Supporting Information

Sulfur Vacancies-Tailored $NiCo_2S_4$ Nanosheet Arrays for Hydrogen Evolution Reaction at All pH Values

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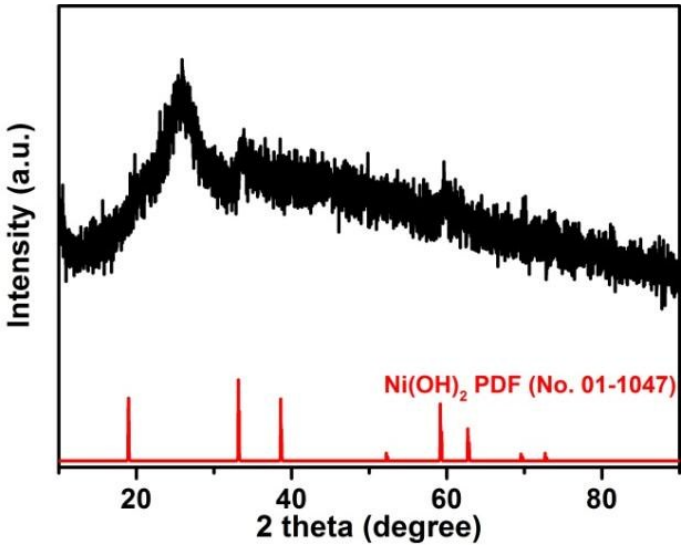

Figure S1. XRD pattern of NiCo hydroxide nanosheet arrays precursors on carbon cloth.

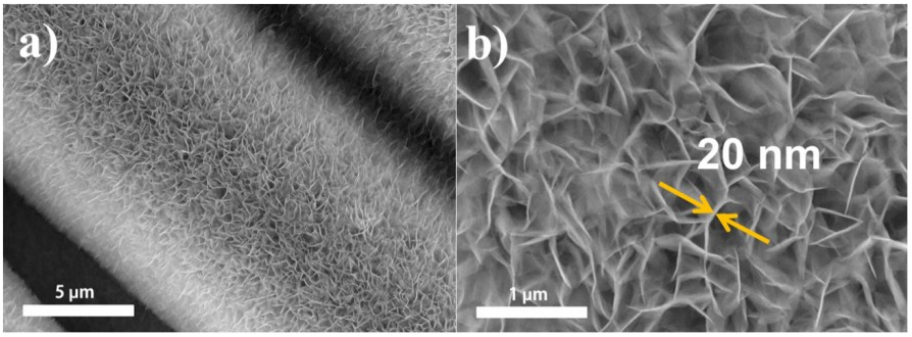

Figure S2. SEM of NiCo hydroxide nanosheet arrays precursors on carbon cloth.

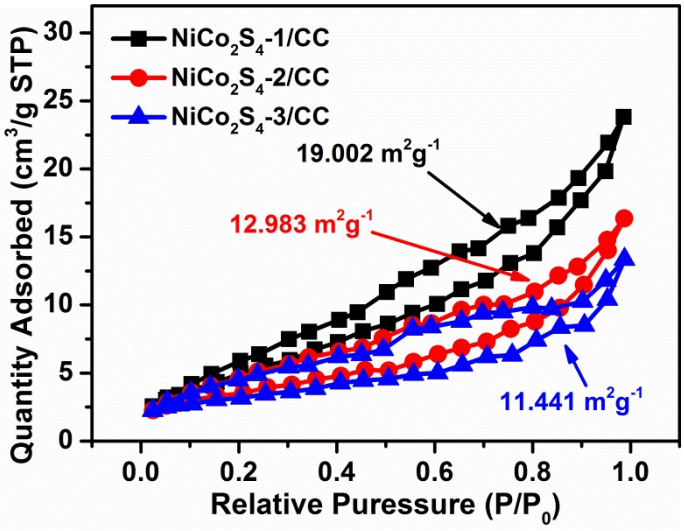

Figure S3. Nitrogen adsorption-desorption isotherms curve of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-2/CC and $NiCo_2S_4$-3/CC.

