Supporting Information

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**Beamline 9.3.2 and APXPS Measurements.** Beamline (BL) 9.3.2 at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory) is equipped with a bending magnet and two grating monochromators [100 lines (l)/mm and 600 l/mm] having a total energy range between 200 eV and 800 eV (soft X-ray range) (21). The analyzer ( Scienta R4000 HiPP) (21) pass energy was set to 100 eV, using a step of 100 meV and a dwell time of 200 ms. Under these conditions, the total resolution (source and analyzer) was equal to about 220 meV at r.t., for photon energies ranging between 280 eV and 660 eV (the maximum flux, around $4.5 \times 10^{10}$ photons $s^{-1}$, is reached at an energy of 490 eV). The incidence angle between the incoming photons and the sample surface was equal to $15^\circ$. The PES measurements were taken in normal emission (NE), at a pressure in the experimental (high pressure) chamber ranging from UHV ($10^{-9}$ torr) to 0.7 Torr (in backfilling configuration), whereas the detection stage in the analyzer was under UHV conditions ($\sim 10^{-9}$–$10^{-10}$ torr). The calibration of the BE scale was carried out using the Au 4f photoelectron peak as reference ($E_{\text{Au}} = 84.0$ eV), from a clean gold polycrystalline surface. The calibration of the photon energy was performed acquiring the Au 4f$_{7/2}$ core level at the desired photon energy and its corresponding II harmonic reflection. The BL, maintained under UHV to avoid contamination of optical elements, is separated from the high-pressure chamber by a 2-mm $\times$ 2-mm $\times$ 100-mm thick Si$_3$N$_4$ window placed at a distance of about 30 cm from the sample.

All of the fits reported in this work have been carried out using a Doniach–Sunjic shape for the Au 4f photoelectron peak, whereas a symmetrical Voigt function (GL:R) ratio ranging from 85/15 to 75/25) was used to fit C 1s and O 1s photoelectron peaks (after Shirley background subtraction). During the fitting procedure, the Shirley background was optimized as well together with the spectral components, increasing in this manner the precision and reliability of the fitting procedure (32–34). The $\chi^2$ minimization was ensured by the use of a nonlinear least-squares routine, with increased stability over simplex minimization (33).

The Cu L$_3$M$_4\alpha$M$_5\beta$ Auger transition was acquired at a photon energy ($\hbar\nu$) of 1,150 eV, using the second harmonic reflection of the 575-eV primary photon energy.

**Simulations of the Cu L$_3$M$_4\alpha$M$_5\beta$ Auger Spectra.** The main Cu Auger transition ($L_3M_4\alpha M_5\beta$) arises from a single $L_3$ ($2P_{3/2}$) core-hole decay via the Auger process involving two $M_4\alpha$ ($3d$) electrons resulting in a final 3$d^0$ configuration. This is expected to lead to a final state term splitting from L-S coupling, namely $3^2F$, $3^2D$, $3^2P$, $3^2G$, and $3^2S$ corresponding to two $d$ holes (35, 36) that constitute the primary excitation spectrum (F(E)) (the final state terms labeled in Fig. S6A with * are indicative of Auger satellite transitions). The final state labeled “sum” denotes the combination of five different final states ($3^2P$, $3^2G$, $3^2P$, $3^2H$, and $3^2D$) that cannot be separated into individual spectral components (36). The Auger transition spectrum can be seen then as the addition of the F(E) and the contribution from electrons that have undergone an increasing number of inelastic scattering (energy loss) events (36), which constitutes the background signal and has a crucial importance for the quantification of the different final states present in the experimental mixed spectrum. The Cu Auger L$_3$M$_4\alpha$M$_5\beta$ spectrum was simulated, for all of the investigated systems, by convolving the final state terms with the multiple inelastic scattering background determined via a Drude–Lindhard continuum medium approach, as reported in previous works by Pauly et al. (36), Tougaard and Yubero (37), Simonsen et al. (38), and Yubero and Tougaard (39). These simulations were then used to fit the experimental signals to obtain the final state term population from the experimental data.

