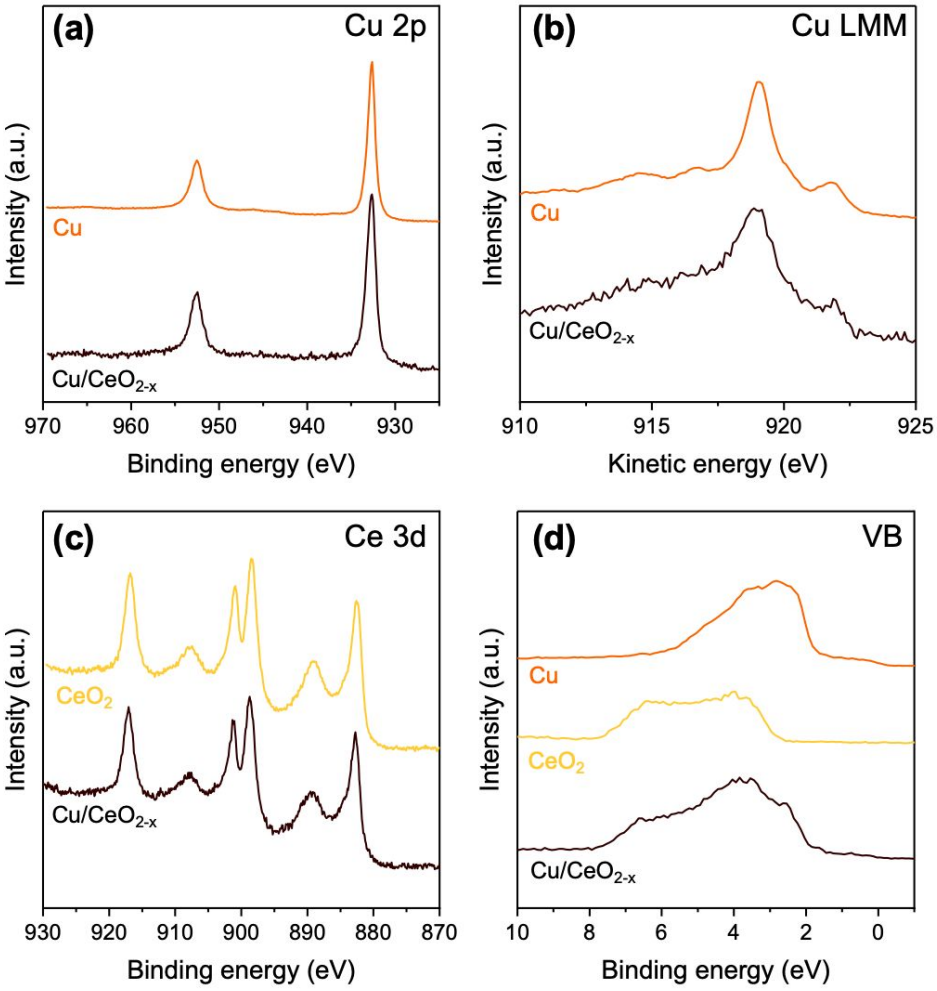
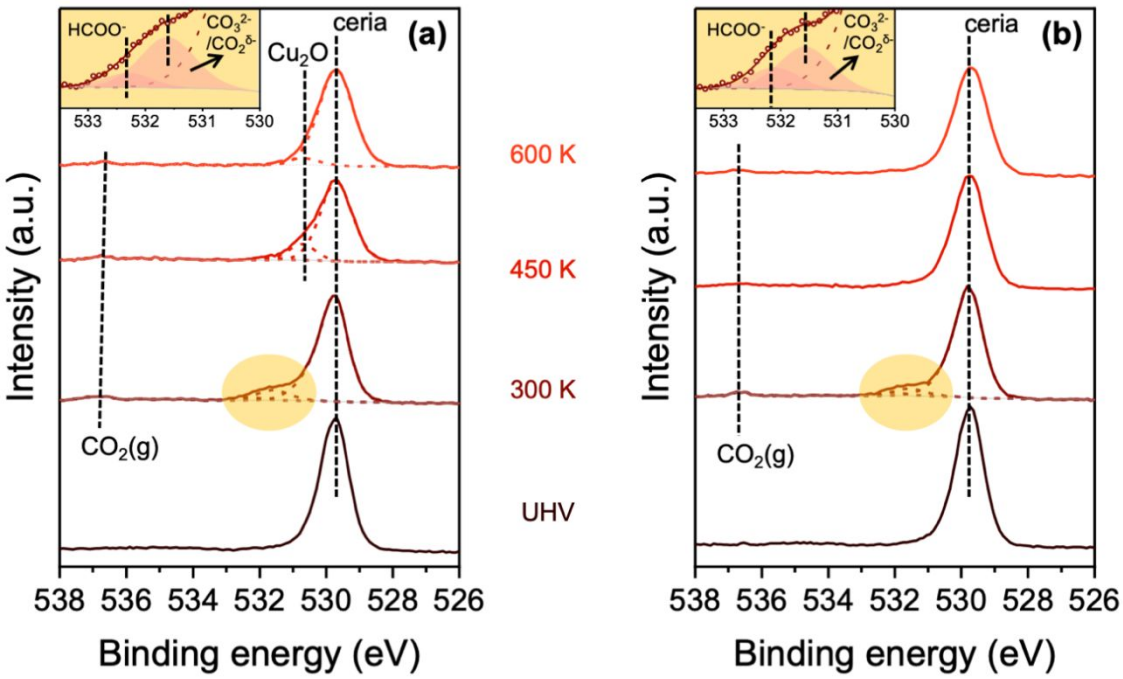


