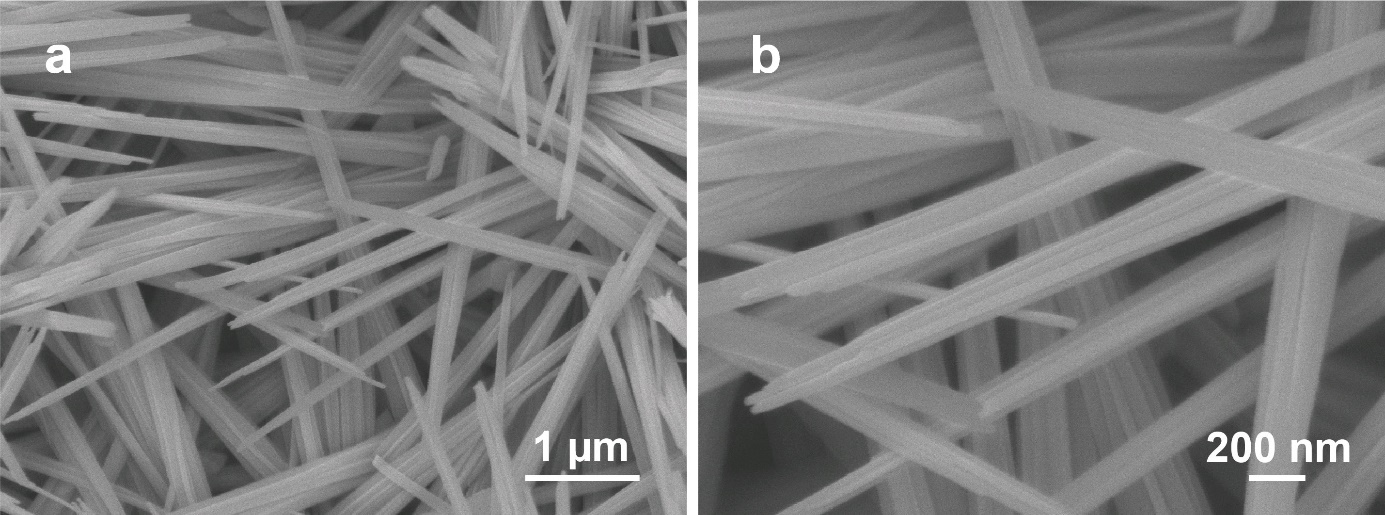
Supplementary Information

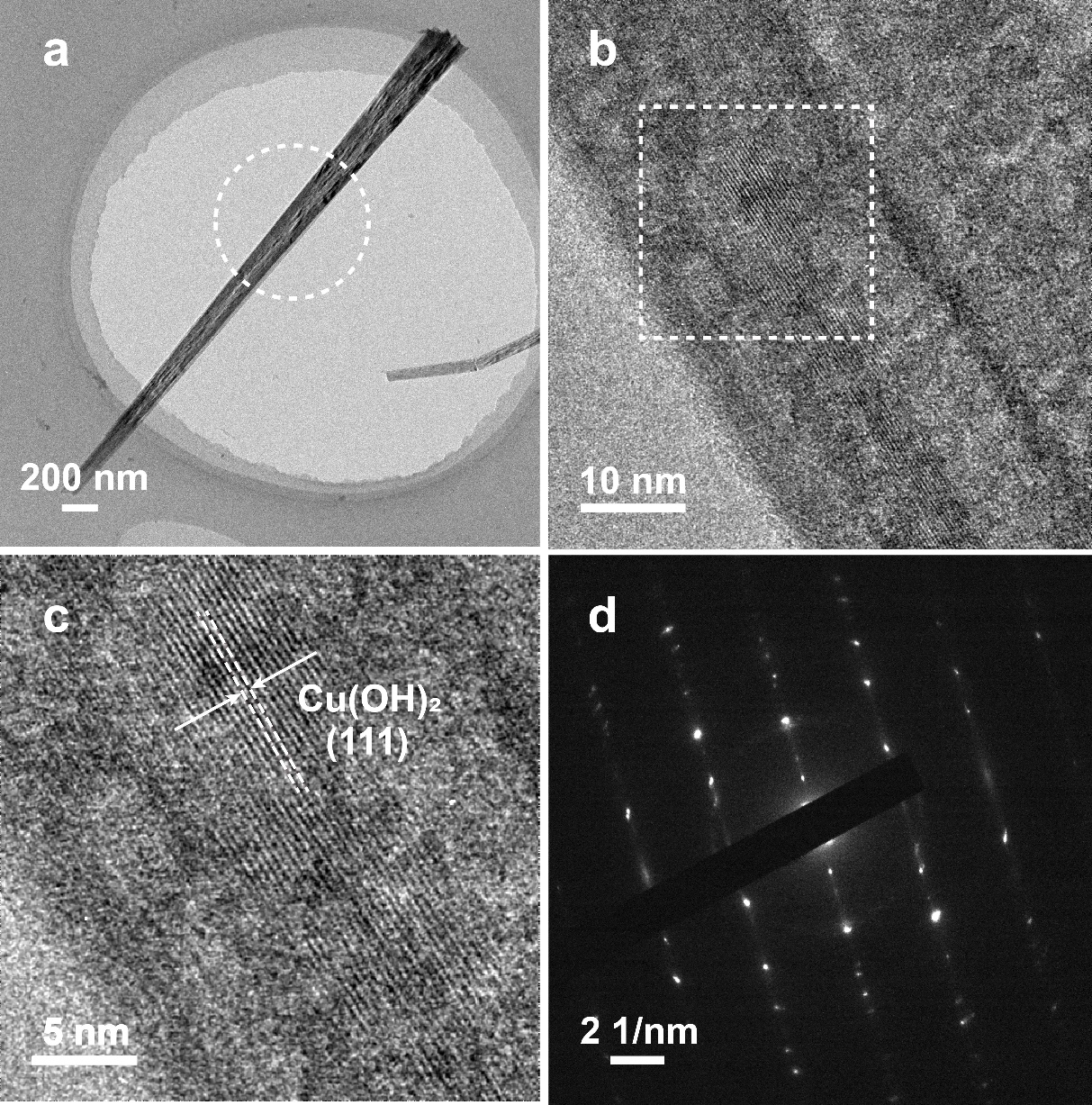
Dynamic restructuring of coordinatively unsaturated copper paddle wheel clusters drives CO2 reduction efficiently

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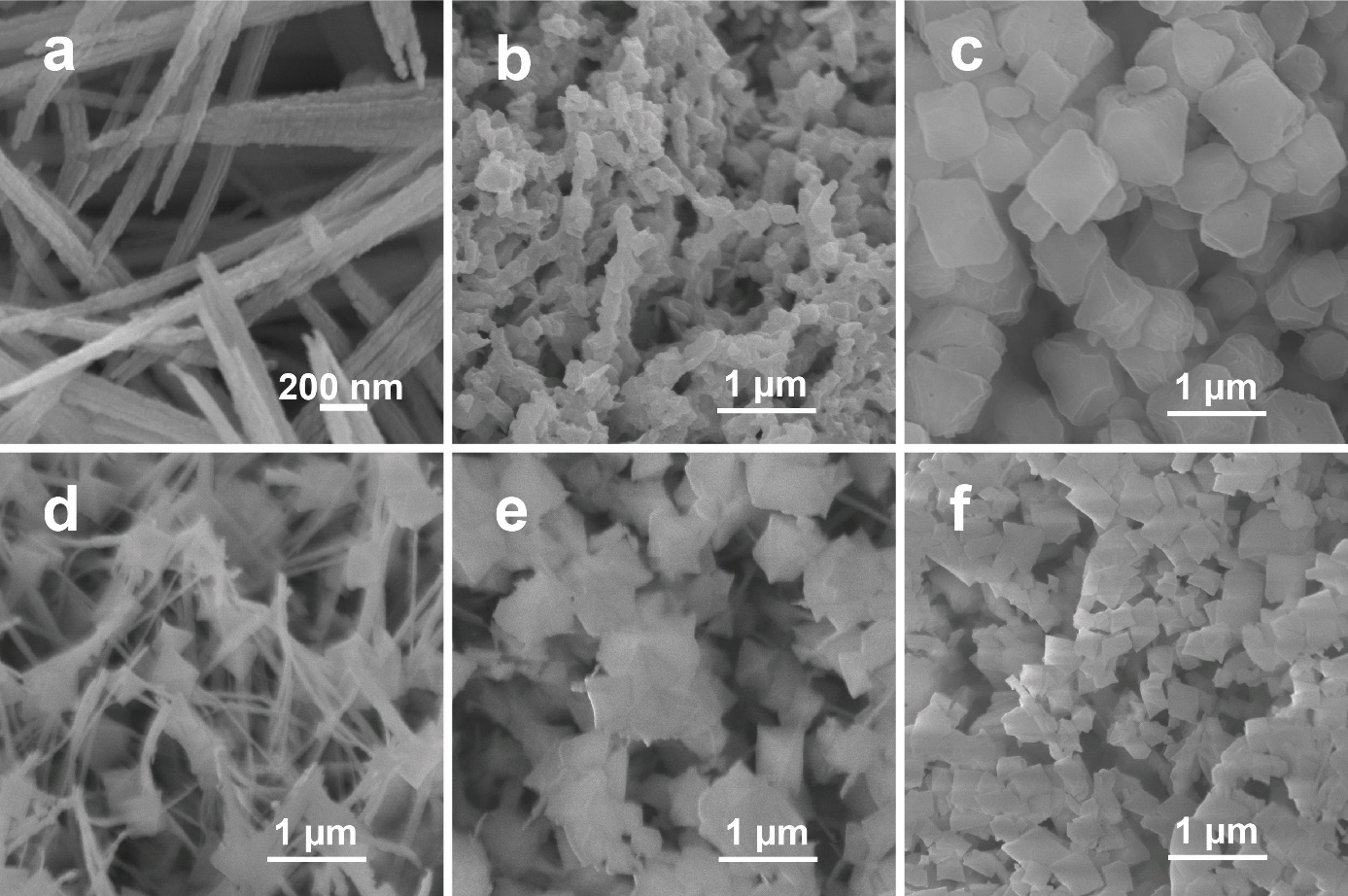
1 Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, Hubei, P. R. China. 2 State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, P. R. China. 3 Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Science, Beijing 100049, P. R. China. 4 State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China. 🖂email: [mlq518@whut.edu.cn](mailto:mlq518@whut.edu.cn); [zhiguo@mail.sic.ac.cn](mailto:zhiguo@mail.sic.ac.cn); [yuying01@mail.ccnu.edu.cn](mailto:yuying01@mail.ccnu.edu.cn).



