Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Data

Tuning composition of $CuCo_2S_4$-$NiCo_2S_4$ solid solutions via solventless pyrolysis of molecular precursors for efficient supercapacitance and water splitting

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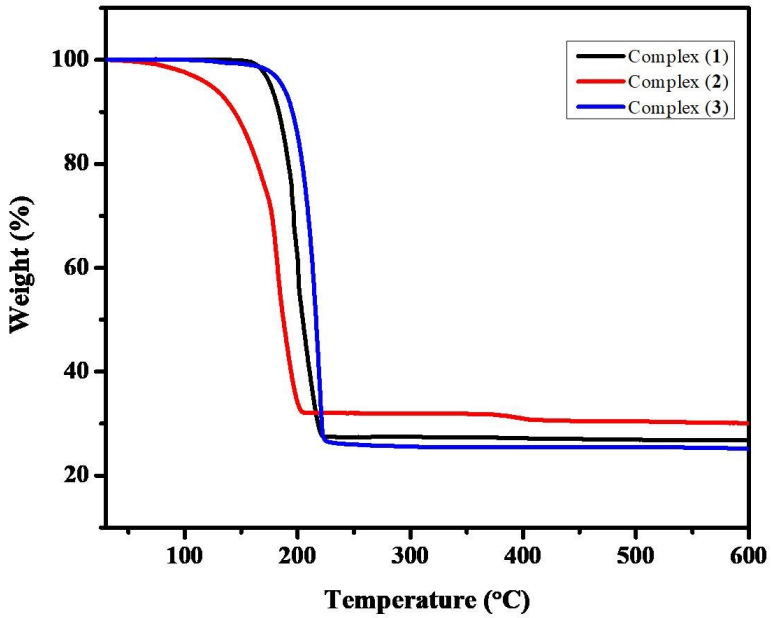

Figure S1. TGA curves of nickel ethyl xanthate (**1**), copper ethyl xanthate (**2**), and cobalt ethyl xanthate (**3**).

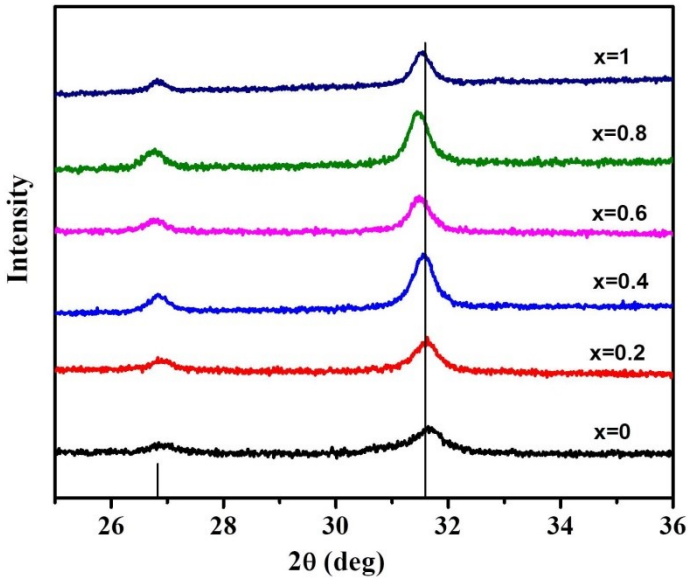

Figure S2. The extended portion of the diffraction patterns of $Ni_{(1-x)}Cu_xCo_2S_4$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) showing the shift in peak positions.