As can be seen from Fig. S6A, Cu$^0$ and Cu$^+$ are characterized by similar final state composition, which leads to the observed limited chemical shift in the core-level spectroscopy. Passing from metallic Cu to Cu$_{0.0}^{+}$, a downward kinetic energy shift can be observed for the poorly shielded $1^F$ and $1^D$ final state terms, as results from the loss of repulsive interaction between the emitted Auger electron and the 4s electron at the Fermi level, as a consequence of the partial ionization of the Cu 4s band passing from metallic Cu to Cu$_{0.0}^{+}$. In addition, an important increase of the satellite $1^F$ term and decrease of the $1^G$ term can be observed, as a function of the surface oxidation. The ratio between these two final state terms can be used to estimate the stoichiometry of the system. Fig. S6A reports the Auger L$_3$M$_4\alpha$M$_5\beta$ spectra for metallic Cu, Cu$_{0.0}^{+}$, and Cu$_{0.0}^{-}$, as references, acquired in UHV conditions ($\sim 10^{-9}$ torr).

We observe that despite the adsorption of CO$_2$ and CO$_2$ plus H$_2$O with partial oxidation of the Cu surface, the Cu surface remains metallic (see Fig. S6A, comparison between the metallic Cu reference and spectra A and B). On the other hand, the same coadsorption on the nominal Cu$_{0.0}^{+}$ and Cu$_{0.0}^{-}$ structures leads to slightly different surface stoichiometry under APXPS conditions (namely to Cu$_{0.0}^{+}$ and Cu$_{0.0}^{-}$, respectively). With the current signal-to-noise ratio, a direct attribution of these observations to a specific surface interaction between CO$_2$, H$_2$O, and the investigated oxidic structures is not yet possible.

**Sample Preparation.** The experiments were performed starting from a Cu polycrystalline surface that was in situ oriented to the (111) plane by repeated Ar sputtering (2 keV, 45 min) and annealing cycles in hydrogen (0.15 Torr) at 1,100 K (for 60 min) (17). The sample preparation as well as the LEED investigation was performed in the preparation chamber connected to the high-pressure chamber available at BL 9.3.2. The sample was then transferred to the high-pressure chamber, using a transfer arm without breaking the UHV conditions (21).

The preparation of different Cu suboxide surfaces (performed in the high-pressure chamber by BL 9.3.2) was adapted from the results obtained by Schedel-Niedrig et al. (18). A first oxidation cycle consisted of a Cu(111) treatment at 625 K for 30 min with 0.3 Torr of molecular oxygen. The sample was then slowly ($\sim 10$ K-min$^{-1}$) cooled down in the same pressure of oxygen to r. t. ($\sim 298$ K). This procedure leads to the formal stoichiometry [determined via the Cu L$_3$M$_4\alpha$M$_5\beta$ Auger analysis (36)] of Cu$_{0.0}^{-}$O. A second cycle performed as described above leads instead to a further surface oxidation, with a formal stoichiometry of Cu$_{0.0}^{-}$O.

**Computational Details of DFT Calculations.** The M06L flavor of DFT (16) was chosen for this study because we found that it describes well both the Cu metal and CO$_2$ molecular crystal, even better than the dispersion-corrected PRE-D3 (29) (see Tables S1 and S2 for details). The calculations were performed with the CRYSTAL14 package (40), which uses local atomic Gaussian-type basis sets. We used all-electron 6-311G(d) basis sets of triple-$\zeta$ quality for H, C, and O, but we added one extra sp shell for the O basis set and reoptimized it. For Cu, we used the SBKJC relativistic effective core potentials (41) and modified associated basis sets of triple-$\zeta$ quality. We used an extra-large grid (consisting of 75 radial points and 974 angular points) for accurate integration. The reciprocal space was sampled by a
Γ-centered Monkhorst–Pack scheme with $3 \times 3 \times 1$ for all slab calculations.

**Discussion.** The difficulty in discriminating between Cu$^0$ and Cu$^+$ using Cu core levels has been well established and is clearly evidenced from Fig. S5A, reporting the Cu $3p$ photoelectron spectra. To overcome this limitation, the various Cu surfaces were characterized by means of the Cu Auger $L_3M_{4,5}M_{4,5}$ transition (using a photon energy of 1,150 eV, Fig. S6A) and the VB (acquired under resonance conditions with the O K edge, at a photon energy of 537 eV, Fig. S5B). Upon passing from metallic Cu to Cu$_{x=1.5,2.5}$O, we observed a downward kinetic energy shift for the poorly shielded $3F$ and $1D$ final state terms (Fig. S6A), due to decreased repulsive interaction between the emitted Auger electron and the $4s$ electron at the Fermi level, as a consequence of the partial ionization of the Cu $4s$ band passing from metallic Cu to Cu$_{x=1.5,2.5}$O (35, 36). In addition, we observe an important increase of the satellite $4F^*$ term and decrease of the $1G$ term as a function of the surface oxidation.