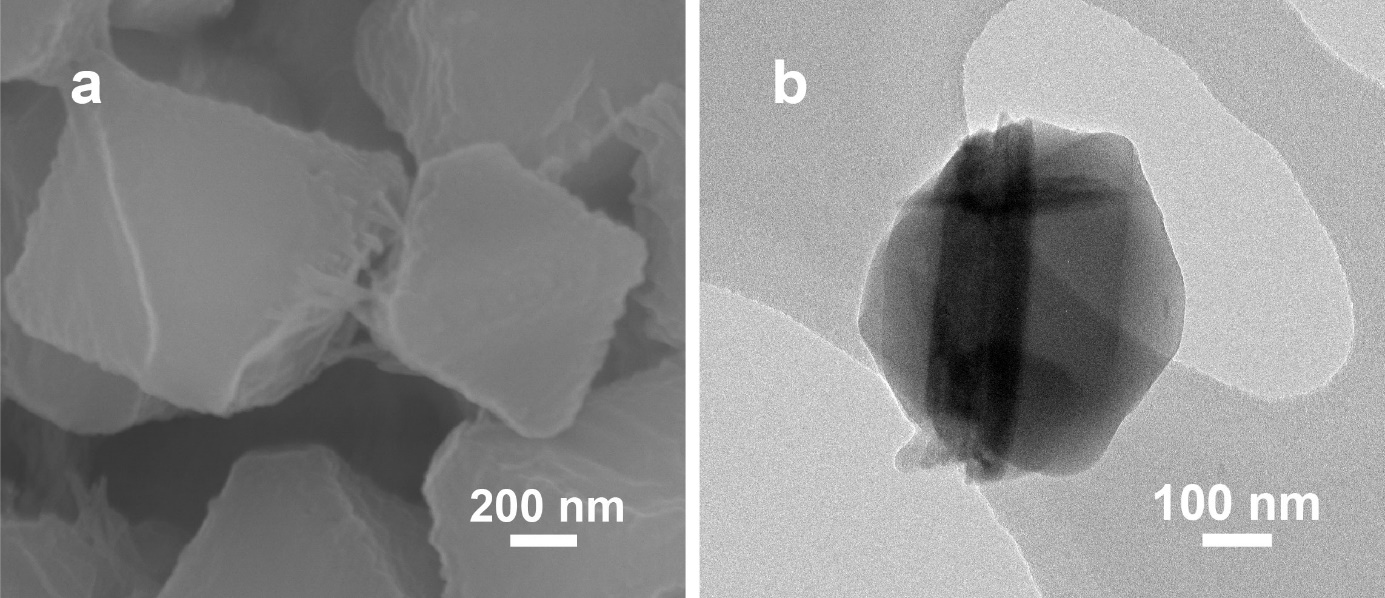
**Supplementary Figure 1.** SEM images of Cu(OH)2 NWs



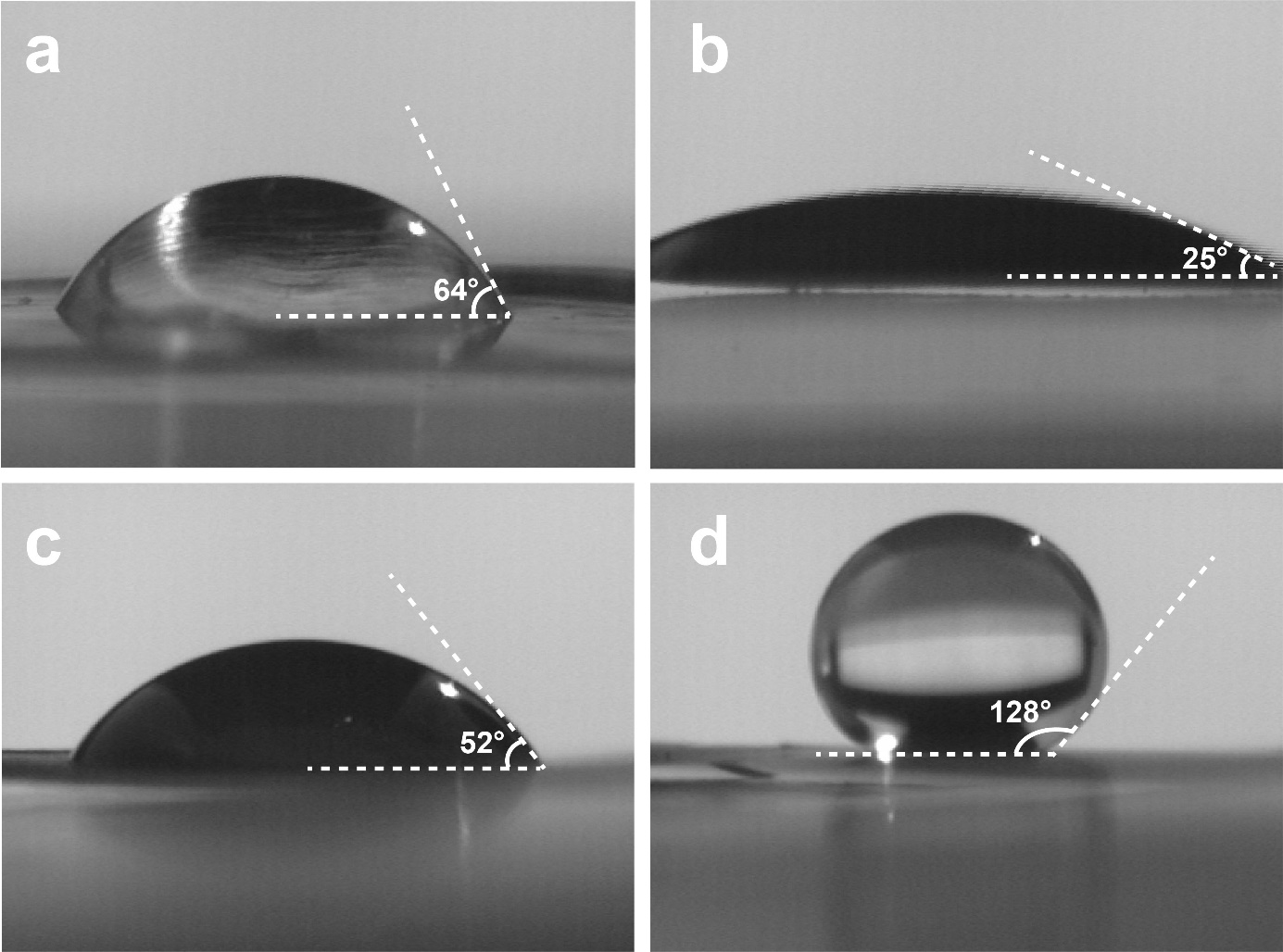
**Supplementary Figure 2.** (a) Low-magnification TEM image, (b, c) HRTEM images and (d) selected area electron diffraction (SAED) pattern of Cu(OH)2 NWs.



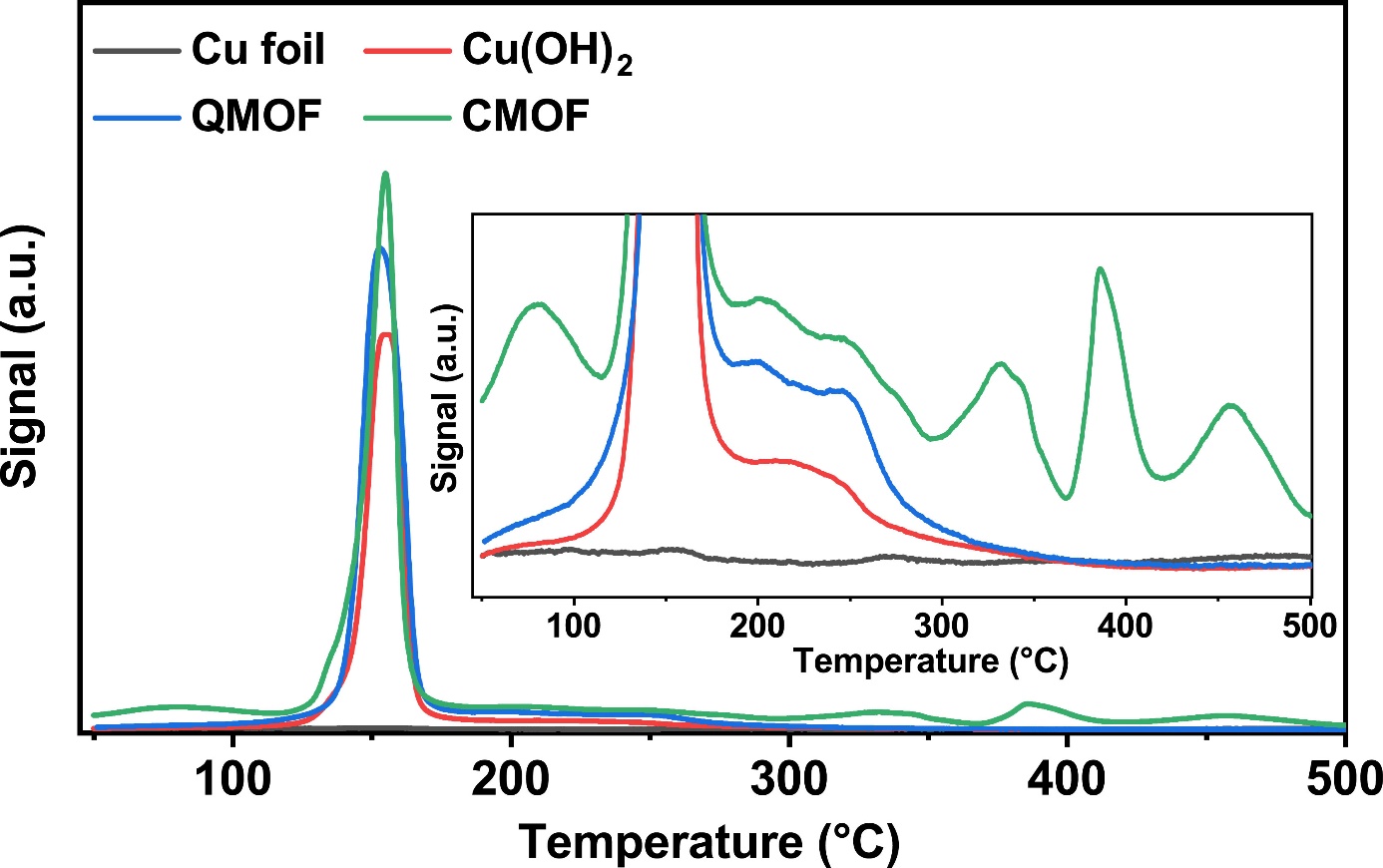
**Supplementary Figure 3.** (a-c) SEM images of samples prepared through “atomized method”. The reaction time was 120 s (a), 240 s (b), 480 s (c). (d-f) SEM images of samples prepared through “immersed method”. The immersed time was 10 s (d), 60 s (e) and 120 s (f).