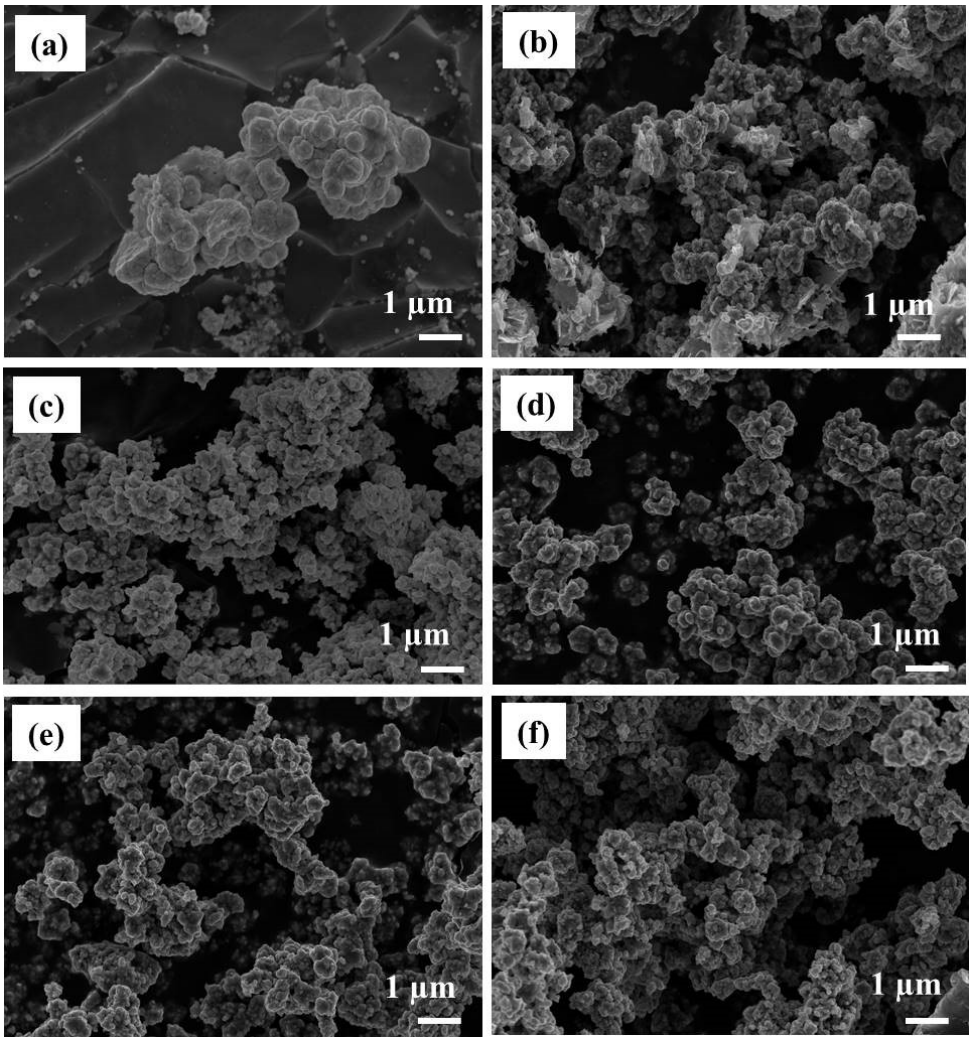

Figure S3. SEM images of $Ni_{(1-x)}Cu_xCo_2S_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) nanoparticles taken at 10.00 KX.

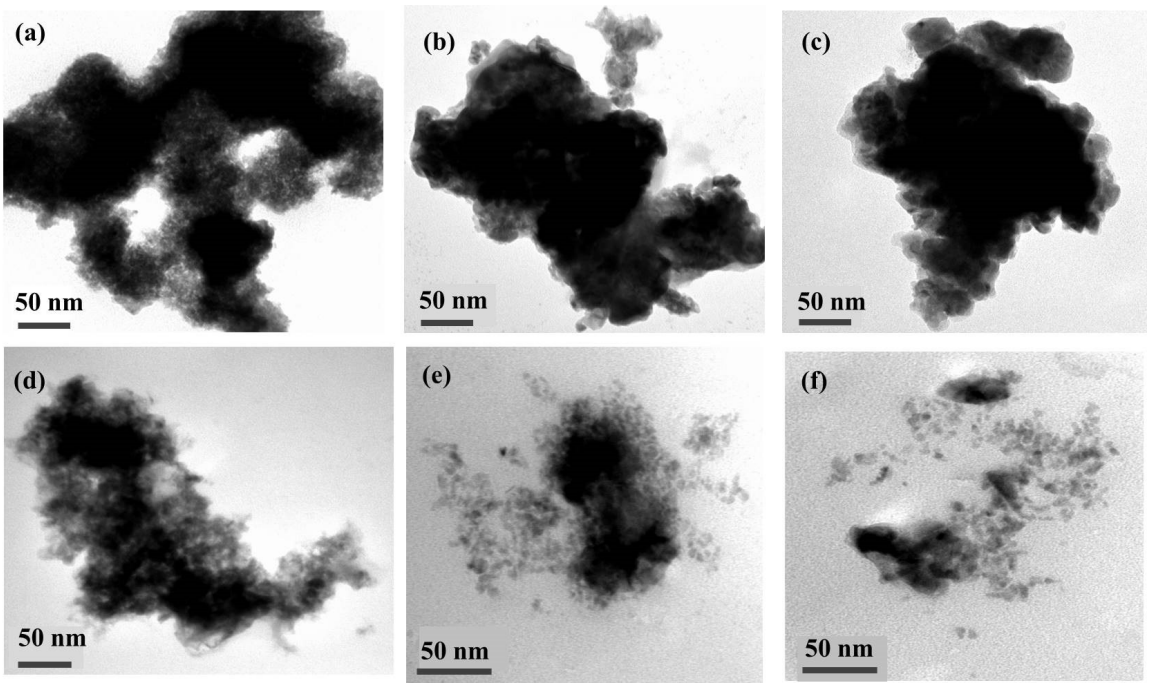

Figure S4. TEM images of $Ni_{(1-x)}Cu_xCo_2S_4$ nanoparticles synthesized at $x = 0$ (a), $x = 0.2$ (b), $x = 0.4$ (c), $x = 0.6$ (d), $x = 0.8$ (e) and $x = 1$ (f).

