

## **Supplementary Information**

**Operando time-resolved X-ray absorption spectroscopy reveals  
the chemical nature enabling highly selective CO<sub>2</sub> reduction**

Lin *et al.*

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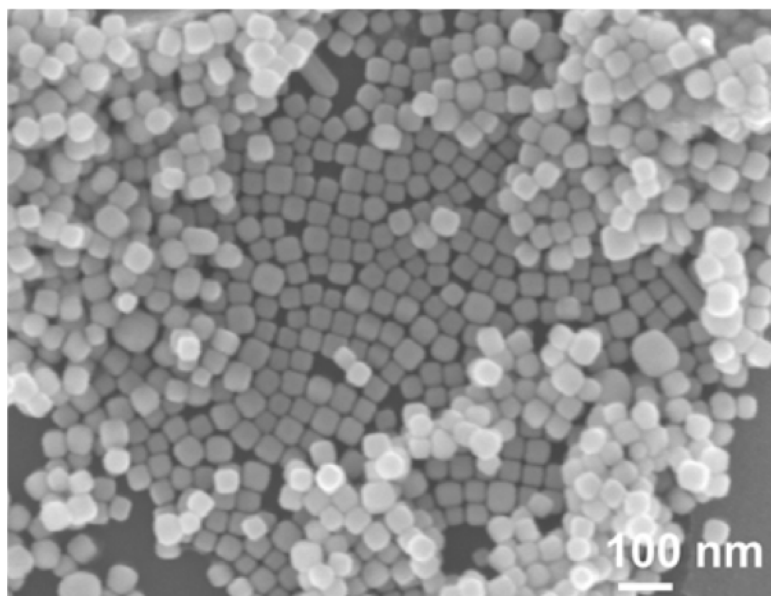
## Supplementary Tables

**Supplementary Table 1.** Cartesian coordinate of Cu/Cu(I) ensemble.

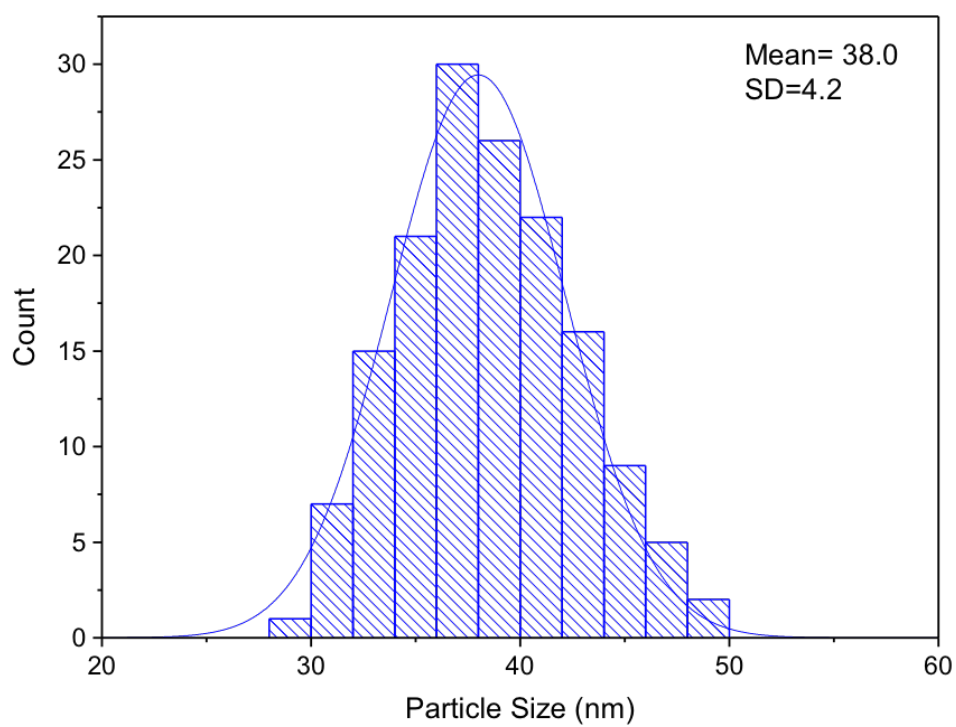
| ELEMENT | X      | Y      | Z     | ELEMENT | X      | Y      | Z     |
|---------|--------|--------|-------|---------|--------|--------|-------|
| Cu      | 3.232  | 2.999  | 0.000 | Cu      | 11.931 | 5.992  | 6.168 |
| Cu      | 3.232  | 6.019  | 0.000 | Cu      | 7.175  | 2.871  | 6.035 |
| Cu      | 3.232  | 9.038  | 0.000 | Cu      | 12.090 | 3.035  | 6.353 |
| Cu      | 3.232  | 12.057 | 0.000 | Cu      | 7.154  | 9.092  | 6.023 |
| Cu      | 7.502  | 2.999  | 0.000 | Cu      | 12.187 | 8.870  | 6.356 |
| Cu      | 11.772 | 2.999  | 0.000 | Cu      | 7.818  | 11.988 | 6.002 |
| Cu      | 7.502  | 6.019  | 0.000 | Cu      | 11.984 | 0.026  | 6.137 |
| Cu      | 11.772 | 6.019  | 0.000 | Cu      | 1.085  | 10.800 | 7.105 |
| Cu      | 7.502  | 9.038  | 0.000 | Cu      | 1.342  | 7.445  | 7.190 |
| Cu      | 11.772 | 9.038  | 0.000 | Cu      | 1.531  | 4.208  | 7.262 |
| Cu      | 7.502  | 12.057 | 0.000 | Cu      | 1.151  | 1.419  | 7.085 |
| Cu      | 11.772 | 12.057 | 0.000 | Cu      | 4.736  | 10.735 | 7.166 |
| Cu      | 5.367  | 10.548 | 1.510 | Cu      | 10.237 | 10.492 | 7.430 |
| Cu      | 9.637  | 10.548 | 1.510 | Cu      | 4.746  | 7.694  | 7.360 |
| Cu      | 5.367  | 7.528  | 1.510 | Cu      | 10.219 | 7.436  | 7.495 |
| Cu      | 9.637  | 7.528  | 1.510 | Cu      | 4.763  | 4.263  | 7.378 |
| Cu      | 5.367  | 4.509  | 1.510 | Cu      | 10.164 | 4.516  | 7.482 |
| Cu      | 9.637  | 4.509  | 1.510 | Cu      | 4.761  | 1.241  | 7.176 |
| Cu      | 5.367  | 1.490  | 1.510 | Cu      | 10.176 | 1.403  | 7.437 |
| Cu      | 9.637  | 1.490  | 1.510 | O       | 2.165  | 2.999  | 1.510 |
| Cu      | 1.097  | 10.548 | 1.510 | O       | 0.030  | 6.019  | 1.510 |
| Cu      | 1.097  | 7.528  | 1.510 | O       | 2.165  | 9.038  | 1.510 |
| Cu      | 1.097  | 4.509  | 1.510 | O       | 0.030  | 12.057 | 1.510 |
| Cu      | 1.097  | 1.490  | 1.510 | O       | 6.435  | 2.999  | 1.510 |
| Cu      | 3.268  | 6.009  | 3.066 | O       | 10.705 | 2.999  | 1.510 |
| Cu      | 3.220  | 3.006  | 3.027 | O       | 4.300  | 6.019  | 1.510 |
| Cu      | 3.197  | 8.990  | 3.045 | O       | 8.570  | 6.019  | 1.510 |
| Cu      | 3.195  | 12.059 | 2.980 | O       | 6.435  | 9.038  | 1.510 |
| Cu      | 7.579  | 6.014  | 3.122 | O       | 10.705 | 9.038  | 1.510 |
| Cu      | 11.783 | 6.008  | 3.038 | O       | 4.300  | 12.057 | 1.510 |

|           |        |        |       |          |        |        |        |
|-----------|--------|--------|-------|----------|--------|--------|--------|
| <b>Cu</b> | 7.457  | 2.983  | 3.109 | <b>O</b> | 8.570  | 12.057 | 1.510  |
| <b>Cu</b> | 11.650 | 3.040  | 3.116 | <b>O</b> | 0.004  | 8.930  | 4.577  |
| <b>Cu</b> | 7.458  | 9.022  | 3.109 | <b>O</b> | 2.024  | 12.053 | 4.375  |
| <b>Cu</b> | 11.664 | 8.954  | 3.116 | <b>O</b> | 12.773 | 3.064  | 4.589  |
| <b>Cu</b> | 7.538  | 12.028 | 3.100 | <b>O</b> | 2.248  | 5.985  | 4.616  |
| <b>Cu</b> | 11.778 | 12.047 | 3.033 | <b>O</b> | 4.192  | 8.968  | 4.577  |
| <b>Cu</b> | 5.305  | 10.504 | 4.619 | <b>O</b> | 8.500  | 9.007  | 4.669  |
| <b>Cu</b> | 9.611  | 10.527 | 4.586 | <b>O</b> | 6.469  | 11.992 | 4.636  |
| <b>Cu</b> | 5.394  | 7.514  | 4.628 | <b>O</b> | 10.752 | 12.022 | 4.546  |
| <b>Cu</b> | 9.610  | 7.485  | 4.600 | <b>O</b> | 4.275  | 2.983  | 4.517  |
| <b>Cu</b> | 5.332  | 1.420  | 4.622 | <b>O</b> | 8.499  | 2.959  | 4.668  |
| <b>Cu</b> | 9.605  | 1.436  | 4.596 | <b>O</b> | 6.525  | 6.003  | 4.673  |
| <b>Cu</b> | 5.434  | 4.464  | 4.615 | <b>O</b> | 10.750 | 5.985  | 4.547  |
| <b>Cu</b> | 9.608  | 4.486  | 4.608 | <b>O</b> | 5.854  | 2.773  | 7.315  |
| <b>Cu</b> | 0.980  | 10.524 | 4.515 | <b>O</b> | 11.065 | 2.962  | 7.850  |
| <b>Cu</b> | 1.117  | 7.450  | 4.683 | <b>O</b> | 9.106  | 5.998  | 7.384  |
| <b>Cu</b> | 0.966  | 1.488  | 4.521 | <b>O</b> | 5.817  | 9.196  | 7.294  |
| <b>Cu</b> | 1.104  | 4.526  | 4.717 | <b>O</b> | 11.175 | 8.963  | 7.858  |
| <b>Cu</b> | 3.001  | 2.649  | 6.015 | <b>O</b> | 9.158  | 11.965 | 7.287  |
| <b>Cu</b> | 2.891  | 9.388  | 6.055 | <b>a</b> | 12.810 | 0.000  | 0.000  |
| <b>Cu</b> | 3.019  | 12.054 | 6.104 | <b>b</b> | 0.000  | 12.077 | 0.000  |
| <b>Cu</b> | 7.860  | 6.004  | 6.029 | <b>c</b> | 0.000  | 0.000  | 22.548 |