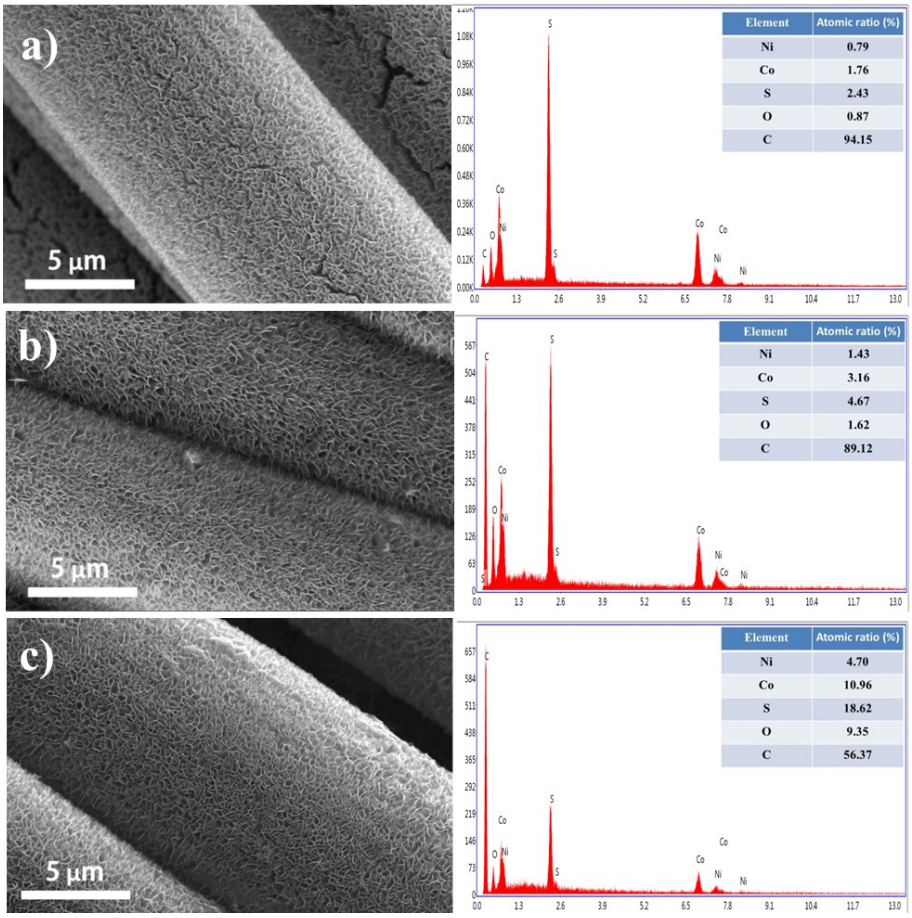

Figure S4. SEM and corresponding EDS for a) $NiCo_2S_4$-1/CC, b) $NiCo_2S_4$-2/CC and c) $NiCo_2S_4$-3/CC.

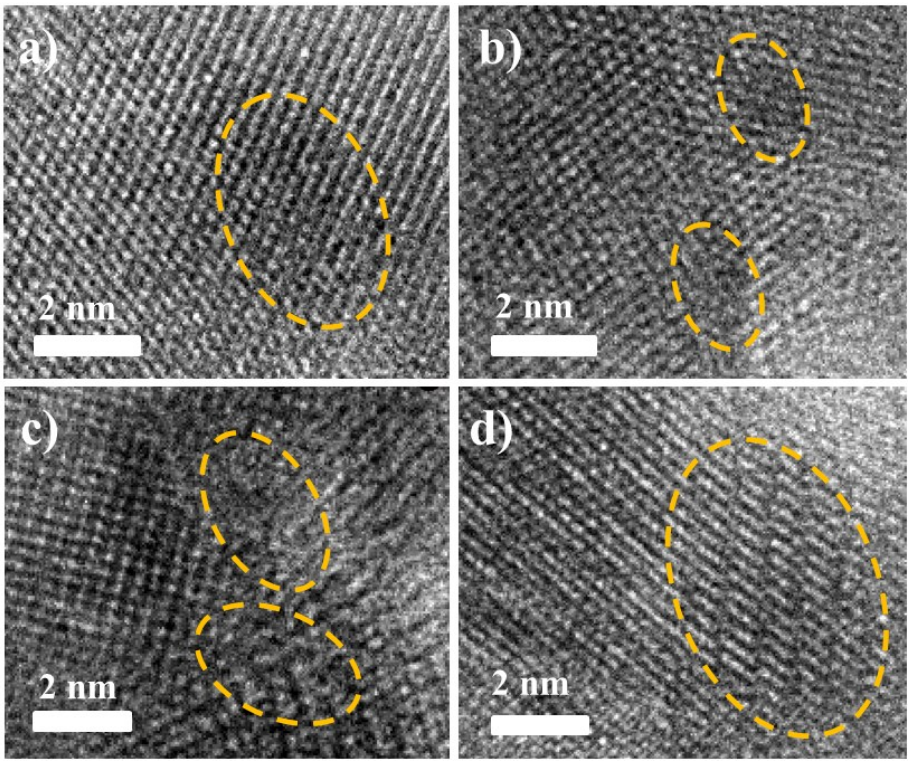

Figure S5. HETEM images of $NiCo_2S_4$-2/CC (a-d)