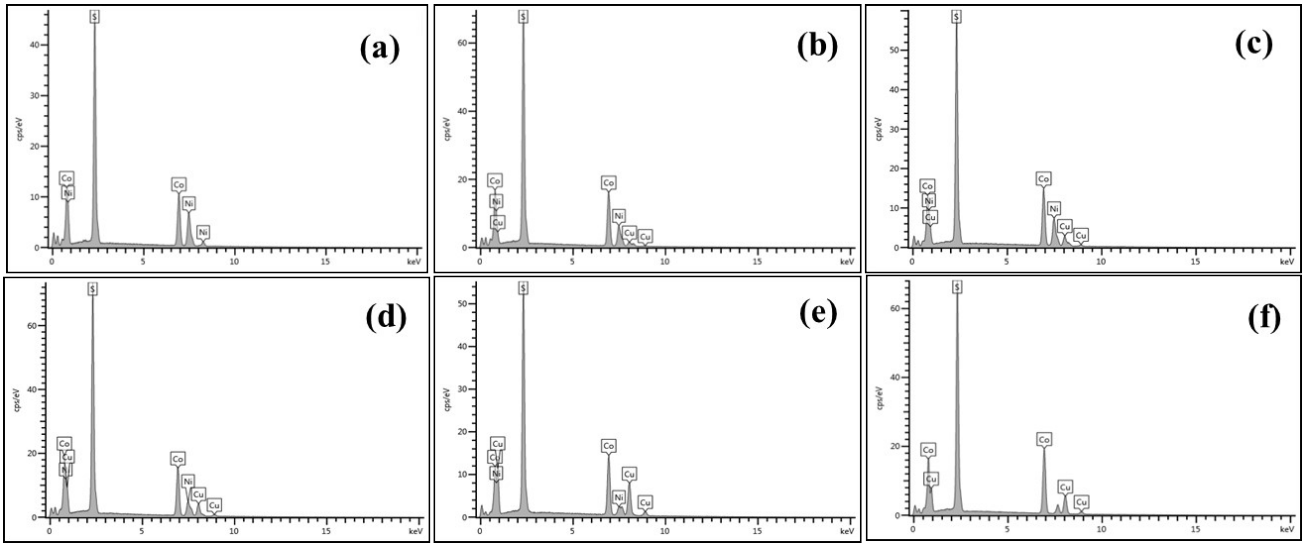

Figure S5. EDX spectra of $Ni_{(1-x)}Cu_xCo_2S_4$ synthesized at $x = 0$ (a), $x = 0.2$ (b), $x = 0.4$ (c), $x = 0.6$ (d), $x = 0.8$ (e), and $x = 1$ (f).

Table S1. Theoretical and experimental atomic percentage compositions of $Ni_{(1-x)}Cu_xCo_2S_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1).

Copper mole fraction (*x*)	**Theoretical Composition (Atomic %)**				**Experimental composition (Atomic %)**			
	Ni	**Co**	**Cu**	**S**	**Ni**	**Co**	**Cu**	**S**
0	14.29	28.57	0	57.14	17.61	28.64	0	53.75
0.2	11.43	28.57	2.86	57.14	12.05	28.96	3.04	55.95
0.4	8.57	28.57	5.71	57.14	9.13	29.56	6.44	54.87
0.6	5.71	28.57	8.57	57.14	5.84	29.63	8.67	55.86
0.8	2.86	28.57	11.43	57.14	3.62	28.20	12.4	55.78
1	0	28.57	14.29	57.14	0	30.92	11.6	57.48