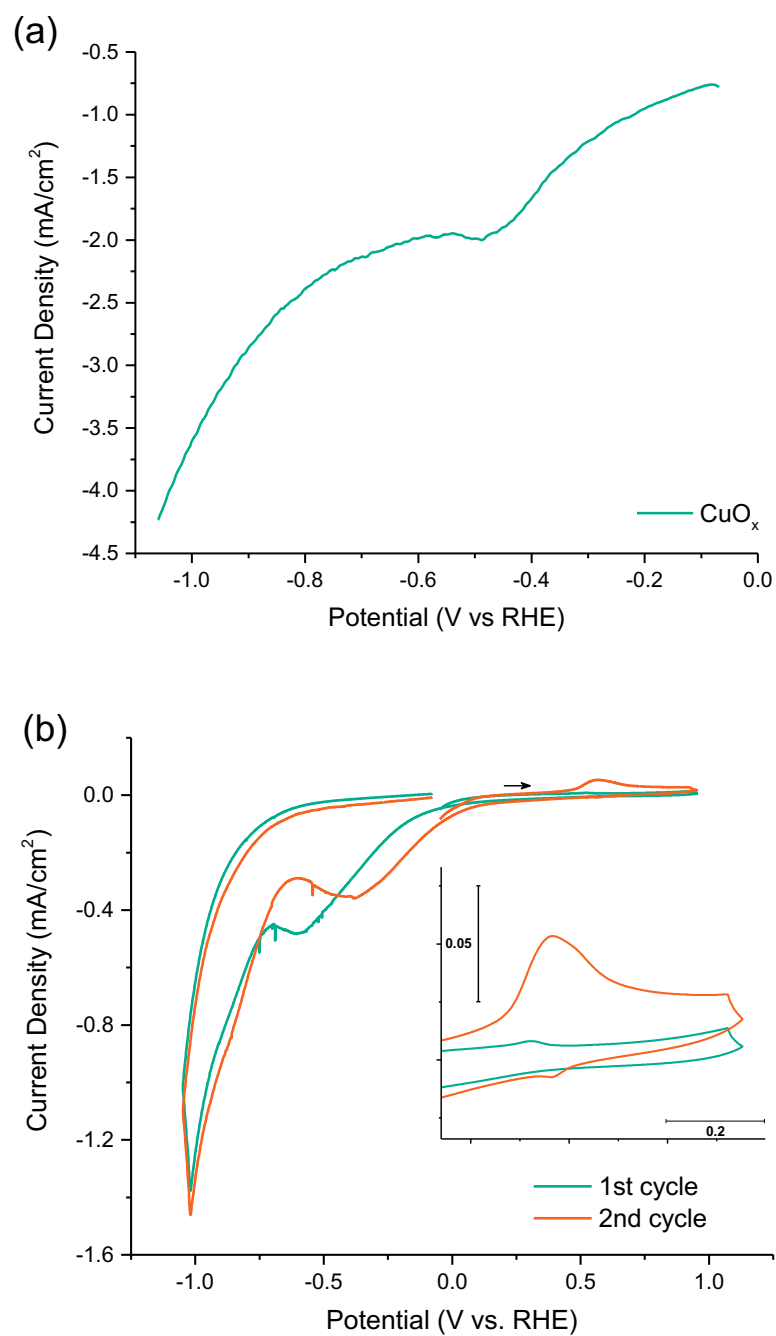
## Supplementary Figures



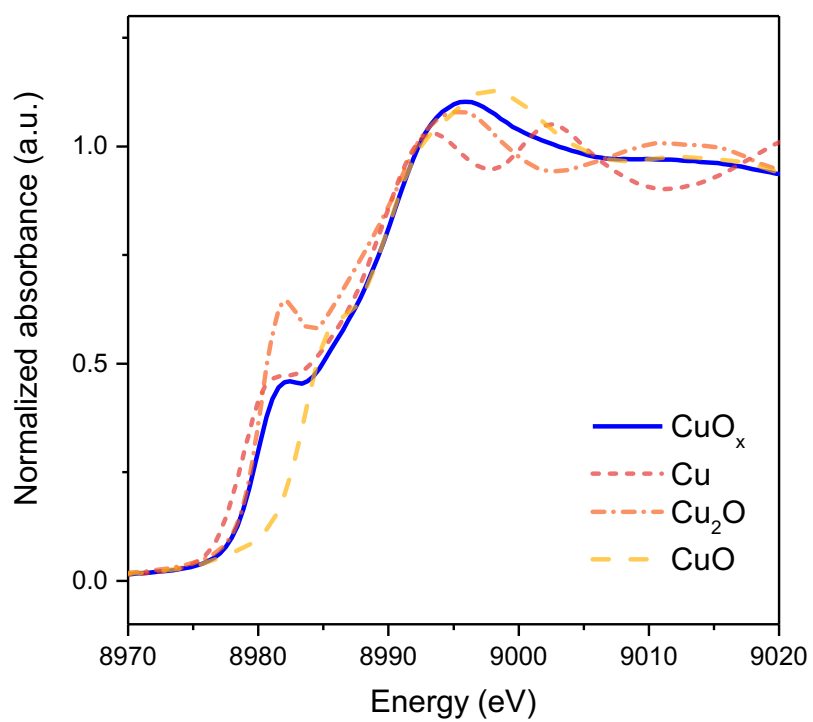
**Supplementary Figure 1.** SEM image of Cu nanocubes.



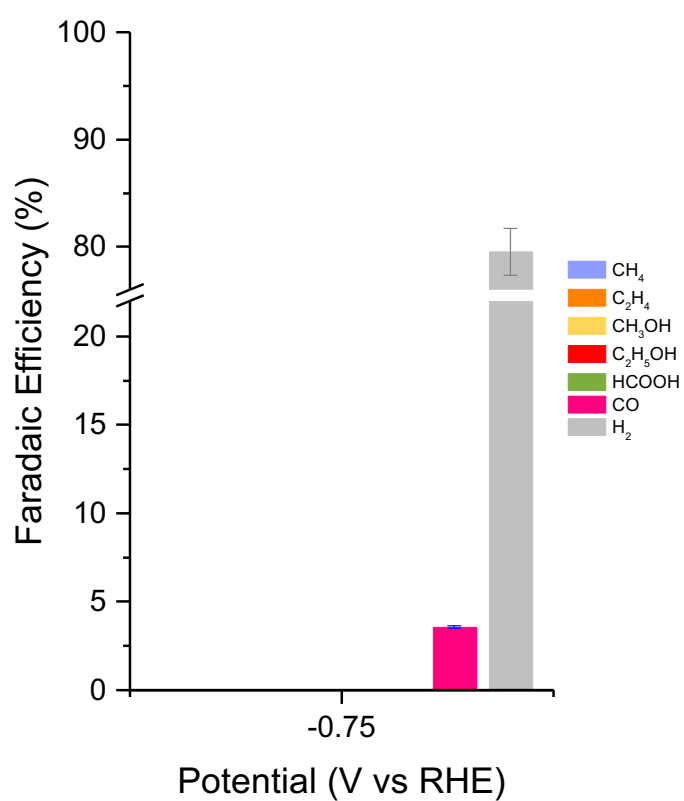
**Supplementary Figure 2.** Particle size distribution statistics of Cu nanocubes.



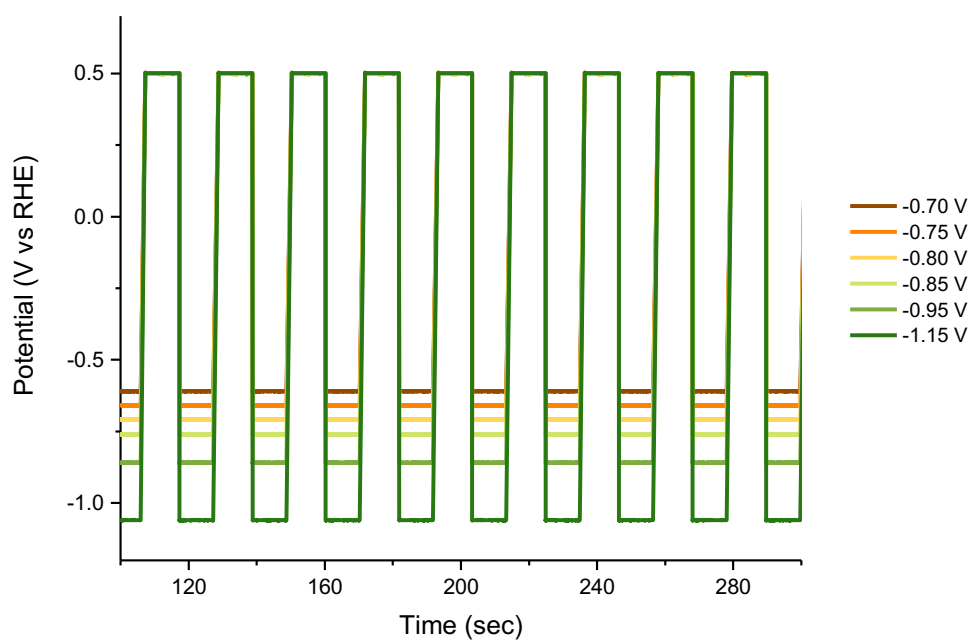
**Supplementary Figure 3.** (a) Linear sweep voltammetry (LSV) of the  $\text{CuO}_x$ . Scan rate: 100 mV/s. Solution composition: 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$ . (b) Cyclic voltammograms (CV) of the  $\text{CuO}_x$  recorded in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at 100 mV/s. In the inset, zoom of the current density values.



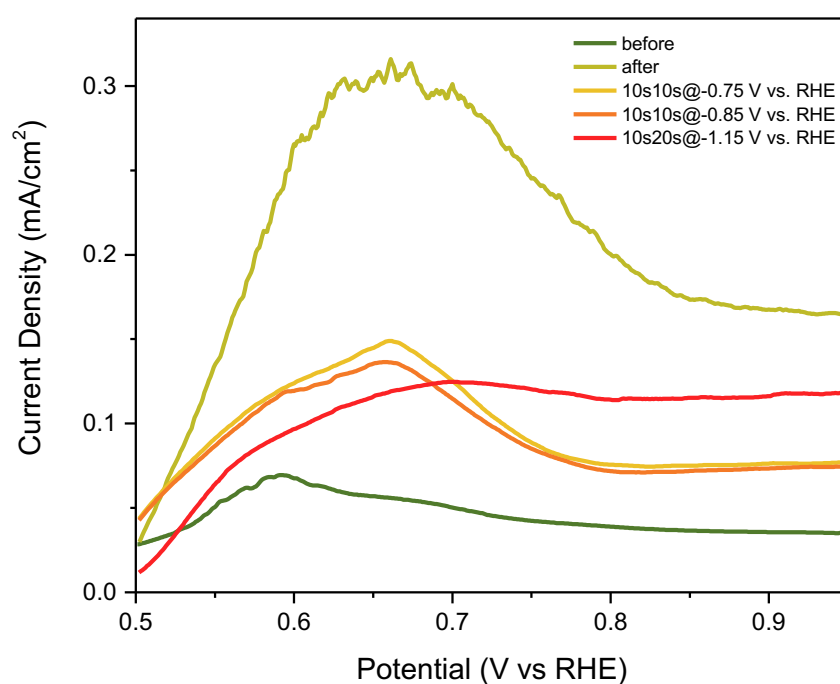
**Supplementary Figure 4.** The Cu K-edge XANES spectra of  $\text{CuO}_x$  and of Cu foil, commercial  $\text{Cu}_2\text{O}$  and CuO as references.