Figure S2 (a) Cu 2p, (b) Cu LMM Auger, (c) Ce 3d region XPS spectra, and (d) X-ray excited valence band spectra of the Cu/CeO2-x model surface, a fully oxidized CeO_2 thin film sample prepared by oxidation (0.5 mbar O_2, 423 K, 60 min) of the reactive deposited ceria thin film, and a sputter-cleaned metallic Cu foil.



Peak assignment	Peak position		FWHM/eV		Peak area	
	CO_2	CO_2+H_2	CO_2	CO_2+H_2	CO_2	CO_2+H_2
CO_3^{2-}/$CO_2^{\delta-}$	531.6	531.6	1.1	1.1	726	461
$HCOO^-$	532.3	532.1	1.0	1.0	159	221

Figure S3 O 1s spectra of the Cu/CeO_{2-x} model surface under UHV and (a) 0.2 mbar of CO_2, and (b) 0.2 mbar CO_2 + 0.6 mbar of H_2 at 300, 450, and 600 K. The peak positions and FWHMs used in the deconvolution is shown in the table below the figures.

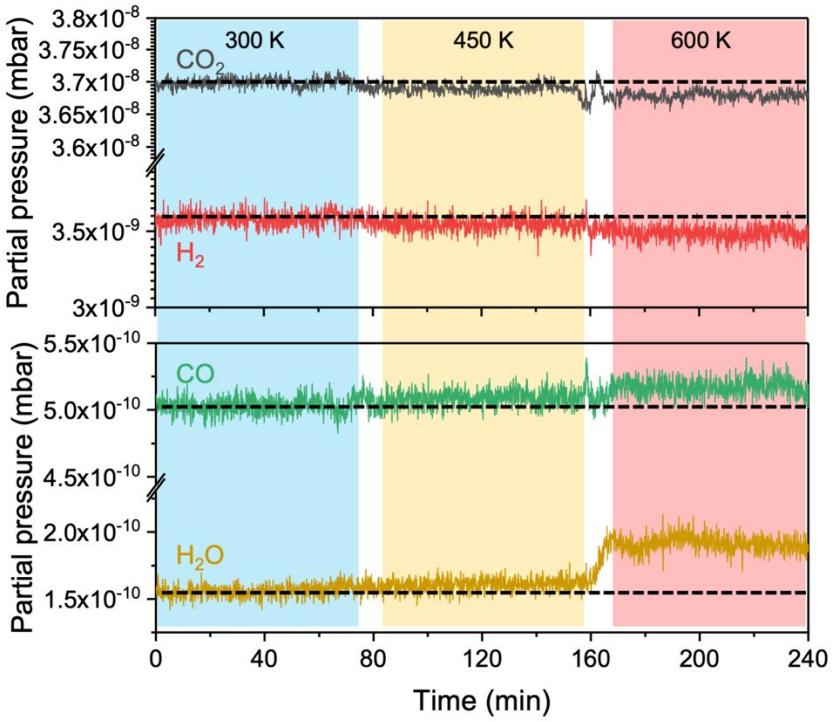


Figure S4 Gas species detected by RGA at the pre-lens stage of the NAP-XPS during measurements of the Cu/CeO_{2-x} model surface under 0.2 mbar CO_2 + 0.6 mbar of H_2 at 300, 450, and 600 K.