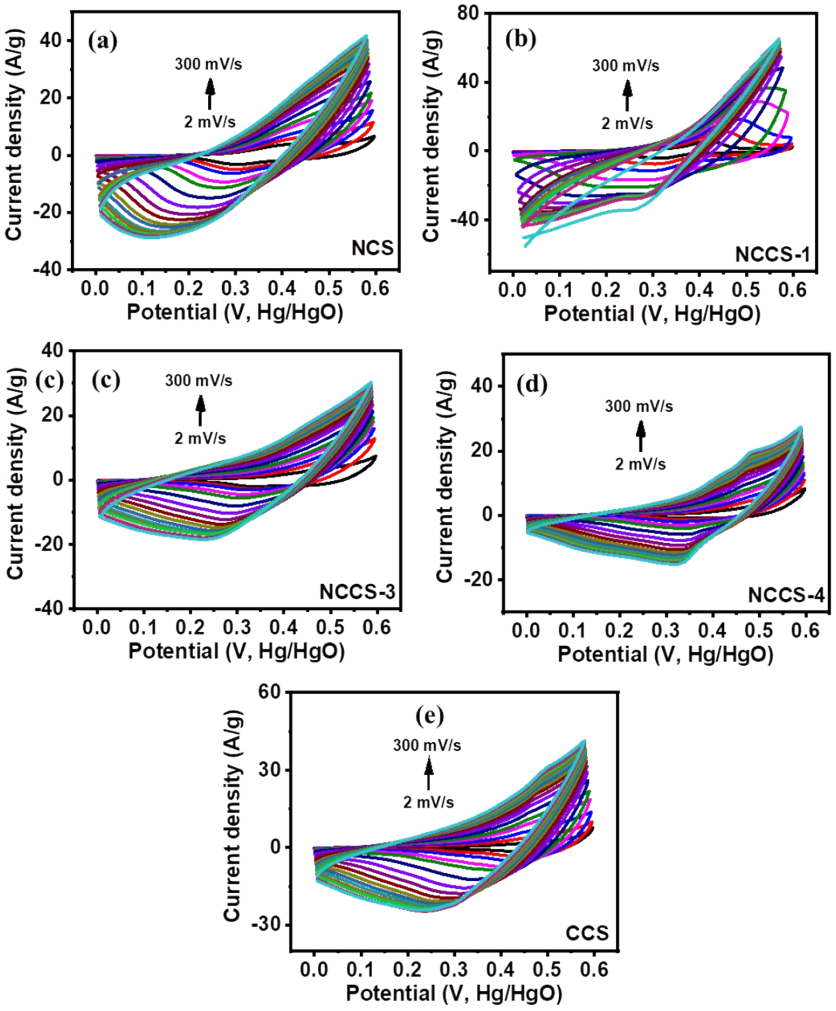

Figure S6. Cyclic voltammograms of (a) NCS, (b) NCCS-1, (c) NCCS-3, (d) NCCS-4, and (e) CCS in KOH at various scan rates of 2-300 mV/s.

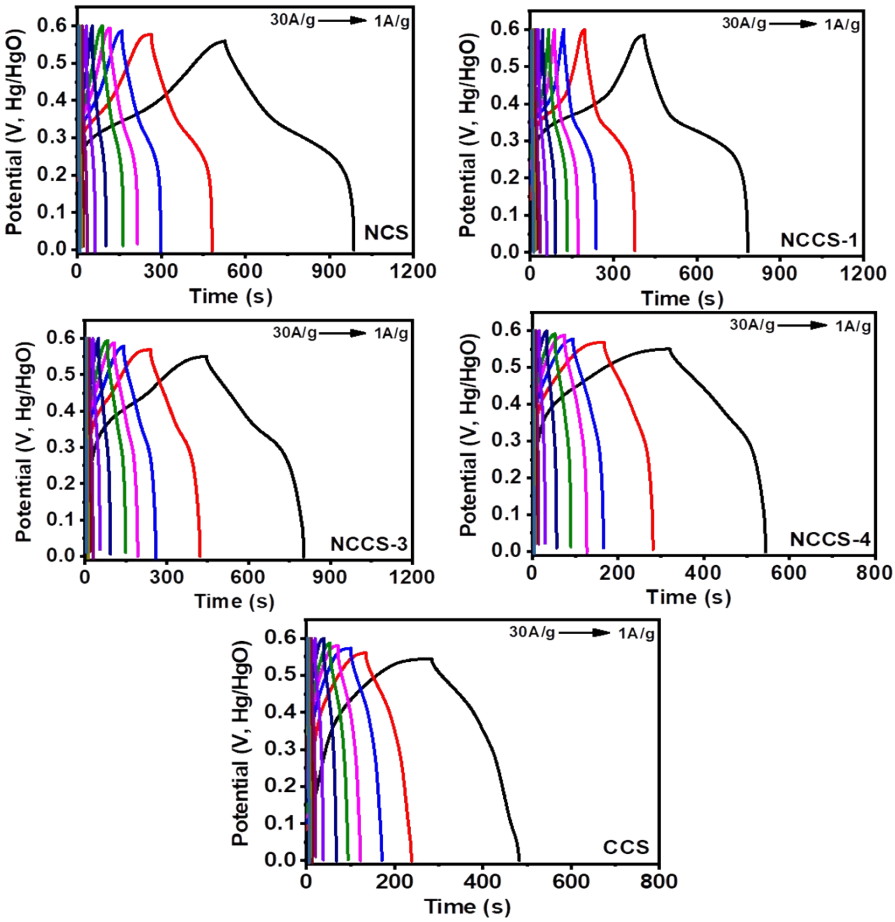

Figure S7. GCD curves of NCS, NCCS-1, NCCS-3, NCCS-4, and CCS at various current densities of 1-30 A/g in KOH.

Table S2. A comparison of the specific capacitance of the NCS and NCCS-2 electrodes with some previously reported nickel and cobalt sulfide-based materials electrode materials.

