Supporting Information

Hierarchical Core-Shell Cu@Cu-Ni-Co Alloy Electrocatalyst for Efficient Hydrogen Evolution in Alkaline Media

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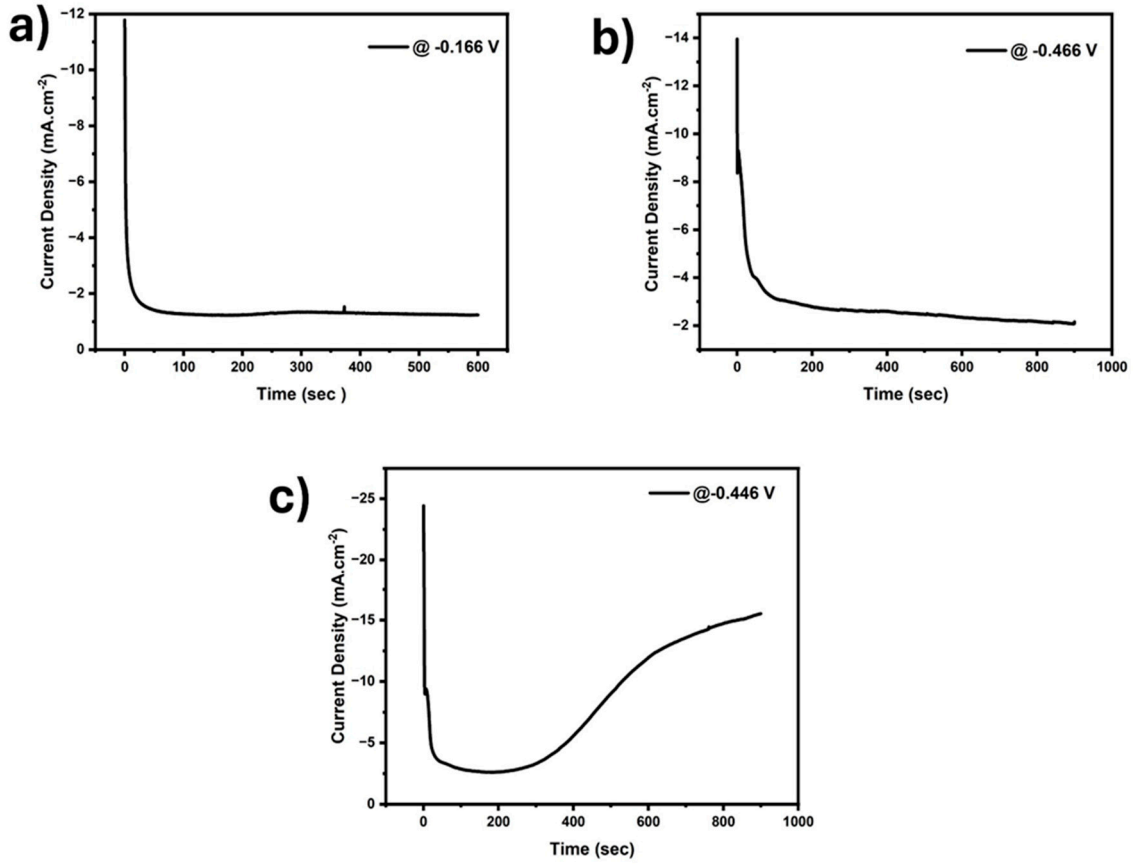

Figure S1. Amperometric i-t curves for electrodeposition: (a) Cu, (b) Cu@Ni-Co, (c) Cu@Cu-Ni-Co.

Table S1. Electrodeposition parameters of various Cu-based electrocatalysts.

	Cu	Cu@Ni-Co	Cu@Cu-Ni-Co
KH_2PO_4 (M)	0.025	0.025	0.025
$CuSO_4$ (M)	0.02	0.02	0.013
$NiCl_2{\cdot}6H_2O$ (M)	-	0.02	0.013
$CoCl_2.6H_2O$ (M)	-	0.02	0.013
pH	3.84	3.68	3.65
E (V vs. RHE)	-0.166	-0.466	-0.446
Time (s)	600	900	900
Temperature (° C)	25	25	25

