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Identifying High-efficiency Oxygen Evolution Electrocatalysts from Co-Ni-Cu Based Selenides through Combinatorial Electrodeposition

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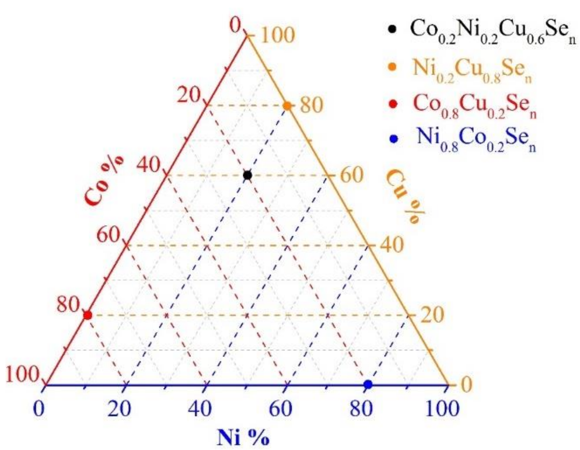

Figure S1. Trigonal phase diagram for exploring compositions of the mixed-metal (Co, Ni, Cu) selenide films examined in this work. Crossing vertices represent compositions of the precursor electrolyte with respect to the relative ratio of the corresponding metals. Color spots indicate typical examples.

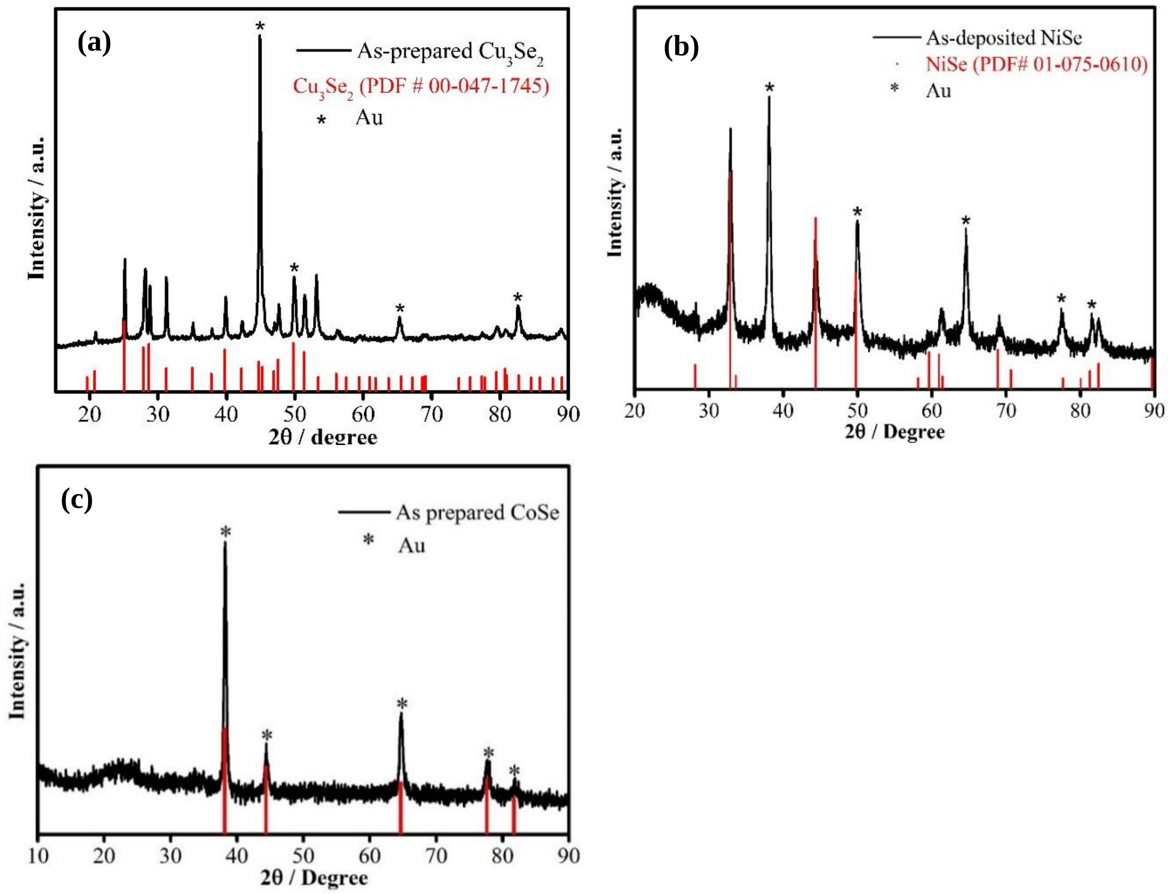

Figure S2. XRD pattern of Cu_3Se_2 (a), NiSe (b) and CoSe (c).