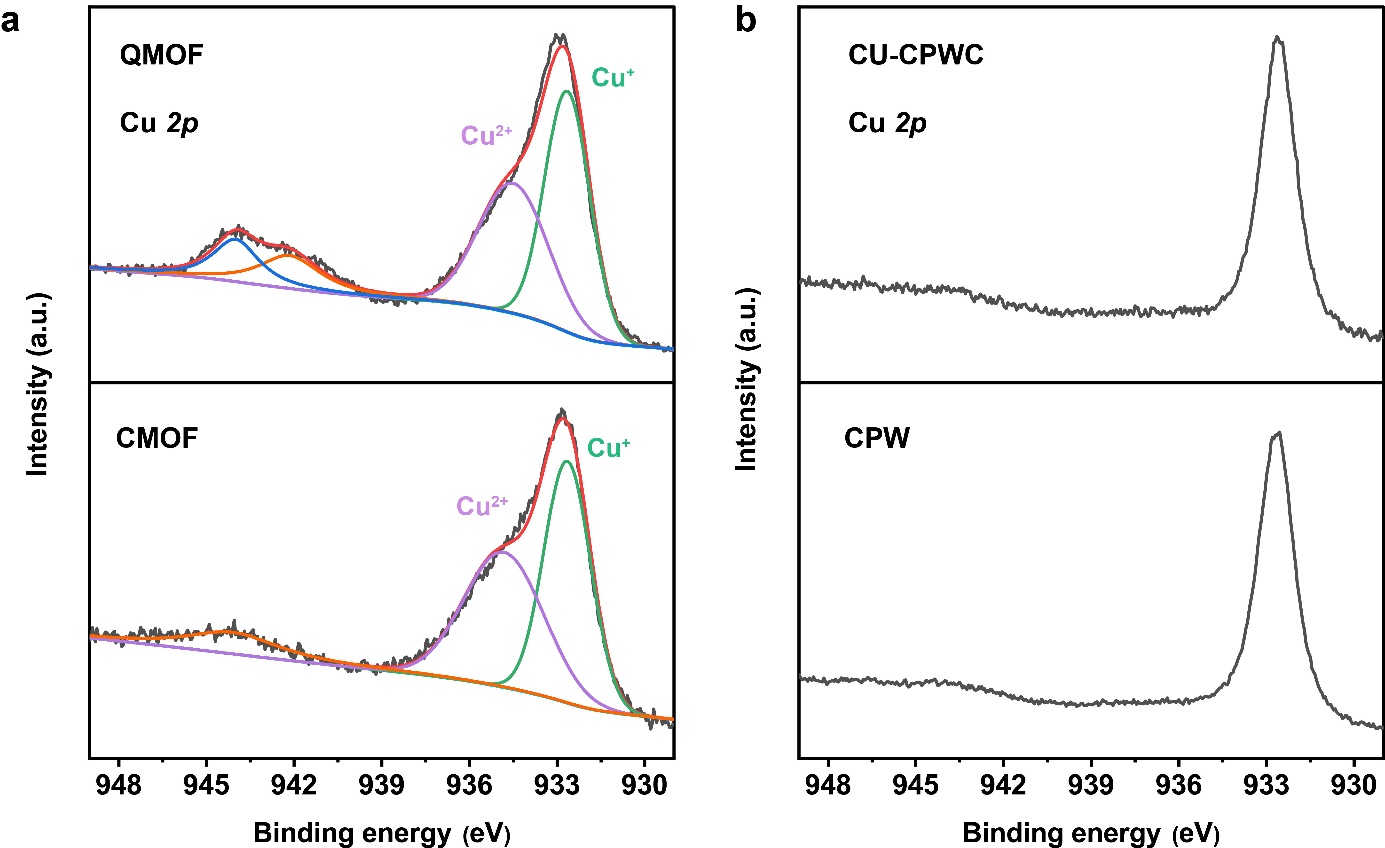
**Supplementary Figure 4.** (a) SEM image of CMOF. (b) TEM image of CMOF.



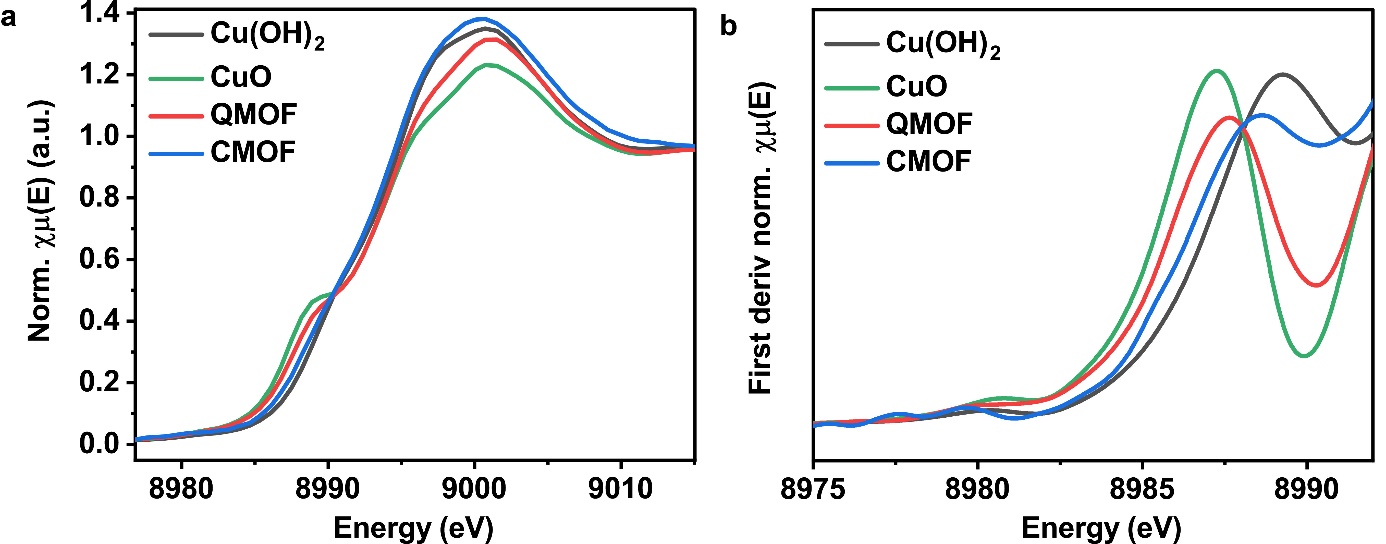
**Supplementary Figure 5.** (a-d) Contact angle of Cu foil, Cu(OH)2 NWs, QMOF and CMOF.



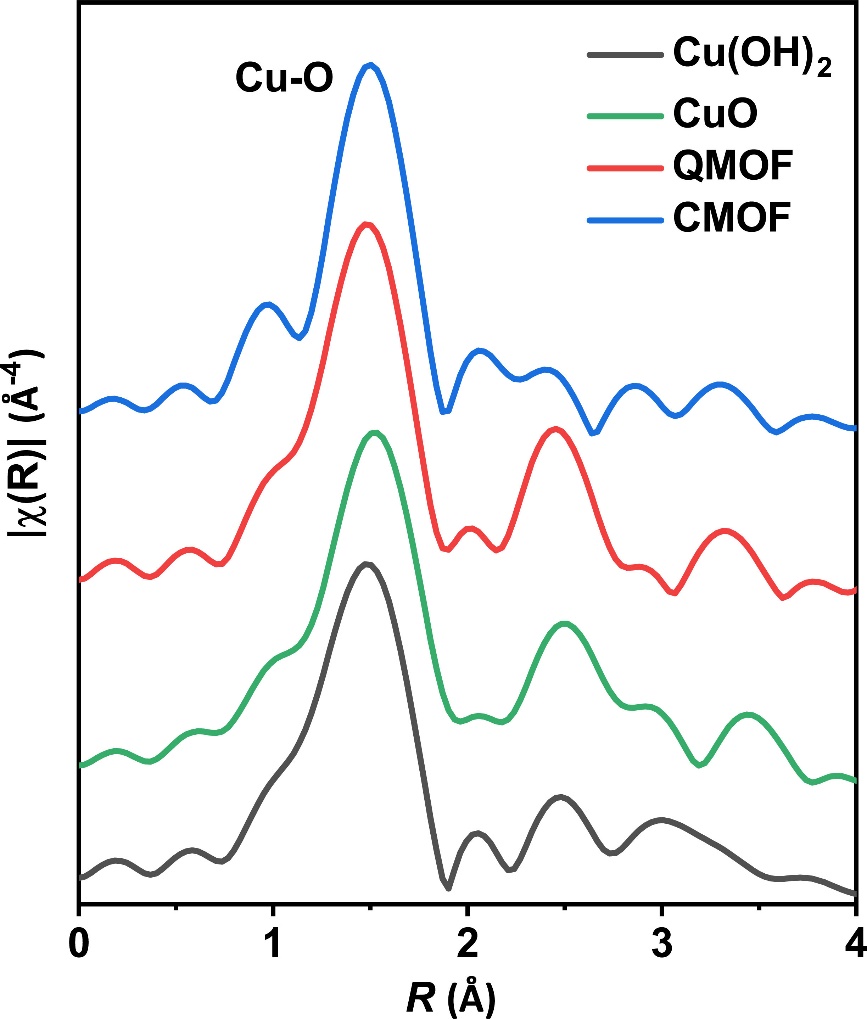
**Supplementary Figure 6.** CO2-temperature programmed desorption (TPD) measurement of Cu foil, Cu(OH)2 NWs, QMOF and CMOF.



