Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Highly Enhanced Bifunctional Electrocatalytic Activity of Mixed Copper-Copper Oxides via Controlling Composition and Fabricating on Nickel Foam

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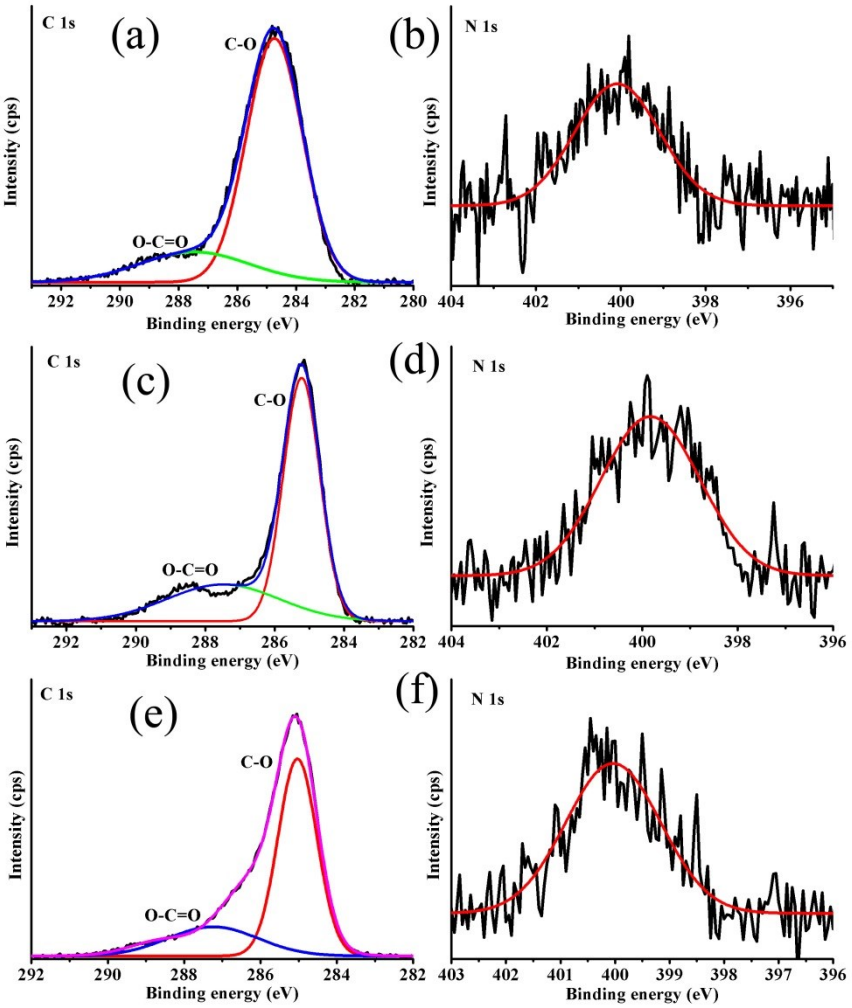

Figure S1. High resolution XPS spectra of C 1s and N 1s (a, b) Cu@NF, (c, d) Cu_2O@NF and (e, f) CuO@NF.