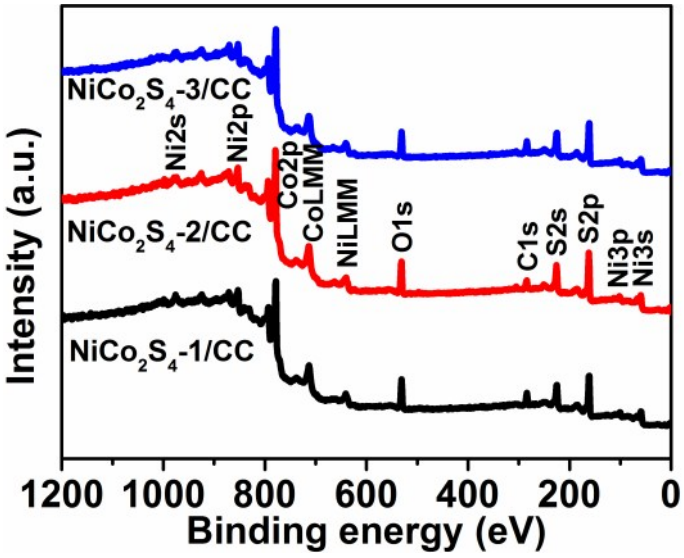

Figure S6. XPS spectra of three samples.

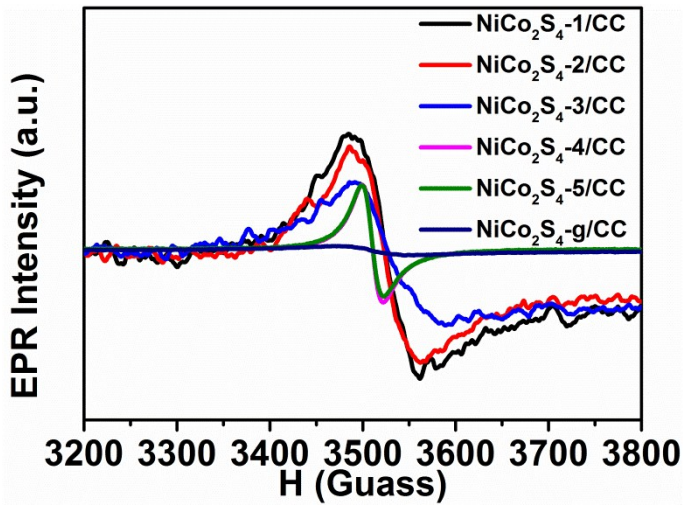

Figure S7. EPR curves of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-2/CC, $NiCo_2S_4$-3/CC, $NiCo_2S_4$-4/CC, $NiCo_2S_4$-5/CC and $NiCo_2S_4$-g/CC.

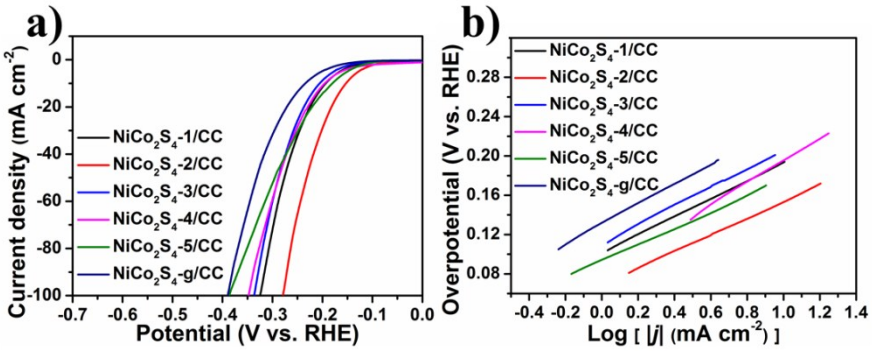

Figure S8. a) LSV and Tafel curves b) of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-2/CC, $NiCo_2S_4$-3/CC, $NiCo_2S_4$-4/CC, $NiCo_2S_4$-5/CC and $NiCo_2S_4$-g/CC.

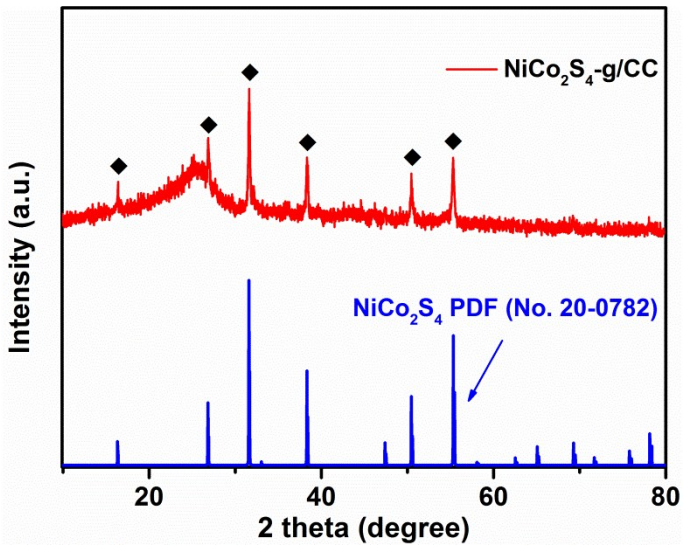

Figure S9. XRD pattern of $NiCo_2S_4$-g/CC.