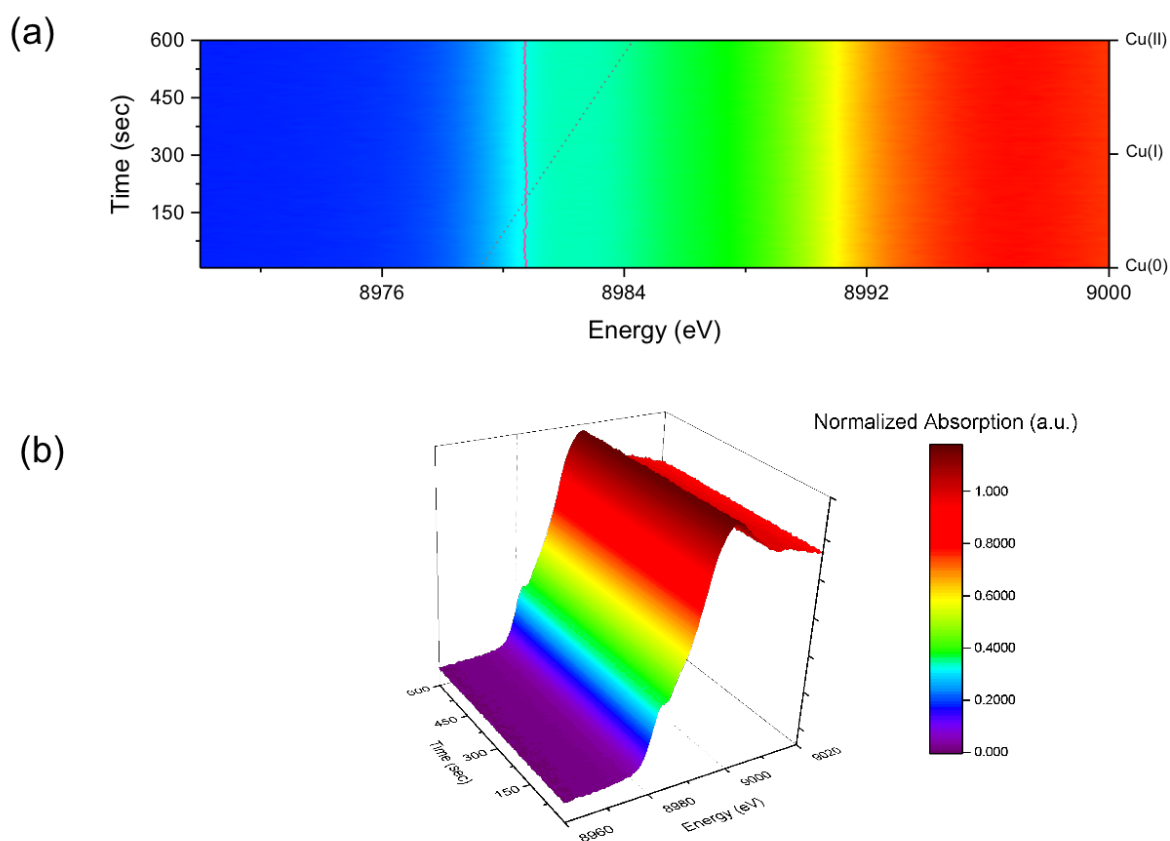
**Supplementary Figure 5.** eCO<sub>2</sub>RR performance of CuO<sub>x</sub> at -0.75 V in 0.5 M CO<sub>2</sub>-saturated KHCO<sub>3</sub> using chronoamperometry. The error bars represented standard deviations based on three individual measurements.



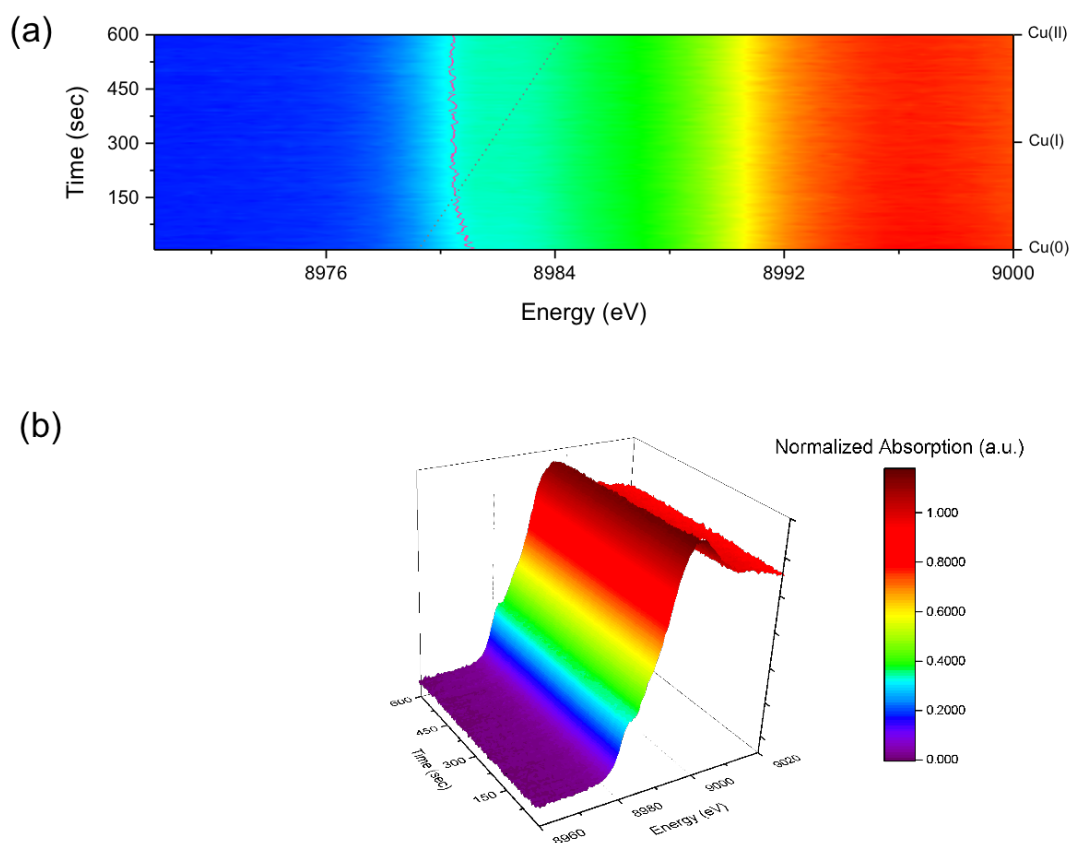
**Supplementary Figure 6.** Potential map of redox shuttle approach with a constant anodic potential (0.5 V vs RHE) and various cathodic potentials as indicated in the figure. The time period of each potential set was 10 seconds.



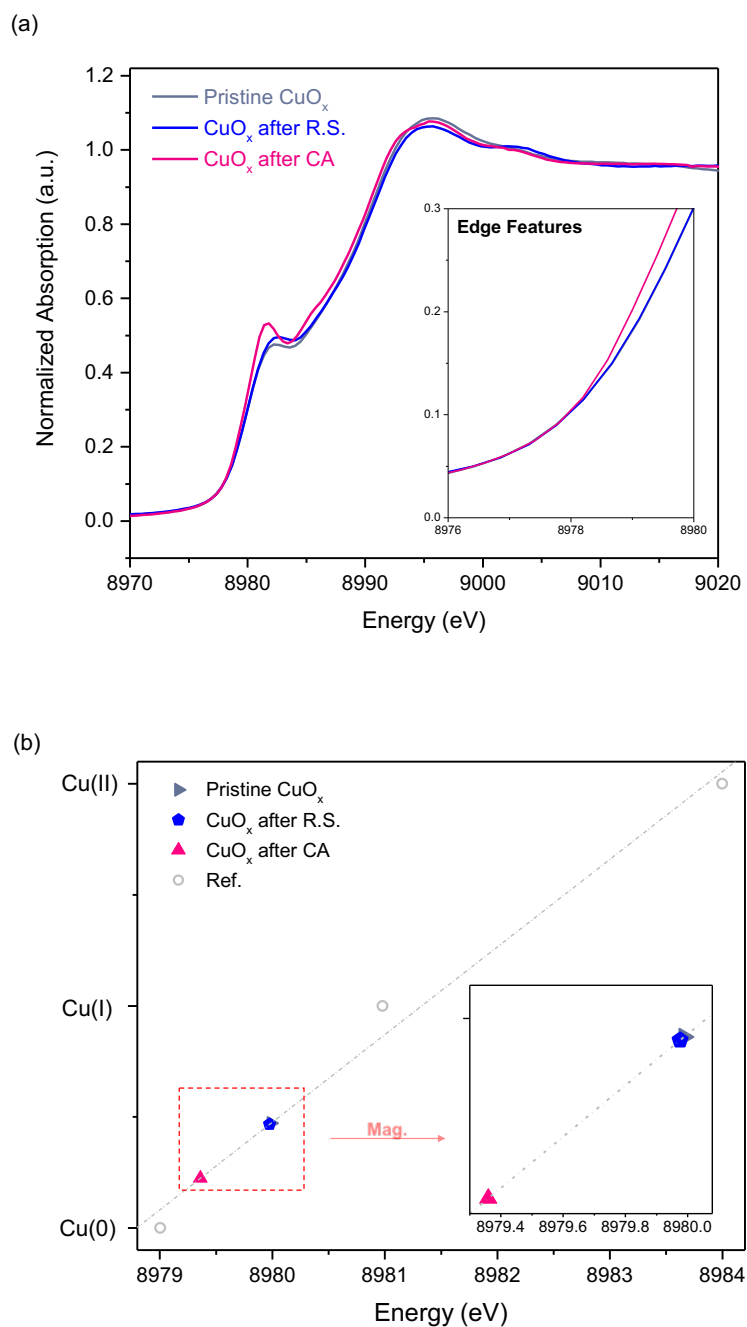
**Supplementary Figure 7.** Cyclic voltammograms (CV) of  $\text{CuO}_x$  recorded in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at 100 mV/s using various techniques.



