Electronic Supplementary Information (ESI)

High-Index Faceted $CuFeS_2$ Nanosheets with Enhanced Behavior for Boosting Hydrogen Evolution Reaction

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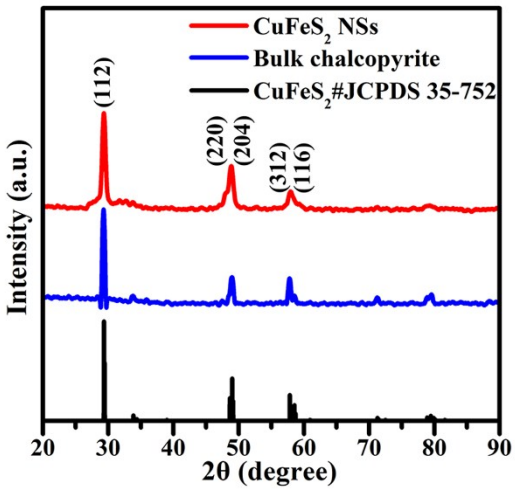

Figure S1. XRD patterns of the as-obtained $CuFeS_2$ NSs and commercial bulk chalcopyrite.

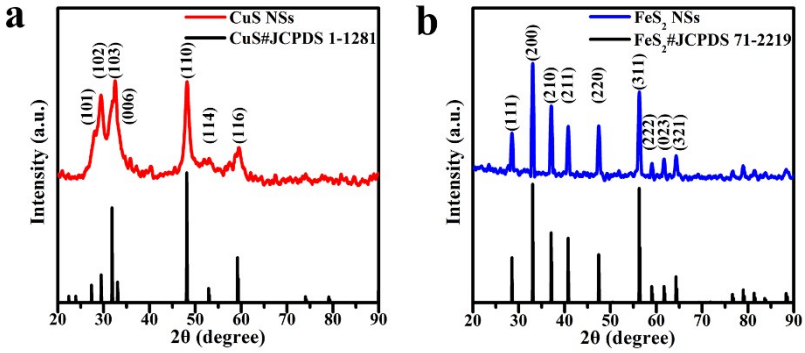

Figure S2. XRD patterns of (**a**) CuS NSs and (**b**) FeS_2 NSs.

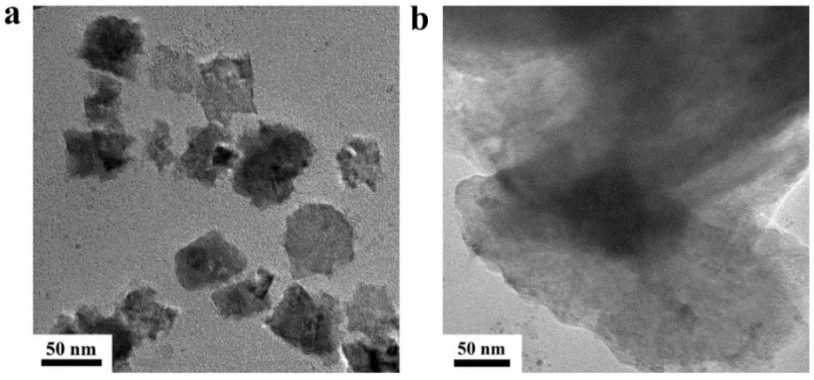

Figure S3. TEM images of (**a**) CuS NSs and (**b**) FeS_2 NSs.

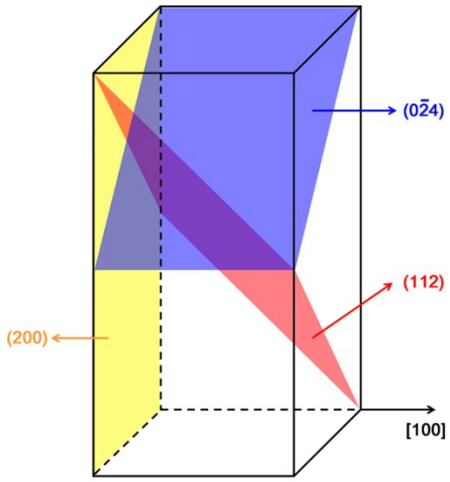

Figure S4. Schematic representation of the relative orientation of (0$\bar{2}$4), (112) and (200) facets in tetragonal $CuFeS_2$ structure.