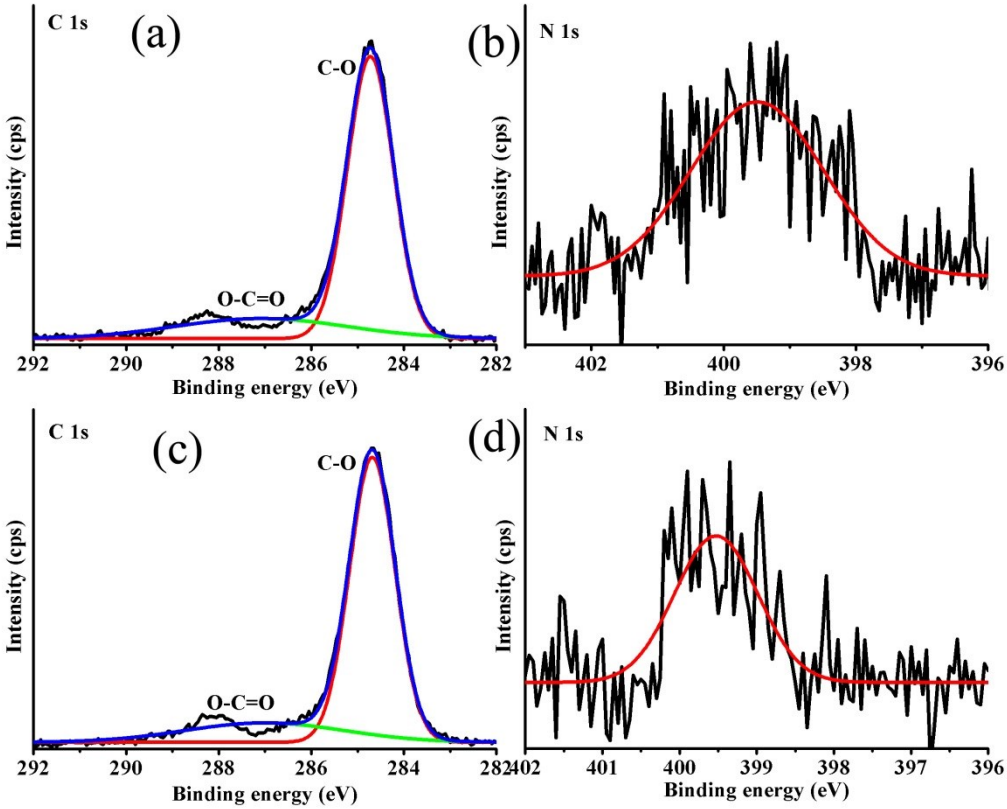

Figure S2. High resolution XPS spectra of C 1s and N 1s (a, b) Cu-Cu_2O-CuO@NF and (c, d) Cu_2O-CuO@NF.

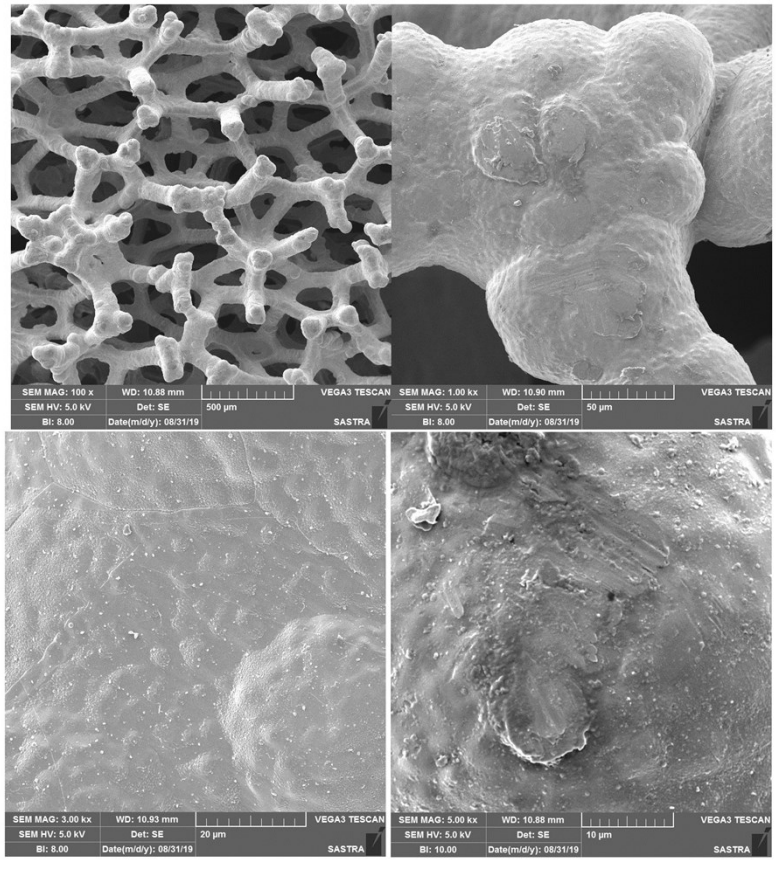

Figure S3. FE-SEM images of bare NF.