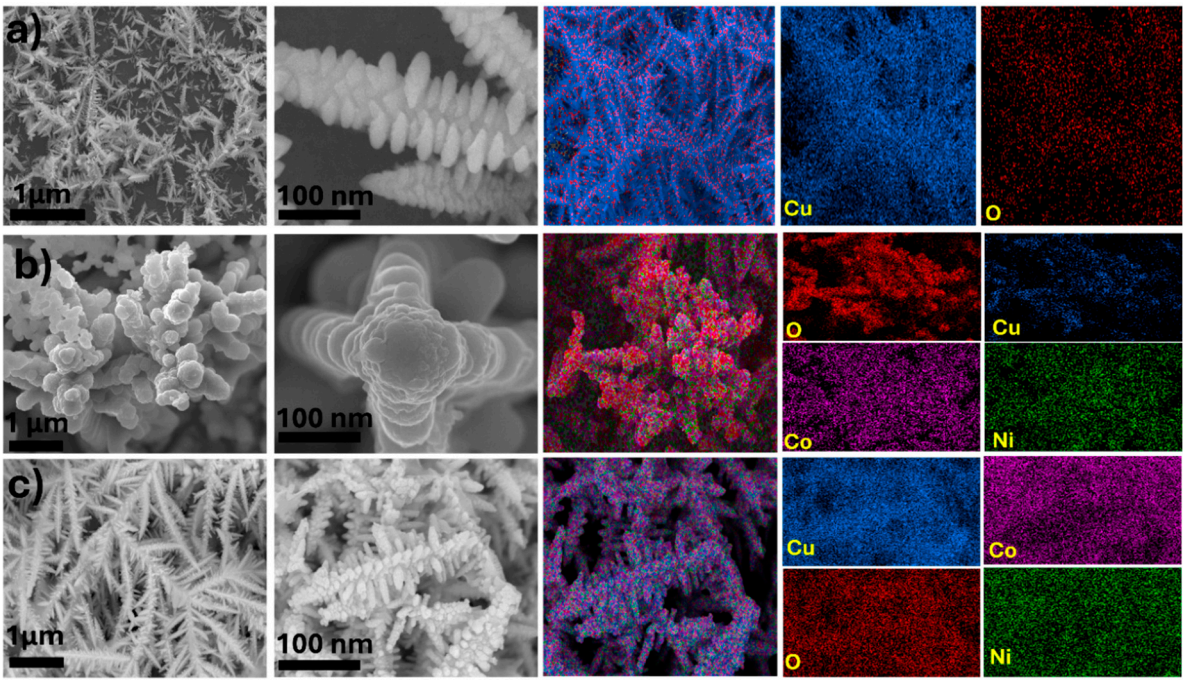

Figure S2. SEM images and EDS mapping of different electrocatalysts:(a) Cu, (b) Cu@Ni-Co, and (c) Cu@Cu-Ni-Co.

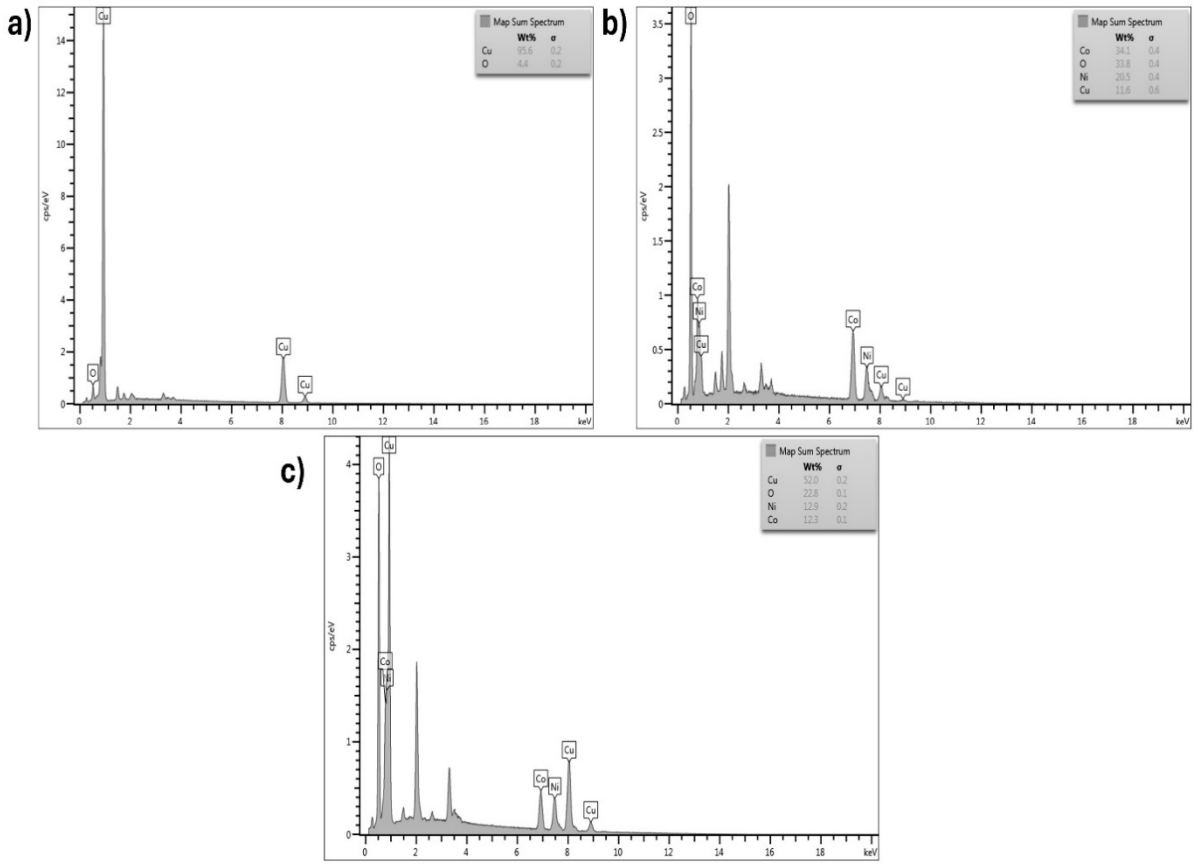

Figure S3. SEM-EDS spectra showing the elemental composition of (a) Cu, (b) Cu@Ni-Co, and (c) Cu@Cu-Ni-Co electrocatalysts.

Table S2. SEM-EDS elemental compositions analysis of Cu, Cu@Ni-Co and Cu@Cu-Ni-Co electrocatalysts.

