Supporting Information

In situ probing dynamic reconstruction of copper-zinc electrocatalyst for CO_2 reduction

Yen-Po Huang,‡[a] Ching-Wei Tung,‡[a] Tai-Lung Chen,[a] Chia-Shuo Hsu,[a] Mei-Yi Liao,*[b] Hsiao-Chien Chen,*[c,d] and Hao Ming Chen*[a,e]

[a]Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

[b]Department of Applied Chemistry, National Pingtung University, Pingtung 90003, Taiwan.

[c]Center for Reliability Science and Technologies, Chang Gung University, Taoyuan 33302, Taiwan

[d]Kidney Research Center, Department of Nephrology, Chang Gung Memorial Hospital, Linkou, Taoyuan 33305, Taiwan

[e]National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

‡These authors contributed equally to this work.

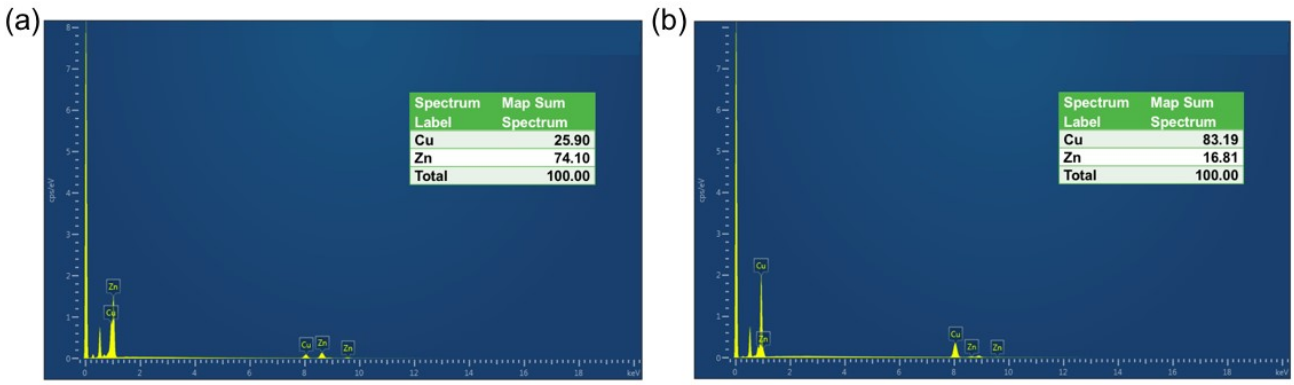

Fig. S1 EDS spectra of (a) s-$Cu_1Zn_3O_x$ and (b) s-$Cu_5Zn_1O_x$.

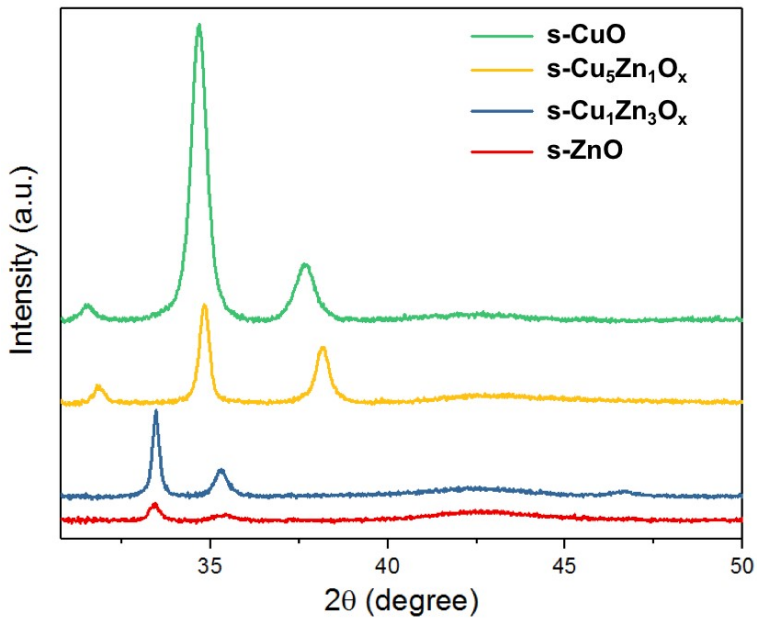

Fig. S2 XRD spectra of s-CuO, s-$Cu_1Zn_3O_x$, s-$Cu_5Zn_1O_x$ and s-ZnO.