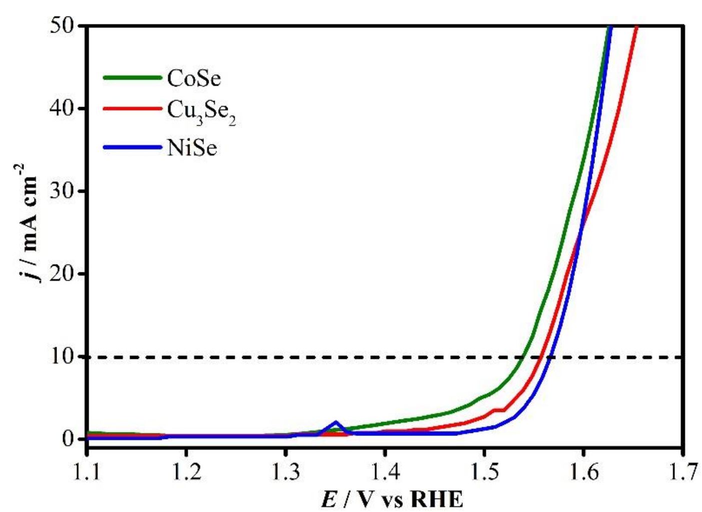

Figure S3. Polarization curves of three binary selenides.

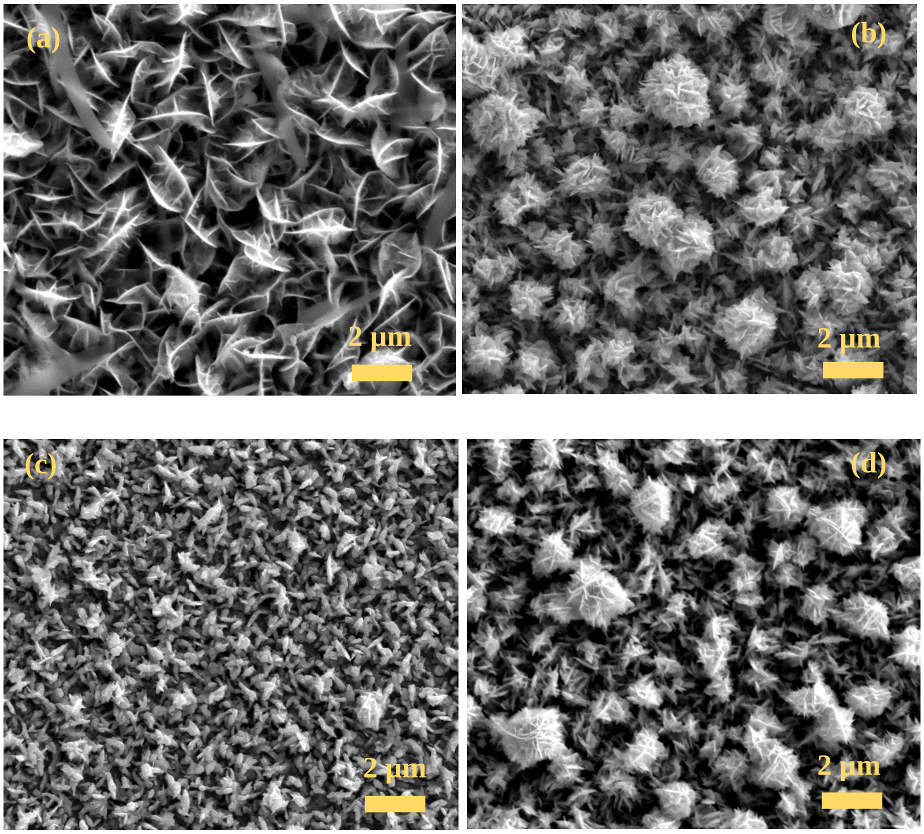

Figure S4. SEM images of selected best performing quaternary $(Co_{0.08}Ni_{0.28}Cu_{0.63})_3Se_2$ (a), $(Co_{0.31}Ni_{0.23}Cu_{0.46})_3Se_2$ (b), $(Co_{0.15}Ni_{0.26}Cu_{0.59})_3Se_2$ (c) and $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ (d).