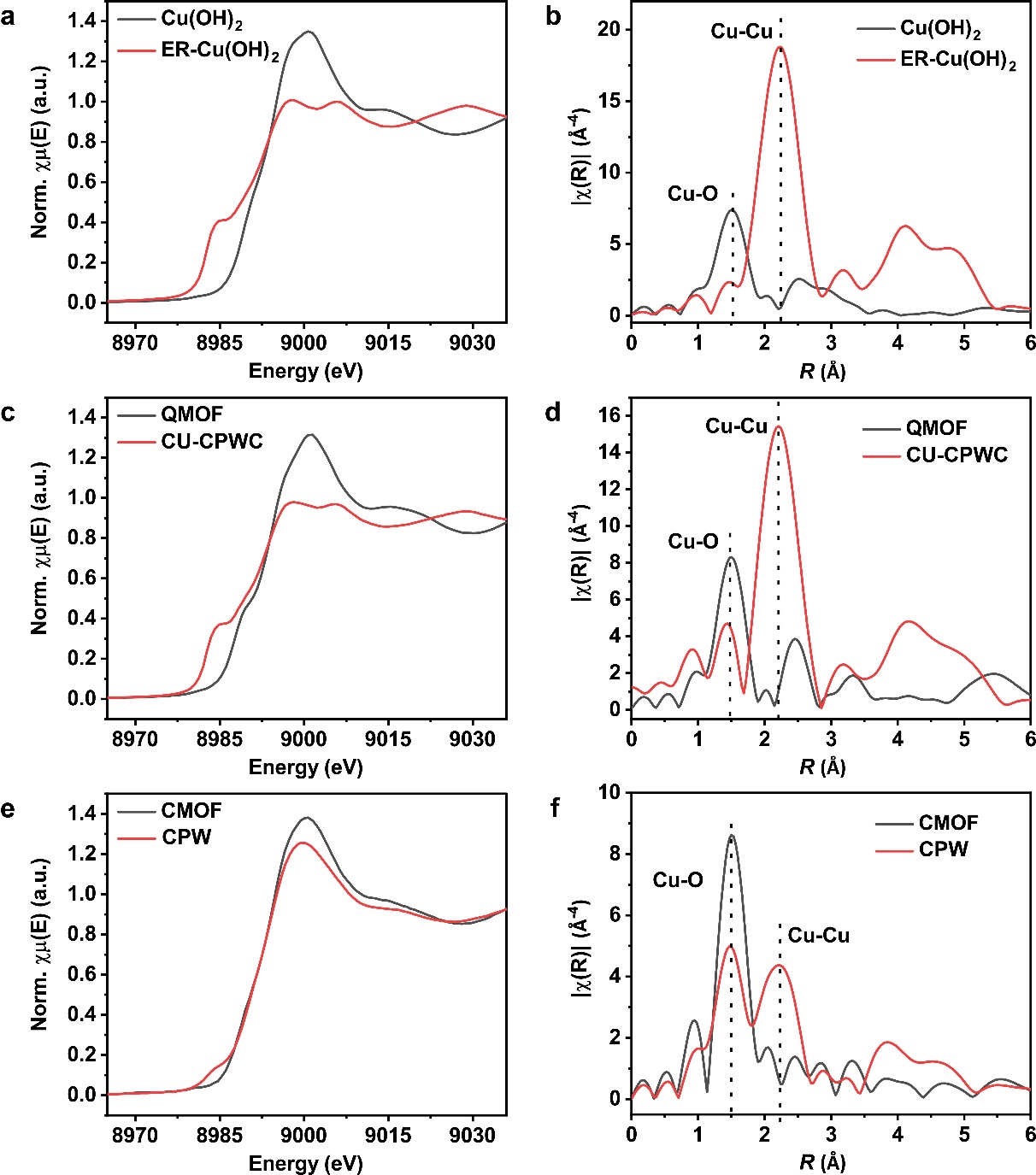
**Supplementary Figure 7.** (a) High-resolution XPS signals of Cu *2p* of QMOF and CMOF. (b) CU-CPWC and CPW.



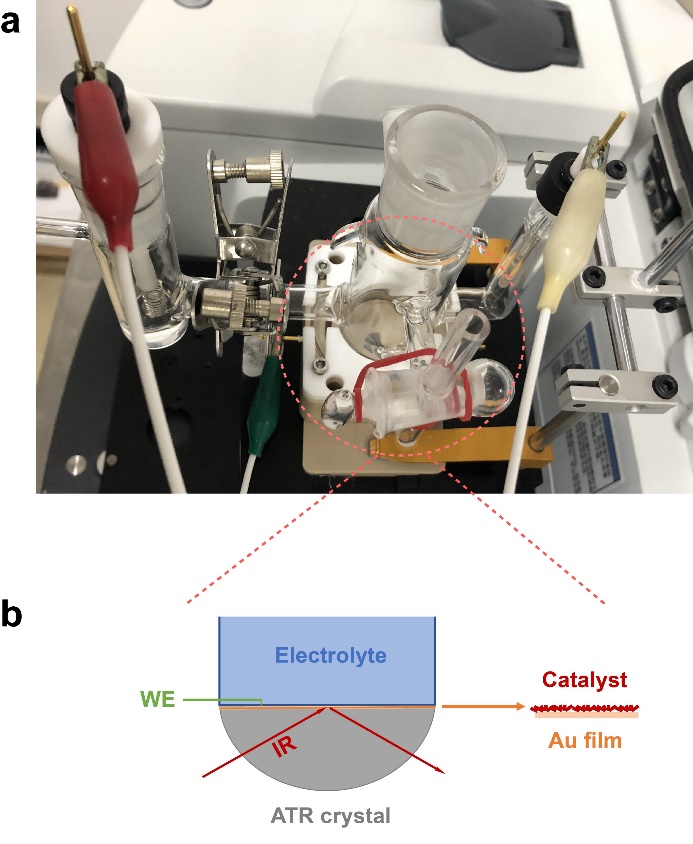
**Supplementary Figure 8.** (a) Normalized Cu K-edge XANES spectra of Cu(OH)2 NWs, CuO, QMOF and CMOF. (b) First-derivative spectra obtained from Cu K-edge XANES spectra.



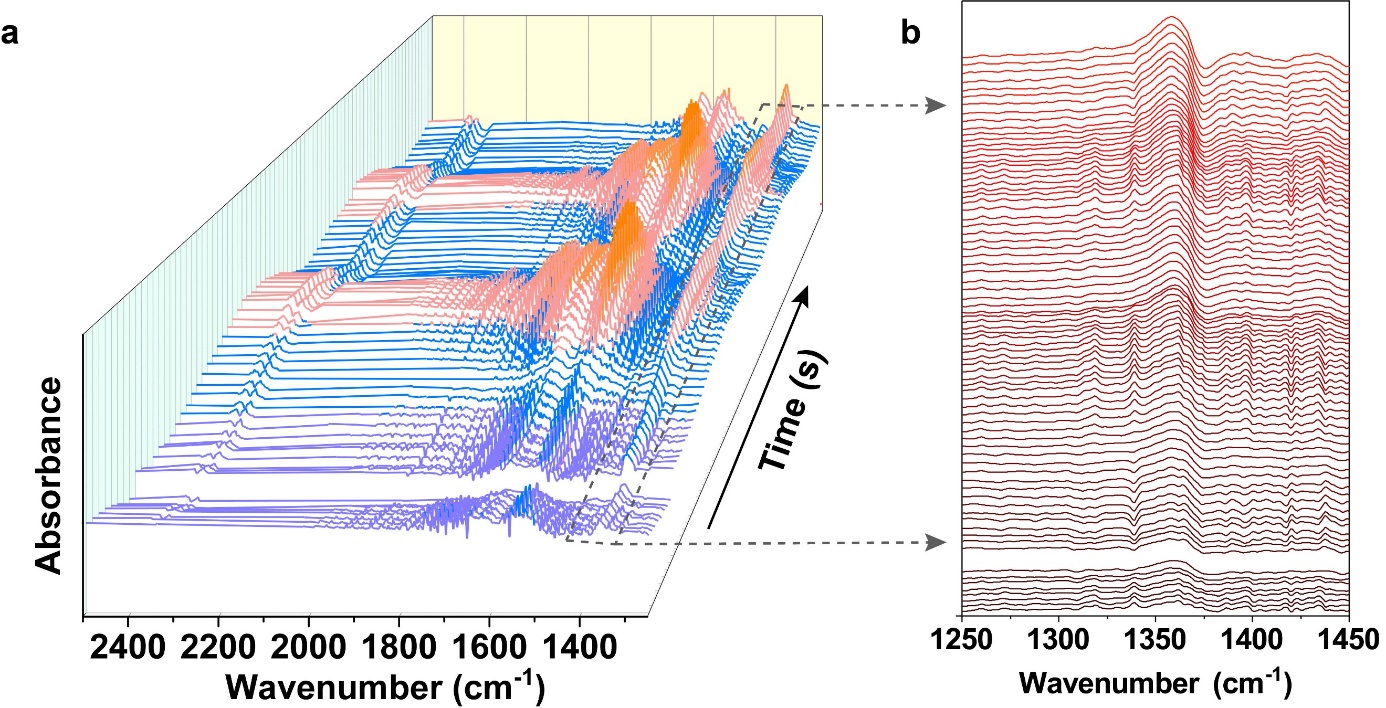
**Supplementary Figure 9.** *K*3-weighted FT-EXAFS spectra of Cu(OH)2 NWs, CuO, QMOF and CMOF.