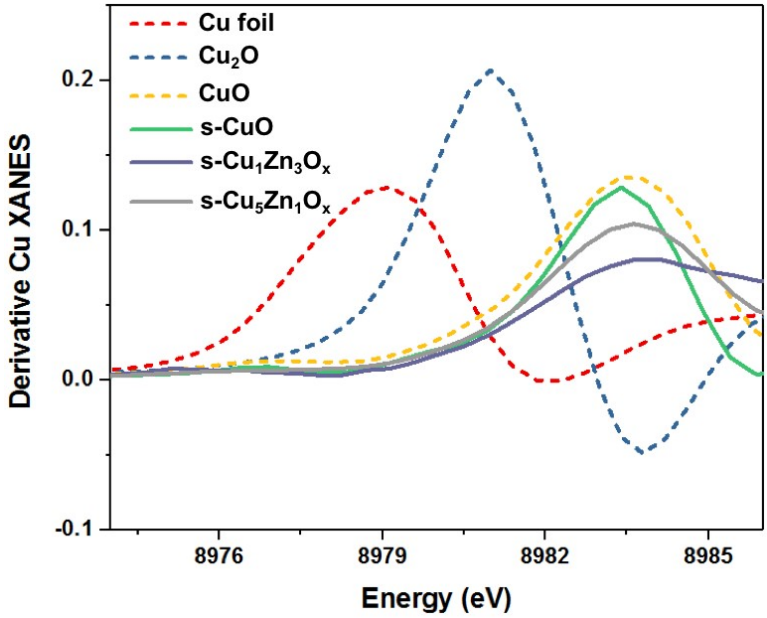

Fig. S3 The first derivative spectra of Cu foil, Cu_2O, CuO, s-CuO, s-$Cu_1Zn_3O_x$ and s-$Cu_5Zn_1O_x$ from XANES spectra of Cu K-edge.

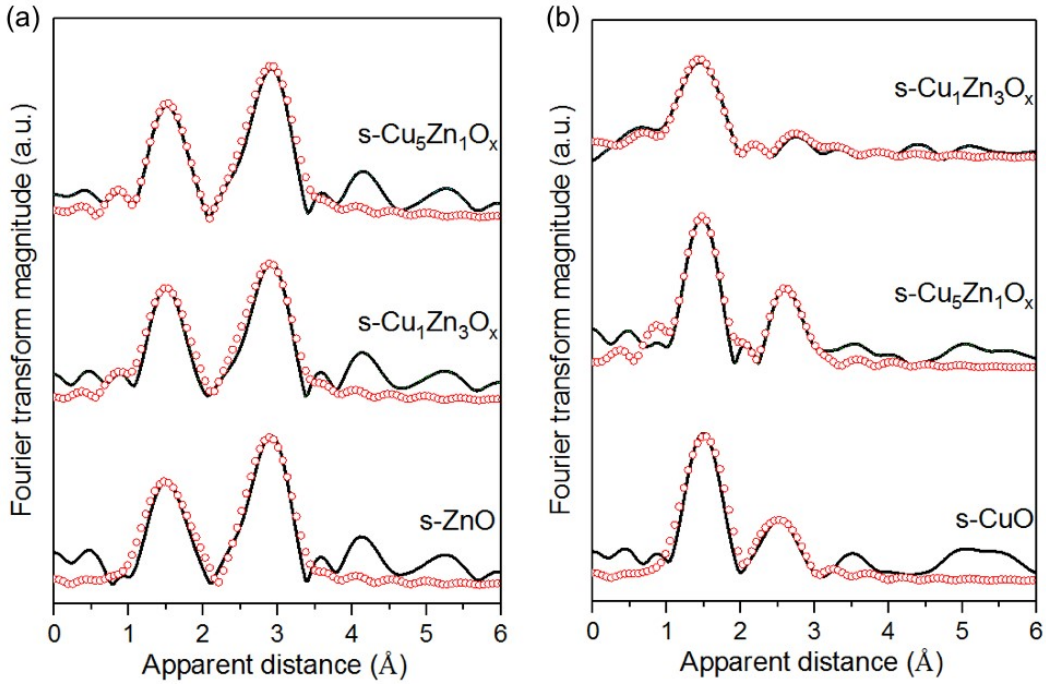

Fig. S4 (a) Zn K-edge and (b) Cu K-edge EXAFS of the sputtered samples.

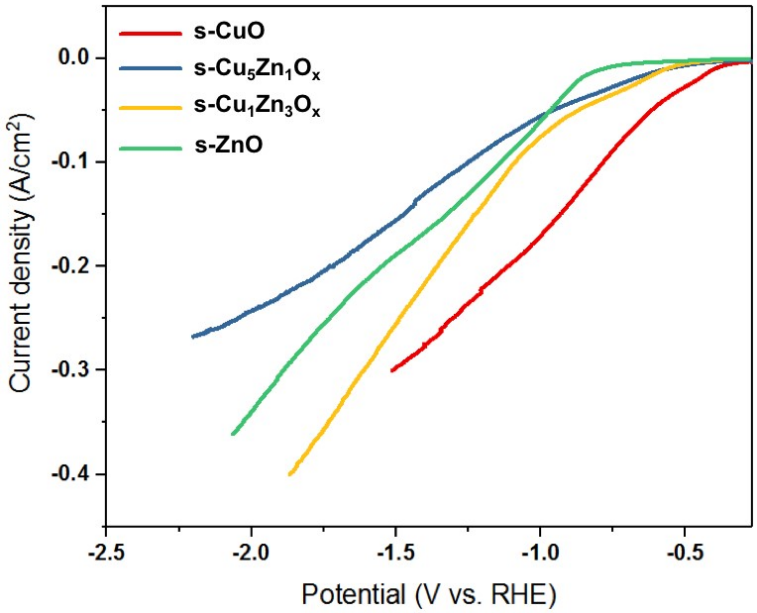

Fig. S5 LSV curves of s-CuO, s-$Cu_1Zn_3O_x$, s-$Cu_5Zn_1O_x$ and s-ZnO in 1.0 M KOH.

