## **Supplementary information**

## Low-temperature dissociation of CO<sub>2</sub> molecules on vicinal Cu surfaces

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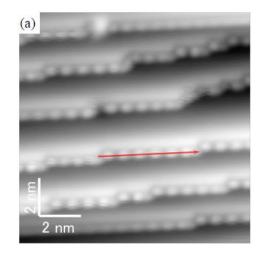
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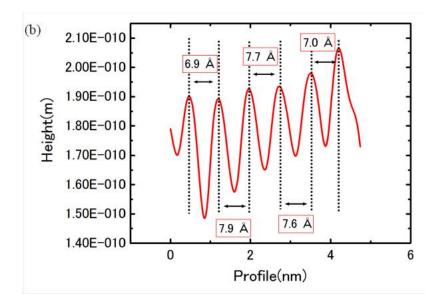
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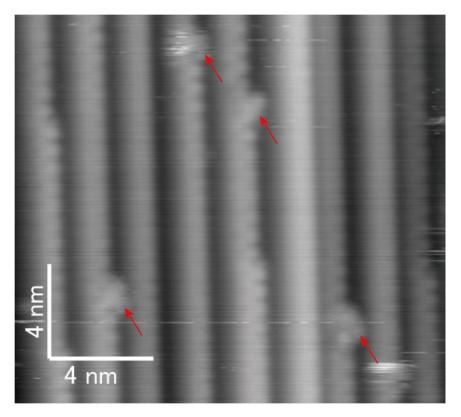
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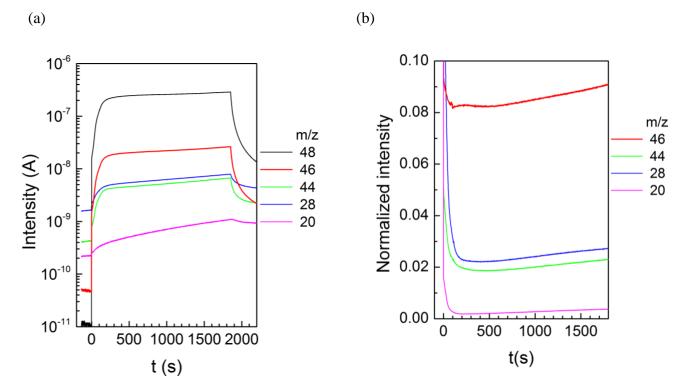




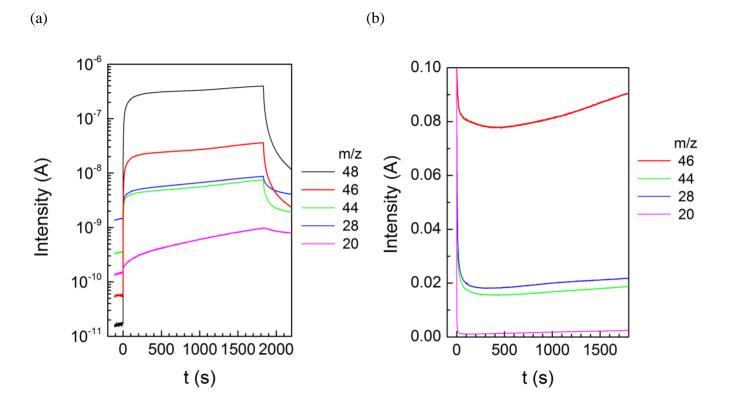
**Figure S1.** (a) An STM image of Cu(997) after 0.3 L CO exposure at 79 K. Vs = +0.5 V and I = 50 pA. (b) A line profile along a red arrow in (a).



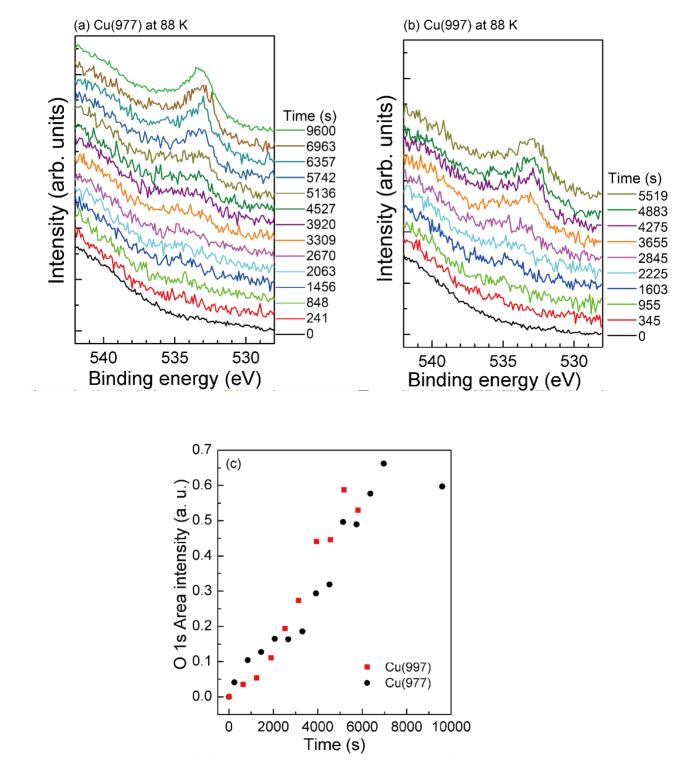
**Figure S2.** An STM image of Cu(997) after 100 L CO<sub>2</sub> exposure at 92 K. Vs = +1.0 V and I = 50 pA. Red arrows in the figure indicate irregular, fuzzy protrusions at kink sites, which are formed after the CO<sub>2</sub> dissociation reaction.



**Figure S3.** (a) QMS spectra during the  $C^{18}O_2$  reaction at a  $CO_2$  pressure of  $1.3 \times 10^{-5}$  Pa on the Cu(997) surface at 82 K as a function of exposure time. (b) Relative QMS intensity normalized by the m/z = 48 signal. The surface was first oppositely oriented from QMS and then faced to QMS at t = 100 s.



**Figure S4.** (a) QMS spectra during the C<sup>18</sup>O<sub>2</sub> reaction at a CO<sub>2</sub> pressure of  $1.3 \times 10^{-5}$  Pa on the cyclohexane-covered Cu(997) surface at 82 K as a function of exposure time. (b) Relative QMS intensity normalized by the m/z = 48 signal. The surface was first oppositely oriented from QMS and then faced to QMS at t = 100 s.



**Figure S5.** O 1s XPS spectra during the CO<sub>2</sub> reaction at a CO<sub>2</sub> pressure of  $3 \times 10^{-6}$  Pa on (a) Cu(977) and (b) Cu(997) at 88 K as a function of exposure time. (c) O 1s total area intensity of the adsorbates.