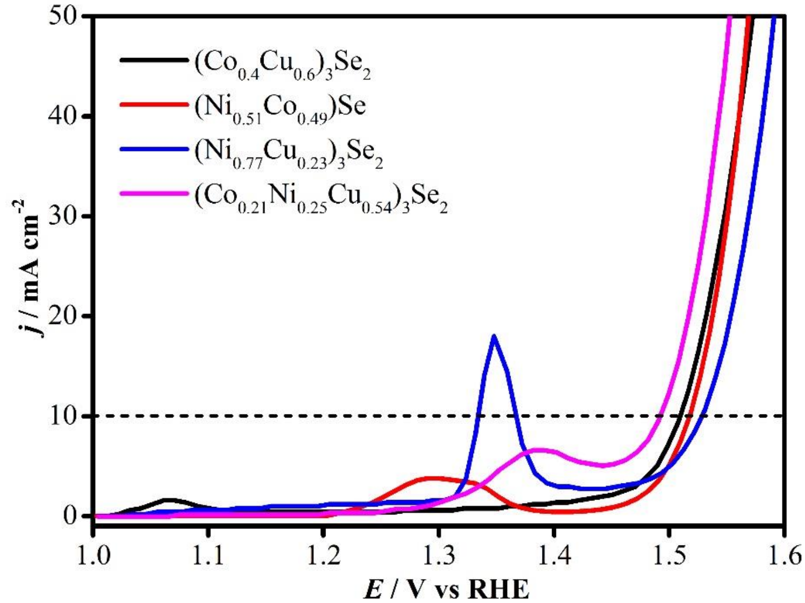

Figure S5. Polarization curves of best quaternary and best ternary selenides.

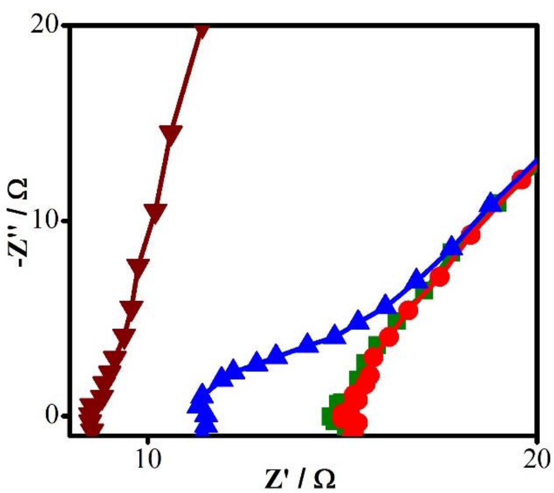

Figure S6. Zoomed-in Nyquist Plots of $(Co_{0.21}Cu_{0.25}Ni_{0.54})_3Se_2$ (green), CoSe (red), NiSe (wine) and Cu_3Se_2 (blue).

Table S1. The EDS atomic ratio of ternaries with respect to their precursor's ratio at applied potential of -0.7 V or -1.0 V vs Ag/AgCl.

$E_{applied}$ / V vs Ag/AgCl	**Precursor Molar Ratio (mM)**				**Averaged atomic % (EDS)**			
	Ni	**Cu**	**Co**	**Se**	**Ni**	**Cu**	**Co**	**Se**
- 0.7 V	2	8	-	10	0	57.2	-	42.8
	4	6	-	10	0	52.5	-	47.5
	6	4	-	10	0.2	43.4	-	56.4
	8	2	-	10	0.3	30.4	-	69.3
	-	8	2	10	-	55.7	0	44.3
	-	6	4	10	-	49.2	1.8	48.9
	-	4	6	10	-	42.2	2.2	55.1
	-	2	8	10	-	33.2	2.6	64.2
- 1.0 V	6	4	-	10	28.6	37.1	-	34.3
	-	4	6	10	-	32	35	33
	6	-	4	10	29.8	-	32.8	37.4

Table S2. Summary of Elemental Analysis of Metal Selenide Films Determined by EDS and Corresponding Kinetic Parameters Extracted from Polarization Curves.