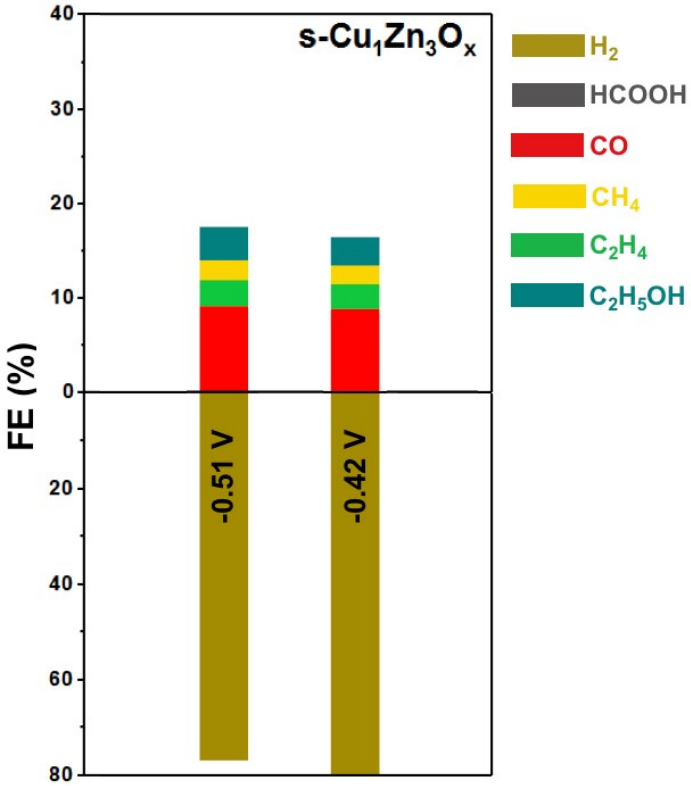

Fig. S6 Faradaic efficiencies for formation of different products in the CO_2RR with s-$Cu_1Zn_3O_x$.

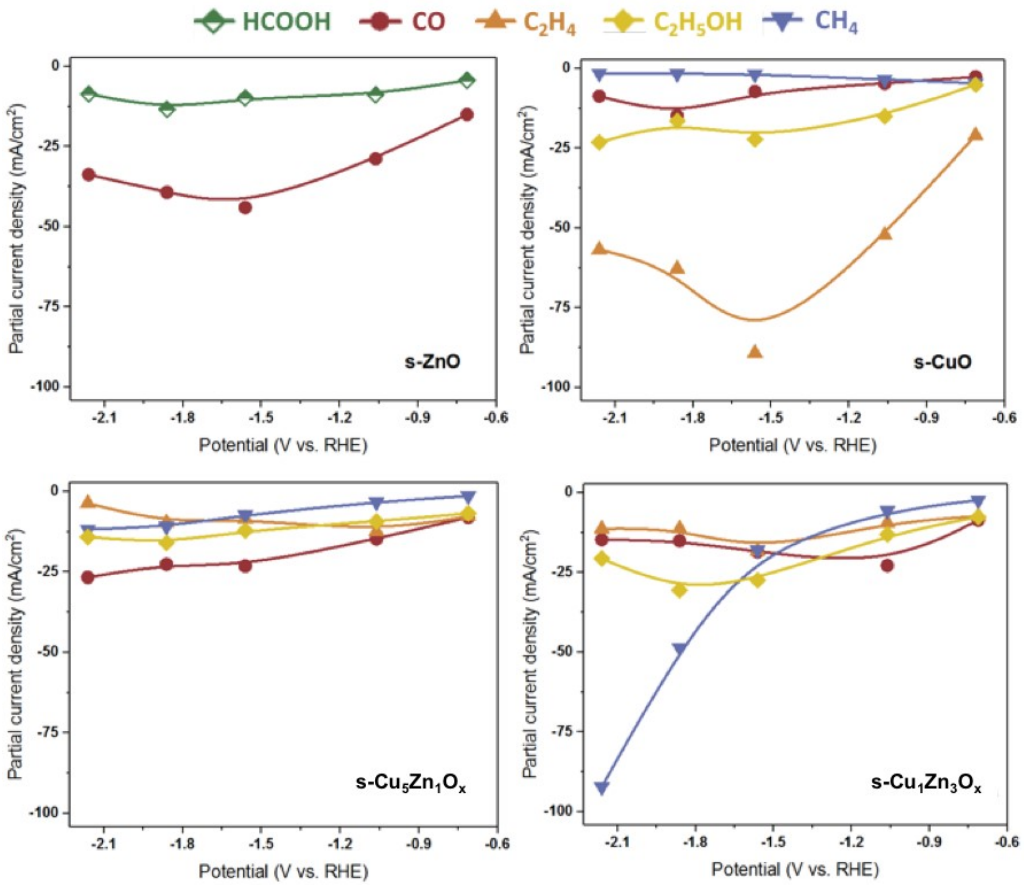

Fig. S7 Products partial current density of s-ZnO, s-CuO, s-$Cu_5Zn_1O_x$ and s-$Cu_1Zn_3O_x$ in 1.0 M KOH.