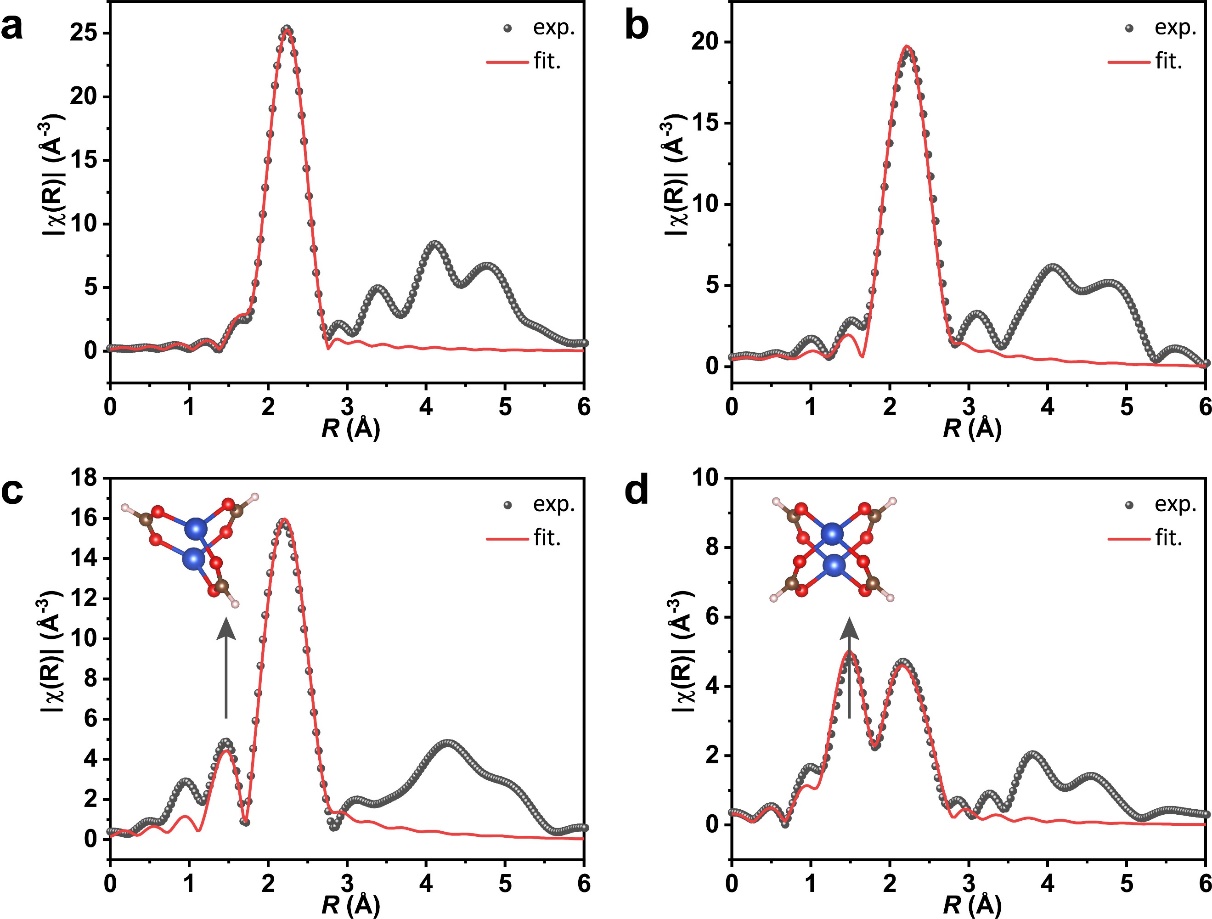
**Supplementary Figure 10.** Comparison of XAS data before and after electrochemical reconstruction: (a, c and e) Cu K-edge XANES spectra, (b, d and f) Corresponding k3-weighted FT-EXAFS spectra of the four samples.



**Supplementary Figure 11.** (a) Electrochemical cell used for ATR-FTIR measurements. (b) Schematic illustration of ATR-FTIR cell.



**Supplementary Figure 12.** (a) *In situ* ATR-SEIRA spectra collected on a QMOF cast Au/Si prism electrode with a time resolution of 2 s, using a single-beam spectrum at ∼−0.4 V vs RHE.

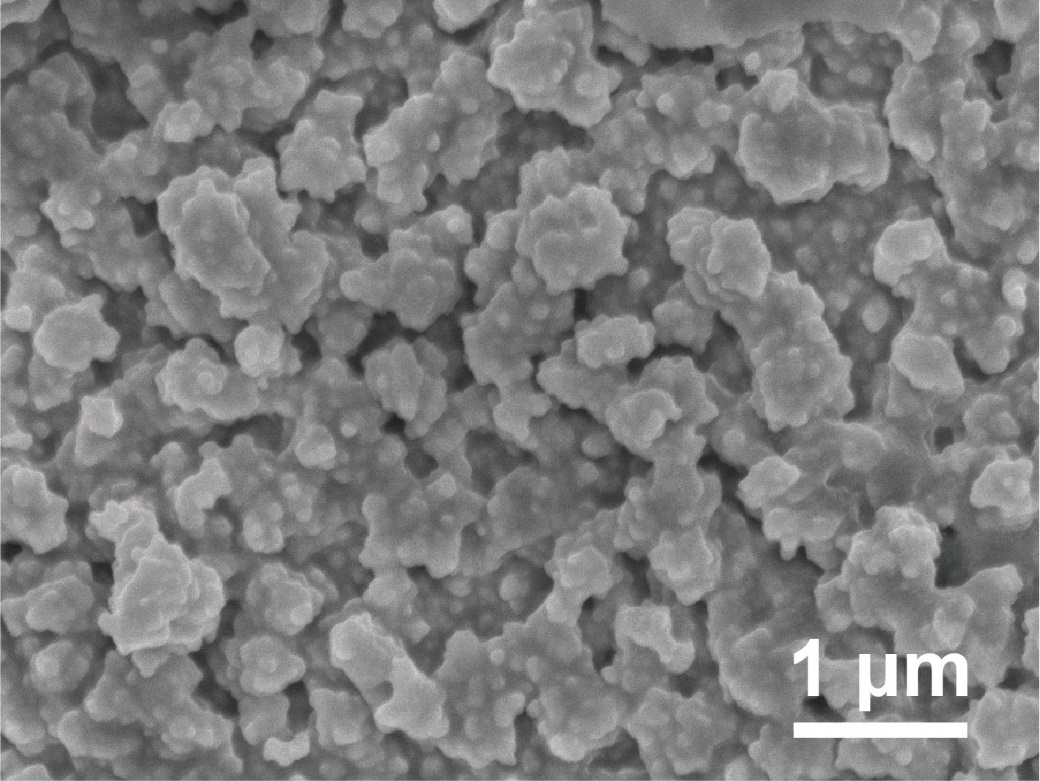


**Supplementary Figure 13.** Corresponding EXAFS *R*-space fitting curves of the four samples. (a) Cu foil, (b) ER-Cu(OH)2, (c) CU-CPWC and (d) CPW.

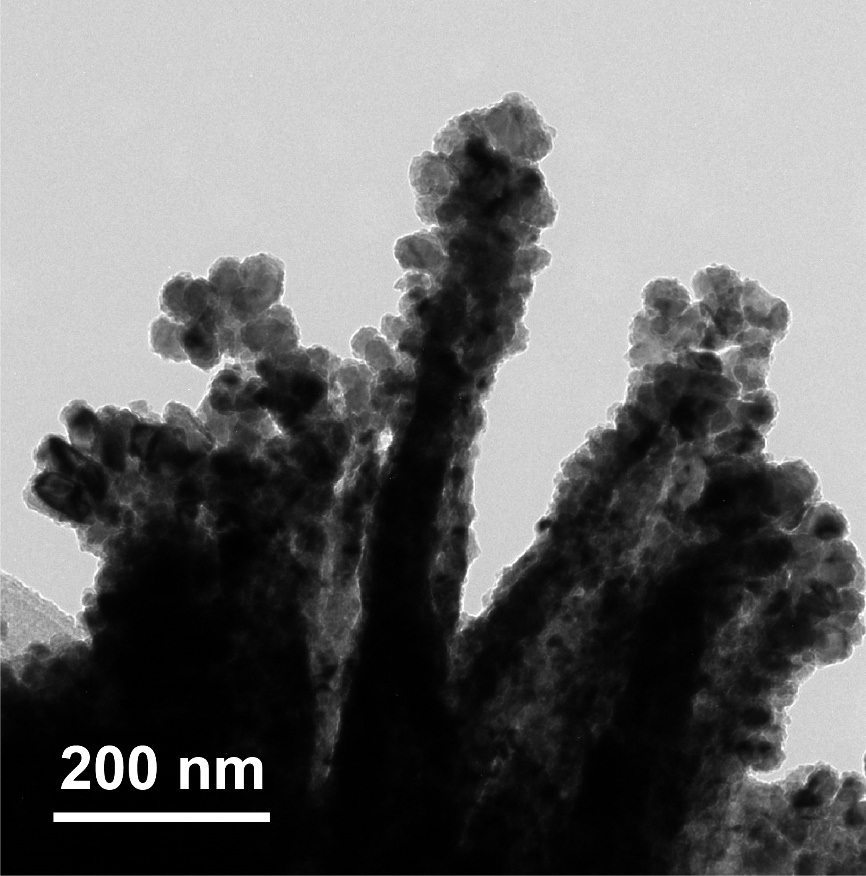
Table S1. Fitting results of Cu K-edge EXAFS dataa.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | Scattering path | CN | R (Å) | σ2 (10-3 Å) | R factor | |
| Cu foil | Cu-Cu | 12 (set) | 2.54 | 8.81 | 0.0011 |
| ER-Cu(OH)2 | Cu-Cu | 9.65 | 2.53 | 8.22 | 0.010 |
| CU-CPWC | Cu-O | 0.51 | 1.88 | 3.22 | 0.0083 |
| Cu-Cu | 7.55 | 2.52 | 7.96 |
| CPW | Cu-O | 2.54 | 1.94 | 6.01 | 0.0048 |
| Cu-Cu | 3.4 | 2.55 | 10.50 |