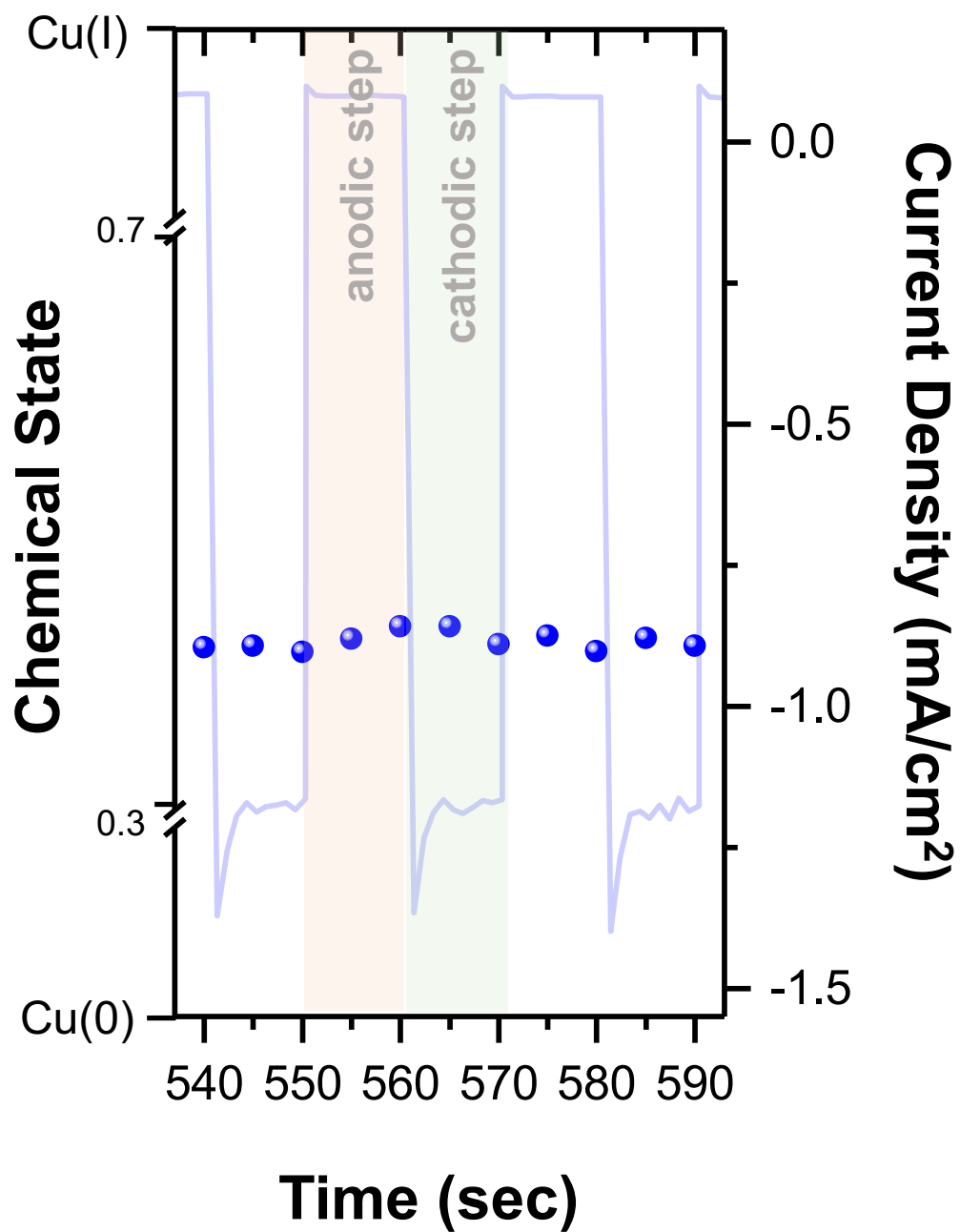
**Supplementary Figure 8.** (a) The double-y plot of the 2D contour plot of *operando* quick-scanning Cu K-edge XANES spectra of  $\text{CuO}_x$  under  $\text{eCO}_2\text{RR}$  in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at -0.75 V using Redox Shuttle (R.S.). The y-axis in the left represents time, while the y-axis in the right represents Cu,  $\text{Cu}_2\text{O}$  and CuO references. (b) The 3D surface plot of *operando* quick-scanning Cu K-edge XANES spectra of  $\text{CuO}_x$  under  $\text{eCO}_2\text{RR}$  in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at -0.75 V using R.S..



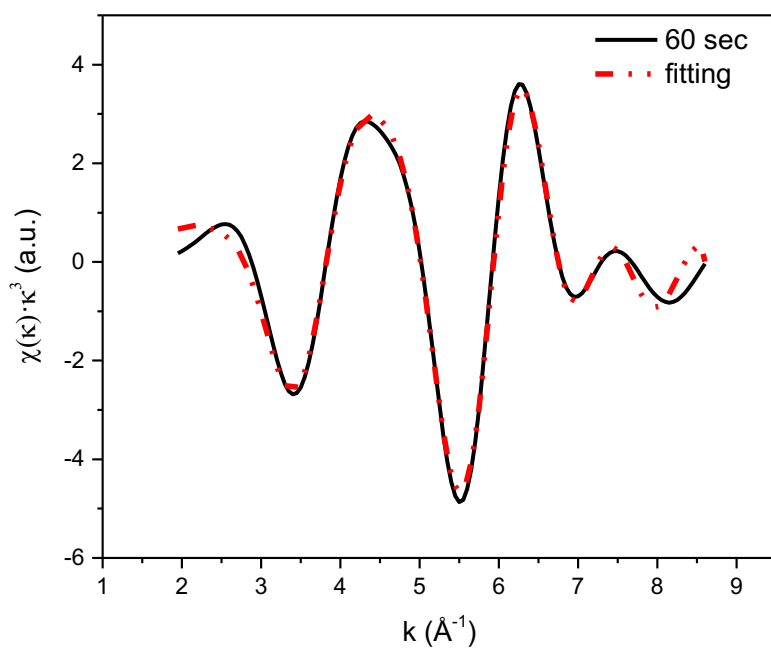
**Supplementary Figure 9.** (a) The double-y plot of the 2D contour plot of *operando* quick-scanning Cu K-edge XANES spectra of  $\text{CuO}_x$  under  $\text{eCO}_2\text{RR}$  in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at -0.75 V using conventional chronoamperometry (CA). The y-axis in the left represents time, while the y-axis in the right represents Cu,  $\text{Cu}_2\text{O}$  and CuO references. (b) The 3D surface plot of *operando* quick-scanning Cu K-edge XANES spectra of  $\text{CuO}_x$  under  $\text{eCO}_2\text{RR}$  in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  at -0.75 V using CA.



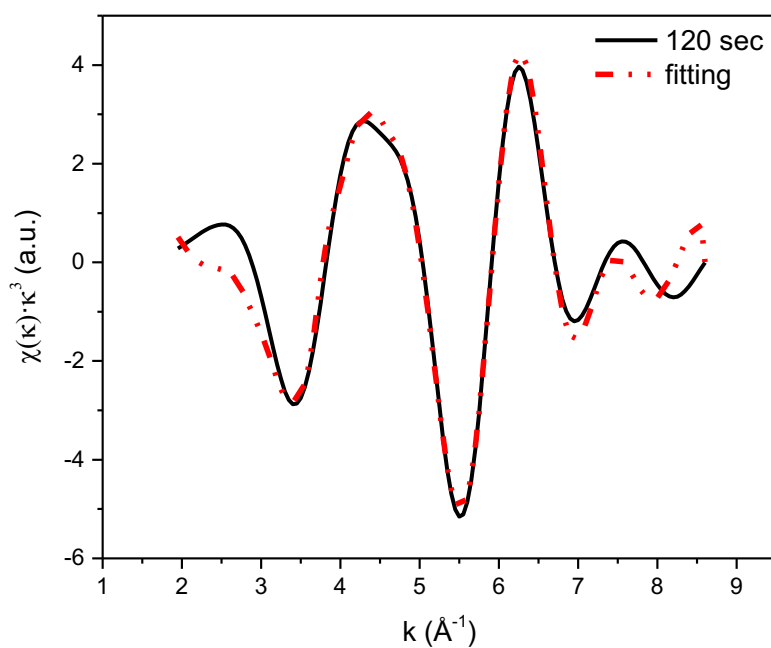
**Supplementary Figure 10.** (a) XANES spectra of pristine  $\text{CuO}_x$ , the  $\text{CuO}_x$  after a  $\text{CO}_2\text{RR}$  electrolysis using R.S., and the  $\text{CuO}_x$  after a  $\text{CO}_2\text{RR}$  electrolysis using CA. (b) Chemical nature of various Cu species – including commercial Cu,  $\text{Cu}_2\text{O}$ , and CuO as references, and the pristine  $\text{CuO}_x$ , the  $\text{CuO}_x$  after the R.S.  $\text{CO}_2\text{RR}$  treatment, and the  $\text{CuO}_x$  after the CA  $\text{CO}_2\text{RR}$  treatment. The working cathodic potential was  $-0.75$  V, and the electrolyte was  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$ . Linear dependence ( $R^2 = 0.99$ ) based on the reference samples is shown by the gray dash line.



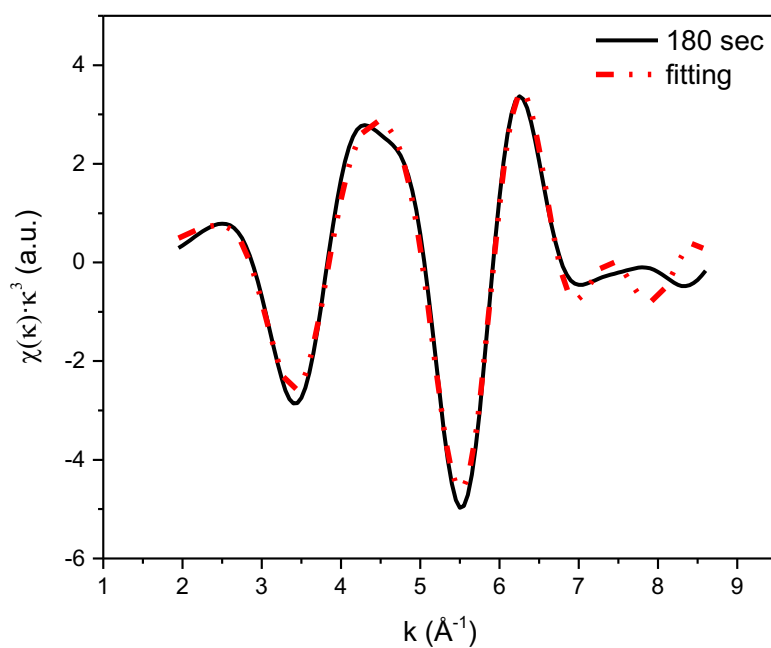
**Supplementary Figure 11.** Magnified portion of Figure 2b. The anodic step of R.S. was highlighted in orange, while the cathodic step was in green.



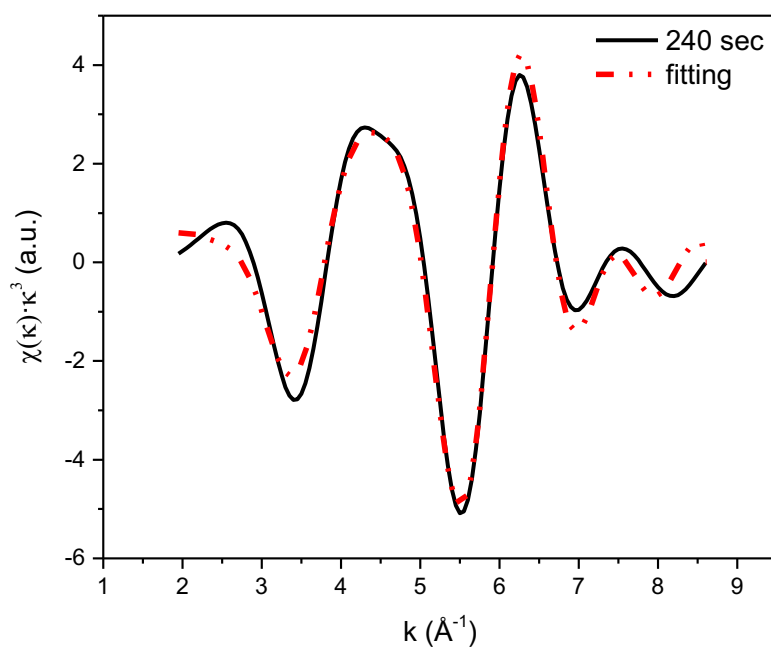
**Supplementary Figure 12.** Snapshot at 60 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