From the VB spectra (as well as the difference VB spectra) reported in Fig. S5B, no unambiguous changes can be detected in the electronic structure of the metallic or oxide surfaces upon CO$_2$ or CO$_2$-H$_2$O coadsorption. With respect to the suboxide structures (Cu$_{x=1.5,2.5}$O), the VB spectra exhibit the typical intensity increase of the $<O\ 2p><Cu\ 3d>$ hybridization bands below the Fermi edge (Fig. S5B), as well documented by the difference VB spectra obtained taking the metallic Cu VB as reference (18). Furthermore, as reported in Fig. S6B, the region below the Fermi level shows the typical increase of the density of states (DOS) at around 0.7 eV expected for Cu$^+$-based suboxidic structures (18) [also confirmed by the increase of the positive slope of the DOS (dDOS/dBE)], obtained by interpolating a straight line where the DOS is centered at 0.7 eV within a range of BEs given by taking the double of the spectral resolution (42, 43).

The coupling of Auger and VB analyses provides then the necessary information to establish in situ copper metallic to subsurface suboxide transitions that occur while changing the experimental conditions.

**Fig. S1.** Survey scan acquired in UHV at 650 eV at r.t. (298 K) on the Cu(111) surface after the cleaning cycle. Insets report the scans over the O 1s and C 1s spectral region (acquired in UHV at r.t. with a photon energy of 632 eV and 387 eV, respectively). It is possible to see that the surface did not present traces of O- or C-based contaminations after the cleaning and annealing procedure (surface preparation).
Fig. S2. C 1s photoelectron peak acquired at r.t. (298 K) as a function of CO₂ and H₂O partial pressures in the analysis chamber [on metallic Cu(111)]. It can be seen that upon H₂O codosing, a downward shift of the l-CO₂ BE takes place with the formation of b-CO₂. b-CO₂ remains stable upon H₂O removal and final pumping of the chamber to HV conditions. Note that the increase in CO₂ partial pressure leads to the emergence and subsequent growth of a gas-phase C 1s core-level signal (the onset occurs between 0.05 Torr and 0.10 Torr). Therefore, the spectral intensity shown here is rescaled by the intensity of the CO₂ gas phase above the onset pressure. Furthermore, the relatively high gas pressure used in this study attenuates the photoelectron intensity coming from the sample surface, leading to an overall apparent decrease of the surface species intensity.
Fig. S3. Multipeak fitting procedure and normalized integrated peak areas for the different chemically shifted components on C 1s (A) and O 1s (B) spectral regions and multipeak fitting procedure results obtained for the different experimental conditions and investigated surfaces (at r.t., 298 K). (Experimental condition A, summarized in Table 1) Pure CO₂ 0.7 Torr on metallic Cu(111); (experimental condition B) CO₂ + H₂O 0.7 Torr on metallic Cu(111); (experimental condition C) CO₂ + H₂O 0.7 Torr on Cuₓ=2.5O; (experimental condition D) CO₂ + H₂O 0.7 Torr on Cuₓ=1.5O; (experimental condition E) pure CO₂ 0.7 Torr on Cuₓ=1.5O.

Fig. S4. Example of gas phases of CO₂ and H₂O detected with APXPS on C 1s (A) and O 1s (B) spectral regions [B: CO₂ + H₂O 0.7 Torr on metallic Cu(111)] (r.t., 298 K).
Fig. S5. Cu 3p (A) and VB (B) reported for the different experimental conditions and investigated surfaces (at r.t., 298 K). (Experimental condition A) Pure CO$_2$ 0.7 Torr on metallic Cu(111); (experimental condition B) CO$_2$ + H$_2$O 0.7 Torr on metallic Cu(111); (experimental condition C) CO$_2$ + H$_2$O 0.7 Torr on Cu$_{x=2.5}$O; (experimental condition D) CO$_2$ + H$_2$O 0.7 Torr on Cu$_{x=1.5}$O; (experimental condition E) pure CO$_2$ 0.7 Torr on Cu$_{x=1.5}$O. Metallic Cu, Cu$_{x=2.5}$O, and Cu$_{x=1.5}$O were collected in UHV as reference.