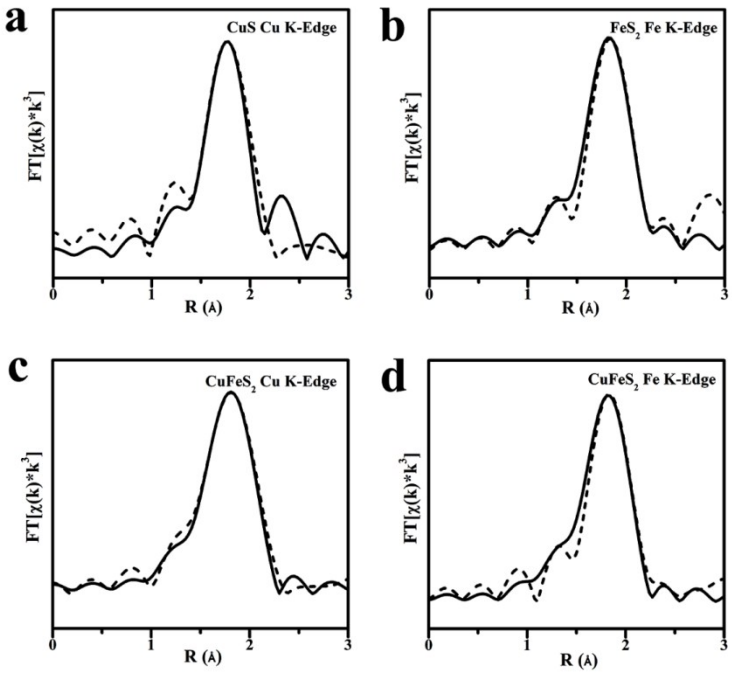

Figure S5. EXAFS data (dotted line) and fits (solid line) in R-space for (**a**) CuS NSs Cu K-Edge, (**b**) FeS_2 NSs Fe K-Edge, (**c**) $CuFeS_2$ NSs Cu K-Edge, and (**d**) $CuFeS_2$ NSs Fe K-Edge.

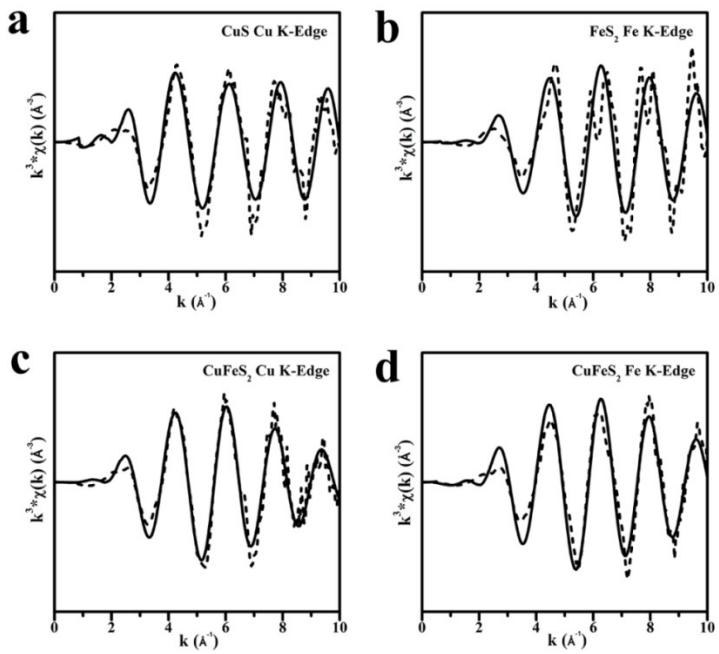

Figure S6. EXAFS data (dotted line) and fits (solid line) in K-space for (**a**) CuS Cu K-Edge, (**b**) FeS_2 Fe K-Edge, (**c**) $CuFeS_2$ Cu K-Edge, and (**d**) $CuFeS_2$ Fe K-Edge.