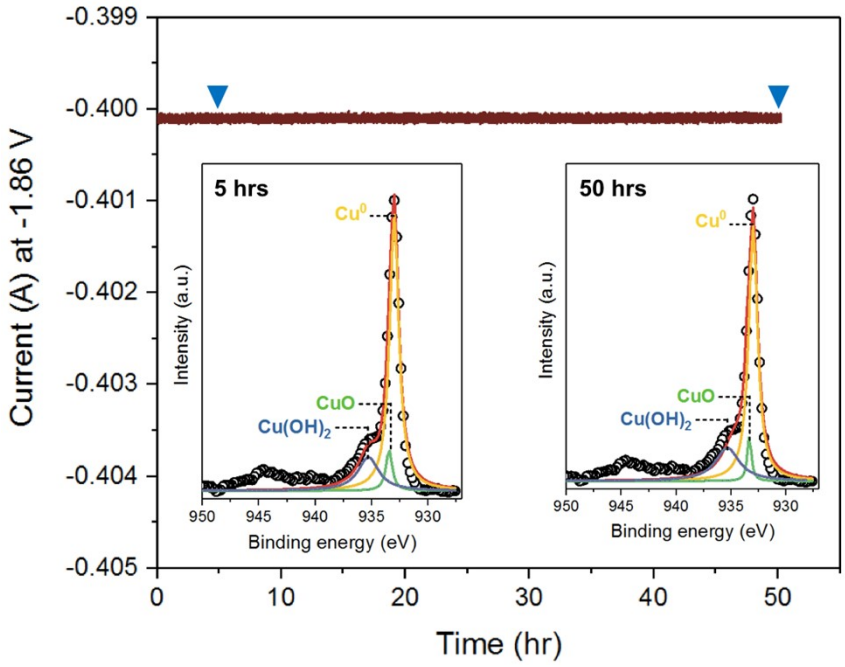

Fig. S8 Stability test of s-$Cu_1Zn_3O_x$ at -1.86 V. (Inset: XPS of Cu 2p at 5 and 50 hrs.)

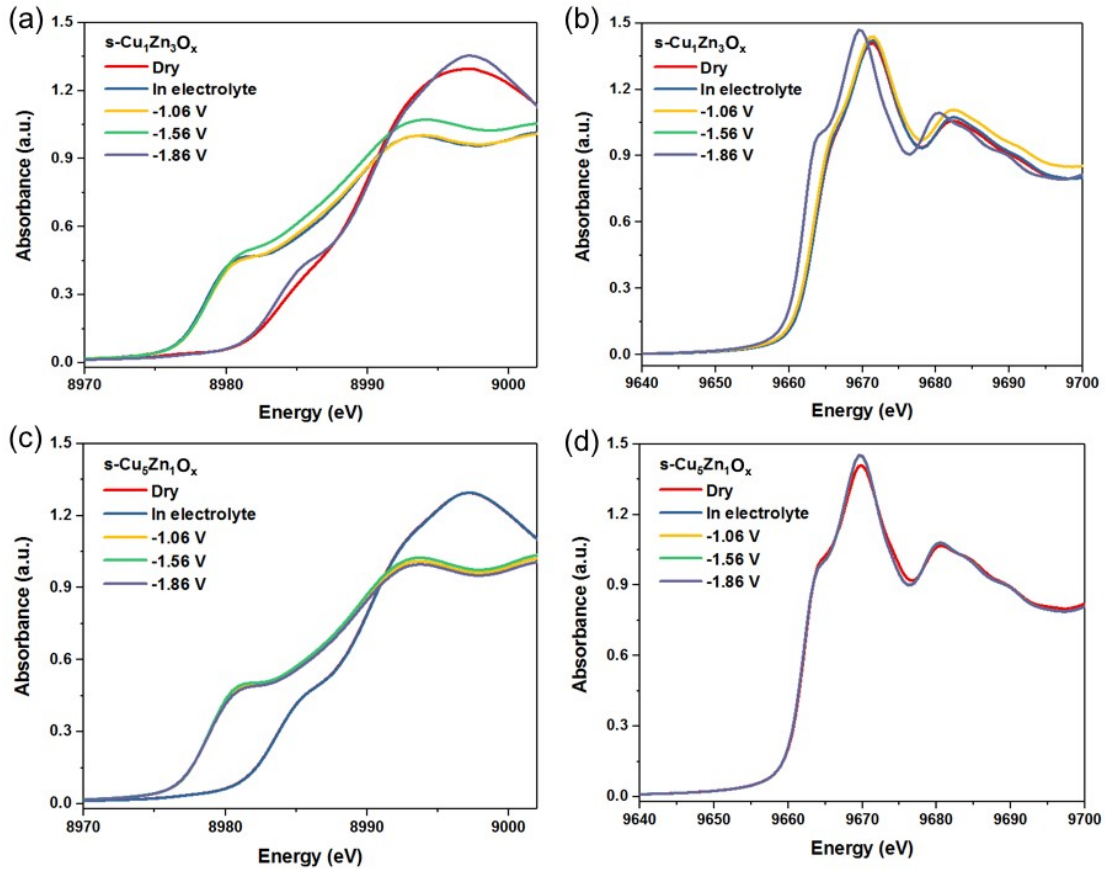

Fig. S9 *In situ* Cu K-edge XANES of (a) s-$Cu_1Zn_3O_x$ and (c) s-$Cu_5Zn_1O_x$. *In situ* Zn K-edge XANES of (b) s-$Cu_1Zn_3O_x$ and (d) s-$Cu_5Zn_1O_x$.