Precursor Molar Ratio (mM)				**Averaged atomic % (EDS)**				**Onset η (V)**	**η 10mA cm^{-2} (V)**	**Tafel Slope**
Ni	**Cu**	**Co**	**Se**	**Ni**	**Cu**	**Co**	**Se**			
10	0	0	10	50.5	0.0	0.0	49.5	0.300	0.335	66.2
0	10	0	10	0.0	63.8	0.0	36.2	0.282	0.326	82.9
0	0	10	10	0.0	0.0	47.0	53.0	0.262	0.308	177.4
1	9	0	10	3.6	56.1	0.0	40.3	0.332	0.373	85.5
2	8	0	10	7.4	53.2	0.0	39.4	0.326	0.356	115.6
3	7	0	10	14.4	49.1	0.0	36.4	0.304	0.337	96.4
4	6	0	10	18.2	46.8	0.0	35.0	0.315	0.363	111.2
5	5	0	10	23.7	43.2	0.0	33.0	0.278	0.311	98.0
6	4	0	10	28.5	33.4	0.0	38.1	0.322	0.359	141.7

7	3	0	10	32.7	30.8	0.0	36.5	0.275	0.306	89.4
8	2	0	10	35.4	15.1	0.0	49.5	0.326	0.369	67.1
9	1	0	10	47.6	14.1	0.0	38.3	0.268	0.299	90.4
0	9	1	10	0.0	57.6	2.6	39.8	0.297	0.323	88.4
0	8	2	10	0.0	48.9	10.1	41.0	0.260	0.284	77.0
0	7	3	10	0.0	50.0	15.6	34.4	0.268	0.290	60.2
0	6	4	10	0.0	45.2	18.3	36.5	0.279	0.302	91.2
0	5	5	10	0.0	38.3	24.9	36.8	0.257	0.278	72.5
0	4	6	10	0.0	31.2	27.7	41.1	0.277	0.299	68.7
0	3	7	10	0.0	31.0	31.6	37.3	0.275	0.299	78.2
0	2	8	10	0.0	16.2	44.6	39.2	0.291	0.315	66.6
0	1	9	10	0.0	9.6	44.7	45.7	0.291	0.312	87.0
1	0	9	10	6.2	0.0	49.2	44.7	0.262	0.292	71.5
2	0	8	10	9.8	0.0	41.1	49.1	0.269	0.298	58.1
3	0	7	10	16.3	0.0	34.6	49.2	0.278	0.306	74.3
4	0	6	10	22.3	0.0	31.2	46.5	0.298	0.325	72.9
5	0	5	10	26.9	0.0	25.7	47.3	0.259	0.289	60.7
6	0	4	10	28.4	0.0	17.4	54.2	0.294	0.318	60.3
7	0	3	10	38.1	0.0	15.2	46.7	0.291	0.315	60.4
8	0	2	10	47.1	0.0	15.8	37.1	0.311	0.339	59.9
9	0	1	10	53.2	0.0	6.2	40.6	0.320	0.346	51.2
1	1	8	10	5.7	11.5	36.9	45.8	0.270	0.299	59.8
1	2	7	10	5.9	15.5	35.4	43.2	0.280	0.310	63.4
1	3	6	10	6.1	19.6	33.8	40.5	0.260	0.289	58.3
1	4	5	10	4.5	36.9	22.9	35.7	0.257	0.284	67.5
1	5	4	10	4.9	38.6	19.7	36.8	0.254	0.282	57.0
1	6	3	10	5.5	44.4	10.7	39.4	0.266	0.298	56.3
1	7	2	10	3.0	53.5	4.4	39.2	0.259	0.287	65.5
1	8	1	10	3.0	56.7	2.8	37.6	0.261	0.296	102.9
2	1	7	10	11.5	11.1	34.9	42.5	0.291	0.327	74.1
2	2	6	10	11.8	19.8	32.2	36.2	0.274	0.311	60.0
2	3	5	10	9.7	29.0	24.0	37.3	0.272	0.304	61.3
2	4	4	10	9.7	28.8	20.2	41.3	0.251	0.283	69.6
2	5	3	10	11.1	40.1	15.3	33.5	0.256	0.288	83.6
2	6	2	10	9.9	45.4	9.8	35.0	0.251	0.283	71.3
2	7	1	10	9.5	52.2	3.9	34.4	0.256	0.288	67.6
3	1	6	10	15.9	12.8	28.3	43.1	0.272	0.313	67.2