Electrode material	Electrolyte	Specific capacitance (F/g)	Current density (A/g)	Reference
β-NiS	3 M KOH	501.5	0.6	[1]
$NiCo_2S_4$	3 M KOH	1298	1	[2]
$NiCo_2S_4$ nanoplates	3 M KOH	437	1	[3]
$NiCo_2S_4$@PPy	5 M KOH	1606.6	1	[4]
Activated carbon@ $NiCo_2S_4$	3 M KOH	651.1	0.6	[5]
Cu-doped $NiCo_2S_4$/graphite	2 M KOH	3080	1	[6]
$NiCo_2S_4$@MnO_2	3 M KOH	520.7	1	[7]
$NiCo_2S_4$/Co_9S_8	3 M KOH	2180	1	[8]
$NiCo_2S_4$@$NiMoO_4$	6 M KOH	1487.6	1	[9]
$CuCo_2S_4$	2 M KOH	515	1	[10]
$CoMoO_4$@ $CuCo_2S_4$	3 M KOH	1414	1	[11]
$CuCo_2S_4$/polyacrylonitrile	6 M KOH	385	1	[12]
$CuCo_2S_4$/CNTs	2 M KOH	557.5	1	[13]
$CuCo_2S_4$@LDH	6 M KOH	1876	1	[14]
$CuCo_2S_4$	2 M KOH	373.4	1	[13]
$CuCo_2S_4$/RGO	3 M KOH	525	1	[15]
$CuCo_2S_4$	2 M KOH	424	1	[16]
NCS	3 M KOH	838	1	**This work**
NCCS-2	3 M KOH	770	1	**This work**

Table S3. Comparison of NCCS-3 HER parameters electrode with other nickel and cobalt sulfide-based materials

Name	Electrolyte	Tafel slope (mV/dec)	Overpotential (mV) @10 mA/cm^2	Reference
Ni_3S_2	1 M KOH	87	230 mV	[17]
NiS_2/rGO	0.5 M H_2SO_4	52	200	[18]
Co_9S_8-Ni_xS_y	1 M KOH	88	163 mV	[17]
CoS_2/RGO-CNT	0.5 M H_2SO_4	51	142 mV	[19]
Ni-Co-S	1 M phosphate solutions	70	280 mV	[20]
$CoNi_2S_4$ nanorod	1 M KOH	53	111	[21]
$CuCo_2S_4$/$NiCo_2S_4$	1 M KOH	90	206	[22]
FeO@$CuCo_2S_4$	1 M KOH	136	107	[23]
$NiCo_2S_4$ nanowires	1 M KOH	37	41	[24]
$NiCo_2S_4$@NCNF	0.5 M H_2SO_4	-	117	[25]
$NiCo_2S_4$@NiCoP	1 M KOH	53	108	[26]
$NiCo_2S_4$	1 M KOH	-	282 mV	[27]
$CoNi_2S_4$	1 M KOH	85	255	[28]
$CuCo_2S_4$	0.5 M H_2SO_4	140	363 mV	[29]
NCCS-3	1 M KOH	150	124 mV	**This work**