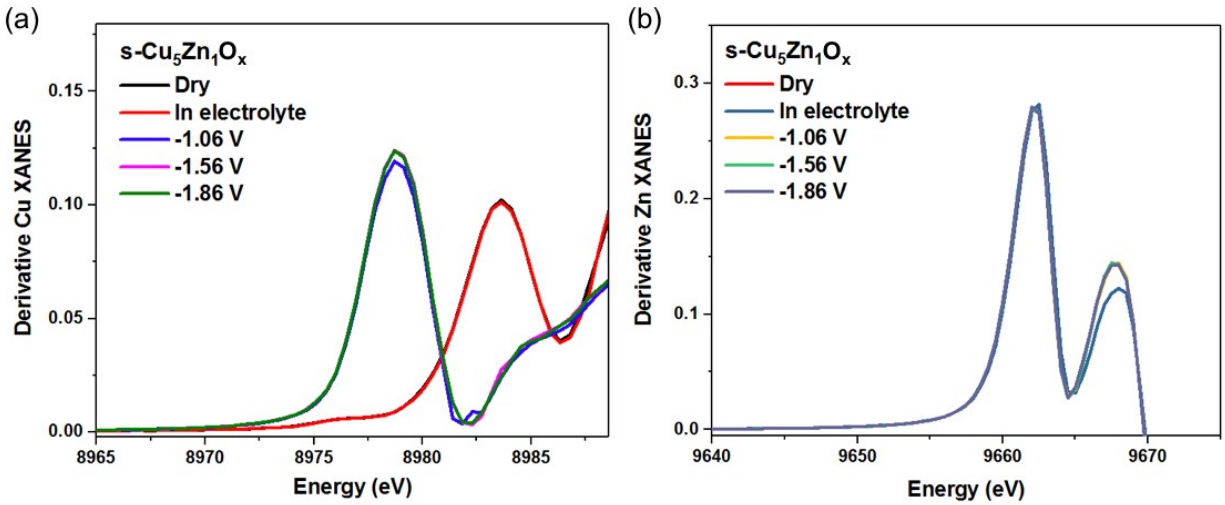

Fig. S10 The first derivative spectra of *in situ* (a) Cu K-edge and (b) Zn K-edge XANES of s-$Cu_5Zn_1O_x$.

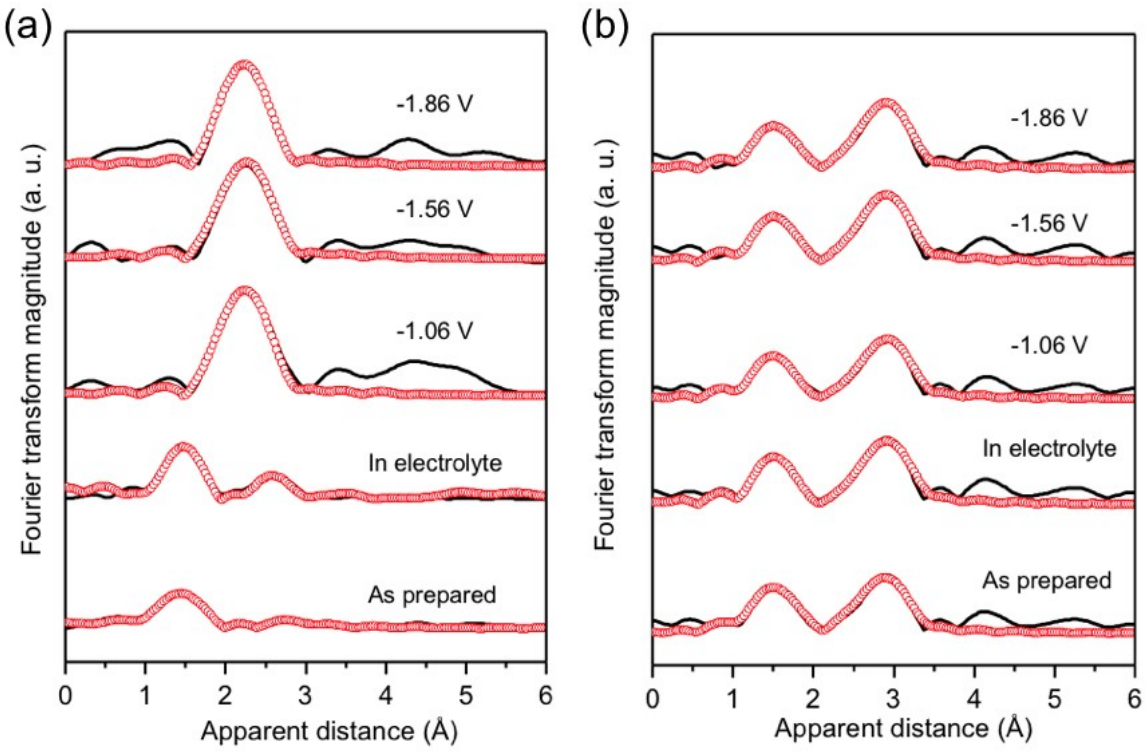

Fig. S11 *In situ* (a) Cu K-edge and (b) Zn K-edge EXAFS of s-$Cu_1Zn_3O_x$.