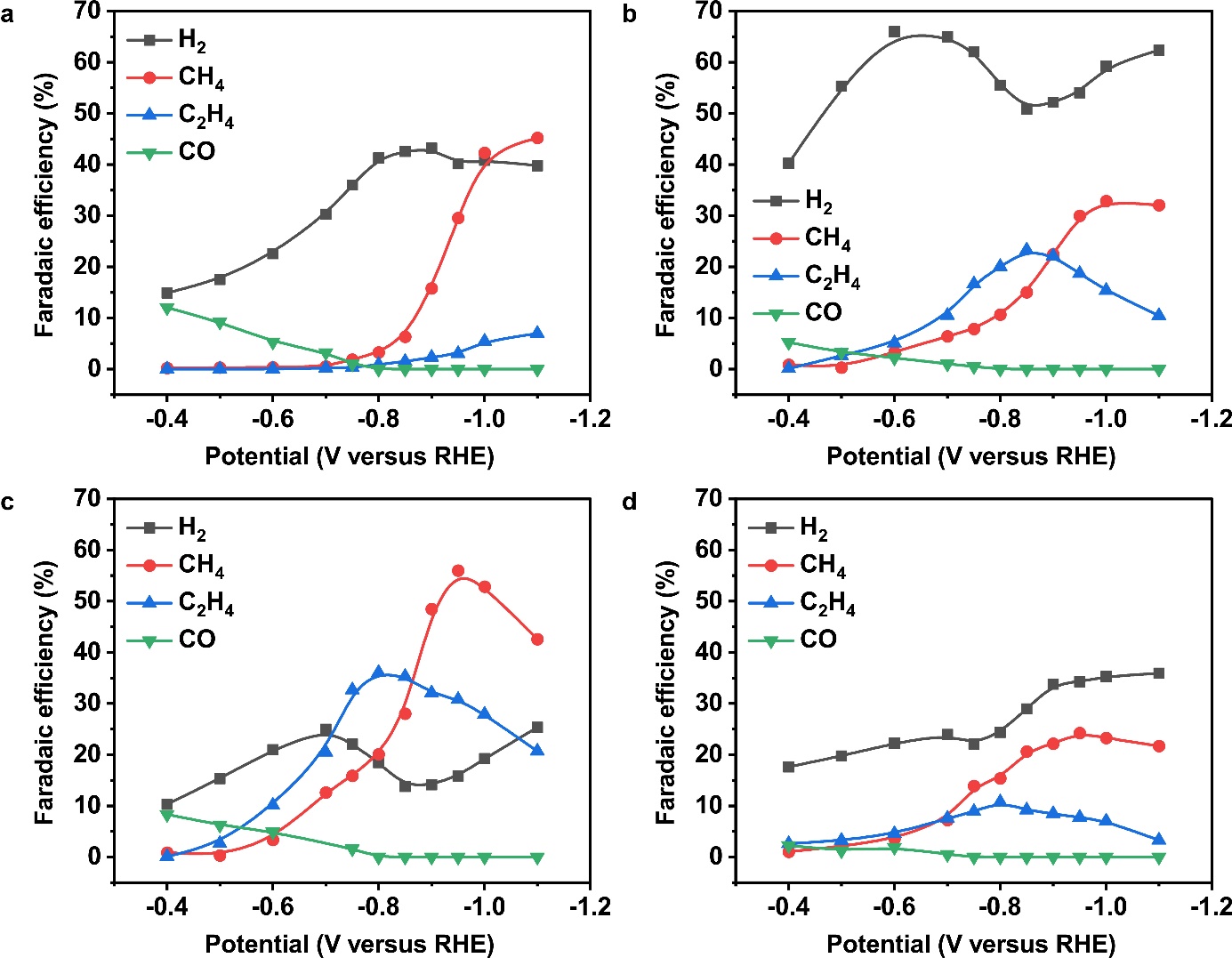
a The lengths of Cu-Cu and Cu-O bonds and coordination numbers of Cu atoms are extracted from the curve-fitting for Cu K-edge EXAFS data. CN: coordination number; σ2: Debye−Waller factor. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as CN ± 20 %; R ± 1 %; σ2 ± 20 %.



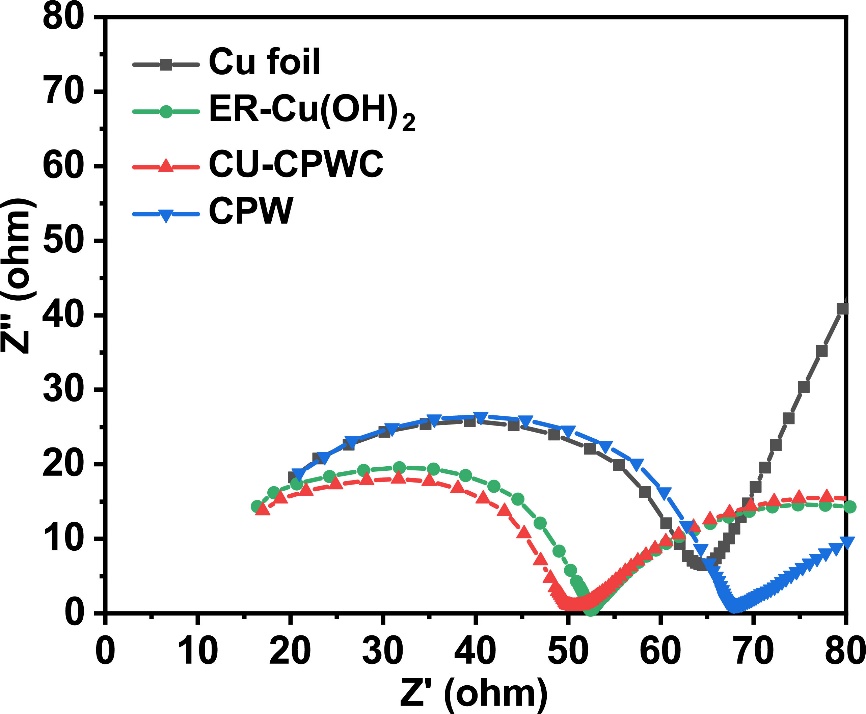
**Supplementary Figure 14.** SEM image of CPW.



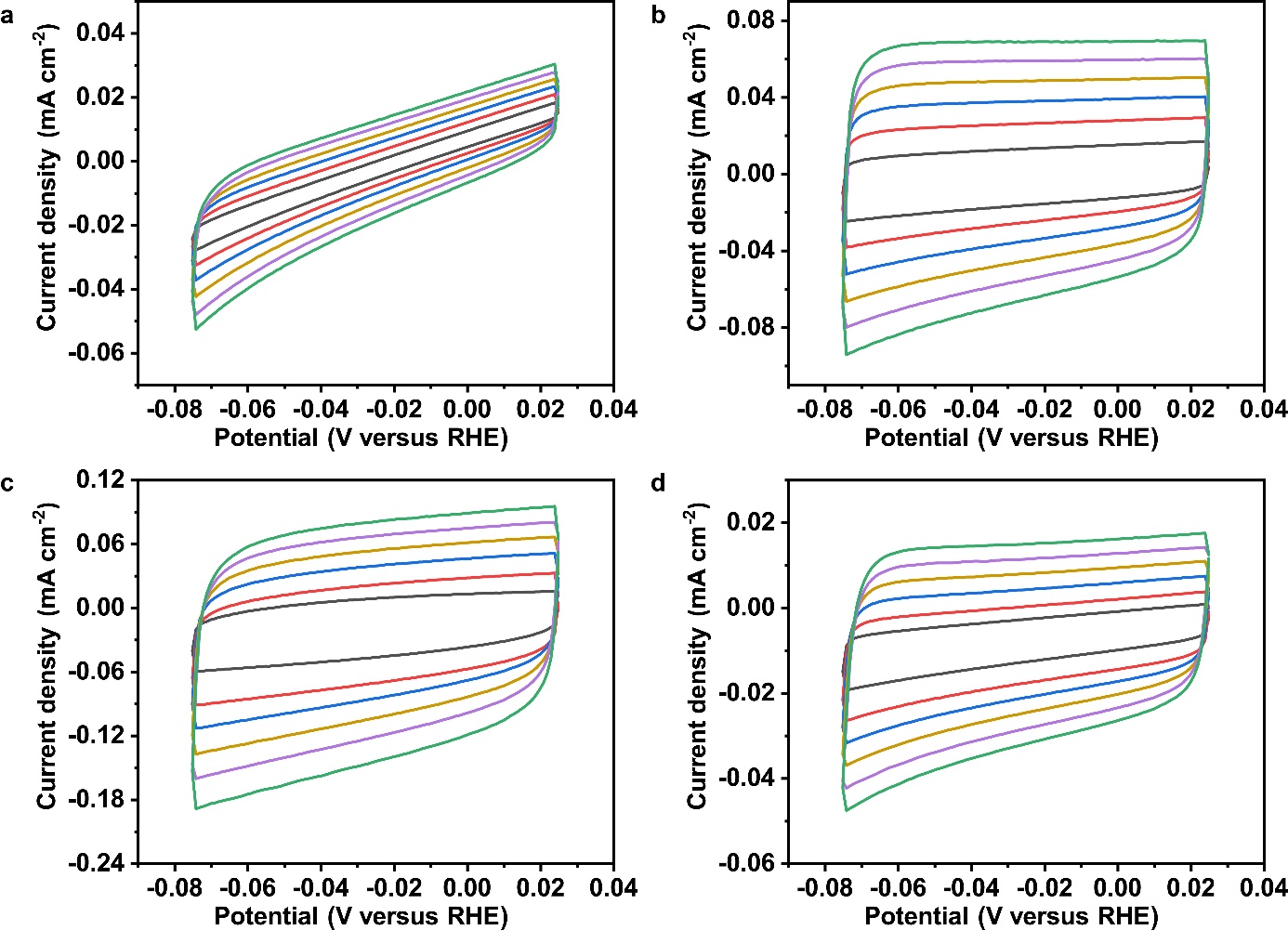
**Supplementary Figure 15.** TEM image of CU-CPWC.