3	2	5	10	15.4	21.3	19.4	43.9	0.261	0.293	57.9
3	3	4	10	14.4	28.9	19.2	37.5	0.248	0.280	78.9
3	4	3	10	16.0	33.9	13.1	37.0	0.241	0.272	53.3
3	5	2	10	14.9	43.8	8.9	32.4	0.264	0.298	56.2
3	6	1	10	16.9	40.1	6.3	36.7	0.264	0.298	74.2
4	1	5	10	22.2	14.4	22.2	41.2	0.256	0.287	55.3
4	2	4	10	20.4	17.4	19.5	42.8	0.280	0.308	51.9
4	3	3	10	17.6	32.0	13.3	37.1	0.263	0.293	53.6
4	4	2	10	17.1	38.5	10.1	34.3	0.246	0.278	93.9
4	5	1	10	19.7	43.8	5.6	30.9	0.256	0.287	74.3
5	1	4	10	26.3	21.5	16.3	35.9	0.290	0.317	73.7
5	2	3	10	21.5	23.6	12.0	42.9	0.265	0.294	114.2
5	3	2	10	18.2	30.6	10.0	41.2	0.259	0.291	87.2
5	4	1	10	22.1	38.4	4.8	34.7	0.270	0.299	82.2
6	1	3	10	34.8	14.4	12.6	38.2	0.273	0.309	69.0
6	2	2	10	32.4	21.7	7.3	38.6	0.268	0.305	78.3
6	3	1	10	29.0	27.3	4.5	39.2	0.270	0.307	64.9
7	1	2	10	43.1	9.7	10.8	36.4	0.296	0.332	71.7
7	2	1	10	39.2	14.8	7.9	38.2	0.280	0.315	78.0
8	1	1	10	46.8	9.5	7.0	36.7	0.279	0.315	91.1

Table S3. The precursor ratio of compounds shown in the plots and their corresponding formulas by EDS atomic ratio.

Precursor ratio			**Molecular formula from EDS atomic ratio**
Ni	**Cu**	**Co**	
10			NiSe
	10		Cu_3Se_2
		10	CoSe
	Co	**Cu**	
	1	9	$(Co_{0.04}Cu_{0.96})_3Se_2$
	2	8	$(Co_{0.17}Cu_{0.83})_3Se_2$
	3	7	$(Co_{0.24}Cu_{0.76})_3Se_2$