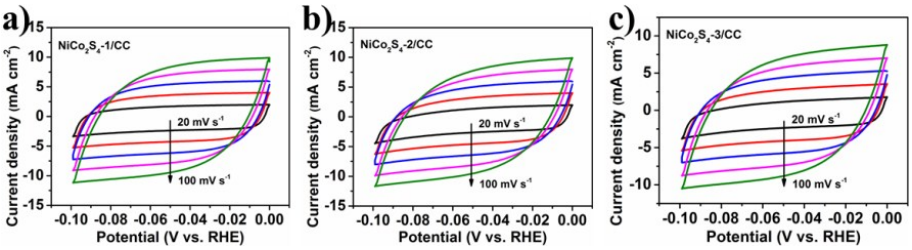

Figure S10. Voltammograms of a) $NiCo_2S_4$-1/CC, b) $NiCo_2S_4$-2/CC and c) $NiCo_2S_4$-1/CC recording at the scan rates of 20, 40, 60, 80, and 100 mV s^{-1} in 1M KOH.

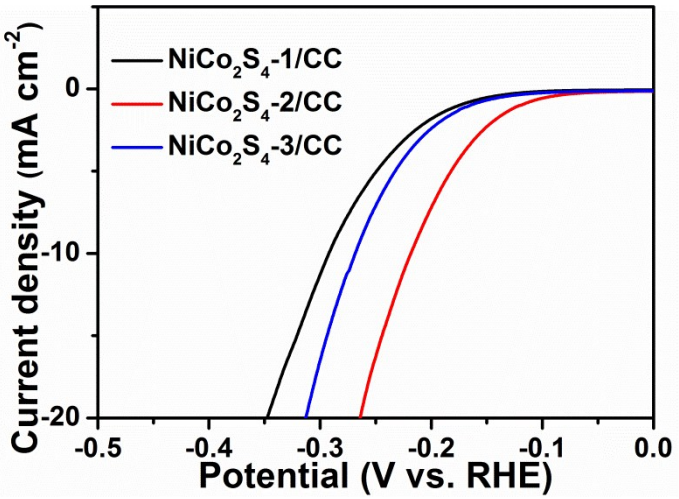

Figure S11. LSV curves of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-1/CC and $NiCo_2S_4$-3/CC normalized by special surface area.

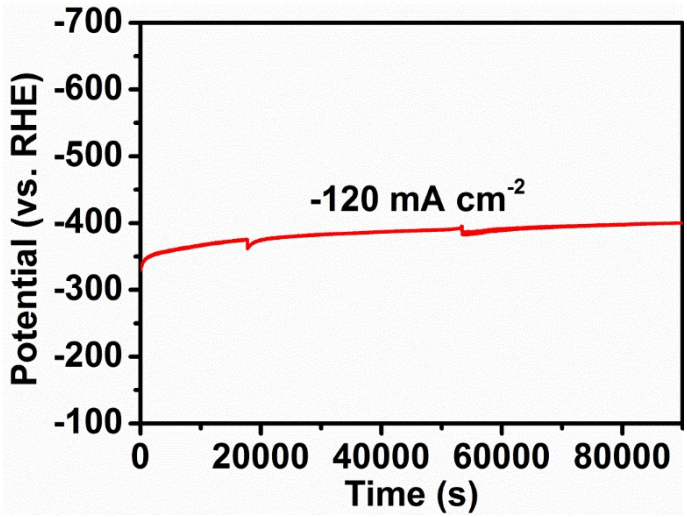

Figure S12. Durability measurement of $NiCo_2S_4$-2/CC with a continuous current density of -120 mA cm^{-2}.