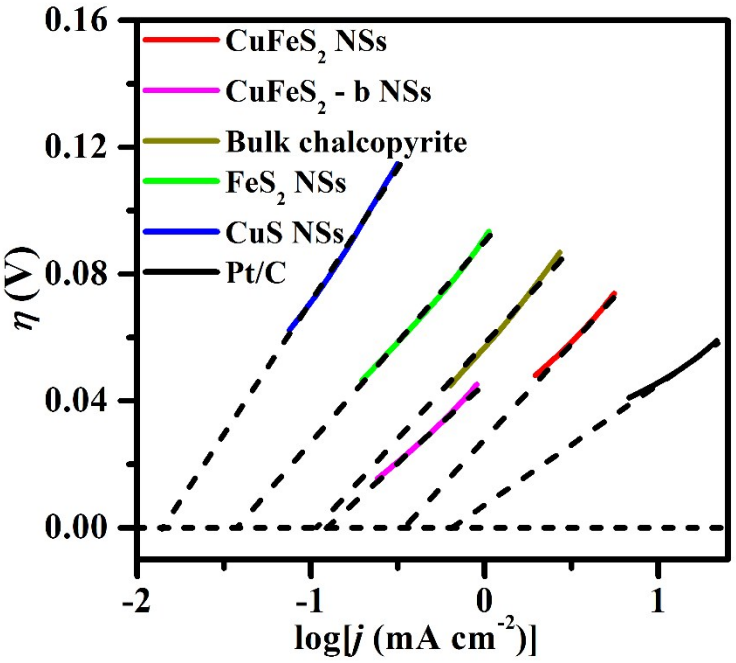

Figure S7. The exchange current density for different catalysts in 0.5 M H_2SO_4.

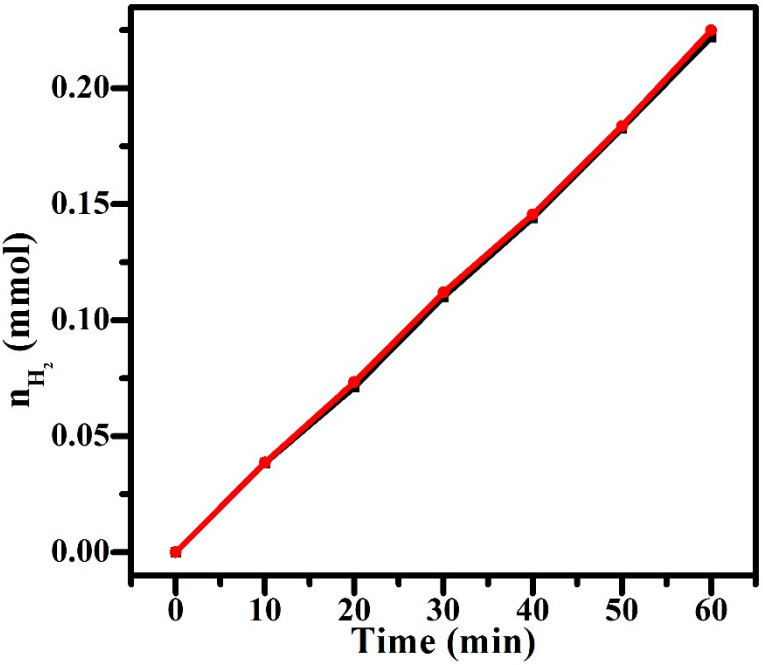

Figure S8. The amount of theoretically calculated (red line) and experimentally measured (black line) hydrogen versus time for $CuFeS_2$ NSs in 0.5 M H_2SO_4.