Electrocatalysts	**EDX wt.%**			
	Cu	**Ni**	**Co**	**O**
Cu	95.6	-	-	4.4
Cu@Ni-Co	11.6	20.5	34.1	33.8
Cu@Cu-Ni-Co	55.3	28.1	10.7	5.8

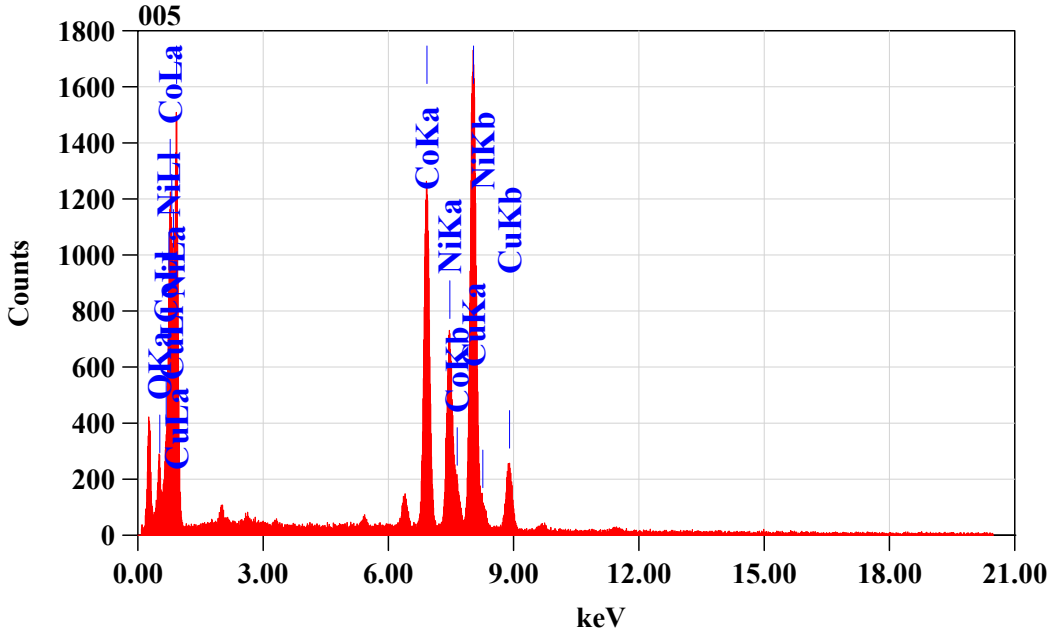

Figure S4. TEM-EDS spectrum of the **Cu@Cu-Ni-Co** electrocatalyst.

Table S3. Elemental composition analysis of the **Cu@Cu-Ni-Co** electrocatalyst based on TEM-EDS measurements.

Electrocatalysts	**EDX wt.%**			
	Cu	**Ni**	**Co**	**O**
Cu@Cu-Ni-Co	50.85	17.72	29.00	2.43

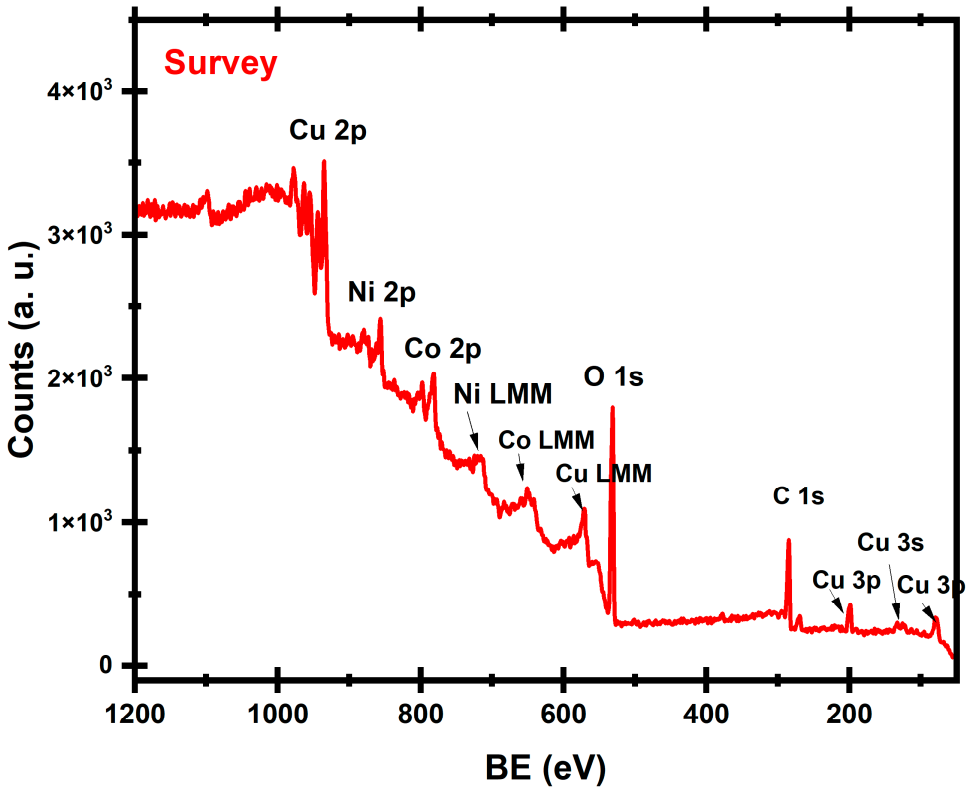

Figure S5. XPS survey of the as-synthesized Cu@Co-Ni-Cu electrocatalyst.