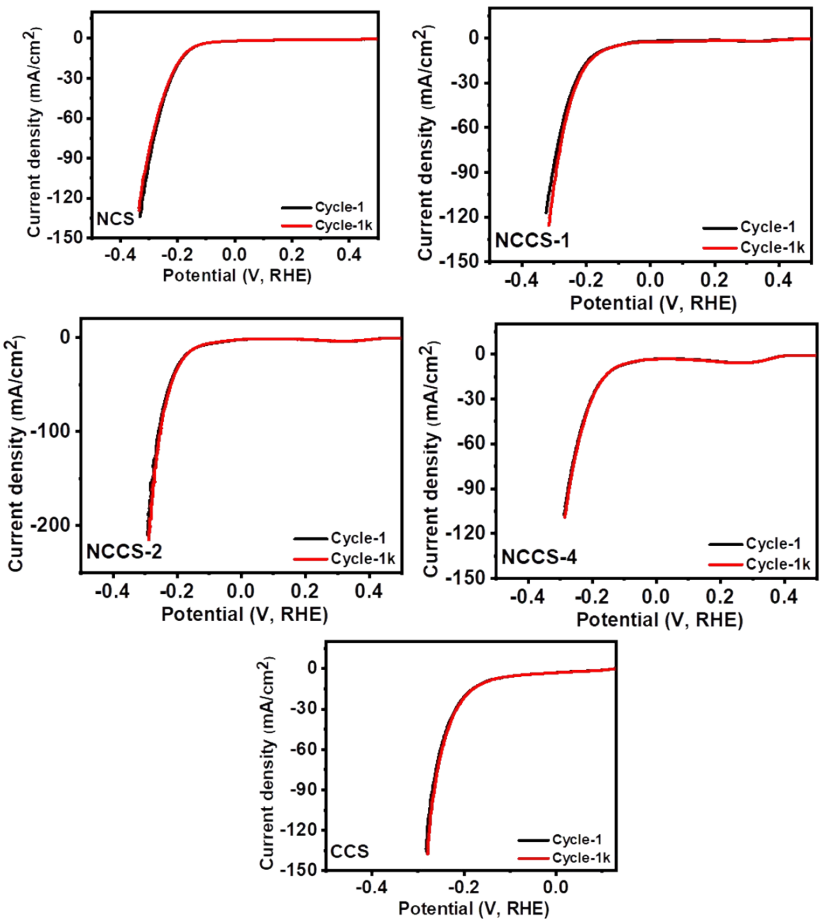

Figure S8. 1st and 1k cycle HER polarization curves for NCS, NCCS-1, NCCS-2, NCCS-4, and CCS in KOH.

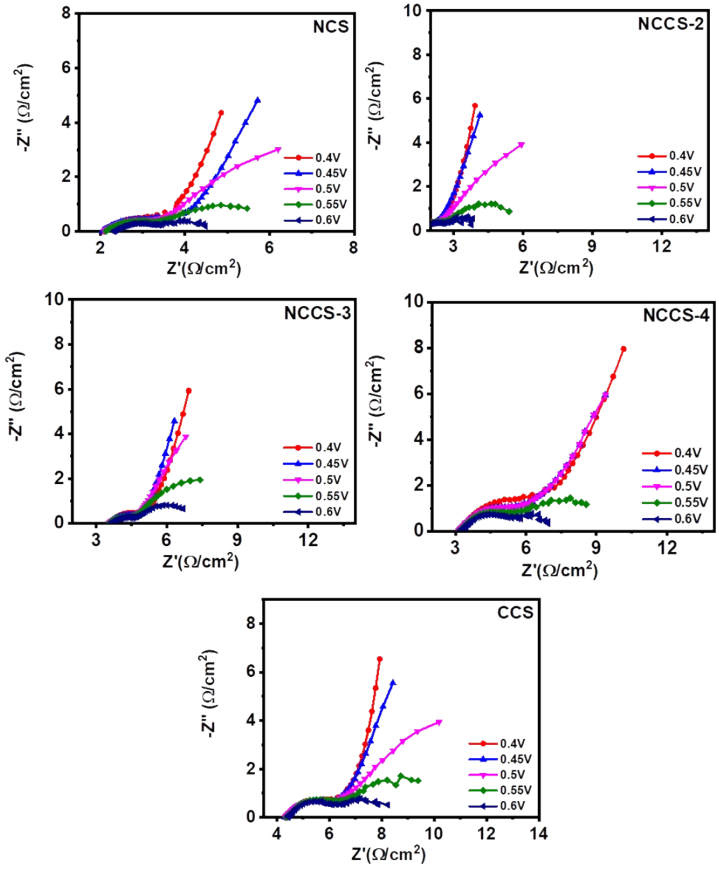

Figure S9. Nyquist plot of NCS, NCCS-2, NCCS-3, NCCS-4, and CCS at various potential (vs SCE) in KOH.

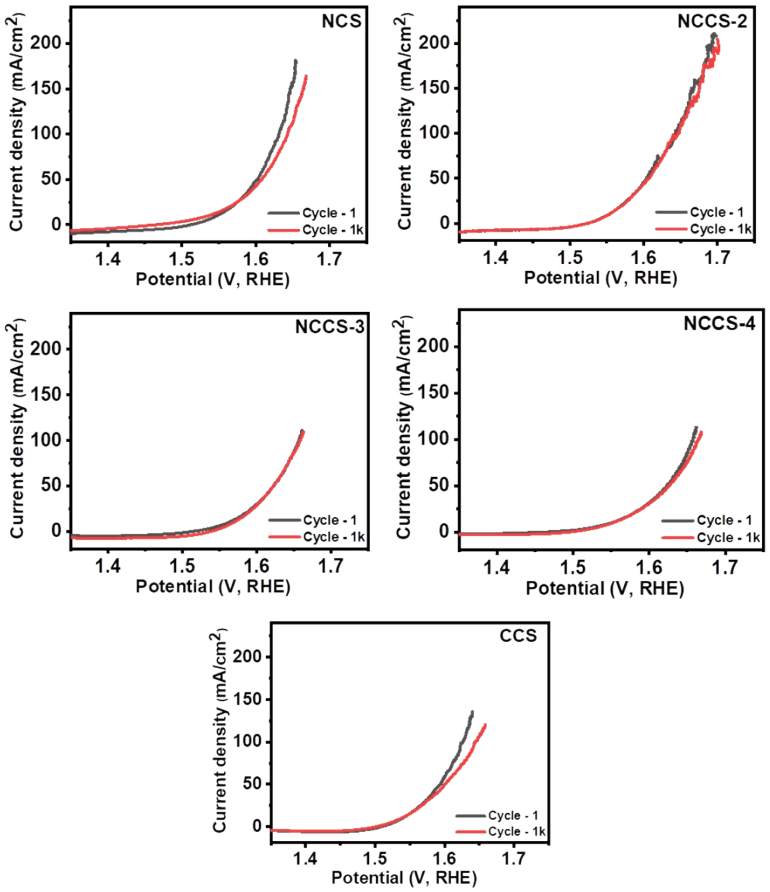

Figure S10. 1st and 1k cycle OER polarization curves for NCS, NCCS-2, NCCS-3, NCCS-4, and CCS in KOH.