Co-Cu Group	4	6	$(Co_{0.29}Cu_{0.71})_3Se_2$
	5	5	$(Co_{0.40}Cu_{0.60})_3Se_2$
	6	4	$(Co_{0.47}Cu_{0.53})_3Se_2$
	7	3	$(Co_{0.5}Cu_{0.5})_3Se_2$
	8	2	$(Co_{0.73}Cu_{0.27})_3Se_2$
	9	1	$(Co_{0.82}Cu_{0.18})_3Se_2$
Ni-Co Group	**Ni**	**Co**	
	1	9	$(Ni_{0.11}Co_{0.89})Se$
	2	8	$(Ni_{0.19}Co_{0.81})Se$
	3	7	$(Ni_{0.32}Co_{0.68})Se$
	4	6	$(Ni_{0.42}Co_{0.58})Se$
	5	5	$(Ni_{0.51}Co_{0.49})Se$
	6	4	$(Ni_{0.62}Co_{0.38})Se$
	7	3	$(Ni_{0.71}Co_{0.29})Se$
	8	2	$(Ni_{0.75}Co_{0.28})Se$
	9	1	$(Ni_{0.9}Co_{0.1})Se$
Ni-Cu Group	**Ni**	**Cu**	
	1	9	$(Ni_{0.06}Cu_{0.94})_3Se_2$
	2	8	$(Ni_{0.12}Cu_{0.88})_3Se_2$
	3	7	$(Ni_{0.23}Cu_{0.77})_3Se_2$
	4	6	$(Ni_{0.28}Cu_{0.72})_3Se_2$
	5	5	$(Ni_{0.35}Cu_{0.65})_3Se_2$
	6	4	$(Ni_{0.46}Cu_{0.54})_3Se_2$
	7	3	$(Ni_{0.52}Cu_{0.48})_3Se_2$
	8	2	$(Ni_{0.7}Cu_{0.3})_3Se_2$
	9	1	$(Ni_{0.77}Cu_{0.23})_3Se_2$
Co	**Ni**	**Cu**	
1	4	5	$(Co_{0.08}Ni_{0.28}Cu_{0.63})_3Se_2$
2	2	6	$(Co_{0.15}Ni_{0.15}Cu_{0.7})_3Se_2$
2	4	4	$(Co_{0.15}Ni_{0.26}Cu_{0.59})_3Se_2$
3	3	4	$(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$
4	1	5	$(Co_{0.31}Ni_{0.08}Cu_{0.61})_3Se_2$
4	3	3	$(Co_{0.31}Ni_{0.23}Cu_{0.46})_3Se_2$

5	1	4	$(Co_{0.36}Ni_{0.07}Cu_{0.57})_3Se_2$

Table S4. Comparison of three binary selenides, best performing ternary selenides and best quaternary selenide.

Catalysts	**Onset η / V**	**η at 10 mA cm^{-2}/V**	**Tafel slope / mV dec^{-1}**
NiSe	0.300	0.335	66.2
Cu_3Se_2	0.282	0.326	82.9
CoSe	0.262	0.308	177.4
$(Co_{0.4}Cu_{0.6})_3Se_2$	0.257	0.278	72.5
$(Ni_{0.51}Co_{0.49})Se$	0.259	0.289	60.7
$(Ni_{0.77}Cu_{0.23})_3Se_2$	0.268	0.299	90.4
$(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$	0.241	0.272	53.3

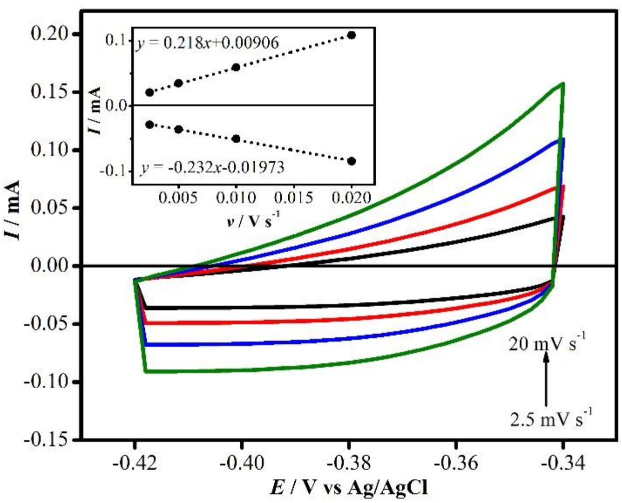

Figure S7. Cyclic voltammograms measured for the $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ after 12 h chronoamperometry in N_2 saturated 1.0 M KOH solution at different scan rates from 2.5 to 20 mV s^{-1}. The inset is a plot of both anodic and cathodic currents measured at -0.36 V vs Ag|AgCl (KCl saturated) as a function of scan rate.

Table S5. Comparison of ECSA and roughness factor (RF) of $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ before and after chronoamperometry.

	ECSA / cm^2	RF
Before	3.68	52.57
After	5.63	80.36

Table S6. Comparison of EDS atomic ratio of $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ before and after electrochemical measurement.