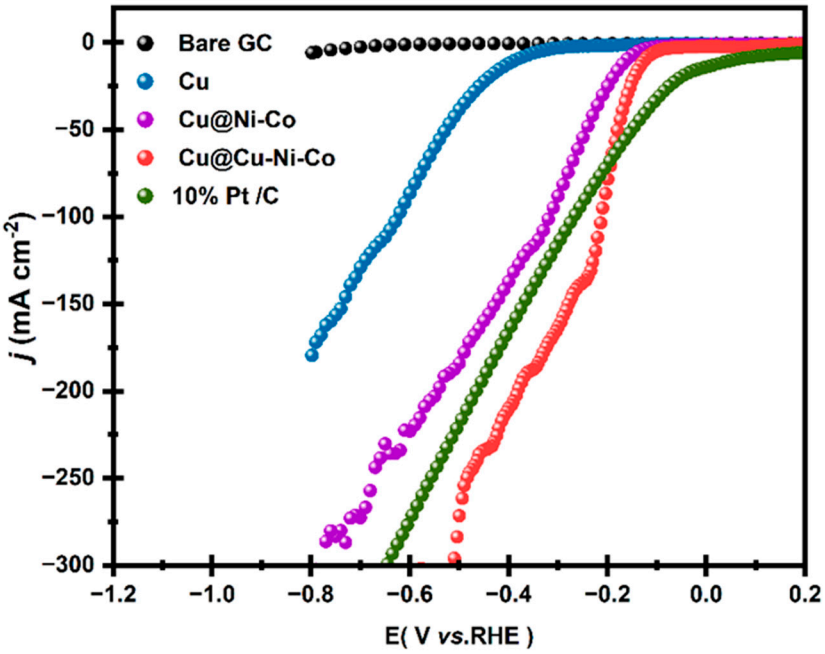

Figure S6. Full range LSV curves of Cu, Cu@Ni-Co, Cu@Cu-Ni-Co, and Pt/C electrocatalysts in 1.0 M NaOH.

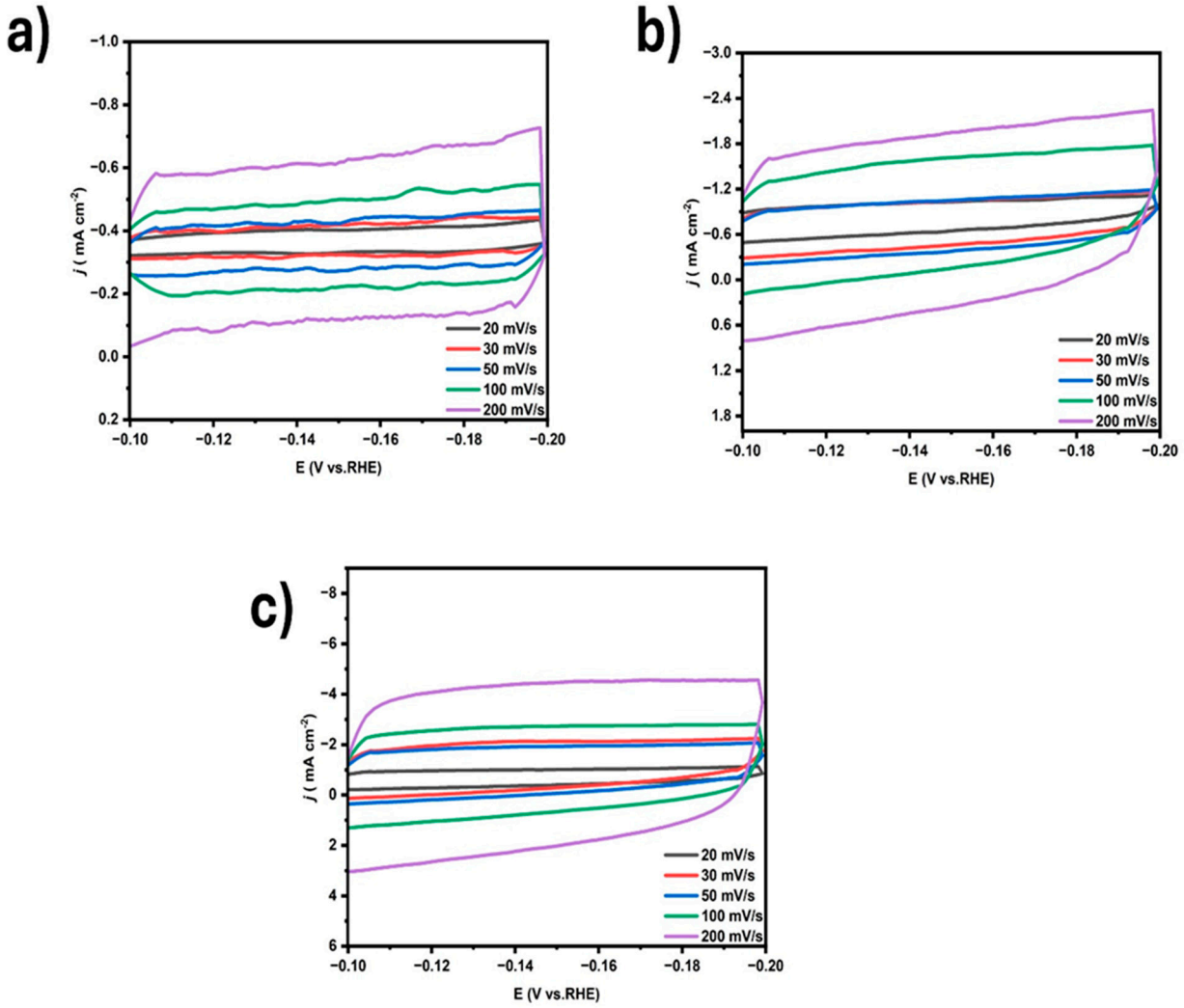

Figure S7. CV curves at different scan rates and their related plots of j vs. $v^{1/2}$ in 1.0 M NaOH for (a) Cu, (b) Cu@Ni-Co and (c) Cu@Cu-Ni-Co electrocatalysts.