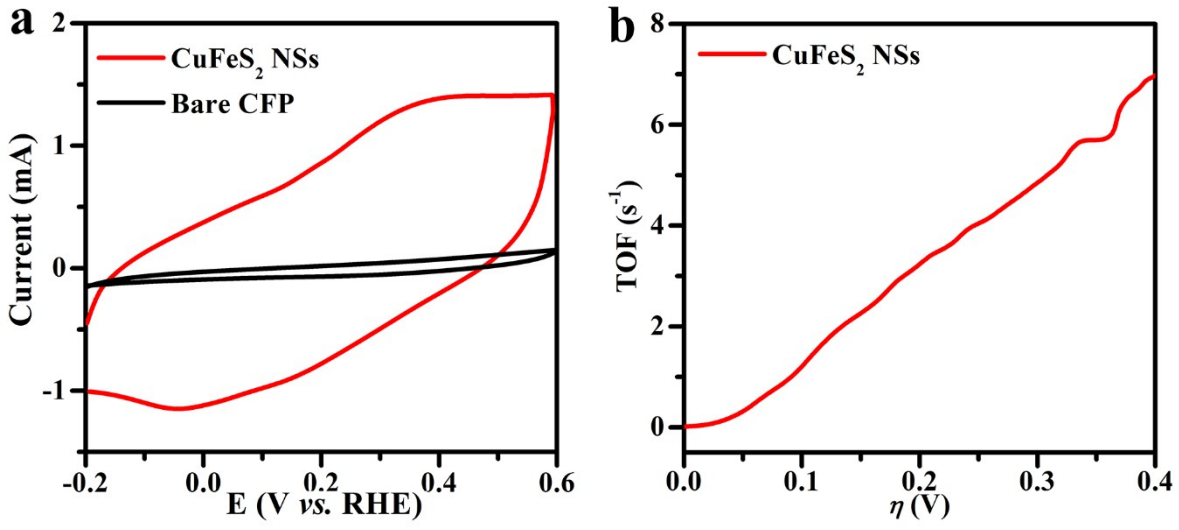

Figure S9. (**a**) CVs of bare CFP and $CuFeS_2$ NSs in pH = 7 phosphate buffer between -0.2 and 0.6 V vs. RHE with a scan rate of 50 mV s^{-1}. (**b**) Turnover frequencies of $CuFeS_2$ NSs in 0.5 M H_2SO_4.

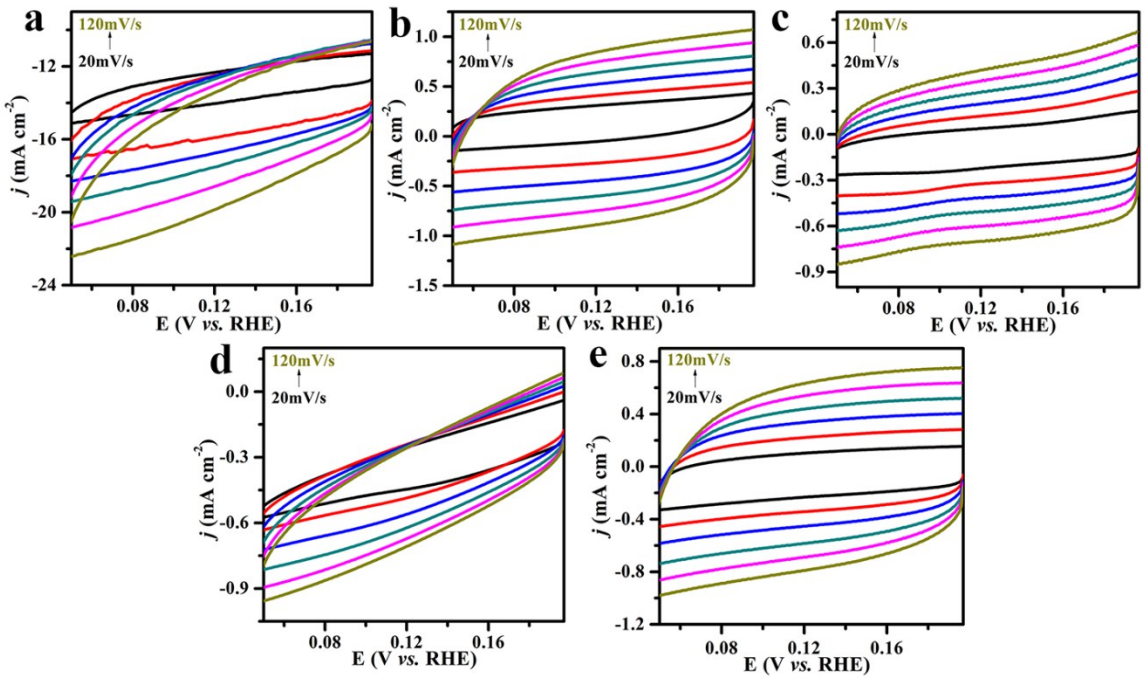

Figure S10. Cyclic voltammograms of (**a**) $CuFeS_2$ NSs, (**b**) $CuFeS_2$ - b NSs, (**c**) Bulk chalcopyrite ($CuFeS_2$), (**d**) CuS NSs and (**e**) FeS_2 NSs, with various scan rates in 0.5 M H_2SO_4.

