Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Selective Electrochemical Reduction of CO_2 to CO on CuO-derived Cu Nanowires

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KEYWORDS: CO_2 reduction, electrochemical reduction of CO_2, Cu nanowires, faradaic efficiency, CO production

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Pt counter electrode

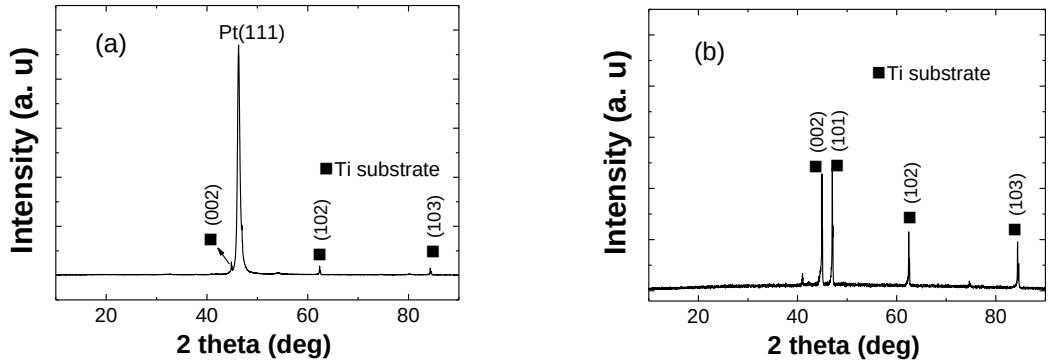

Fig. S1 XRD patterns of Pt film (a) deposited by magnetron sputtering and Ti foil (b).

Pt films (~160 nm) were deposited on Ti foils by using direct current magnetron sputtering (60 W) at 0.3 Pa for 20 min (deposition rate is 0.133 nm/s). The XRD pattern of the Pt film sputtered on Ti foil was shown in Fig. S1 (a). The Pt film coated on Ti foil was used as the counter electrode (anode) in the three-electrode configuration measurement.

Surface preparation of polycrystalline Cu

It is important to remove impurities on the surface of Cu foil.[1,2] SEM images of the copper electrode surface are displayed after polishing by sandpaper in Fig. S2 (a) and subsequent electropolishing in Fig. S2 (b) in order to have a surface free of impurities. In our study the Cu foils were electropolished at 4.0 V for 5 min in 85% phosphoric acid.[3]

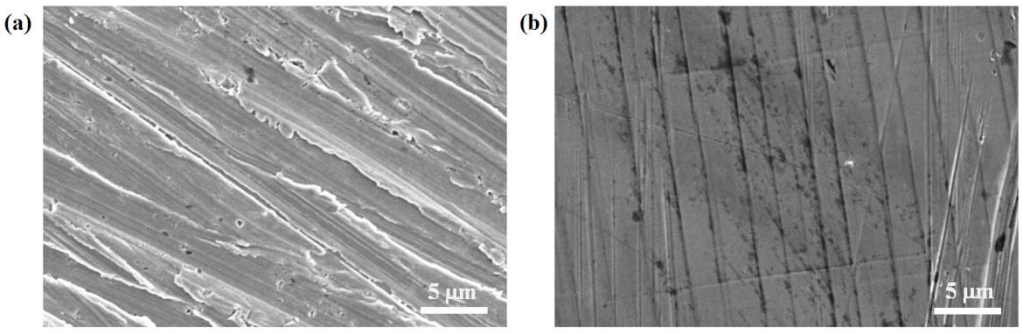

Fig. S2 SEM images of Cu foil before (a) and after (b) electropolishing in 85 % phosphoric acid.

The annealing temperature and time

Some examples of annealed $Cu(OH)_2$ nanowires at different annealing conditions were shown in Fig. S3.