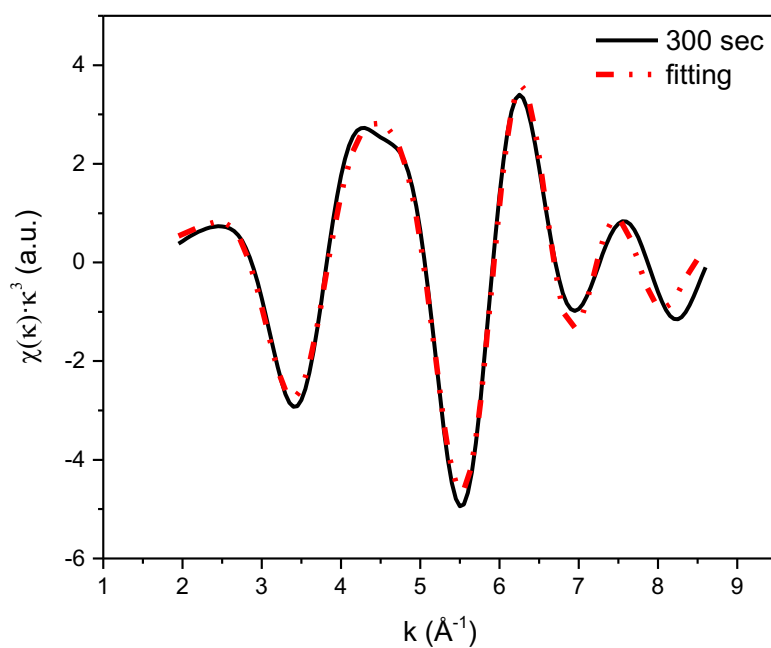
**Supplementary Figure 13.** Snapshot at 120 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



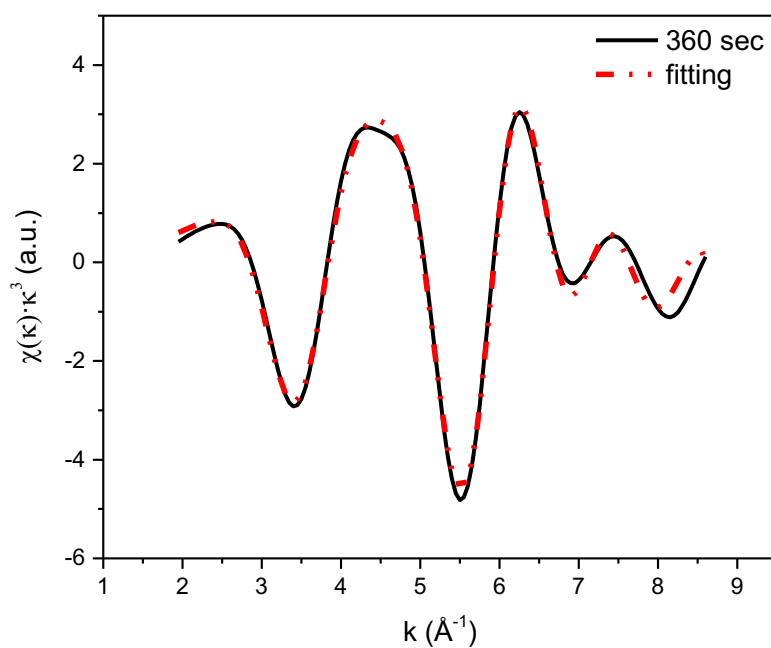
**Supplementary Figure 14.** Snapshot at 180 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



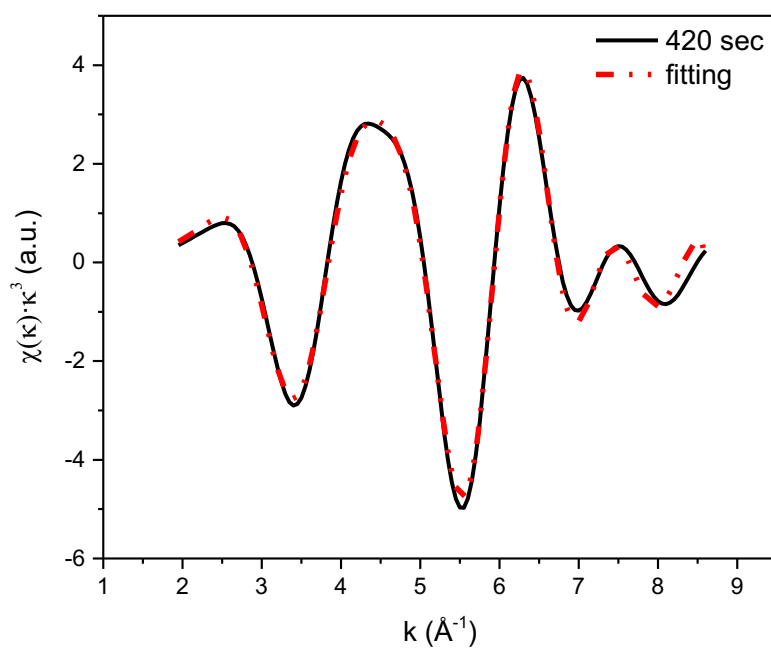
**Supplementary Figure 15.** Snapshot at 240 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



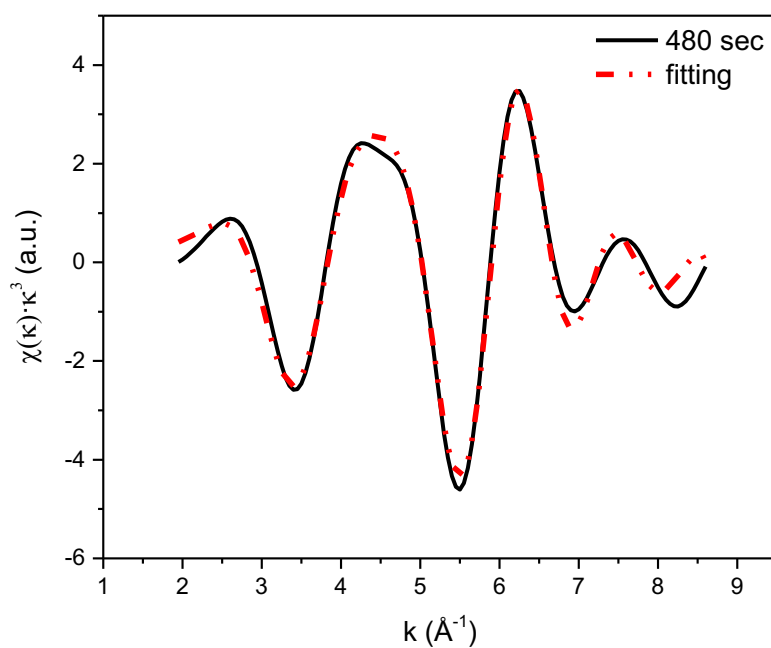
**Supplementary Figure 16.** Snapshot at 300 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



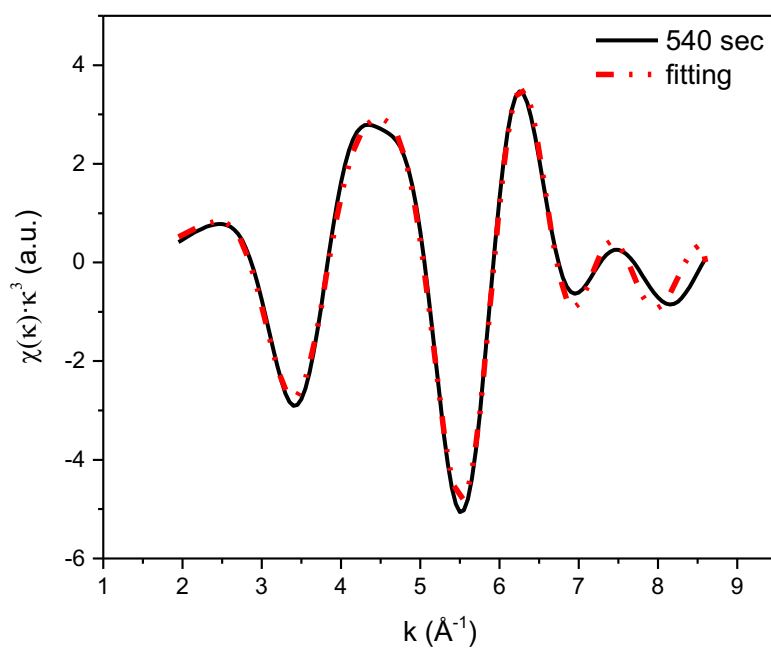
**Supplementary Figure 17.** Snapshot at 360 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



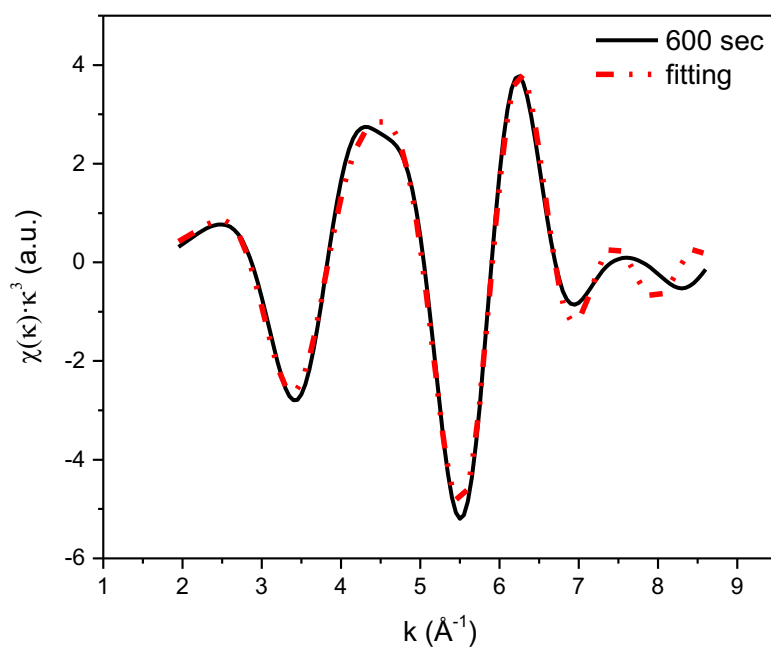
**Supplementary Figure 18.** Snapshot at 420 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



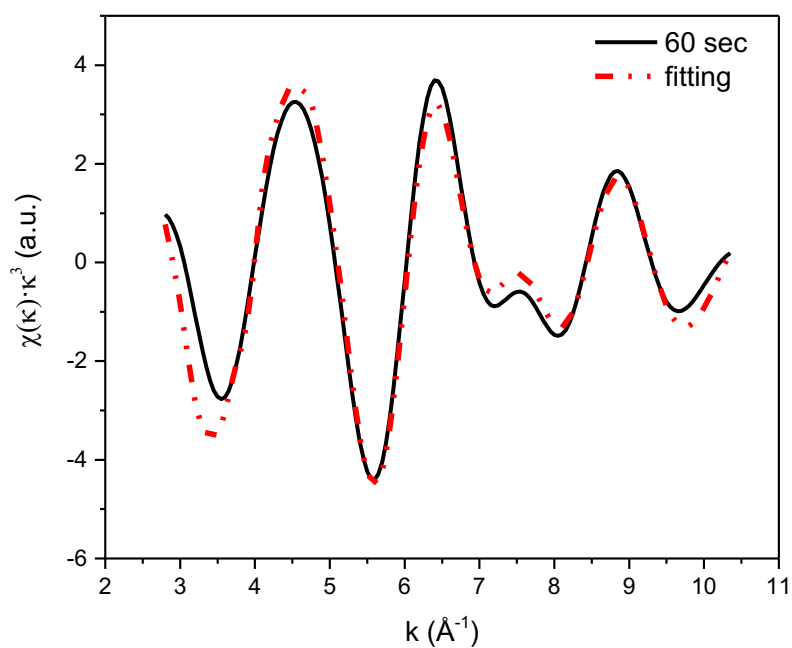
**Supplementary Figure 19.** Snapshot at 480 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