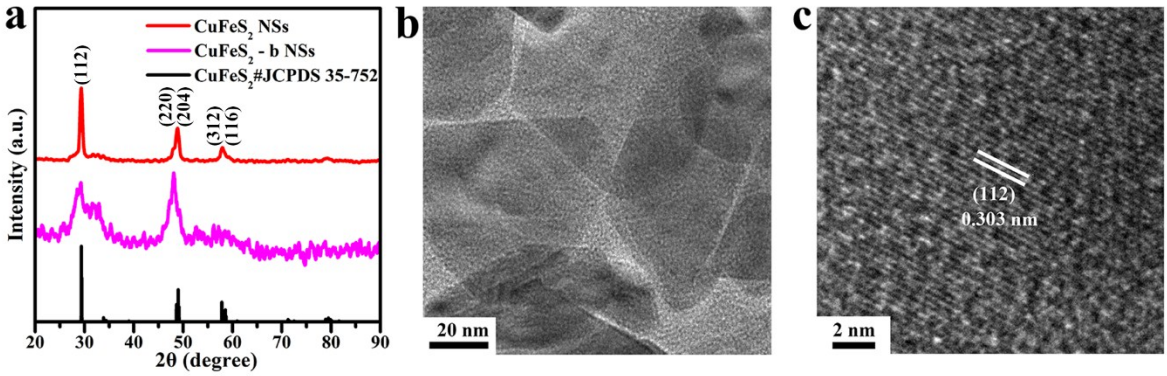

Figure S11. (**a**) The XRD patterns, (**b**) TEM image and (**c**) HRTEM image of $CuFeS_2$ - b NSs.

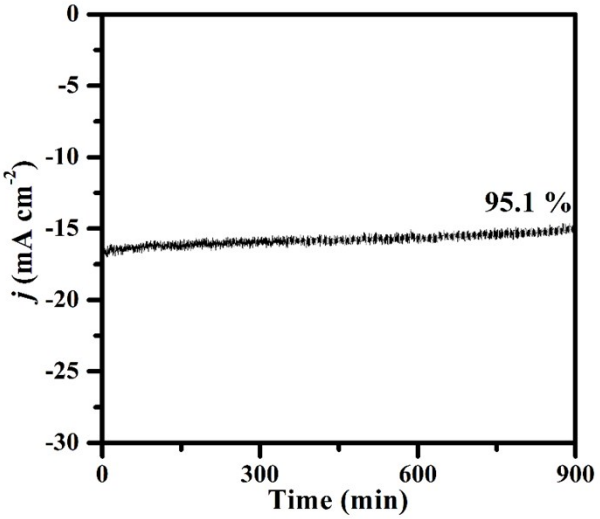

Figure S12. Chronoamperometric response curves for HER stability of $CuFeS_2$ NSs in 0.5 M H_2SO_4.