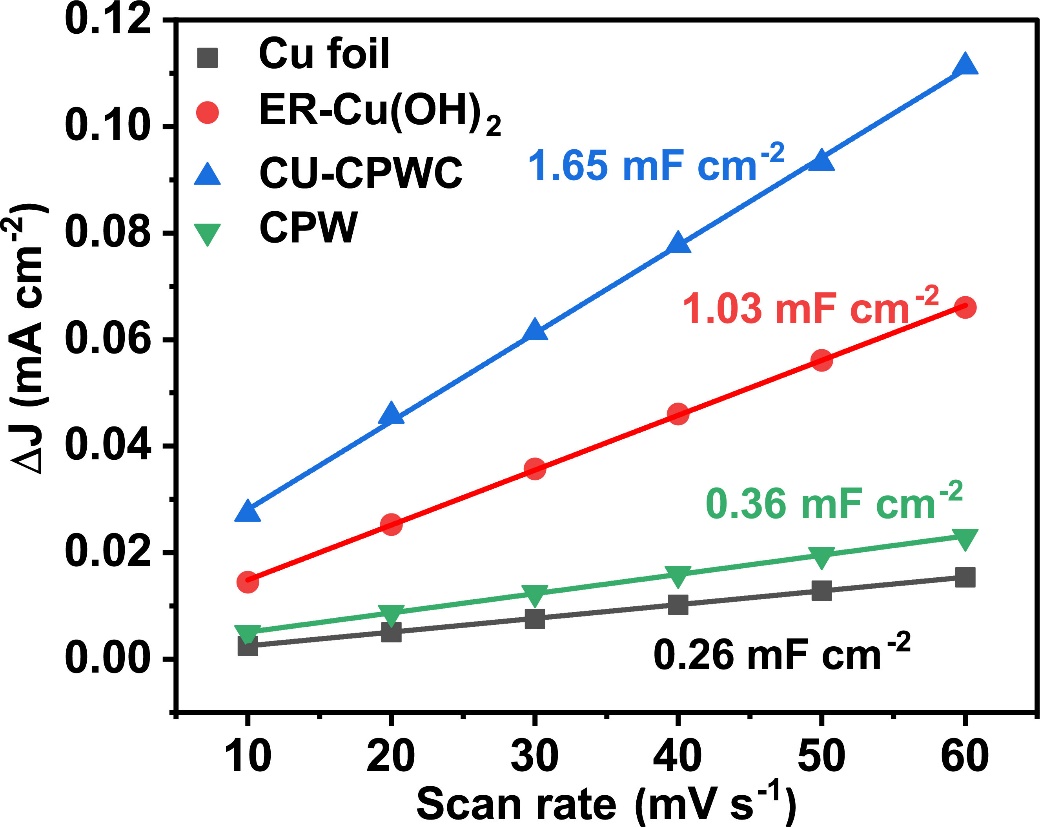
**Supplementary Figure 16.** Product distribution of CO2 reduction on Cu foil (a), ER-Cu(OH)2 NWs (b), CU-CPWC (c), and CPW (d).



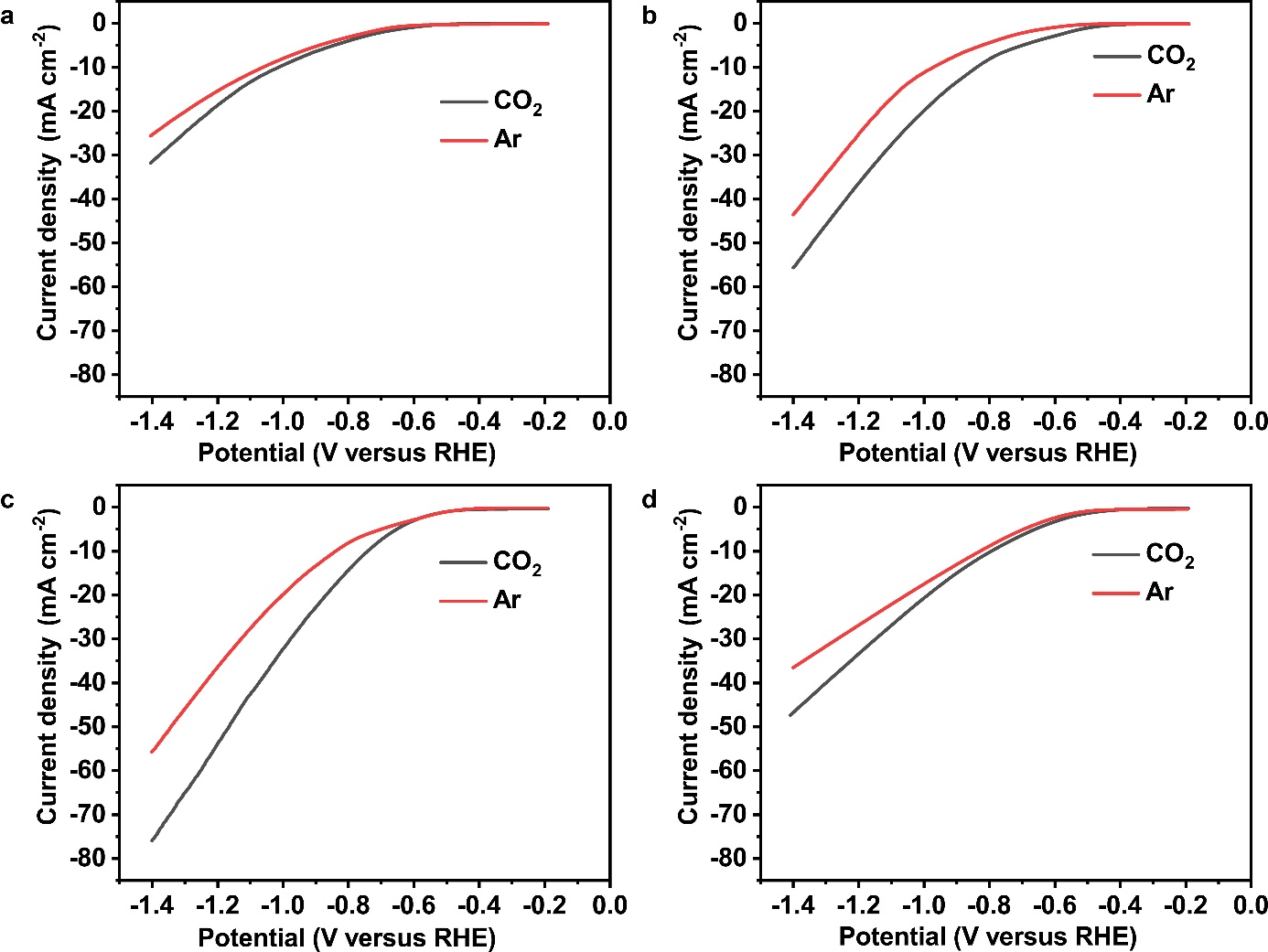
**Supplementary Figure 17.** Nyquist plots of the four samples in CO2-saturated KHCO3 electrolyte.



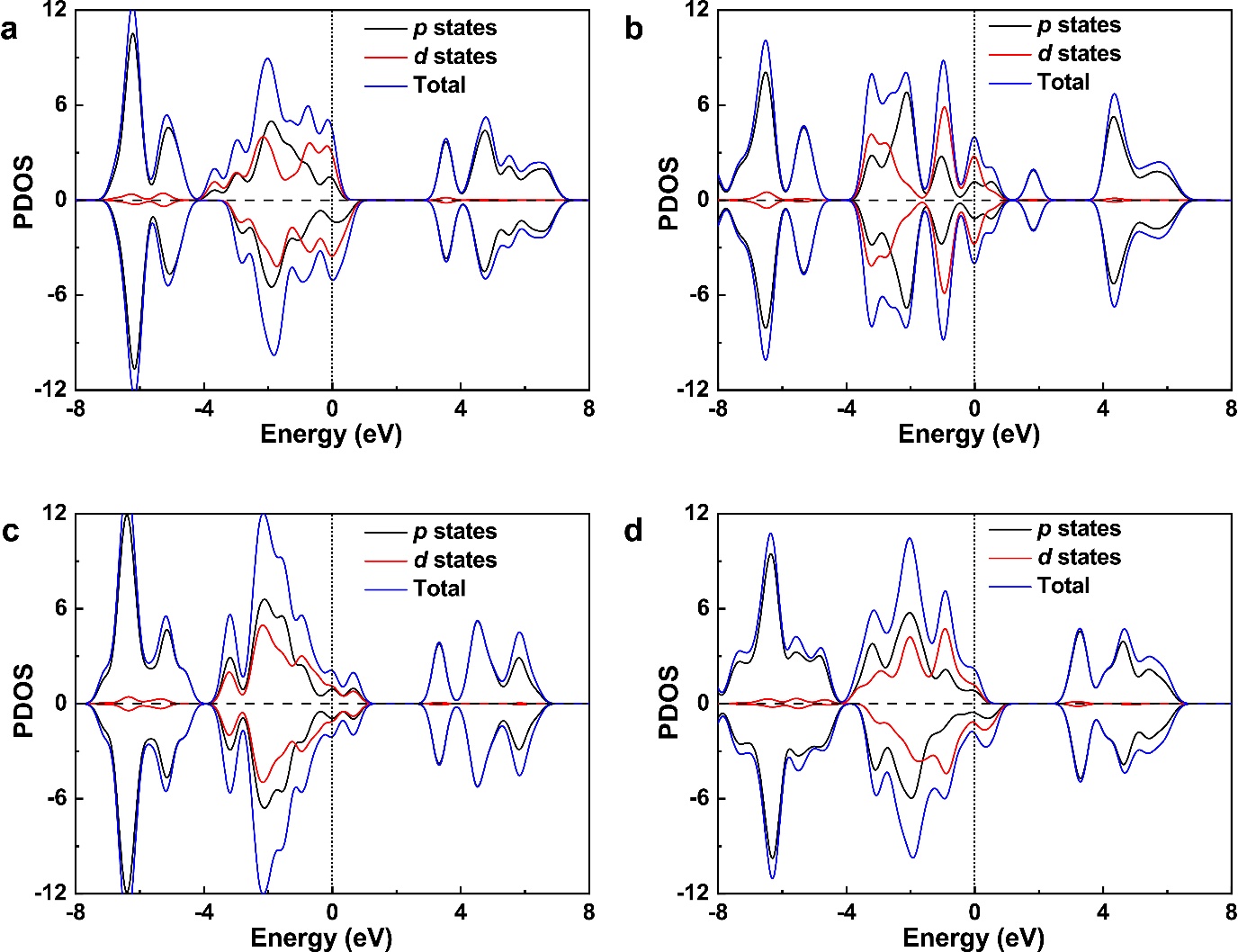
**Supplementary Figure 18.** Cyclic voltammetry scans on Cu foil (a), ER-Cu(OH)2 NWs (b), CU-CPWC (c), and CPW (d) between 0.025 and -0.075 V vs. RHE in CO2-saturated 0.1 M KHCO3 solution at scan rates of 10, 20, 30, 40, 50 and 60 mV s-1.