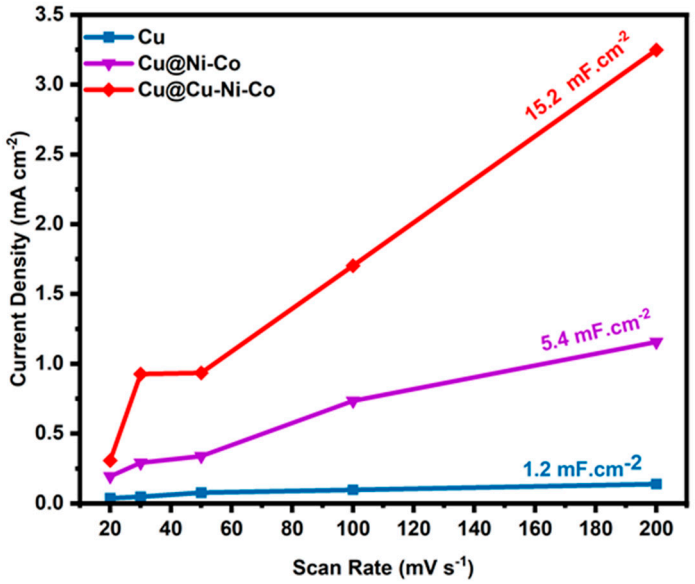

Figure S8. Double layer capacitance (C_{dl}) for Cu, Cu@Ni-Co and Cu@Cu-Ni-Co electrocatalysts in 1.0 M NaOH.

ECSA Calculations

The electrochemical activity surface area (ECSA) was determined using the formula $ECSA = \frac{C_{dl}}{C_s}$.

The double layer capacitance (C_{dl})and was obtained using the slope of plots of j vs. $v^{1/2}$

Where j is defined as $\frac{j_a - j_c}{2}$, where j_a represents the anodic current and j_c represents the cathodic current, and $v^{1/2}$ corresponds to the potential at half the potential window.

The specific capacitance (C_s) was taken from the literature as *0.040 mF cm^{-2} [1].*

Table S4. The double layer capacitance(C_{dl}) , specific capacitance (C_s) and electrochemical activity surface area ($ECSA$) of different Cu-based electrocatalysts in 1.0 M NaOH.

Catalyst	C_{dl} (F/cm^2)	$C_s(F/cm^2)$	$ECSA(cm^2)$
Cu	0.0012	0.00004	30
Cu@Ni-Co	0.0054	0.00004	135
Cu@Cu-Ni-Co	0.0152	0.00004	380

Table S5. The resistance of solution and the charge transfer resistance of various Cu-based electrocatalysts in 1.0 M NaOH.

Catalyst	R_s (Ω)	R_{ct} (Ω)	CPE ($S \cdot s^n$) $\times 10^{-4}$	Zω ($\Omega/s^{½}$)$\times 10^{-5}$
Cu	12.93	197.07	1.058	7.314
Cu@Ni-Co	11.55	82.64	2.976	42.42
Cu@Cu-Ni-Co	9.04	15.76	20.16	2482

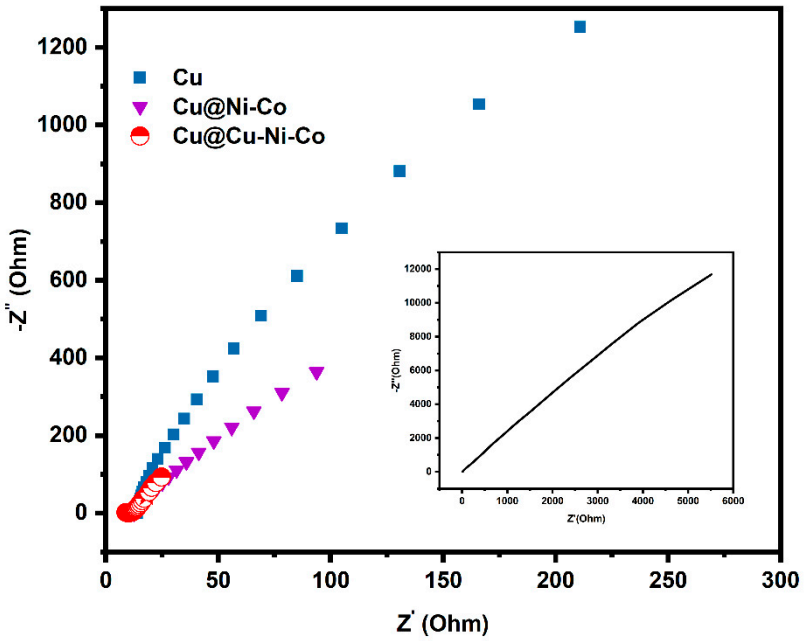

Figure S9. Nyquist plots of Cu, Cu@Ni-Co, and Cu@Cu-Ni-Co electrocatalysts in 1.0 M NaOH, the inset depicts Nyquist Plots for GC.