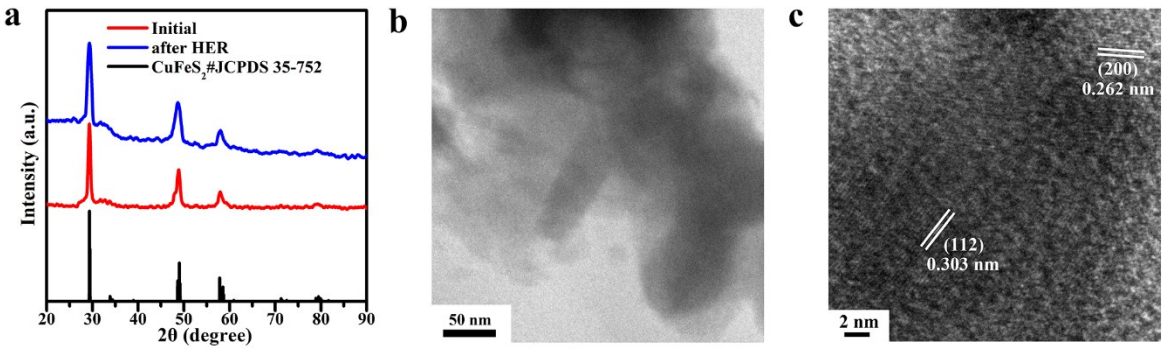

Figure S13. (**a**) The XRD patterns, (**b**) TEM image and (**c**) HRTEM image of $CuFeS_2$ NSs after stability measurement in 0.5 M H_2SO_4.

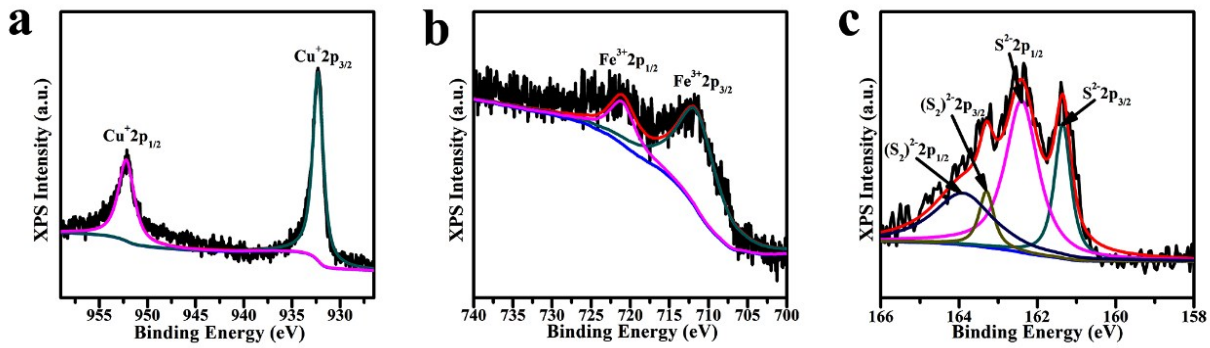

Figure S14. XPS spectra of (**a**) Cu 2p, (**b**) Fe 2p and (**c**) S 2p of $CuFeS_2$ NSs after stability measurement in 0.5 M H_2SO_4.

Table S1. EXAFS Fitting results for Cu-center (top rows) and Fe center (bottom row) for the three catalysts investigated. CNs = Coordination Numbers, R = Vector distance (± 0.02 Å), σ^2 = Debye-Waller factor (± 0.001 Å^2).

Vector	CuS NSs			FeS_2 NSs			$CuFeS_2$ NSs		
	CNs	R(Å)	σ^2(Å^2)	CNs	R(Å)	σ^2(Å^2)	CNs	R(Å)	σ^2(Å^2)
Cu_2-S_2	3	2.41	0.004						
Cu_1-S_1	3	2.25	0.004	-	-	-	4	2.28	0.01
Cu_1-S_2	1	2.57	0.004						
Fe-S	-	-	-	6	2.26	0.006	4	2.26	0.008

Table S2. EXAFS Fitting results for Cu-center (top rows) and Fe center (bottom row) for the $CuFeS_2$ NSs before and after HER. CN = Coordination Numbers, R = Vector distance (± 0.02 Å), σ^2 = Debye-Waller factor (± 0.001 Å^2).

Vector	$CuFeS_2$ NSs before HER			$CuFeS_2$ NSs after HER		
	CNs	R(Å)	σ^2(Å^2)	CNs	R(Å)	σ^2(Å^2)
Cu-S	4	2.28	0.01	3.7	2.28	0.00023
Fe-S	4	2.26	0.008	2.6	2.26	0.00016

Table S3. Summary on the HER performance of reported catalysts by using a graphite rod as the counter electrode in 0.5 M H_2SO_4.