Table S4. Comparison of OER parameters NCCS-1 with other nickel and cobalt sulfide-based materials.

Name	Electrolyte	Tafel slope (mV/dec)	Overpotential (mV) @10 mA/cm^2	Reference
NiS_X	1 M KOH	56	408 mV	[30]
Ni_3S_2 NWs/Ni	1 M KOH	84.8	317	[31]
Co-S nanosheets	1 M KOH	64	361 mV	[32]
Co_9S_8-CuS-FeS	1 M KOH	79	300 mV	[33]
NiCoS	1 M KOH	73.7	~ 410 mV	[34]
$NiCo_2S_4$	1 M KOH	72	309	[35]
NiCoS/$Ti_3C_2T_x$	1 M KOH	58	365 mV	[34]
$NiCo_2S_4$ NN/CC	1 M KOH	84	316	[36]
$NiCo_2S_4$ sphere	0.1 M KOH	65	> 500 mV	[37]
MoS_2/$NiCo_2S_4$/NF	1 M KOH	52	220	[38]
Fe-doped α-NiS	1 M KOH	79	266	[39]
$CuCo_2S_4$/g-C_3N_4	1 M KOH		242	[40]
$CuCo_2S_4$	1 M KOH	86	310 mV	[41]
$CuCo_2S_4$	1 M KOH	115	395	[42]
NCCS-1	1 M KOH	47	268 mV	**This work**

References

[1] C. Wei, C. Cheng, J. Zhao, Y. Wang, Y. Cheng, Y. Xu, W. Du, H. Pang, *Chemistry–An Asian Journal* **2015**, *10*, 679-686.

[2] G. Xiang, Y. Meng, G. Qu, J. Yin, B. Teng, Q. Wei, X. Xu, *Science Bulletin* **2020**, *65*, 443-451.

[3] J. Pu, F. Cui, S. Chu, T. Wang, E. Sheng, Z. Wang, *ACS Sustainable Chemistry & Engineering* **2014**, *2*, 809-815.

[4] T. Yi, S. Qi, Y. Li, L. Qiu, Y. Liu, Y. Zhu, J. Zhang, Y. Li, *Energy Technology* **2020**, *8*, 2000096.

[5] T. Wang, Q. Le, G. Zhang, S. Zhu, B. Guan, J. Zhang, S. Xing, Y. Zhang, *Electrochimica Acta* **2016**, *211*, 627-635.

[6] M. Zhang, H. Zheng, H. Zhu, M. Zhang, R. Liu, X. Zhu, X. Li, H. Cui, *Journal of Alloys and Compounds* **2022**, 163633.

[7] H. Chen, X. L. Liu, J. M. Zhang, F. Dong, Y. X. Zhang, *Ceramics International* **2016**, *42*, 8909-8914.

[8] X. Han, Q. Chen, H. Zhang, Y. Ni, L. Zhang, *Chemical Engineering Journal* **2019**, *368*, 513-524.

[9] S. Chen, Z. Zhang, W. Zeng, J. Chen, L. Deng, *ChemElectroChem* **2019**, *6*, 590-597.

[10] S. Guo, W. Chen, M. Li, J. Wang, F. Liu, J. Cheng, *Electrochimica Acta* **2018**, *271*, 498-506.

[11] T. Xie, J. Xu, J. Wang, C. Xuan, C. Ma, L. Su, F. Dong, L. Gong, *Energy & Fuels* **2020**, *34*, 16791-16799.

[12] L. Chen, Y. Zuo, Y. Zhang, Y. Gao, *Materials Letters* **2018**, *215*, 268-271.

[13] H. Li, Z. Li, Z. Wu, M. Sun, S. Han, C. Cai, W. Shen, X. Liu, Y. Fu, *Journal of colloid and interface science* **2019**, *549*, 105-113.

[14] H.-B. Li, G.-F. Xiao, H.-Y. Zeng, X.-J. Cao, K.-M. Zou, S. Xu, *Electrochimica Acta* **2020**, *352*, 136500.

[15] K. Annamalai, Y.-s. Tao, *New Carbon Materials* **2016**, *31*, 336-342.

[16] J. Cheng, S. Gao, P. Zhang, B. Wang, X. Wang, F. Liu, *Journal of Alloys and Compounds* **2020**, *825*, 153984.