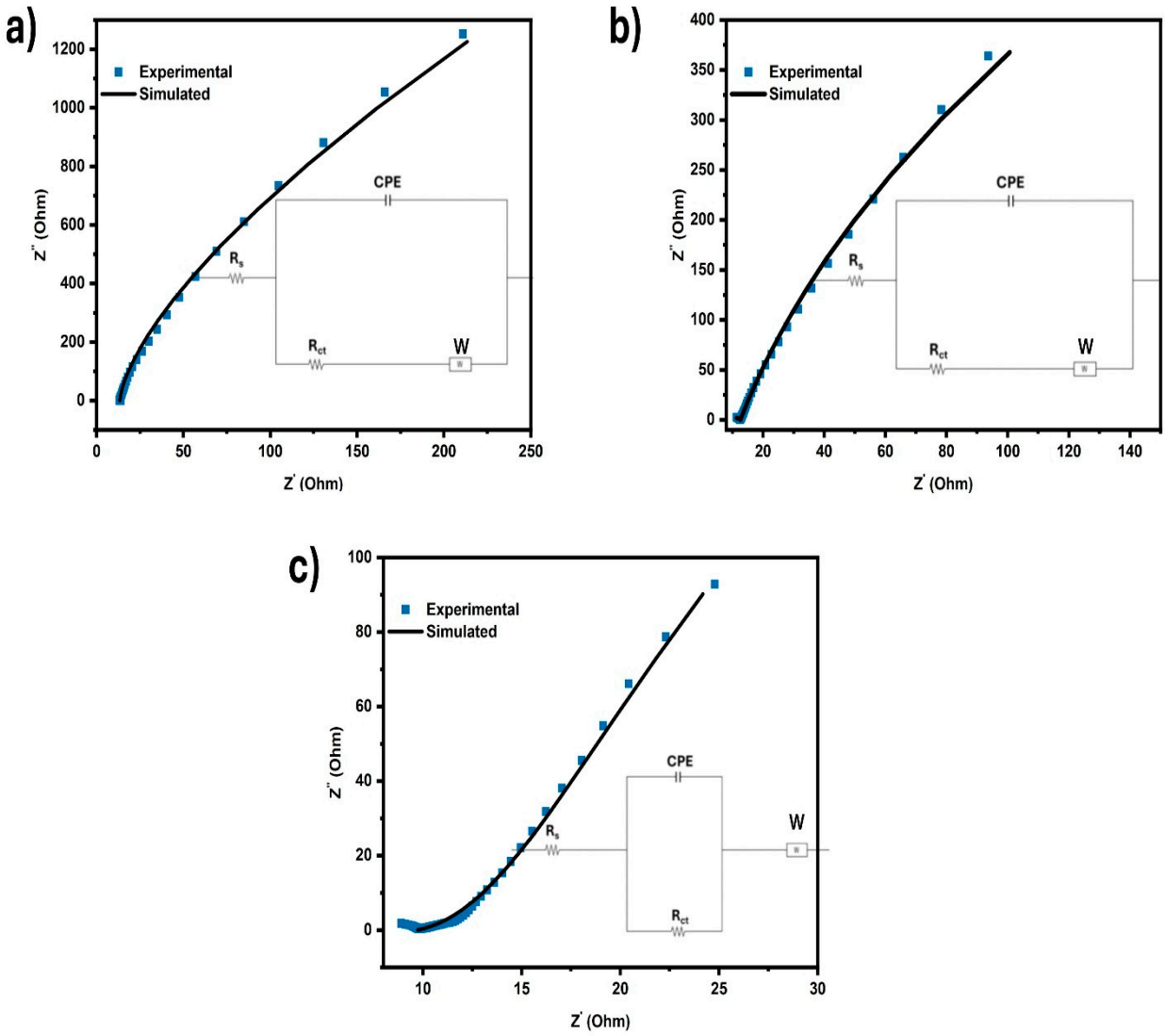

Figure S10. Experimental and simulated Nyquist plots of (a) Cu, (b) Cu@Ni-Co and (c) Cu@Cu-Ni-Co, electrocatalysts, the insets show electrical equivalent circuit.

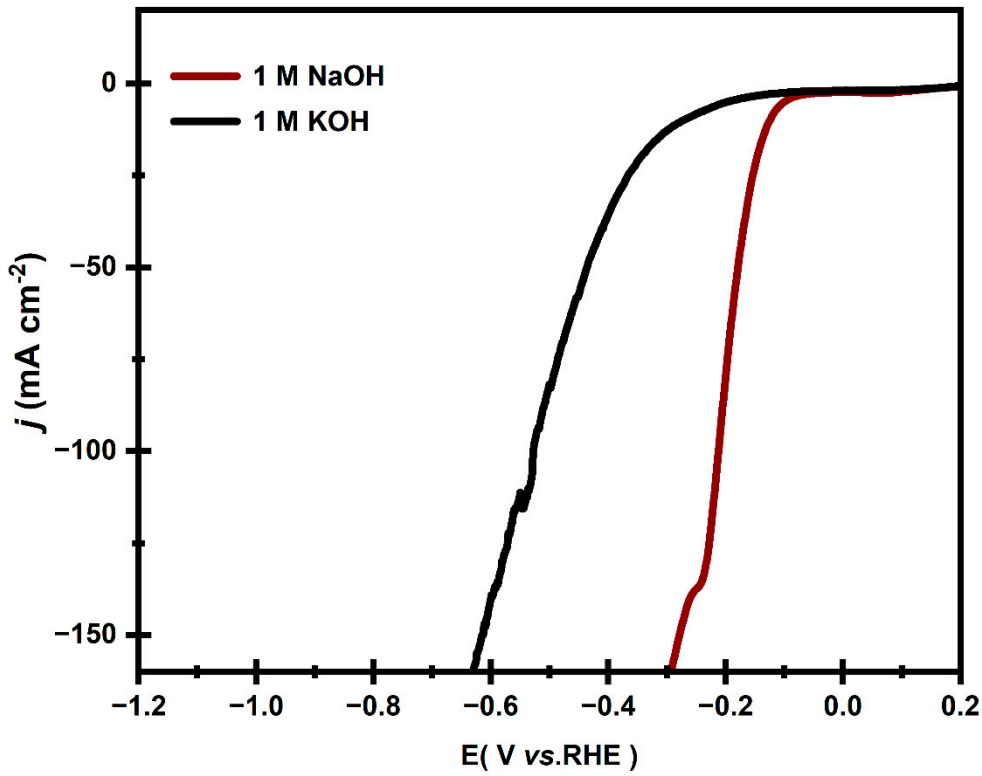

Figure S11. LSV curves of the Cu@Cu-Ni-Co electrocatalyst recorded in 1.0 M NaOH and 1.0 M KOH, demonstrating enhanced catalytic activity in NaOH, as evidenced by a lower overpotential and higher current density.