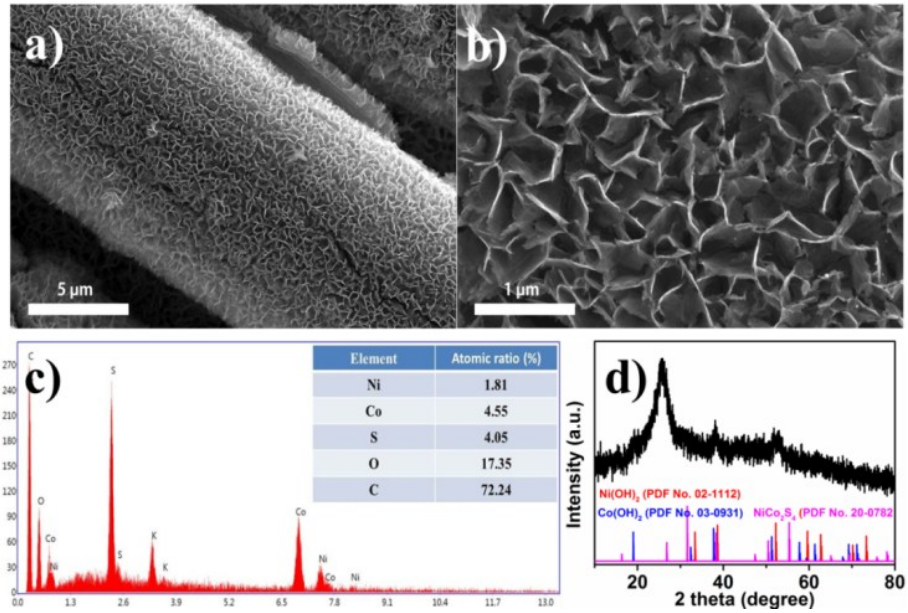

Figure S13. a-b) SEM images of $NiCo_2S_4$-2/CC electrode after 36000 s durability measurement. c) Corresponding EDS spectrum. d) XRD pattern of $NiCo_2S_4$-2/CC electrocatalyst after 36000 s stable test.

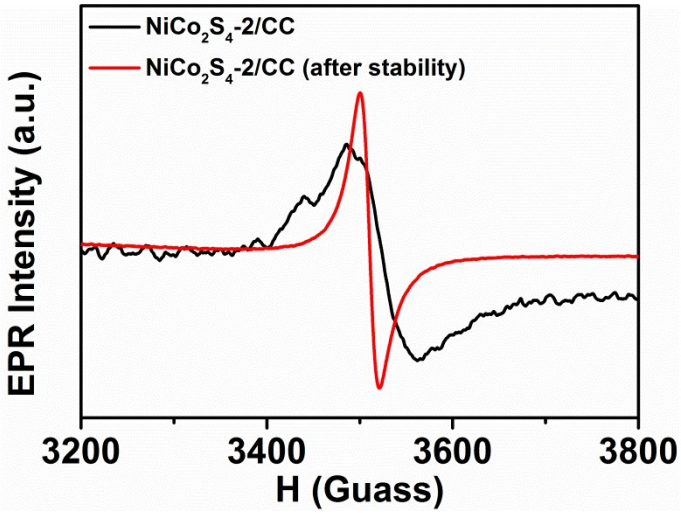

Figure S14. EPR curve after 10 h of continuous test.

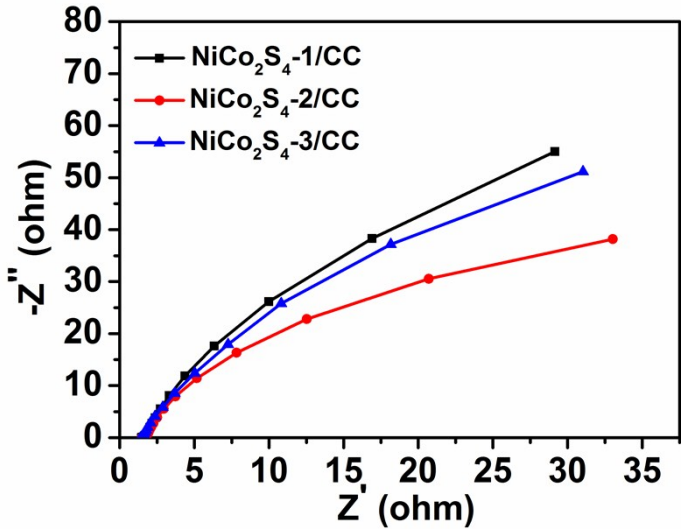

Figure S15. Nyquist plots of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-2/CC, and $NiCo_2S_4$-3/CC in 0.5 M H_2SO_4.