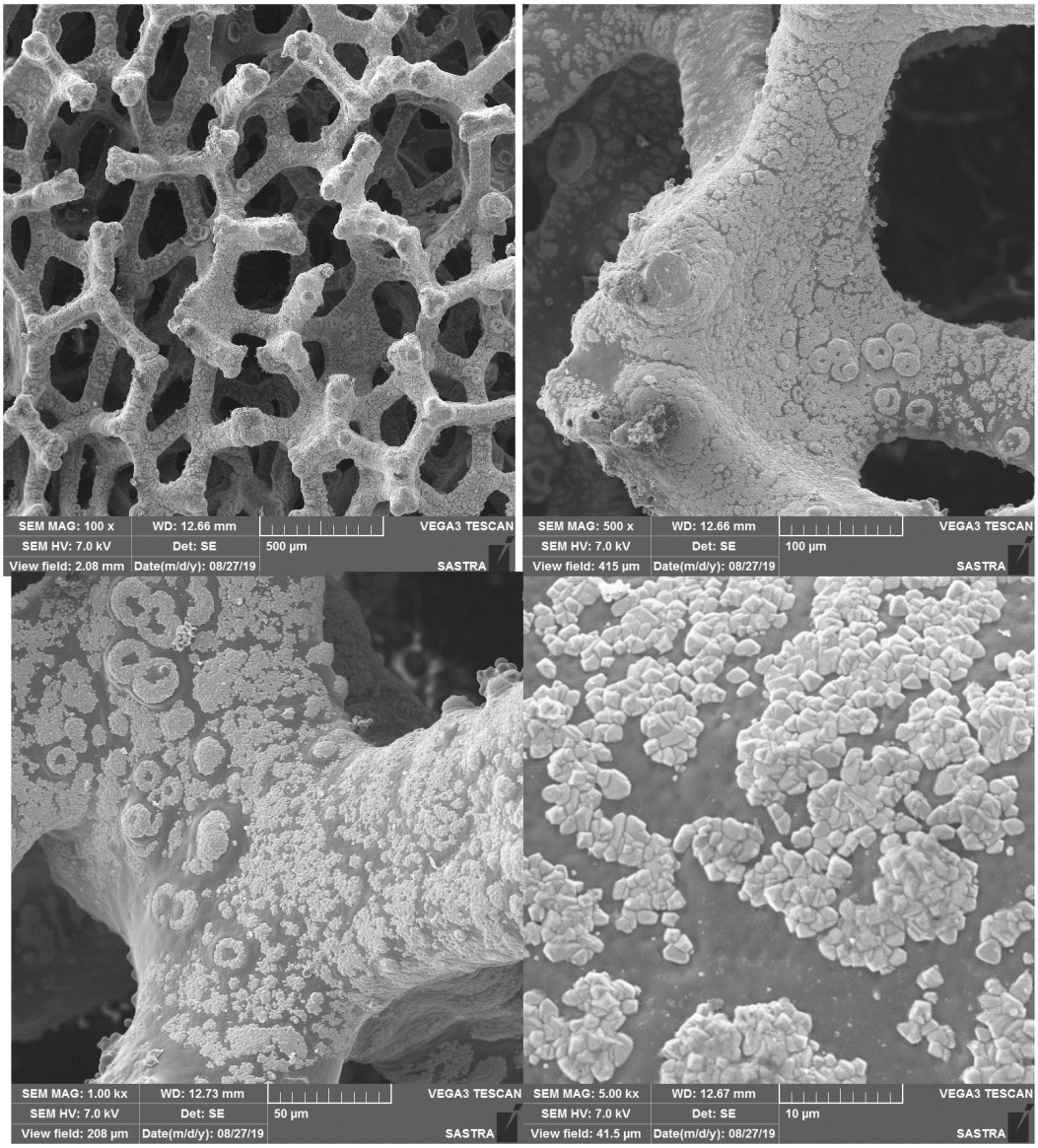

Figure S4. FE-SEM images of Cu@NF.