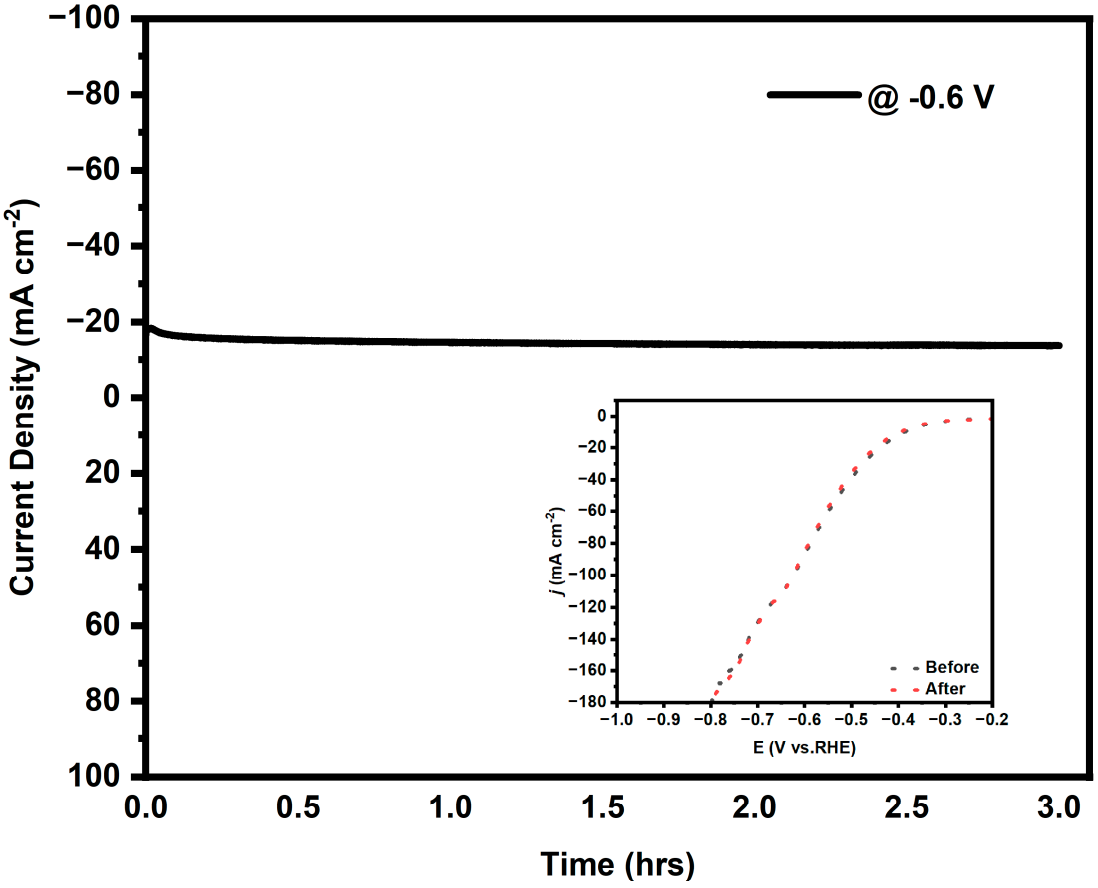

Figure S12. it-amperometric curves at -0.6 V over 3 hours and inset: LSV curves before and after 1000 CV cycles in 1 M NaOH for Cu.