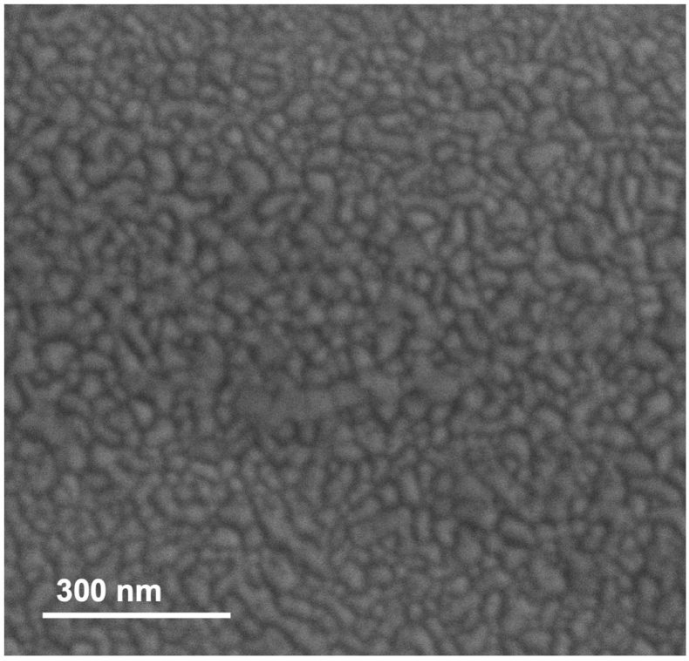


Figure S5 SEM image of as-prepared Cu/CeO_{2-x} model surface.

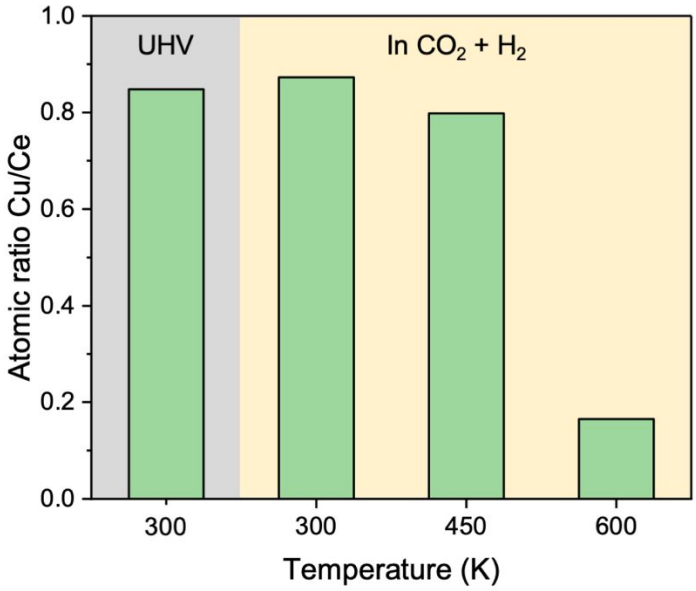


Figure S6 The atomic ratio of Cu/Ce on the Cu/CeO_{2-x} model surface under UHV and 0.2 mbar of CO_2 + 0.6 mbar of H_2 at 300, 450, and 600 K, determined by the Cu 2p and Ce 3d peak areas after correction by their corresponding RSFs