[17] D. Ansovini, C. J. J. Lee, C. S. Chua, L. T. Ong, H. R. Tan, W. R. Webb, R. Raja, Y.-F. Lim, *Journal of Materials Chemistry A* **2016**, *4*, 9744-9749.

[18] R. Chen, Y. Song, Z. Wang, Y. Gao, Y. Sheng, Z. Shu, J. Zhang, X. a. Li, *Catalysis Communications* **2016**, *85*, 26-29.

[19] S. Peng, L. Li, X. Han, W. Sun, M. Srinivasan, S. G. Mhaisalkar, F. Cheng, Q. Yan, J. Chen, S. Ramakrishna, *Angewandte Chemie* **2014**, *126*, 12802-12807.

[20] A. Irshad, N. Munichandraiah, *ACS applied materials & interfaces* **2017**, *9*, 19746-19755.

[21] Y. Ge, J. Wu, X. Xu, M. Ye, J. Shen, *International Journal of Hydrogen Energy* **2016**, *41*, 19847-19854.

[22] L. Ma, J. Liang, T. Chen, Y. Liu, S. Li, G. Fang, *Electrochimica Acta* **2019**, *326*, 135002.

[23] A. T. A. Ahmed, A. S. Ansari, S. Pawar, B. Shong, H. Kim, H. Im, *Applied Surface Science* **2021**, *539*, 148229.

[24] Y. Wu, X. Liu, D. Han, X. Song, L. Shi, Y. Song, S. Niu, Y. Xie, J. Cai, S. Wu, *Nature communications* **2018**, *9*, 1-9.
[25] J. Xu, J. Rong, F. Qiu, Y. Zhu, K. Mao, Y. Fang, D. Yang, T. Zhang, *Journal of colloid and interface science* **2019**, *555*, 294-303.
[26] H. Su, X. Du, X. Zhang, *International Journal of Hydrogen Energy* **2019**, *44*, 30910-30916.
[27] J. Tie, J. Han, G. Diao, J. Liu, Z. Xie, G. Cheng, M. Sun, L. Yu, *Applied Surface Science* **2018**, *435*, 187-194.
[28] D. Wang, X. Zhang, Z. Du, Z. Mo, Y. Wu, Q. Yang, Y. Zhang, Z. Wu, *International Journal of Hydrogen Energy* **2017**, *42*, 3043-3050.
[29] Y. Sun, D. Li, J. Lu, Y. Zhang, L. Li, J. Liang, *Crystal Research and Technology* **2019**, *54*, 1800248.
[30] H. Li, Y. Shao, Y. Su, Y. Gao, X. Wang, *Chemistry of Materials* **2016**, *28*, 1155-1164.
[31] D. Zhang, J. Li, J. Luo, P. Xu, L. Wei, D. Zhou, W. Xu, D. Yuan, *Nanotechnology* **2018**, *29*, 245402.
[32] T. Liu, Y. Liang, Q. Liu, X. Sun, Y. He, A. M. Asiri, *Electrochemistry Communications* **2015**, *60*, 92-96.
[33] S. Zhang, Y. Sun, F. Liao, Y. Shen, H. Shi, M. Shao, *Electrochimica Acta* **2018**, *283*, 1695-1701.
[34] H. Zou, B. He, P. Kuang, J. Yu, K. Fan, *ACS applied materials & interfaces* **2018**, *10*, 22311-22319.
[35] S. M. N. Jeghan, G. Lee, *Nanotechnology* **2020**.
[36] S. Hyun, S. Shanmugam, *ACS omega* **2018**, *3*, 8621-8630.
[37] Z. Zhang, X. Wang, G. Cui, A. Zhang, X. Zhou, H. Xu, L. Gu, *Nanoscale* **2014**, *6*, 3540-3544.
[38] X. Xu, W. Zhong, L. Zhang, G. Liu, W. Xu, Y. Zhang, Y. Du, *Surface and Coatings Technology* **2020**, *397*, 126065.
[39] G. B. Shombe, M. D. Khan, A. M. Alenad, J. Choi, T. Ingsel, R. K. Gupta, N. Revaprasadu, *Sustainable Energy & Fuels* **2020**, *4*, 5132-5143.
[40] R. Biswas, P. Thakur, G. Kaur, S. Som, M. Saha, V. Jhajhria, H. Singh, I. Ahmed, B. Banerjee, D. Chopra, *Inorganic Chemistry* **2021**, *60*, 12355-12366.
[41] H. Luo, H. Lei, Y. Yuan, Y. Liang, Y. Qiu, Z. Zhu, Z. Wang, *Catalysts* **2019**, *9*, 459.
[42] A. M. Wiltrout, C. G. Read, E. M. Spencer, R. E. Schaak, *Inorganic chemistry* **2016**, *55*, 221-226.