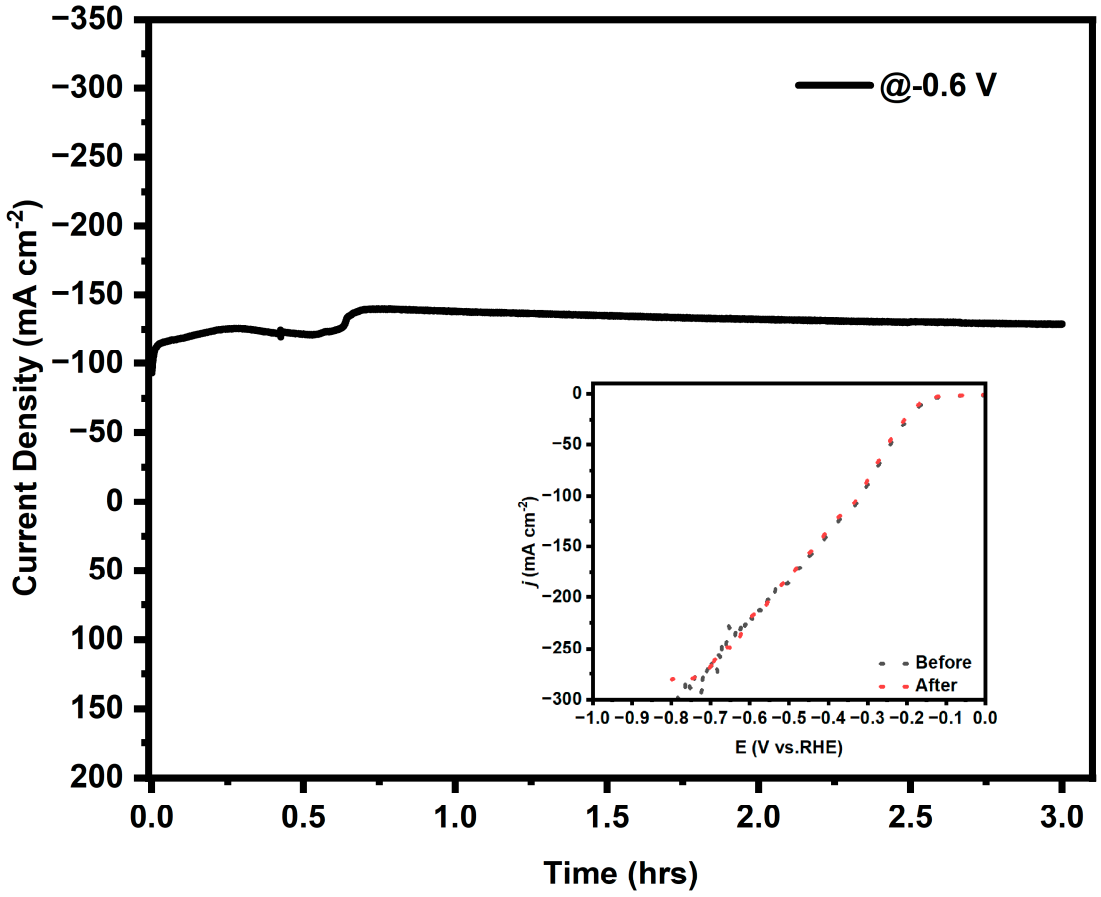

Figure S13. It-amperometric curves at -0.6 V over 3 hours and inset: LSV curves before and after 1000 CV cycles in 1 M NaOH for Cu@Ni-Co.

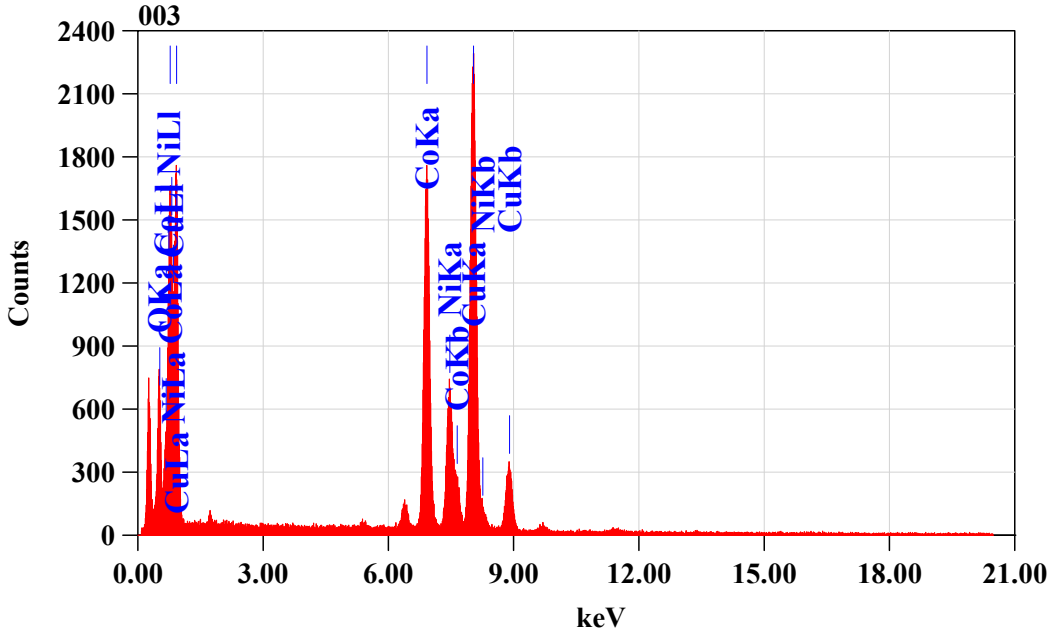

Figure S14. TEM-EDS spectrum of the post-electrolysis Cu@Cu-Ni-Co electrocatalyst.

Table S6. Elemental composition analysis of the post-electrolysis **Cu@Cu-Ni-Co** electrocatalyst based on TEM-EDS measurements.

Electrocatalysts	**EDX wt.%**			
	Cu	**Ni**	**Co**	**O**
Cu@Cu-Ni-Co	50.40	12.71	30.34	6.54

Table S7. Comparison of the HER activity of our Cu-based electrocatalysts and previous reported Cu-based electrocatalysts in alkaline electrolyte.

Electrocatalyst	Electrolyte	Overpotential @ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Reference
Cu@Cu-Ni-Co	**1 M NaOH**	**125**	**79.1**	**This work**
Cu@Ni-Co	1 M NaOH	162	89.8	This work
Cu	1 M NaOH	386	169.5	This work
CuS/Ag	0.5 M KOH	375	316	[2]
CuS	1 M KOH	447	244	[3]
Cu_2O/CuS/Co	1 M KOH	74.77	150.29	[4]
$Mo_{80}Ni_{10}Cu_{10}$	1M NaOH	426	139	[5]
$Mo_{10}Ni_{80}Cu_{10}$	1M NaOH	324	126	[5]
GQDs@ Ru	1 M KOH	30	59	[6]
Cu_3P/CF	1 M KOH	143	-	[7]
Ni-Cu	1.0 M KOH	140	140.8	[8]

Ni/Cu/CF	1.0 M KOH	38	42.7	[9]
Cu NWs	1.0 M KOH	234	120.4	[10]
CF LDH	1.0 M KOH	194	46.5	[10]
RuCu/C	1.0 M KOH	252	119	[11]
$Cu_{90}Co_{10}P$	1.0 M KOH	236	102	[12]
Ni–Co	1.0 M KOH	131	193	[13]
Ni-Co/Ni-Co-O-P@CS	1.0 M KOH	90	51	[14]
Ni–Cu–Fe@G	1.0 M KOH	111	60	[15]
$Ni_{2/3}Fe_{1/3}$/rGO	1.0 M KOH	560	210	[16]
Ni-Cu	1.0 M KOH	194	155.4	[17]
Ni–Se–Cu	1.0 M KOH	40	117.5	[17]
NiMo/Cu-NS/NF-2	1.0 M KOH	89	104	[18]
CoO_x@CN	1.0 M KOH	232	115	[19]

Pt/C	1.0 M KOH	53	49.9	[20]

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