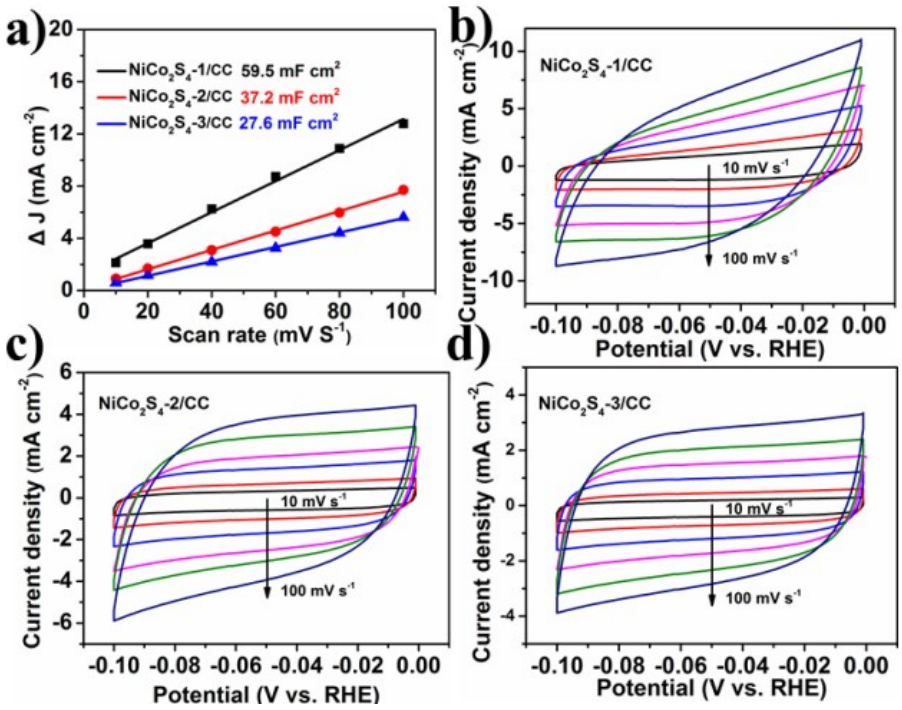

Figure S16. C_{dl} (a) and different cyclic voltammograms of $NiCo_2S_4$-1/CC (b), $NiCo_2S_4$-2/CC (c) and $NiCo_2S_4$-3/CC (d) in 0.5 M H_2SO_4

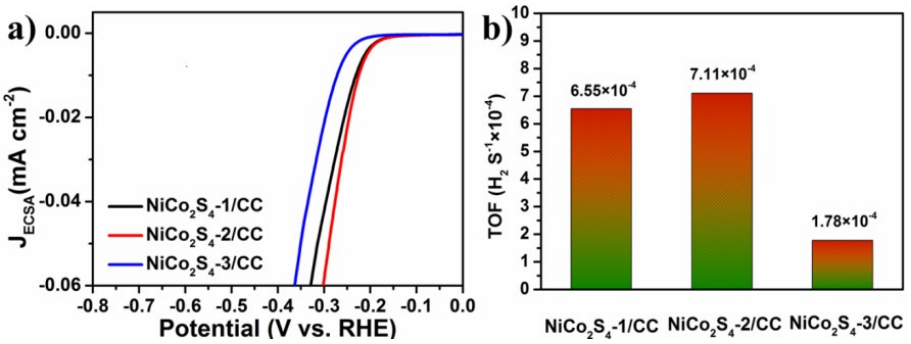

Figure S17. a) Polarization curves of as-prepared samples normalized by ECSA in 0.5 M H_2SO_4, b) Calculated TOF vaule at overpotential of -200 mV in 0.5 M H_2SO_4.

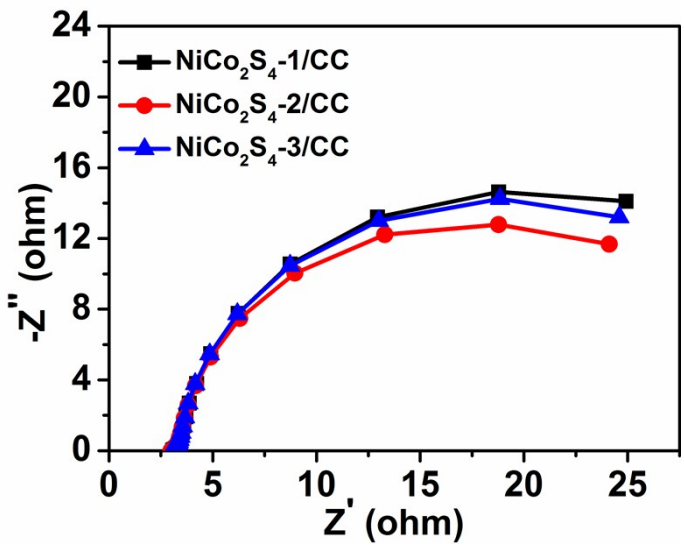

Figure S18. Nyquist plots of $NiCo_2S_4$-1/CC, $NiCo_2S_4$-2/CC, and $NiCo_2S_4$-3/CC in 1 M PBS.