Catalyst	Loading (mg cm^{-2})	η_{onset} (mV *vs.* RHE)	η_{10} (mV *vs.* RHE)	Tafel slope (mV dec^{-1})	j_0	Reference
W_2C/MWNT	~ 0.56	~ 50	123	45	-	1
Mo_2C@NC	~ 0.28	60	124	60	0.096	2
$CoSe_2$ NW/CC	~ 1.3	-	130	32	-	3
Mo_2C/NCF	~ 0.28	85	144	55	-	4
3DHP- Mo_2C	0.28	35	97	60	0.28	5
MoSSe	~ 0.28	-	164±2	48±2	-	6
1T MoS_2	0.05	-	~ 200	~ 40	-	7
Mo_2C-NCNT	~ 3	72	147	71	0.1146	8
MoC_x	0.8	~ 25	142	53	0.023	9
α-Mo_2C	0.102	-	198	56	-	10
$CuFeS_2$ NSs	**~ 0.2**	**28.1**	**88.7**	**47**	**0.35**	**This Work**

Table S4. Summary on the TOF of reported catalysts.

Catalyst	TOF (s^{-1})	Overpotential at the corresponding TOF (mV)	Reference
Defect-rich MoS_2 NSs	0.725	300	11
MoS_3-CV films	0.8	220	12
CoP/CC	0.725	75	13
	4	240	
CoP	0.8	82	14
	4	246	
Ni_2P/Ti	0.725	205	15
m-Mo_2C/G(2:1)	0.8	128	16
	4	233	
MoO_3-MoS_2	4	272	17
$CuFeS_2$ NSs	**0.725**	**75**	**This work**
	0.8	**80**	
	4	**240**	

References

1. Q. Gong, Y. Wang, Q. Hu, J. Zhou, R. Feng, P. N. Duchesne, P. Zhang, F. Chen, N. Han, Y. Li, C. Jin, Y. Li, S.-T. Lee, *Nat. Commun.* 2016, **7**, 13216-13223.
2. Y. Liu, G. Yu, G.-D. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, *Angew. Chem. Int. Ed.* 2015, **54**, 10752-10757.
3. Q. Liu, J. Shi, J. Hu, A. M. Asiri, Y. Luo, X. Sun, *ACS Appl. Mater. Interfaces* 2015, **7**, 3877-3881.
4. Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong, Y. Li, *ACS Nano* 2016, **10**, 11337-11343.
5. H. Ang, H. Wang, B. Li, Y. Zong, X. Wang, Q. Yan, *small* 2016, **12**, 2859-2865.
6. Q. Gong, L. Cheng, C. Liu, M. Zhang, Q. Feng, H. Ye, M. Zeng, L. Xie, Z. Liu, Y. Li, *ACS Catal.* 2015, **5**, 2213-2219.
7. D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nano Lett.* 2013, **13**, 6222-6227.
8. K. Zhang, Y. Zhao, D. Fu, Y. Chen, *J. Mater. Chem. A* 2015, **3**, 5783-5788.
9. H. Wu, B. Xia, L. Yu, X.-Y. Yu, X. Lou, *Nat. Commun.* 2015, **6**, 6512-6519.
10. L. Ma, L. R. L. Ting, V. Molinari, C. Giordano, B. S. Yeo, *J. Mater. Chem. A,* 2015, **3**, 8361-8368.
11. J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. Lou, Y. Xie, *Adv. Mater.* 2013, **25**, 5807-5813.
12. D. Merki, S. Fierro, H. Vrubel, X. Hu, *Chem. Sci.* 2011, **2**, 1262-1267.
13. J. Tian, Q. Liu, A. M. Asiri, X. Sun, *J. Am. Chem. Soc.* 2014, **136**, 7587-7590.
14. J. Li, X. Zhou, Z. Xia, Z. Zhang, J. Li, Y. Ma, Y. Qu, *J. Mater. Chem. A* 2015, **3**, 13066-13071.
15. Z. Pu, Q. Liu, C. Tang, A. M. Asiri, X. Sun, *Nanoscale* 2014, **6**, 11031-11034.
16. L. Huo, B. Liu, G. Zhang, J. Zhang, *ACS Appl. Mater. Interfaces* 2016, **8**, 18107-18118.
17. Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara, T. F. Jaramillo, *Nano Lett.* 2011, **11**, 4168-4175.