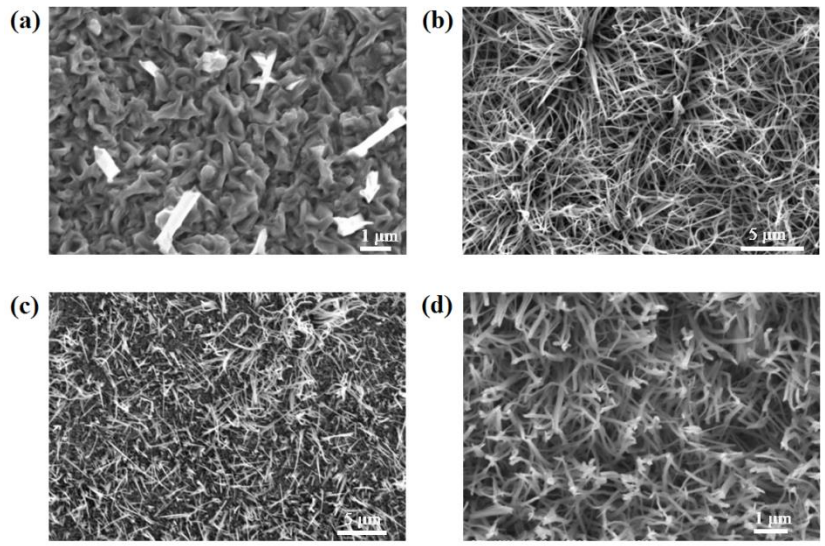

Fig. S3 SEM images of annealed $Cu(OH)_2$ nanowires in argon at 500 ºC (a) and 300 ºC (b) for 1 hour, and in air at 450 ºC for 1 hour (c) and 230 ºC in air for 2 hours (d), respectively.

SEM images of nanowires after electrolysis.

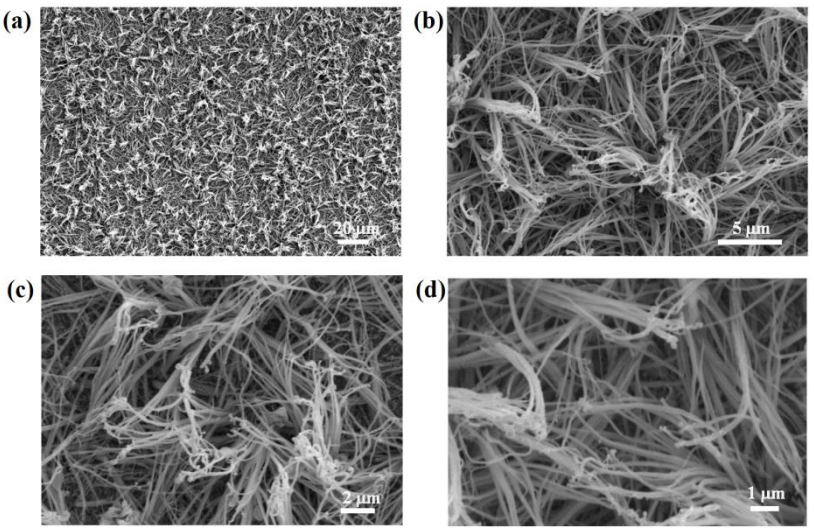

Fig. S4 SEM images of CuO nanowires after CO_2 reduction electrolysis.

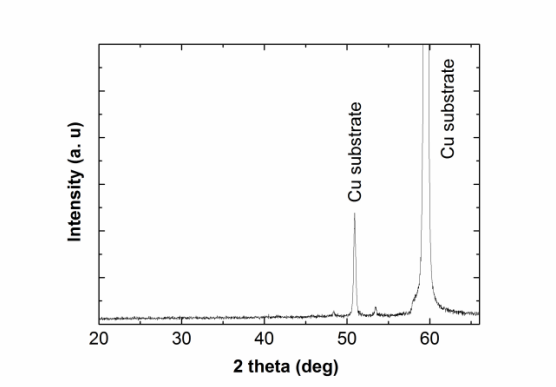

Fig. S5 XRD pattern of the CuO nanowire arrays after CO_2 reduction electrolysis.

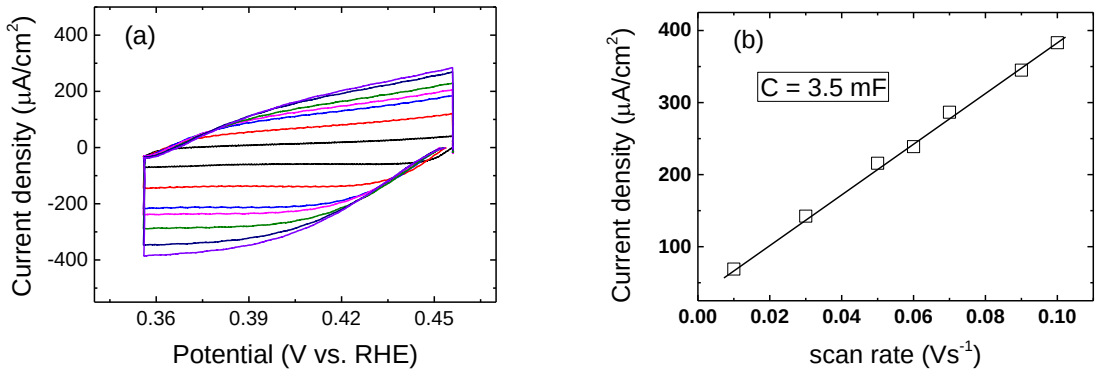

Fig. S6 Determination of double-layer capacitance for the Cu nanowire arrays. (a) the cyclic voltammograms were measured in a non-faradaic region of the voltammogram at the following scan rate: 0.01, 0.03, 0.05, 0.06, 0.07, 0.09 and 0.1 V/s in N_2 bubbled 0.1 M phosphate buffer. The working electrode was held at each potential vertex for 15 s before starting the next sweep. (b) The relationship between the current density and the CV scan rate.