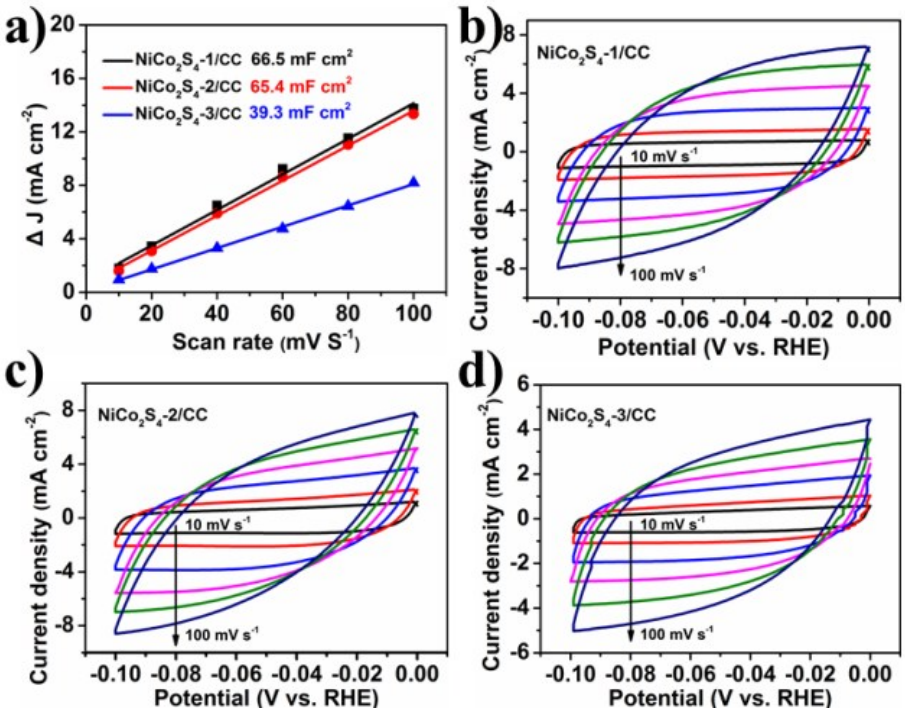

Figure S19. C_{dl} (a) and different cyclic voltammograms of $NiCo_2S_4$-1/CC (b), $NiCo_2S_4$-2/CC (c) and $NiCo_2S_4$-3/CC (d) in 1 M PBS.

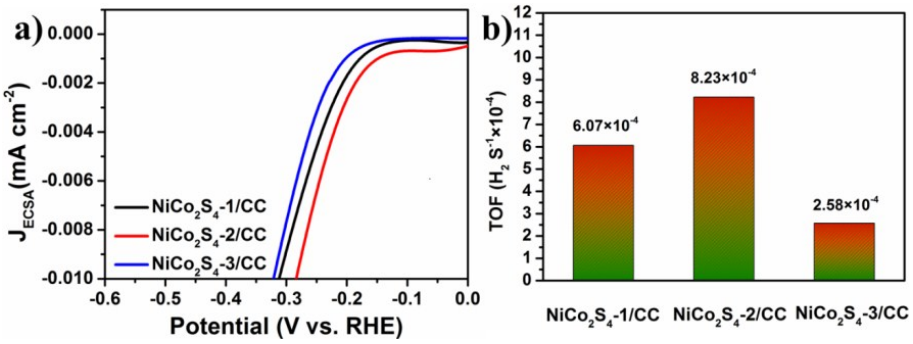

Figure S20. a) Polarization curves of as-prepared samples normalized by ECSA in 0.5 M H_2SO_4, b) Calculated TOF value at overpotential of -200 mV in 1 M PBS.

Table S1. EDS and ICP-OES results of Ni, Co and S in $NiCo_2S_4$.

	EDS (Ni: Co: S) molar ratio	**ICP (Ni: Co: S) molar ratio**	**$NiCo_2S_4$ (Ni/Co: S by ICP) molar ratio**
$NiCo_2S_4$-1/CC	0.79:1.76:2.43	0.82:1.72:2.46	1:2.09:3.0
$NiCo_2S_4$-2/CC	1.43:3.16:4.67	0.61:1.40:2.13	1:2.29:3.5
$NiCo_2S_4$-3/CC	4.70:10.96:18.62	1.03:2.11:3.82	1:2.05:3.71

Table S2. Comparison of HERR performances of $NiCo_2S_4$-2/CC with previously reported non-precious metal HER electrocatalysts.

Catalyst	Substrate	Electrolyte	J ($mA\ cm^{-2}$)	η (mV vs RHE)	Ref.
$NiCo_2S_4$/CC	CC[a]	1M KOH	10	150	This work
$NiCo_2S_4$/NF	NF[a]	1M KOH	10	210	[1]
$NiCo_2S_4$@$NiCo_2O_4$/NF	NF[c]	1M KOH	10	190	[2]
$NiCo_2S_4$	GCE[d]	1M KOH	10	148	[3]
$NiCo_2S_4$/NF	NF	1M KOH	10	169	[4]
$NiCo_2S_4$/NF	NF	1M KOH	10	191	[5]
$NiCo_2S_4$@Pd	GCE	1M KOH	10	87	[6]
N-$NiCo_2S_4$	NF	1M KOH	10	41	[7]
Ni-Co-S-P/Graphene	GCE	1M KOH	10	117	[8]
Co_9S_8-Ni_xS_y/NF	NF	1M KOH	10	163	[9]
MoS_2-Ni_xS_y/NF	CFP[e]	1M KOH	10	139	[10]
Co_9S_8-$NiCo_2S_4$	GCE	1M KOH	10	172	[11]
NiCoS@C-dot	GCE	1M KOH	10	232	[12]
CoS@Ni_3S_2	NF	1M KOH	10	204	[13]
Ni_2P/Ni_3S_2	NF	1M KOH	10	130	[14]
MoS_2	RDE[f]	1M KOH	10	154	[15]
CoS_2	GCE	1M KOH	10	193	[16]
N-Ni_3S_2/NF	NF	1M KOH	10	155	[17]
Se-(NiCo)S_x/(OH)x	NF	1M KOH	10	103	[18]
CoP	GCE	1M KOH	10	154	[19]
rGO@NiMnCo	GCE	1M KOH	10	151	[20]