Fig. S6. APXPS investigation of the surface chemistry for various surfaces and conditions (performed at r.t., 298 K). (A) Cu L$_3$M$_4$M$_4$ Auger transition for the investigated systems and the reference spectra for metallic Cu, Cu$_{x=2.5}$O, and Cu$_{x=1.5}$O acquired under UHV conditions. The deconvolution of the spectra was performed accordingly with the final state simulation of the primary excitation spectrum F(E). (B) VB spectra at the Fermi edge for the investigated systems and the reference spectra for metallic Cu, Cu$_{x=2.5}$O, and Cu$_{x=1.5}$O acquired under UHV conditions. (Experimental condition A) Pure CO$_2$ 0.7 Torr on metallic Cu(111); (experimental condition B) CO$_2$ + H$_2$O 0.7 Torr on metallic Cu(111); (experimental condition C) CO$_2$ + H$_2$O 0.7 Torr on Cu$_{x=2.5}$O; (experimental condition D) CO$_2$ + H$_2$O 0.7 Torr on Cu$_{x=1.5}$O; (experimental condition E) pure CO$_2$ 0.7 Torr on Cu$_{x=1.5}$O.

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Fig. S7. Illustration of structures for (A) reacted COOH<sub>ad</sub> plus OH<sub>ad</sub> and (B) HCOOH plus surface O<sub>ad</sub>. This complements the structures shown in Fig. 4. On a pristine Cu(111) surface, $\Delta G(A) = +1.36$ eV, $\Delta G(B) = +1.26$ eV; on Cu(111) with 1/4 ML O<sub>sub</sub>, $\Delta G(A) = +0.20$ eV, $\Delta G(B) = -0.05$ eV; on Cu(111) with 1/2 ML O<sub>sub</sub>, $\Delta G(A) = +0.71$ eV, $\Delta G(B) = +0.48$ eV. All free energies are referenced to $p_{CO_2} = p_{H_2O} = 0.35$ Torr, and T = 298 K.

Fig. S8. O 1s and C 1s photoelectron peaks acquired under APXPS conditions at r.t. (298 K) on Cu<sub>x</sub>=1 sO and at r.t. and at a total pressure of CO<sub>2</sub> and O<sub>2</sub> (1:1) of 0.7 Torr. The relative abundance of the different chemically shifted components is expressed in percentage of the total integrated area of each photoelectron spectrum.

Table S1. The performance of M06L and PBE-D3 on Cu fcc metal

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{cohesive}}, \text{kJ/mol}$</th>
<th>a, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment (44)</td>
<td>340</td>
<td>3.595</td>
</tr>
<tr>
<td>M06L</td>
<td>411</td>
<td>3.603</td>
</tr>
<tr>
<td>PBE-D3</td>
<td>394</td>
<td>3.569</td>
</tr>
</tbody>
</table>

Note that the zero-point phonon effects were removed from the reference (Experiment).

Table S2. The performance of M06L and PBE-D3 on CO<sub>2</sub> molecular crystal (ground-state Pa3 structure)

<table>
<thead>
<tr>
<th>Method</th>
<th>$H_{\text{sublimation}}, \text{kJ/mol}$</th>
<th>a, Å</th>
<th>$R_{CO}, \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)/CBS (45)</td>
<td>27</td>
<td>5.475</td>
<td>1.162</td>
</tr>
<tr>
<td>M06L</td>
<td>28</td>
<td>5.426</td>
<td>1.162</td>
</tr>
<tr>
<td>PBE-D3</td>
<td>24</td>
<td>5.673</td>
<td>1.168</td>
</tr>
</tbody>
</table>

Note that the zero-point phonon effects were removed from the reference (coupled cluster singles, doubles, and perturbative triples [CCSD(T)] calculation extrapolated to the complete basis set (CBS) limit).

Other Supporting Information Files

Dataset S1 (PDF)