	EDS (Atomic %)			
	Ni	**Cu**	**Co**	**Se**
As-deposited	16.1	33.9	13.1	37.0
After activity	15.3	35.6	12.4	36.7

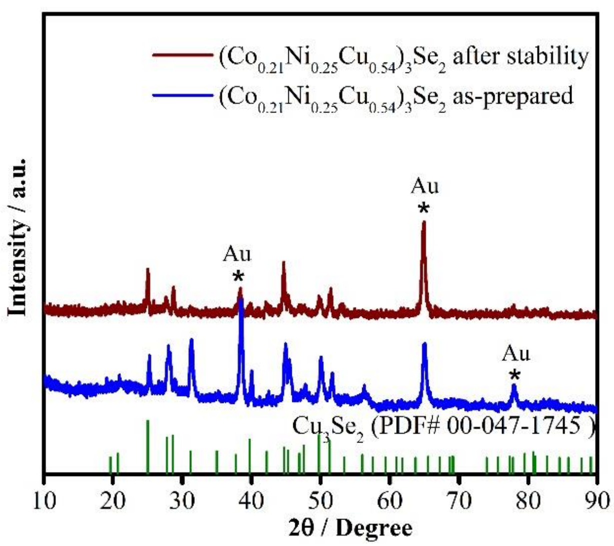

Figure S8. XRD patterns of as-prepared $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ and $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ after 12 h chronoamperometry along with reference Cu_3Se_2 (PDF # 00-047-1745).