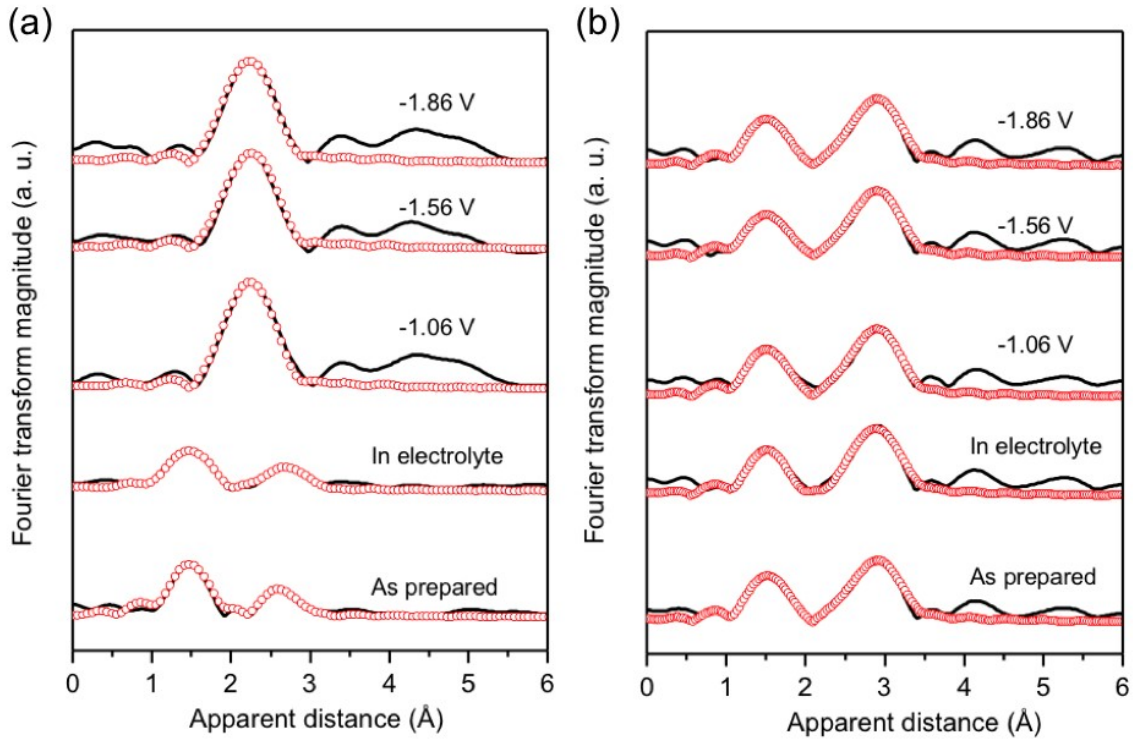

Fig. S12 *In situ* (a) Cu K-edge and (b) Zn K-edge EXAFS of s-$Cu_5Zn_1O_x$.

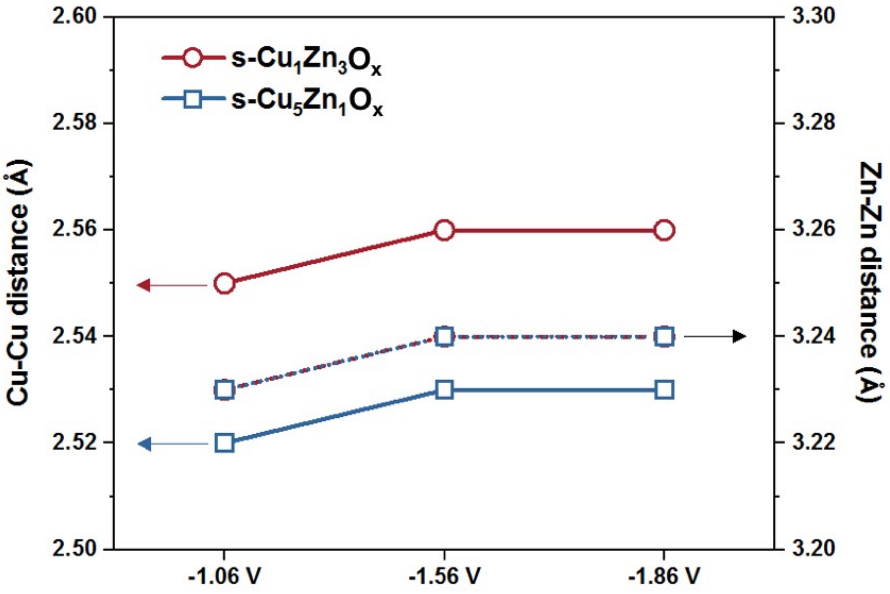

Fig. S13 Cu-Cu and Zn-Zn bond distance as a function of potential for s-Cu_1Zn_3 and s-$Cu_5Zn_1O_x$.