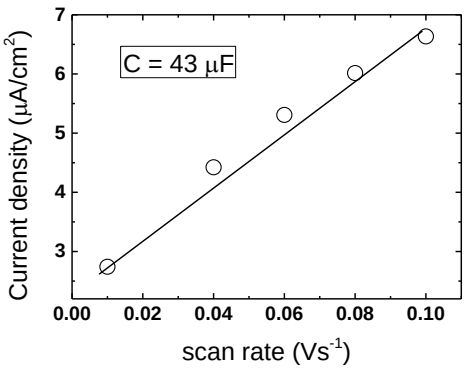

Fig. S7 The relationship between the current density and the CV scan rate for polycrystalline Cu.

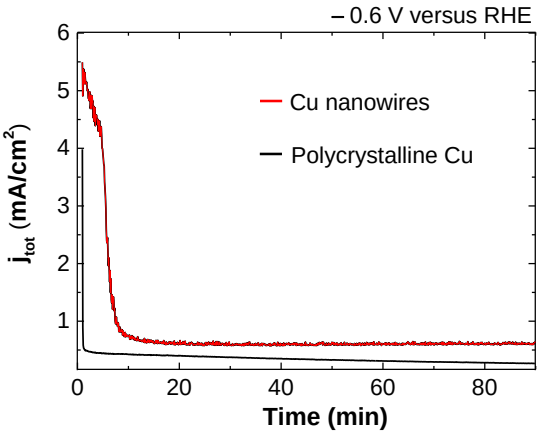

Fig. S8 CO_2 reduction current as a function of time at -0.6 V vs. RHE.

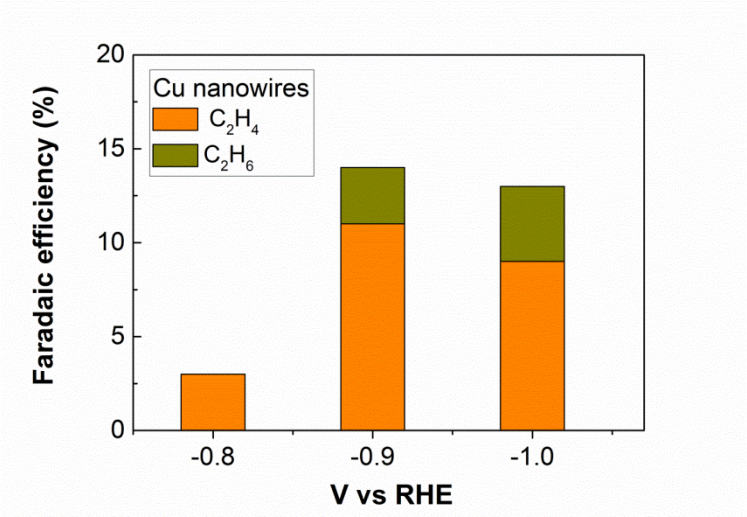

Fig. S9 Faradaic efficiency for $C_2H_4$and C_2H_6 at various potentials in CO_2-saturated 0.1 M $KHCO_3$ electrolytes at ambient temperature and pressure.

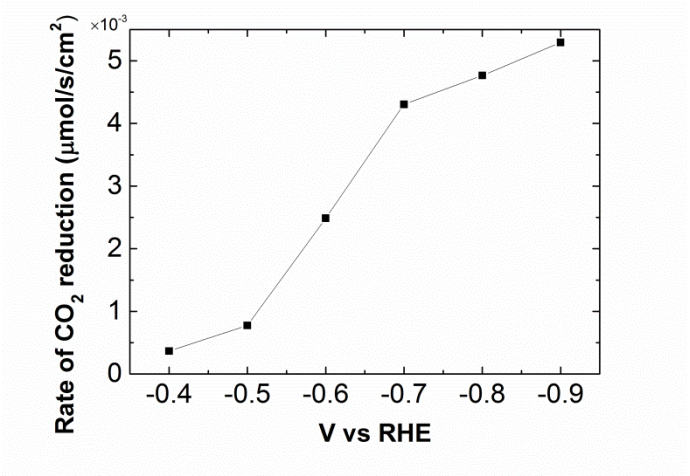

Fig. S10 Total rate of CO_2 reduction as a function of potentials.

The total rate of CO_2 reduction is calculated at a given potential as follow:

$$RR_{CO_2} = \frac{J_{CO}}{2F} + \frac{J_{HCOOH}}{2F} + \frac{J_{C_2H_4}}{6F} + \frac{J_{C_2H_6}}{7F} \quad (1)$$

where J_{CO}, J_{HCOOH}, $J_{C_2H_4}$ and $J_{C_2H_6}$ are the partial current density for each reduction product (CO, HCOOH, C_2H_4 and C_2H_6) of CO_2, and F is the faraday constant. The partial current density for each reduction product of CO_2 is calculated through multiplying the total geometric current density by the faradaic efficiency for each product at a given potential.