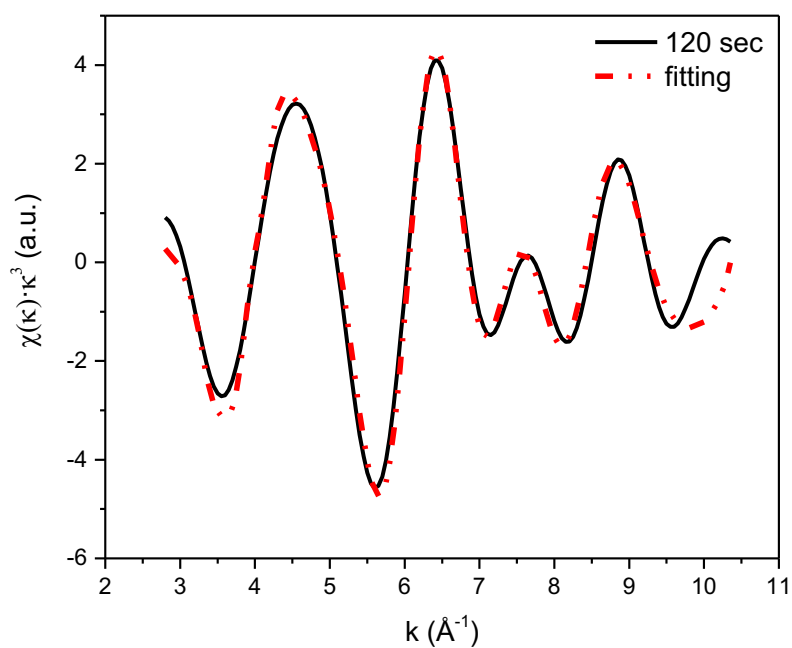
**Supplementary Figure 20.** Snapshot at 540 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



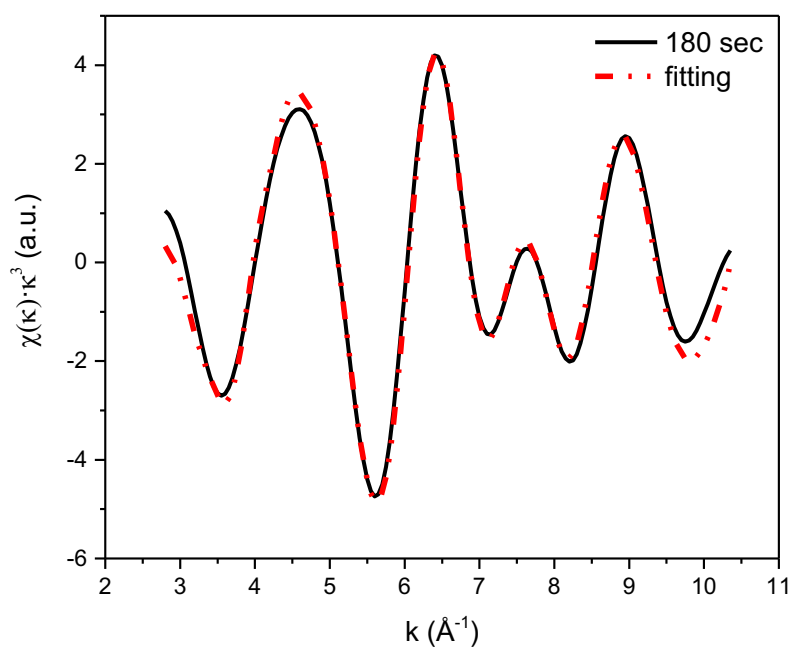
**Supplementary Figure 21.** Snapshot at 600 sec of time-resolved EXAFS fitting curves in  $k$ -space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach.



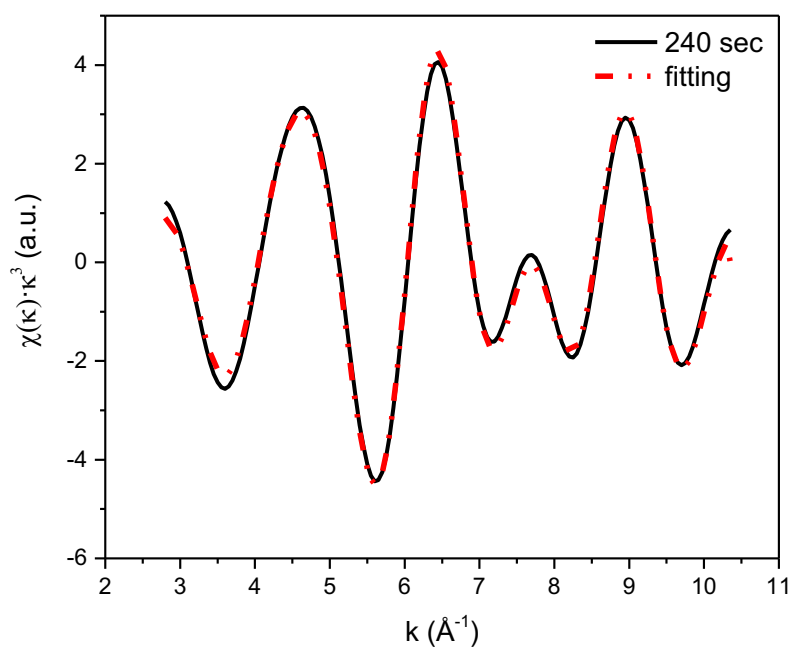
**Supplementary Figure 22.** Snapshot at 60 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



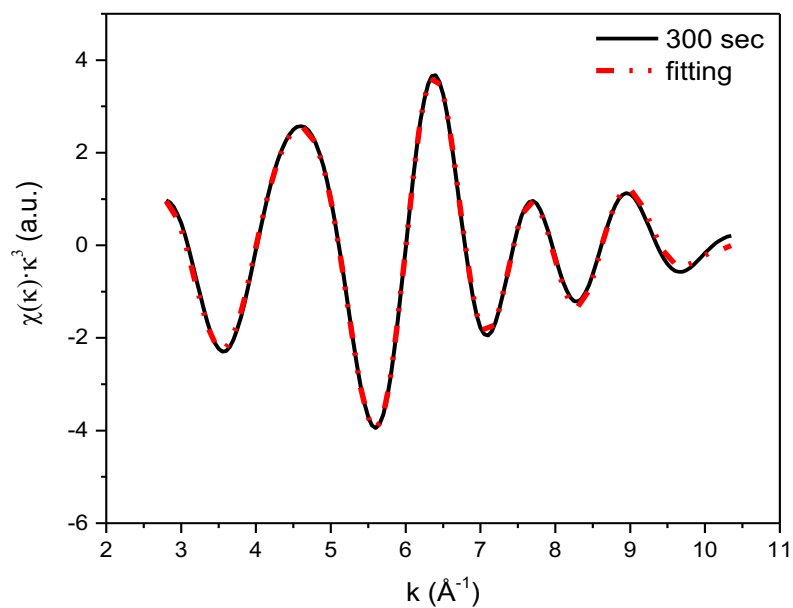
**Supplementary Figure 23.** Snapshot at 120 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at -0.75 V in 0.5 M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



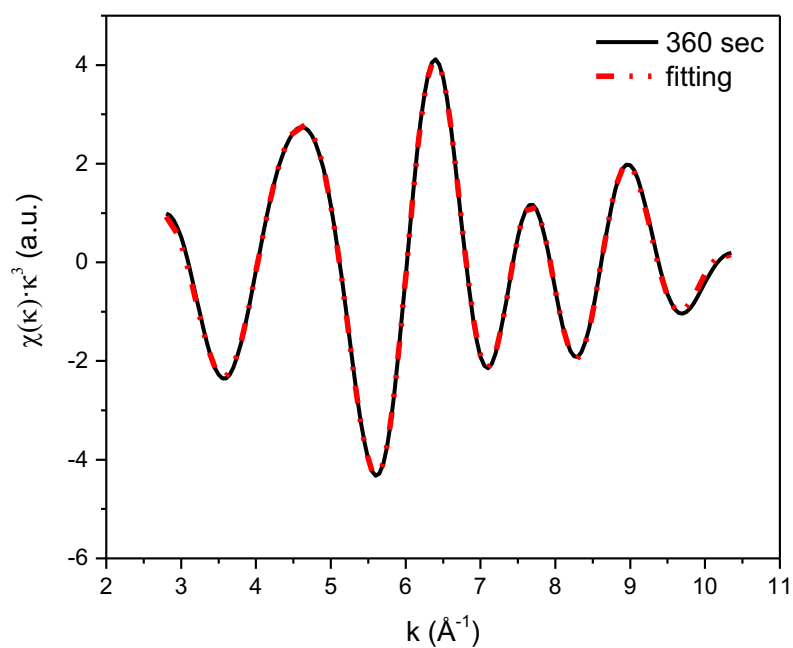
**Supplementary Figure 24.** Snapshot at 180 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



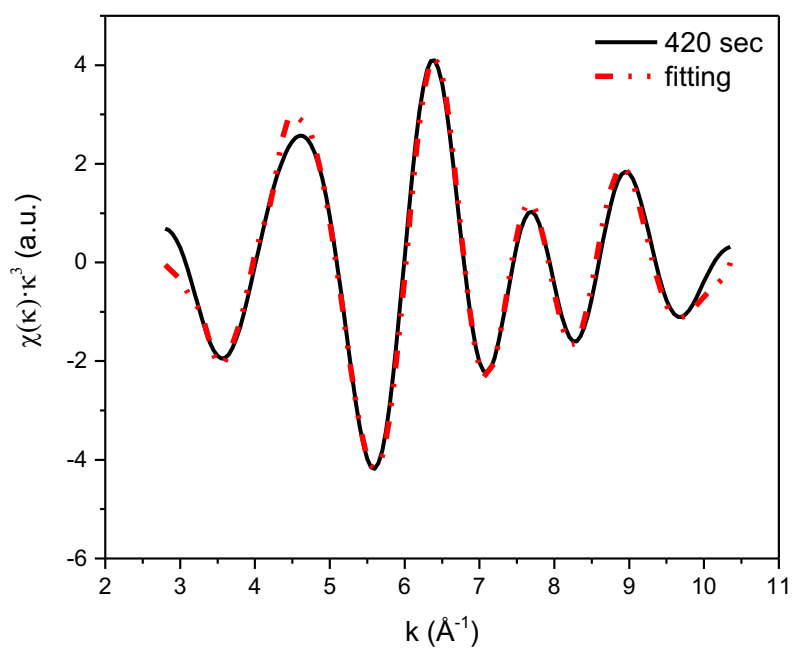
**Supplementary Figure 25.** Snapshot at 240 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