CC[a]: Carbon Cloth
NF[b]: Ni Foam
GCE[c]: Glassy Carbon Electrode
CFP[d]: Carbon Fiber Paper
RDE[f]: Rotating Disk Electrode

References

1. A. Sivanantham, P. Ganesan, and S. Shanmugam, *Adv. Funct. Mater.*, 2016, **26,** 4661-4672.
2. X. Du, W. Lian, and X. Zhang, *Int. J. Hydrogen Energy*, 2018, **43,** 20627-20635.
3. C. Zequine, S. Bhoyate, K. Siam, P. K. Kahol, N. Kostoglou, C. Mitterer, S. J. Hinder, M. A. Baker, G. Constantinides, C. Rebholz, G. Gupta, X. Li, and R. K. Gupta, *Surf. Coat. Technol*., 2018, **354,** 306-312.
4. J. Yu, C. Lv, L. Zhao, L. Zhang, Z. Wang, and Q. Liu, *Adv. Mater. Interface*, 2018, **5,** 1701396.
5. Y. Gong, Y. Lin, Z. Yang, J. Wang, H. Pan, Z. Xu, and Y. Liu, *ChemistrySelect*, 2019, **4,** 1180-1187.
6. G. Sheng, J. Chen, Y. Li, H. Ye, Z. Hu, X. Z. Fu, R. Sun, W. Huang, and C. P. Wong, *ACS Appl Mater Interfaces*, 2018, **10,** 22248-22256.
7. Y. Wu, X. Liu, D. Han, X. Song, L. Shi, Y. Song, S. Niu, Y. Xie, J. Cai, S. Wu, J. Kang, J. Zhou, Z. Chen, X. Zheng, X. Xiao, and G. Wang, *Nat Commun*, 2018, **9,** 1425.
8. H. J. Song, H. Yoon, B. Ju, G.-H. Lee, and D.-W. Kim, *Adv. Energy Mater*, 2018, **8,** 1802319.
9. D. Ansovini, C. J. Jun Lee, C. S. Chua, L. T. Ong, H. R. Tan, W. R. Webb, R. Raja, and Y.-F. Lim, *J. Mater. Chem. A*, 2016, **4,** 9744-9749.
10. L. Sun, T. Wang, L. Zhang, Y. Sun, K. Xu, Z. Dai, and F. Ma, *J. Power Sources*, 2018, **377,** 142-150.
11. M. Basu, *Chem. Asian J.*, 2018, **13,** 3204-3211.
12. Y. Ali, V.-T. Nguyen, N.-A. Nguyen, S. Shin, and H.-S. Choi, *Int. J.Hydrogen Energy*, 2019, **44,** 8214-8222.
13. S. Shit, S. Chhetri, W. Jang, N. C. Murmu, H. Koo, P. Samanta, and T. Kuila, *ACS Appl. Mater Interfaces*, 2018, **10,** 27712-27722.
14. L. Zeng, K. Sun, X. Wang, Y. Liu, Y. Pan, Z. Liu, D. Cao, Y. Song, S. Liu, and C. Liu, *Nano Energy*, 2018, **51,** 26-36.
15. Y. Yin, J. Han, Y. Zhang, X. Zhang, P. Xu, Q. Yuan, L. Samad, X. Wang, Y. Wang, Z. Zhang, P. Zhang, X. Cao, B. Song, and S. Jin, *J. Am. Chem. Soc.*, 2016, **138,** 7965-7972.
16. X. Ma, W. Zhang, Y. Deng, C. Zhong, W. Hu, and X. Han, *Nanoscale*, 2018, **10,** 4816-4824.
17. T. Kou, T. Smart, B. Yao, I. Chen, D. Thota, Y. Ping, and Y. Li, *Adv. Energy Mater.*, 2018, **8,** 1703538.
18. C. Hu, L. Zhang, Z. J. Zhao, A. Li, X. Chang, and J. Gong, *Adv. Mater.*, 2018, **30,** e1705538.
19. H. Li, X. Zhao, H. Liu, S. Chen, X. Yang, C. Lv, H. Zhang, X. She, and D. Yang, *Small*, 2018, **14,** e1802824.
20. R. Miao, J. He, S. Sahoo, Z. Luo, W. Zhong, S.-Y. Chen, C. Guild, T. Jafari, B. Dutta, S. A. Cetegen, M. Wang, S. P. Alpay, and S. L. Suib, *ACS Catal.*, 2016, **7,** 819-832.