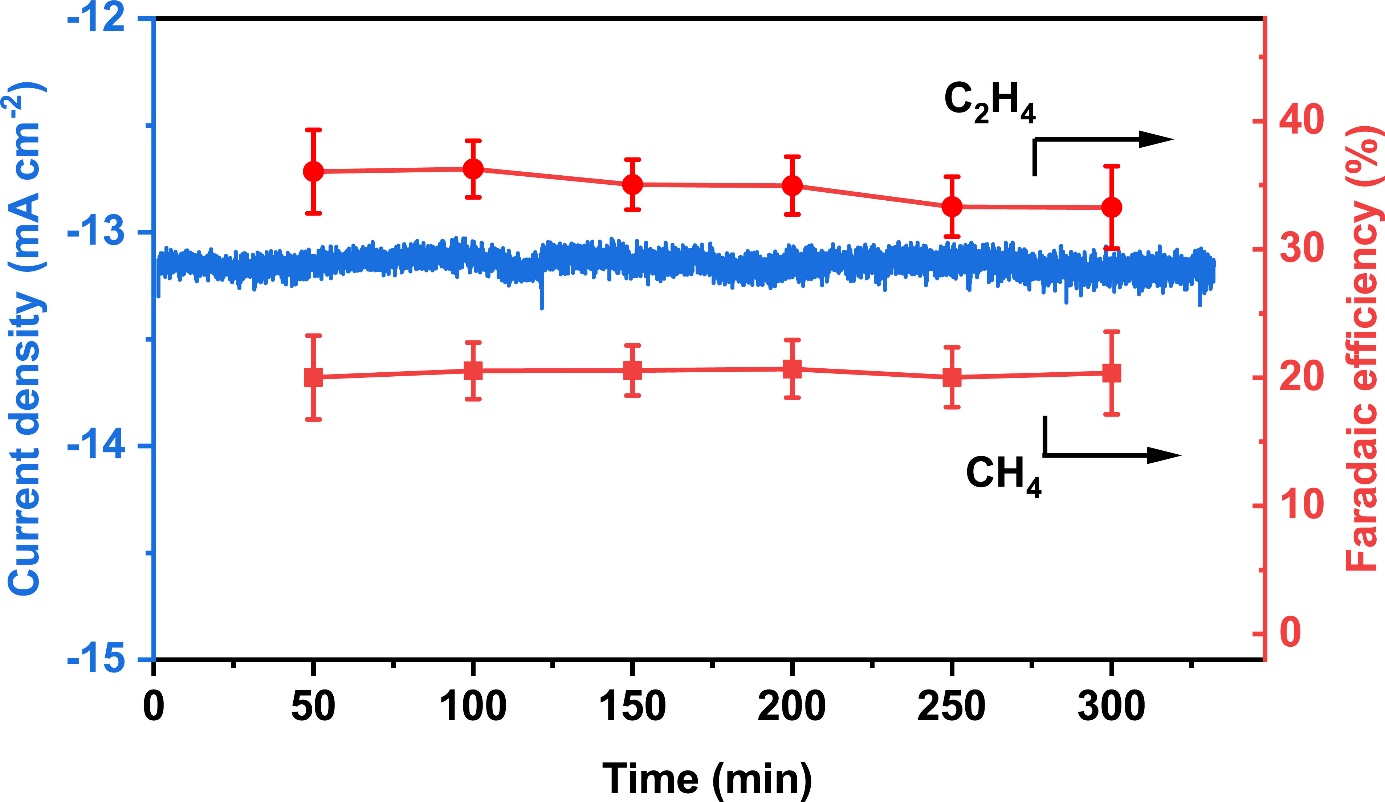
**Supplementary Figure 19.** Extracted currents at -0.02 V vs. RHE as a function of scan rate, leading to a slope indicating a capacitance of 0.26, 1.03. 1.65 and 0.36 mF cm-2 for Cu foil, ER-Cu(OH)2, CU-CPWC and CPW, respectively.



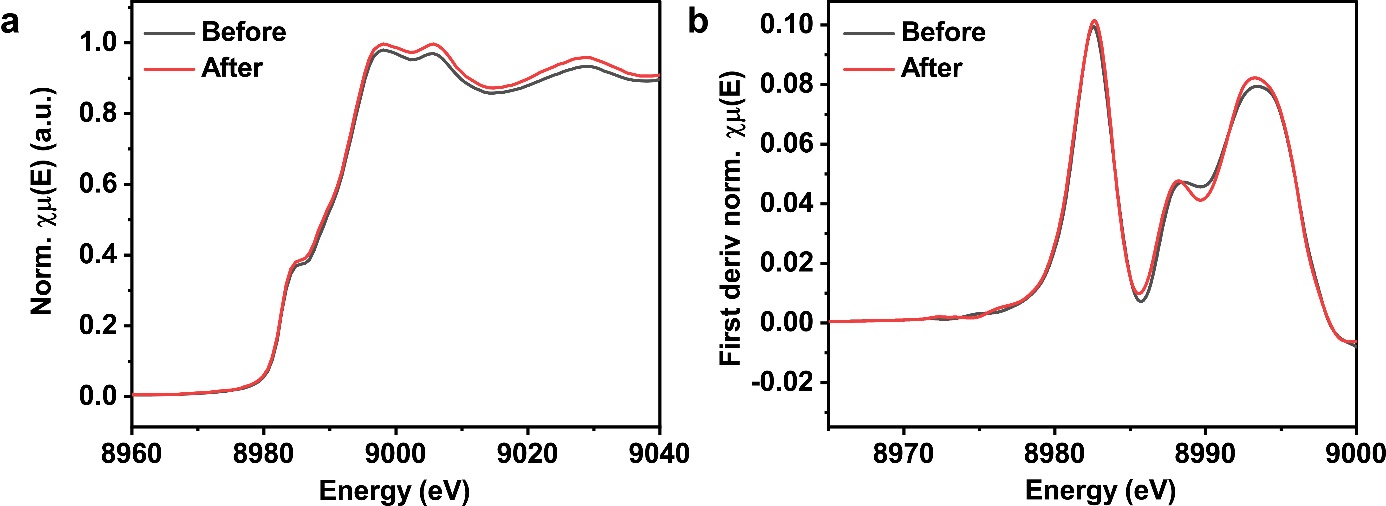
**Supplementary Figure 20.** Comparison of LSV curves in Ar-saturated and CO2-saturated KHCO3 electrolyte for Cu foil (a), ER-Cu(OH)2 NWs (b), CU-CPWC (c) and CPW (d).



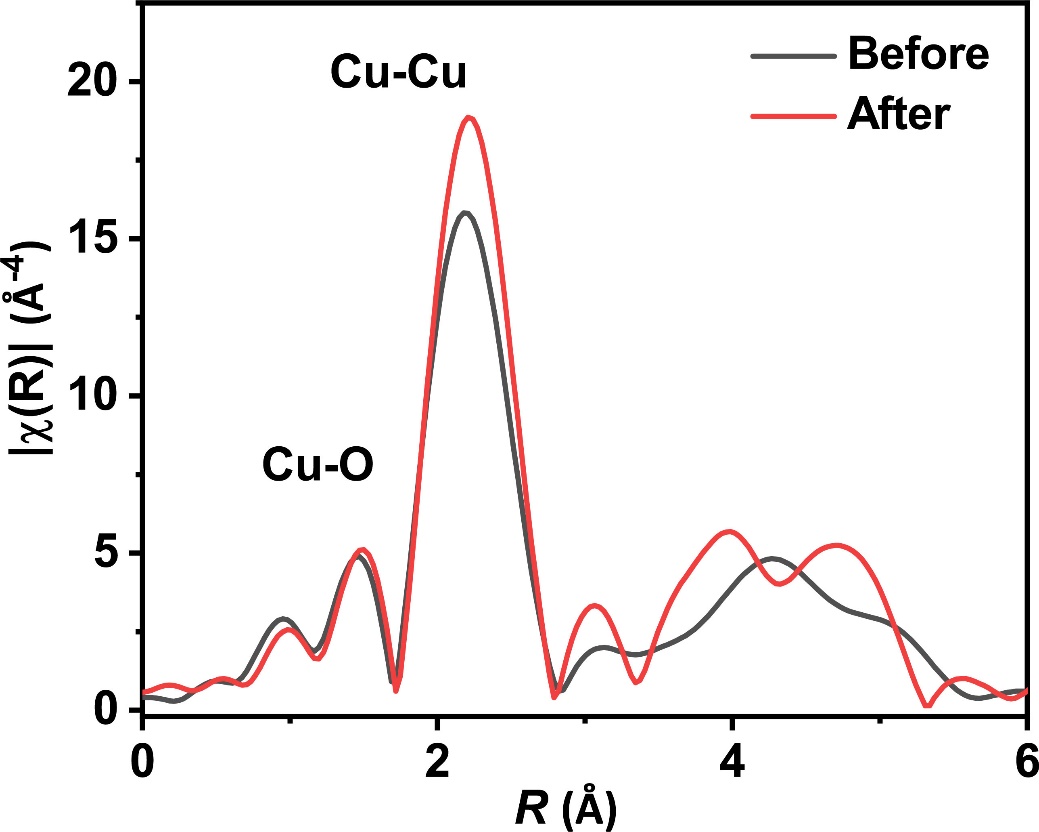
**Supplementary Figure 21.** Spin-orbit projected density of states of Cu-CPWC with CO (a) and CHO (b) adsorption. Spin-orbit projected density of states of Cu-CPW with CO (c) and CHO (d) adsorption.



**Supplementary Figure 22.** Chronoamperometry test of CU-CPWC operated at -0.80 V vs. RHE in 0.1 M KHCO3.



**Supplementary Figure 23.** (a) Comparison of normalized Cu K-edge XANES spectra before and after stability testing of CU-CPWC. (b) First-derivative spectra obtained from (a).



**Supplementary Figure 24.** Comparison of *k*3-weighted FT-EXAFS spectra before and after stability testing of CU-CPWC.