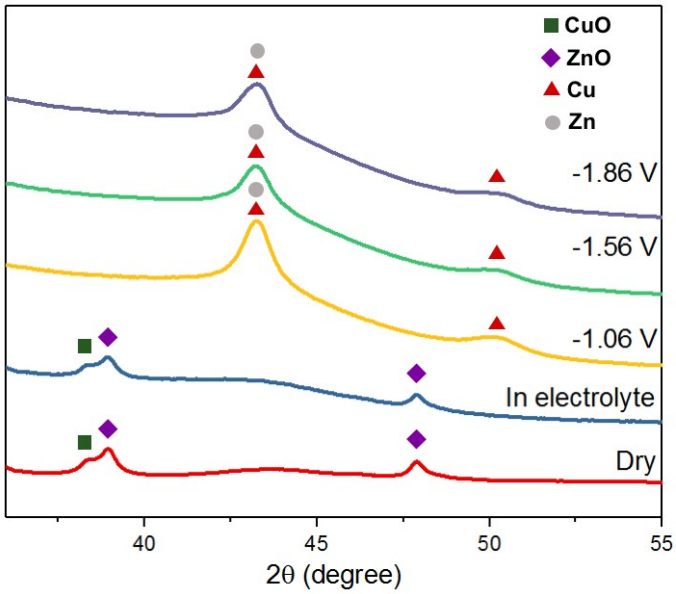

Fig. S14 *In situ* synchrotron XRD for s-$Cu_1Zn_3O_x$ during CO_2RR.

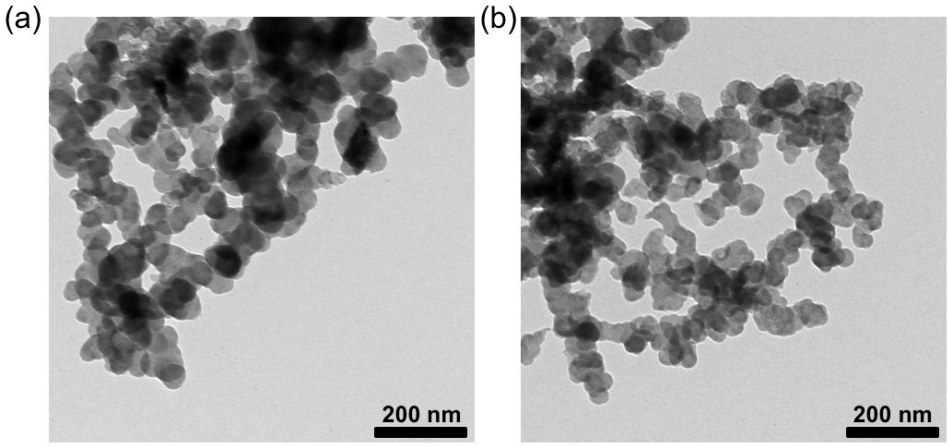

Fig. S15 TEM images of s-$Cu_1Zn_3O_x$ (a) before and (b) after CO_2RR at applied potential of -1.86 V.

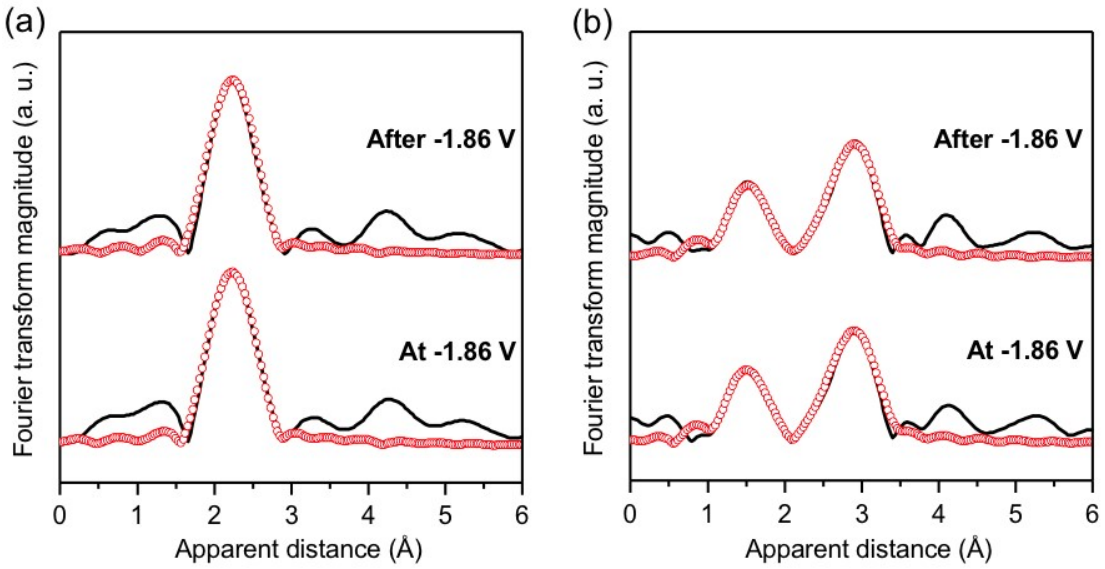

Fig. S16 Comparison of (a) Cu K-edge and (b) Zn K-edge EXAFS of s-$Cu_5Zn_1O_x$ when and after -1.86 V was applied.