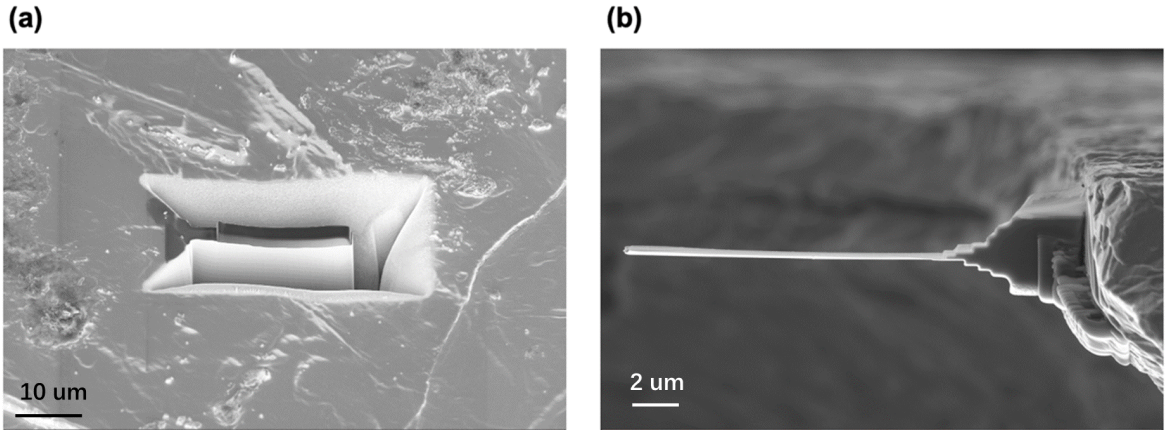


Figure S7 TEM lamella of the thin-film Cu/CeO_{2-x} sample prepared by FIB: (a) the cut volume with surface protection by carbon before lift-out, (b) the electron-transparent TEM lamella glued on Mo grid after thinning.

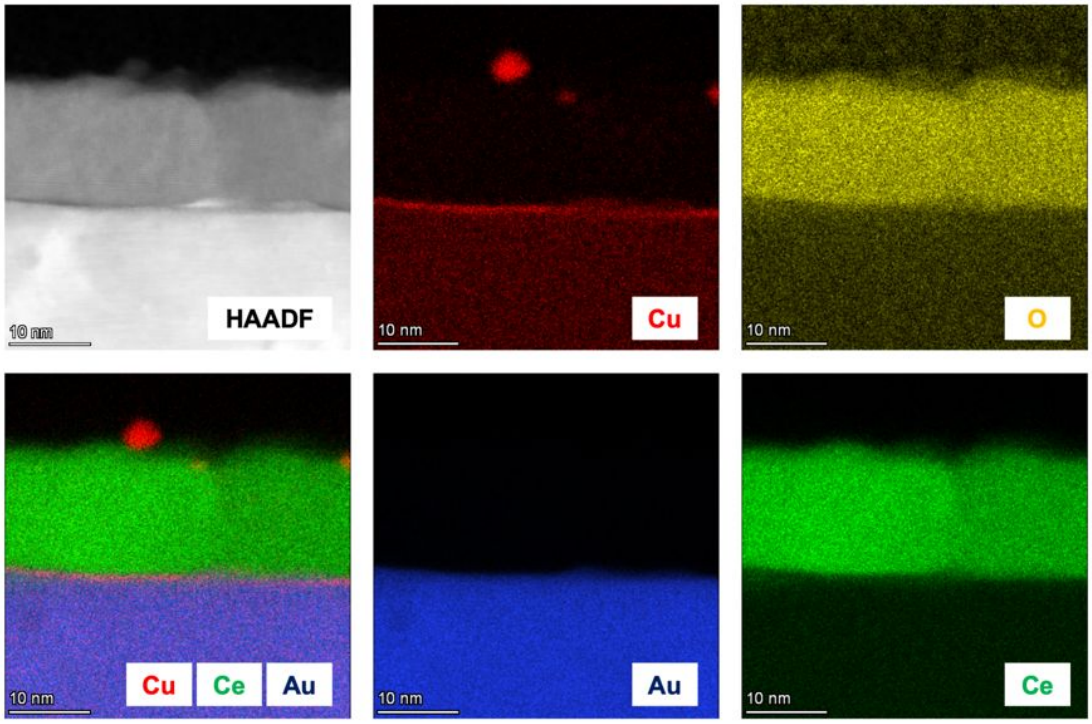


Figure S8 Additional cross-sectional STEM-HAADF image, and STEM-EDX elemental map of the Cu/CeO_{2-x} model surface after exposure to 0.2 mbar of CO_2 + 0.6 mbar of H_2 at 600 K for 1 h.