## Supplementary Information

## Insights into autonomously formed oxygen-evacuated Cu<sub>2</sub>O electrode for the selective production of C<sub>2</sub>H<sub>4</sub> from CO<sub>2</sub>

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Figure S1. Schematic diagram of the H-type cell used for the electrochemical CO<sub>2</sub> reduction.



**Figure S2.** Faradaic efficiencies for all products;  $H_2$  ( $\diamondsuit$ ), CO ( $\blacktriangle$ ), HCOO<sup>-</sup> ( $\bigtriangledown$ ), CH<sub>4</sub> ( $\blacksquare$ ), and C<sub>2</sub>H<sub>4</sub> ( $\bullet$ ) on (a) Cu<sub>2</sub>O and (b) Cu at different applied potentials. CO<sub>2</sub> electrolysis was performed for 30 min at each potential in a CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution.



Figure S3. Current density profiles of (a)  $Cu_2O$  and (b) Cu during  $CO_2$  electrolysis for 2 h.



**Figure S4.** Partial current densities during CO<sub>2</sub> electrolysis of (a) Cu<sub>2</sub>O and (b) Cu for 2 h. H<sub>2</sub> ( $\diamondsuit$ ), CO ( $\blacktriangle$ ), HCOO<sup>-</sup> ( $\bigtriangledown$ ), CH<sub>4</sub> ( $\blacksquare$ ), and C<sub>2</sub>H<sub>4</sub> ( $\bullet$ ).



Cu	0.36	1
Cu <sub>2</sub> O	0.87	2.42

**Figure S5.** Cyclic voltammograms (CVs) for the measurement of the surface roughness factor on Cu<sub>2</sub>O (a) and Cu (b) electrodes in 0.1 M HClO<sub>4</sub> at a scan rate of 40 mV s<sup>-1</sup>, with Ar bubbling.



**Figure S6.** Potential profile during CO<sub>2</sub> electrolysis on Cu electrode at a constant current density of 10 mA cm<sup>-2</sup> for 1 h. Faradaic efficiencies of  $C_2H_4$  (a),  $CH_4$  (b) and  $H_2$  (c) were almost same as the product distribution on Cu electrode at constant potential of -1.9 V.



**Figure S7.** SEM images for the Cu electrode (a) before and (b) after CO<sub>2</sub> electrolysis and the Cu<sub>2</sub>O electrode (c) before and (d) after CO<sub>2</sub> electrolysis at -1.9 vs. Ag/AgCl.



**Figure S8.** TEM images for the Cu electrode (a) before and (b) after  $CO_2$  electrolysis and the Cu<sub>2</sub>O electrode (c) before and (d) after  $CO_2$  electrolysis at -1.9 vs. Ag/AgCl.



**Figure S9.** Auger spectra of  $Cu_2O$  before (a) and after (b)  $CO_2$  electrolysis and Cu before (c) and after (d)  $CO_2$  electrolysis.  $CO_2$  reduction was carried out for 2 h.