Table S1. Structural parameters extracted of s-ZnO, s-$Cu_1Zn_3O_x$ and s-$Cu_5Zn_1O_x$ from Zn K-edge EXAFS. Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
s-ZnO	Zn-O	4.0(1)	1.98(1)	0.0088(1)
	Zn-Zn	11.8(1)	3.19(2)	0.0084(1)
s-$Cu_1Zn_3O_x$	Zn-O	3.8(2)	1.97(1)	0.0088(1)
	Zn-Zn	11.1(1)	3.24(2)	0.0084(1)
s-$Cu_5Zn_1O_x$	Zn-O	3.7(1)	1.97(1)	0.0088(1)
	Zn-Zn	11.0(1)	3.23(2)	0.0084(1)

Table S2. Structural parameters extracted of s-CuO, s-$Cu_5Zn_1O_x$ and s-$Cu_1Zn_3O_x$ from Cu K-edge EXAFS. Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
s-CuO	Cu-O	4.1(1)	1.96(1)	0.0084(1)
	Cu-Cu	11.6(2)	3.23(1)	0.0082(1)
s-$Cu_5Zn_1O_x$	Cu-O	3.3(2)	1.93(1)	0.0054(1)
	Cu-Cu	2.1(2)	2.97(2)	0.0050(1)
s-$Cu_1Zn_3O_x$	Cu-O	3.4(2)	1.91(1)	0.0054(1)
	Cu-Cu	1.2(2)	3.03(2)	0.0050(1)

Table S3. Structural parameters extracted of s-Cu_1Zn_3 from *in situ* Cu K-edge EXAFS during CO_2RR. Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
As prepared	Cu-O	3.4(2)	1.91(1)	0.0054(1)
	Cu-Cu	1.2(2)	3.03(2)	0.0050(1)
In electrolyte	Cu-O	3.3(2)	1.94(1)	0.0054(1)
	Cu-Cu	2.3(1)	2.94(2)	0.0050(1)
-1.06 V	Cu-Cu	11.9(1)	2.55(1)	0.0106(1)
-1.56 V	Cu-Cu	11.3(1)	2.56(1)	0.0106(1)
-1.86 V	Cu-Cu	10.9(1)	2.56(1)	0.0106(1)
After -1.86 V	Cu-Cu	10.8(1)	2.56(1)	0.0106(1)

R[Å]: Apparent distance

CN: Coordination number

DW: Debye-Waller parameter

Table S4. Structural parameters extracted of s-Cu_5Zn_1 from *in situ* Cu K-edge EXAFS during CO_2RR. Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
As prepared	Cu-O	3.3(2)	1.93(1)	0.0054(1)
	Cu-Cu	2.1(2)	2.97(2)	0.0050(1)
In electrolyte	Cu-O	3.4(2)	1.95(1)	0.0054(1)
	Cu-Cu	2.2(1)	2.99(1)	0.0050(1)
-1.06 V	Cu-Cu	11.9(1)	2.52(1)	0.0106(1)
-1.56 V	Cu-Cu	12.0(1)	2.53(1)	0.0106(1)
-1.86 V	Cu-Cu	12.1(1)	2.53(1)	0.0106(1)

R[Å]: Apparent distance

CN: Coordination number

DW: Debye-Waller parameter

Table S5. Structural parameters extracted of s-Cu_1Zn_3 from *in situ* Zn K-edge EXAFS during CO_2RR. Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
As prepared	Zn-O	3.8(2)	1.97(1)	0.0088(1)
	Zn-Zn	11.1(1)	3.24(2)	0.0084(1)
In electrolyte	Zn-O	3.9(2)	1.97(1)	0.0088(1)
	Zn-Zn	11.3(1)	3.23(2)	0.0084(1)
-1.06 V	Zn-O	3.7(1)	1.97(1)	0.0088(1)
	Zn-Zn	11.0(1)	3.23(2)	0.0084(1)
-1.56 V	Zn-O	3.6(2)	1.97(1)	0.0088(1)
	Zn-Zn	10.7(1)	3.24(2)	0.0084(1)
-1.86 V	Zn-O	3.3(2)	1.97(1)	0.0088(1)
	Zn-Zn	10.4(2)	3.24(2)	0.0084(1)
After -1.86 V	Zn-O	3.4(2)	1.97(1)	0.0088(1)
	Zn-Zn	10.4(2)	3.24(2)	0.0084(1)

R[Å]: Apparent distance

CN: Coordination number

DW: Debye-Waller parameter

Table S6. Structural parameters extracted of s-Cu_5Zn_1 from *in situ* Zn K-edge EXAFS during CO_2RR.

Fourier-transforms (FT) were performed in the k-range between 2.5 $Å^{-1}$ and 10 $Å^{-1}$.

Condition	Path	Coordination number	R(Å)	DW($Å^2$)
As prepared	Zn-O	3.3(1)	1.99(1)	0.0088(1)
	Zn-Zn	11.4(1)	3.23(2)	0.0084(1)
In electrolyte	Zn-O	3.8(1)	1.97(1)	0.0088(1)
	Zn-Zn	11.8(1)	3.23(2)	0.0084(1)
-1.06 V	Zn-O	3.8(1)	1.97(1)	0.0088(1)
	Zn-Zn	11.8(1)	3.23(2)	0.0084(1)
-1.56 V	Zn-O	4.0(2)	1.98(1)	0.0088(1)
	Zn-Zn	11.8(1)	3.24(2)	0.0084(1)
-1.86 V	Zn-O	4.0(2)	1.98(1)	0.0088(1)
	Zn-Zn	11.8(1)	3.24(2)	0.0084(1)

R[Å]: Apparent distance

CN: Coordination number

DW: Debye-Waller parameter