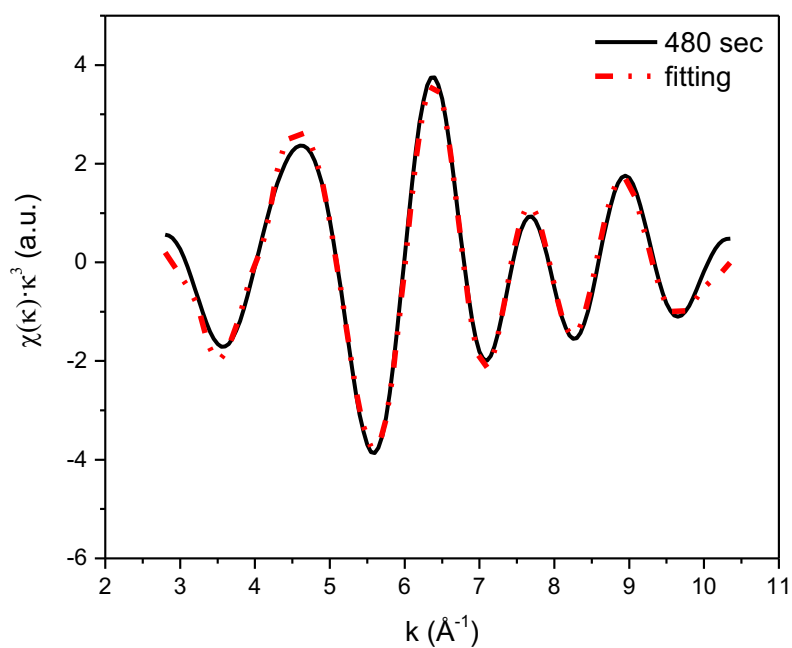
**Supplementary Figure 26.** Snapshot at 300 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



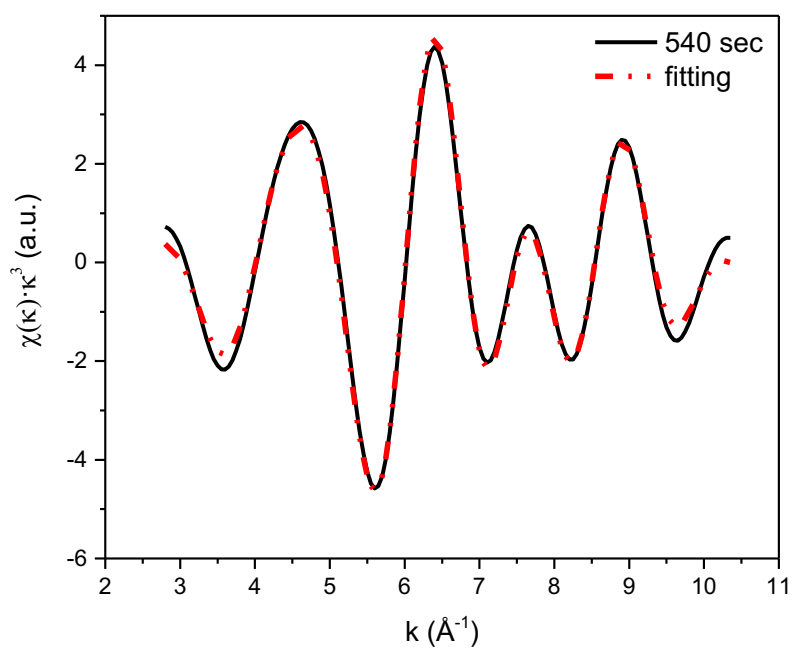
**Supplementary Figure 27.** Snapshot at 360 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



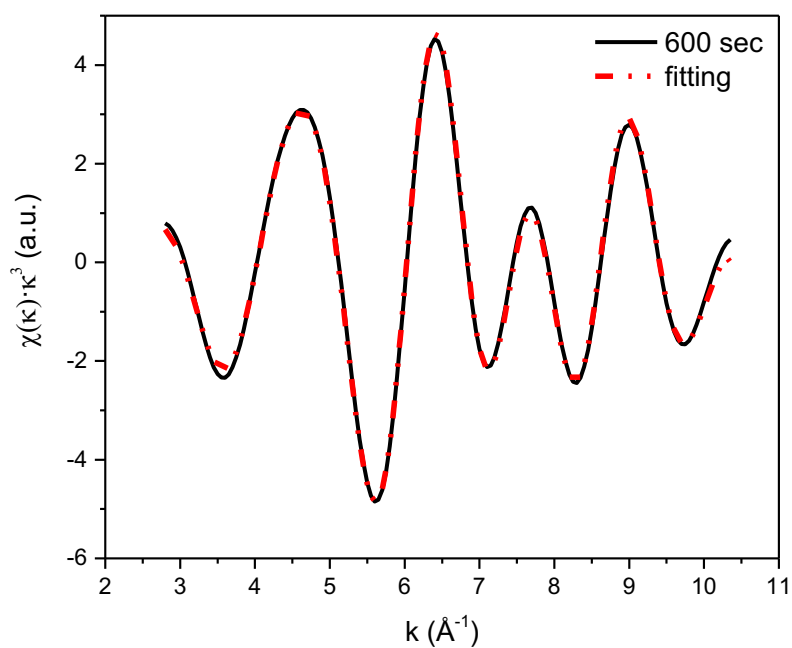
**Supplementary Figure 28.** Snapshot at 420 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



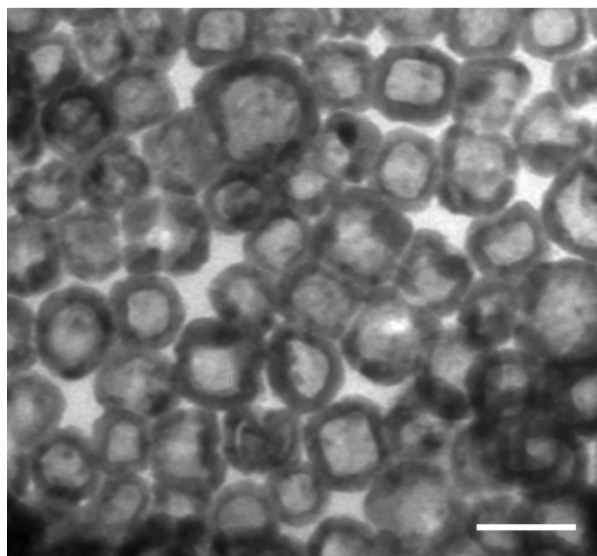
**Supplementary Figure 29.** Snapshot at 480 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



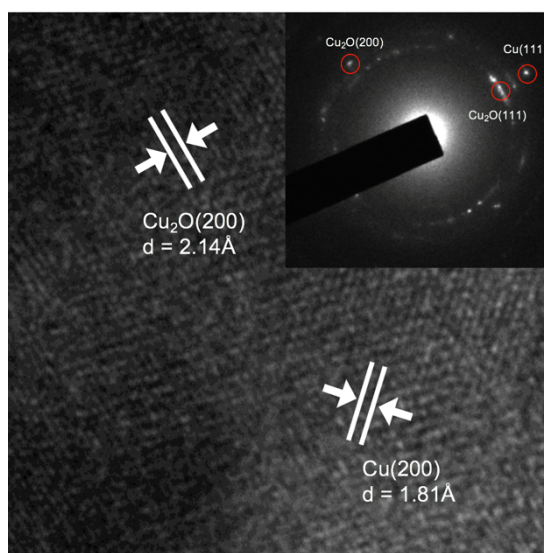
**Supplementary Figure 30.** Snapshot at 540 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.



**Supplementary Figure 31.** Snapshot at 600 sec of time-resolved EXAFS fitting curves in k-space for  $\text{CuO}_x$  at  $-0.75$  V in  $0.5$  M  $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using chronoamperometry.

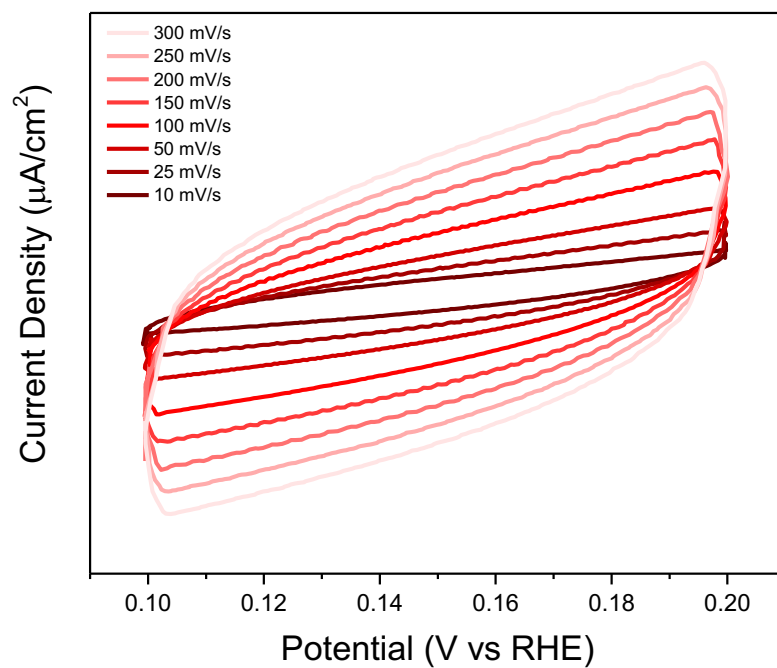


**Supplementary Figure 32.** TEM image of the  $\text{CuO}_x$  after 6-hours  $\text{CO}_2\text{RR}$  electrolysis. The electrochemical reaction was at  $-0.75\text{ V}$  in  $0.5\text{ M}$   $\text{CO}_2$ -saturated  $\text{KHCO}_3$  using redox shuttle approach. Scale bar present in the image is  $50\text{ nm}$ .

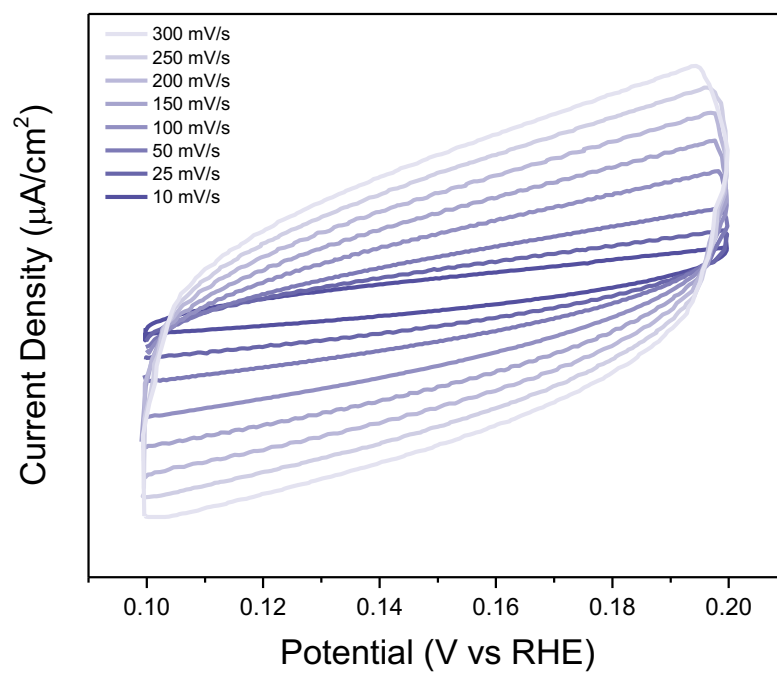


**Supplementary Figure 33.** HR-TEM image and SAED pattern (inset) of post- $\text{CuO}_x$ . The  $\text{CuO}_x$  was used for a 6-hours  $\text{eCO}_2\text{RR}$  using redox shuttle approach in  $0.5\text{ M}$   $\text{CO}_2$ -saturated  $\text{KHCO}_3$ .