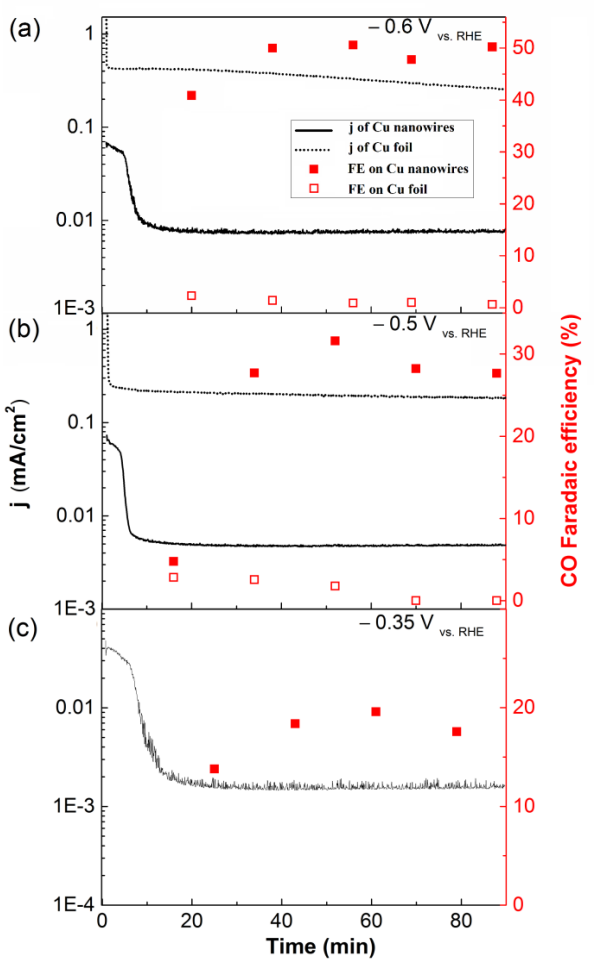

Fig. S11 CO_2 reduction performance of CuO-derived Cu nanowires. CO_2 reduction activity of CuO-derived Cu nanowires and polycrystalline Cu at (a) -0.6 V and (b) -0.5 V, and CuO-derived Cu nanowires at (c) -0.35 V vs. RHE in CO_2-saturated 0.1 M $KHCO_3$ electrolytes (no CO production was observed for polycrystalline Cu at -0.35 V vs. RHE). The logarithm of current density (current density on Cu nanowires is normalized by measured surface roughness in Fig. S9) is shown on the left axis and the faradaic efficiency for CO is shown on the right axis (■ and □ represent CO faradaic efficiency on Cu nanowires and Cu foil respectively).

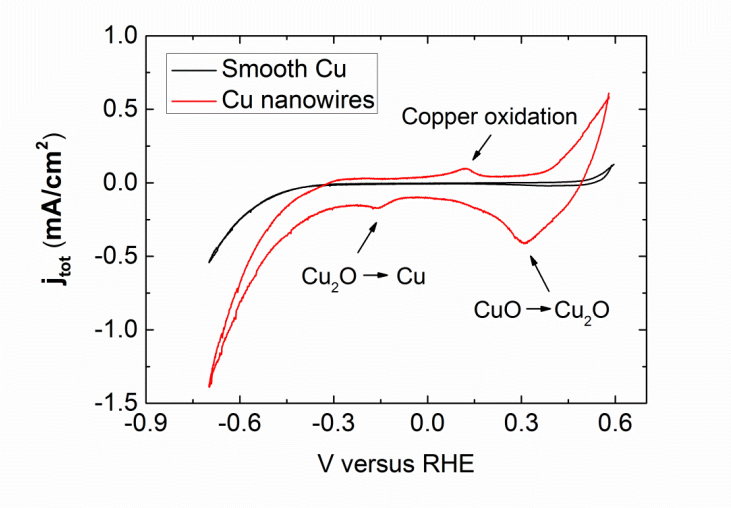

Fig. S12 Cyclic voltammetry (CV) of smooth Cu and Cu nanowire arrays in CO_2-saturated 0.1 M $KHCO_3$ electrolytes at ambient temperature and pressure (scan rate is 0.02 V/s).

References

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(2) Gattrell, M.; Gupta, N.; Co, A. *J. Electroanal. Chem.* **2006**, *594*, 1–19.

(3) Li, C. W.; Kanan, M. W. *J. Am. Chem. Soc.* **2012**, *134* 7231–7234.