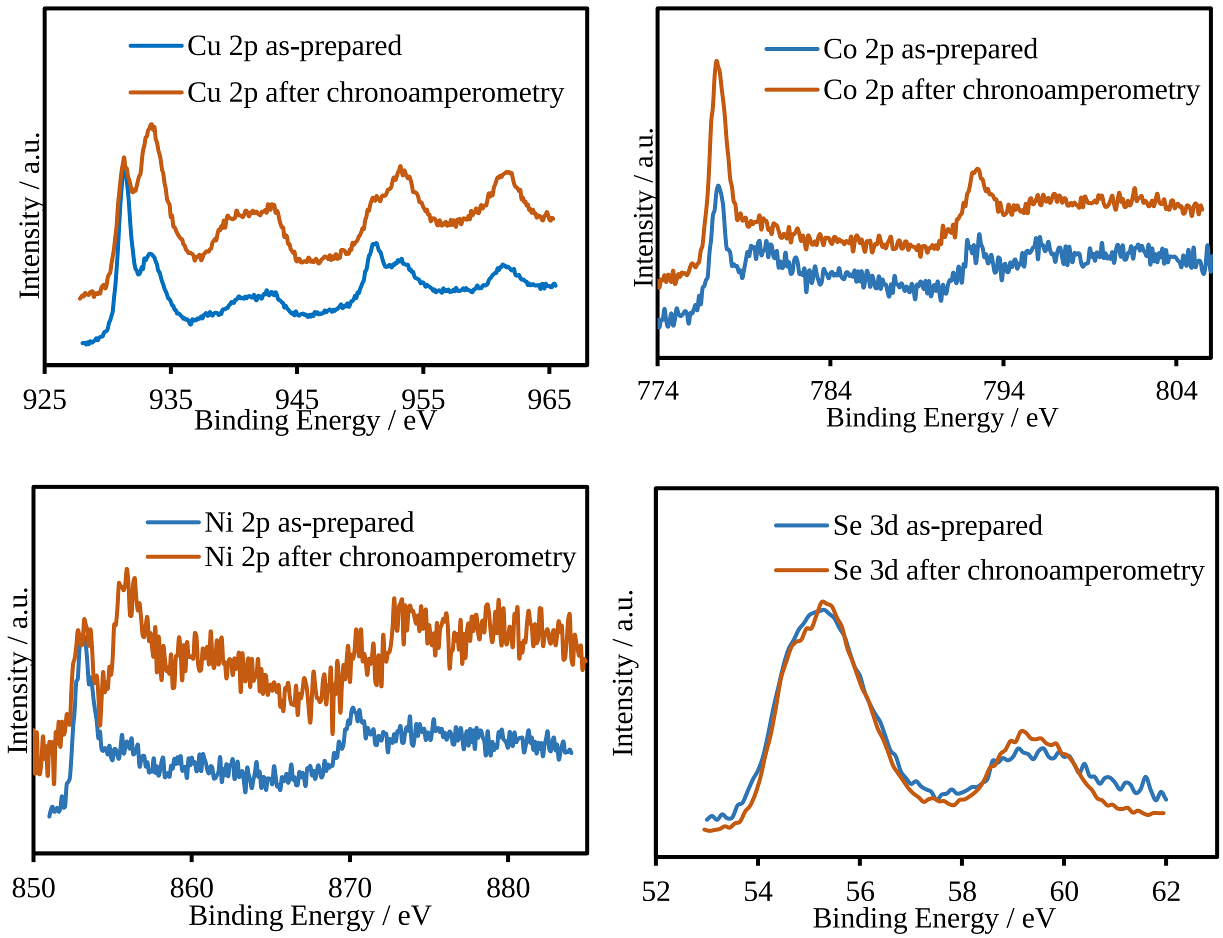

Figure S9. Comparison of XPS spectra of $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ catalyst before and after chronoamperometry.

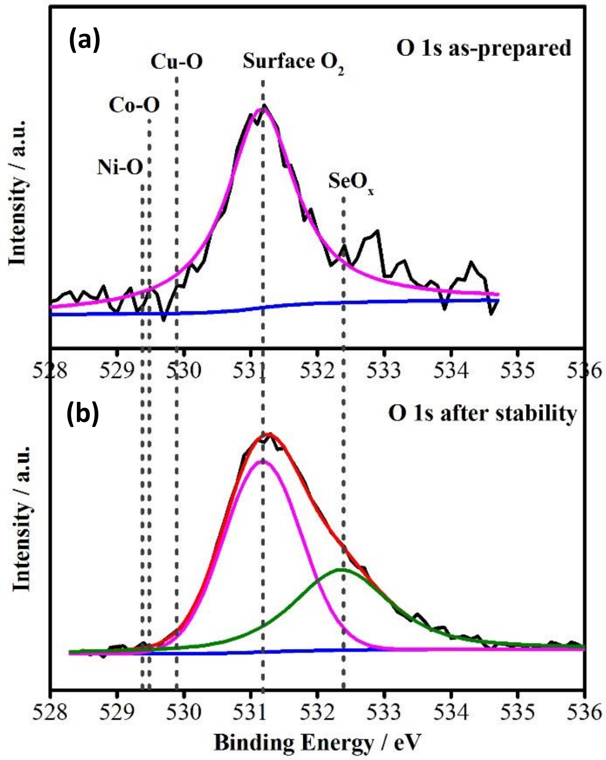

Figure S10. Comparison of XPS spectra of $(Co_{0.21}Ni_{0.25}Cu_{0.54})_3Se_2$ catalyst before and after chronoamperometry.

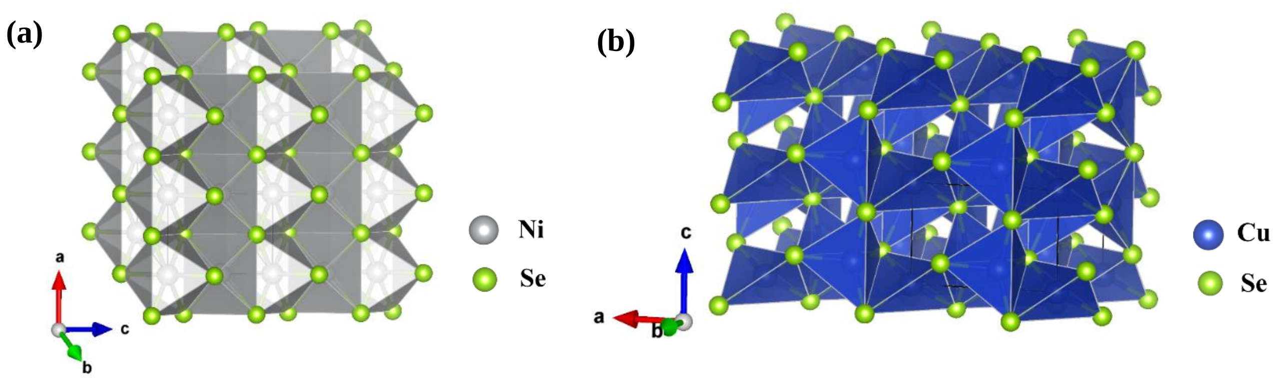

Figure S11. Crystal structure of (a) NiSe and (b) Cu_3Se_2.