(a)

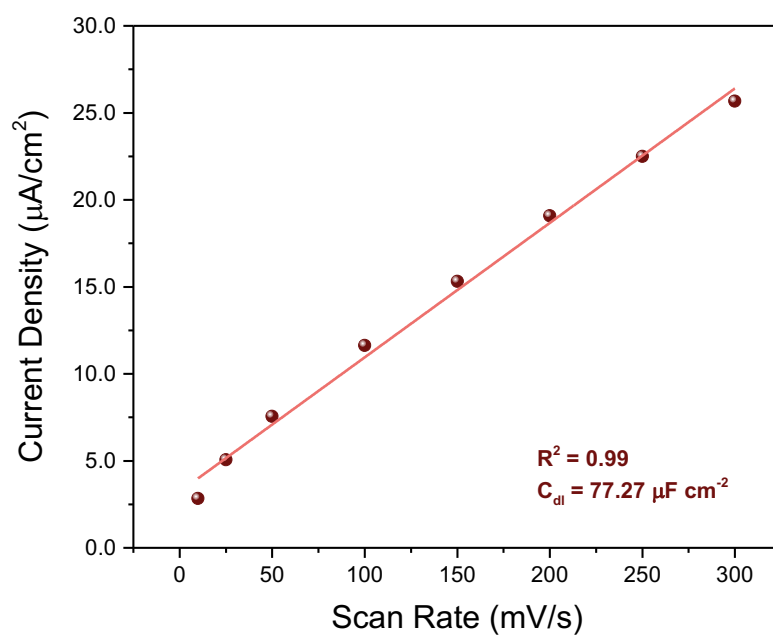


(b)

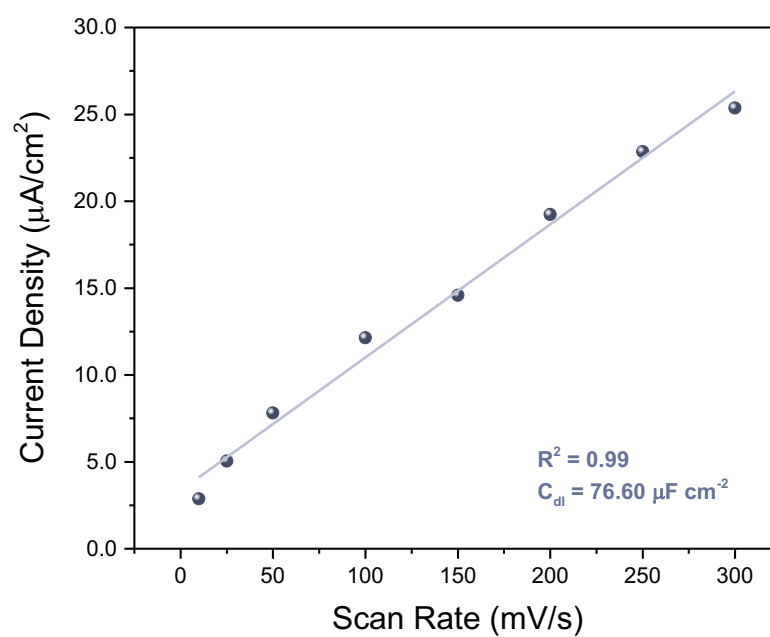


**Supplementary Figure 34.** Cyclic voltammograms in the region of 0.1-0.2 V for the CuO<sub>x</sub> (a) before and (b) after CO<sub>2</sub>RR treatment using Redox Shuttle (R.S.) at -0.75 V in 0.5 M N<sub>2</sub>-saturated KHCO<sub>3</sub>.

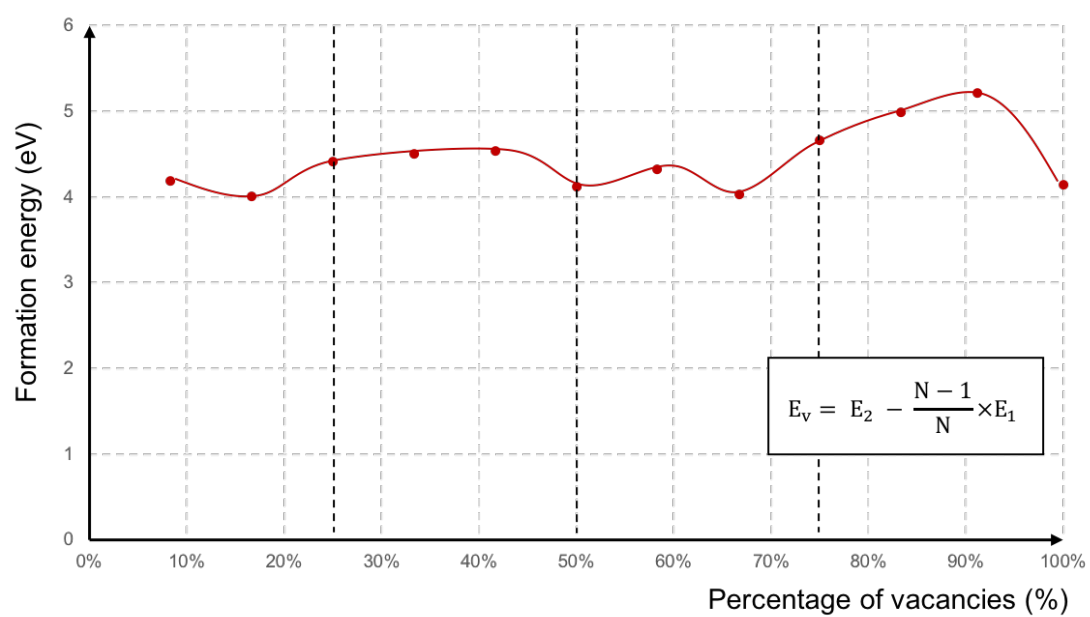
(a)



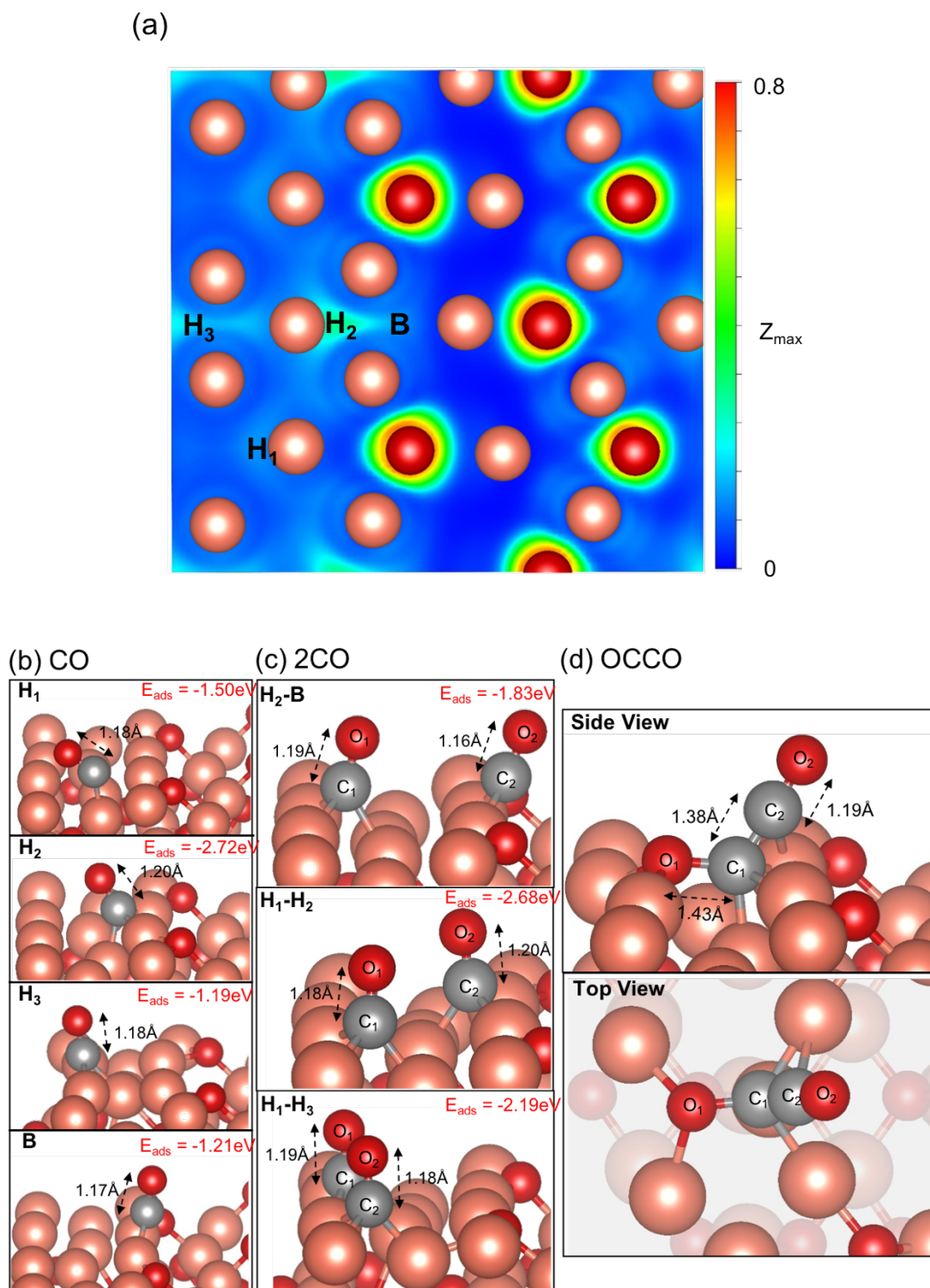
(b)



**Supplementary Figure 35.** Current density difference as a function of scan rate for the  $\text{CuO}_x$  (a) before and (b) after Redox Shuttle (R.S.)  $\text{CO}_2\text{RR}$  treatment at  $-0.75 \text{ V}$  in  $0.5 \text{ M N}_2$ -saturated  $\text{KHCO}_3$ .



**Supplementary Figure 36.** The profile of the formation energy for various ratios of Cu and Cu(I).



**Supplementary Figure 37.** (a) The electron-localization function plots of the ensemble. The schematic representations of the optimized structures of (b) CO, (c) 2CO and (d) OCCO on the ensemble. Surface reconstruction induced by CO adsorption-desorption perturbation has been considered for all surfaces.

## Supplementary Note 1

We applied the  $\text{CuO}_x$  to conducting  $\text{CO}_2\text{RR}$  either using conventional chronoamperometry (CA) or using Redox Shuttle (R.S.) for 30 mins, and immediately took CVs to investigate corresponding electrochemical oxidation responses (the procedure of the CVs the same as those in Figure 2). As depicted in Supplementary Fig. 7, the CV results showed that when the cycle time of R.S. was 20 sec (10 sec for reduction and 10 sec for oxidation), the oxidation responses between the applied potentials of -0.75 V and of -0.85 V were nearly the same, suggesting compositions of Cu species in both potentials were the same. Furthermore, when the applied potential went to a more negative one, namely -1.05 V, the corresponding electrochemical response was similar to those in -0.65 and in -0.85 V, despite the oxidation period increasing to 20 sec. On the contrary, using CA for 30 mins in -1.05 V (denoted as after), the oxidation amount of Cu species increased considerably, compared with that before  $\text{CO}_2\text{RR}$ . Overall, the results highly suggested R.S. enabled the composition of Cu species in  $\text{CuO}_x$  to be well preserved under  $\text{CO}_2\text{RR}$ , while CA did not.