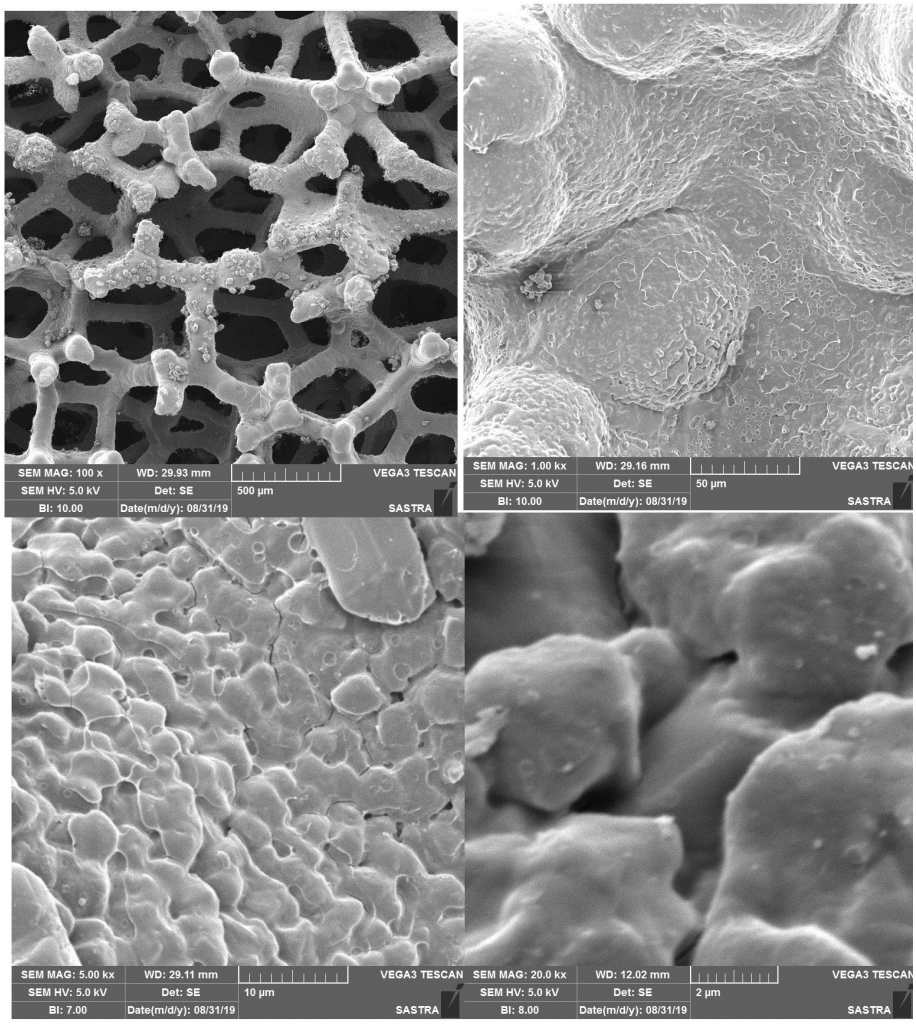

Figure S5. FE-SEM images of Cu_2O@NF.

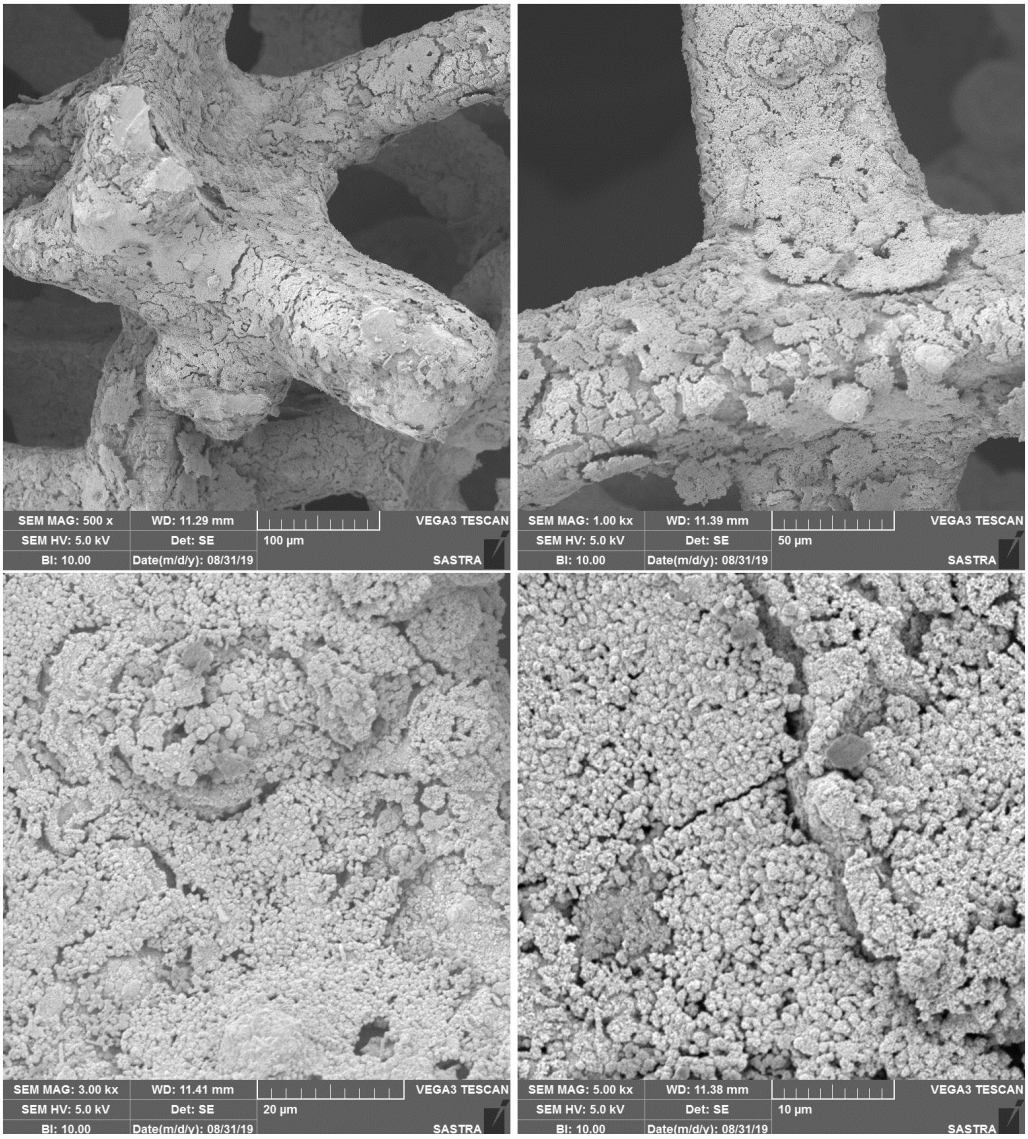

Figure S6. FE-SEM images of CuO@NF.

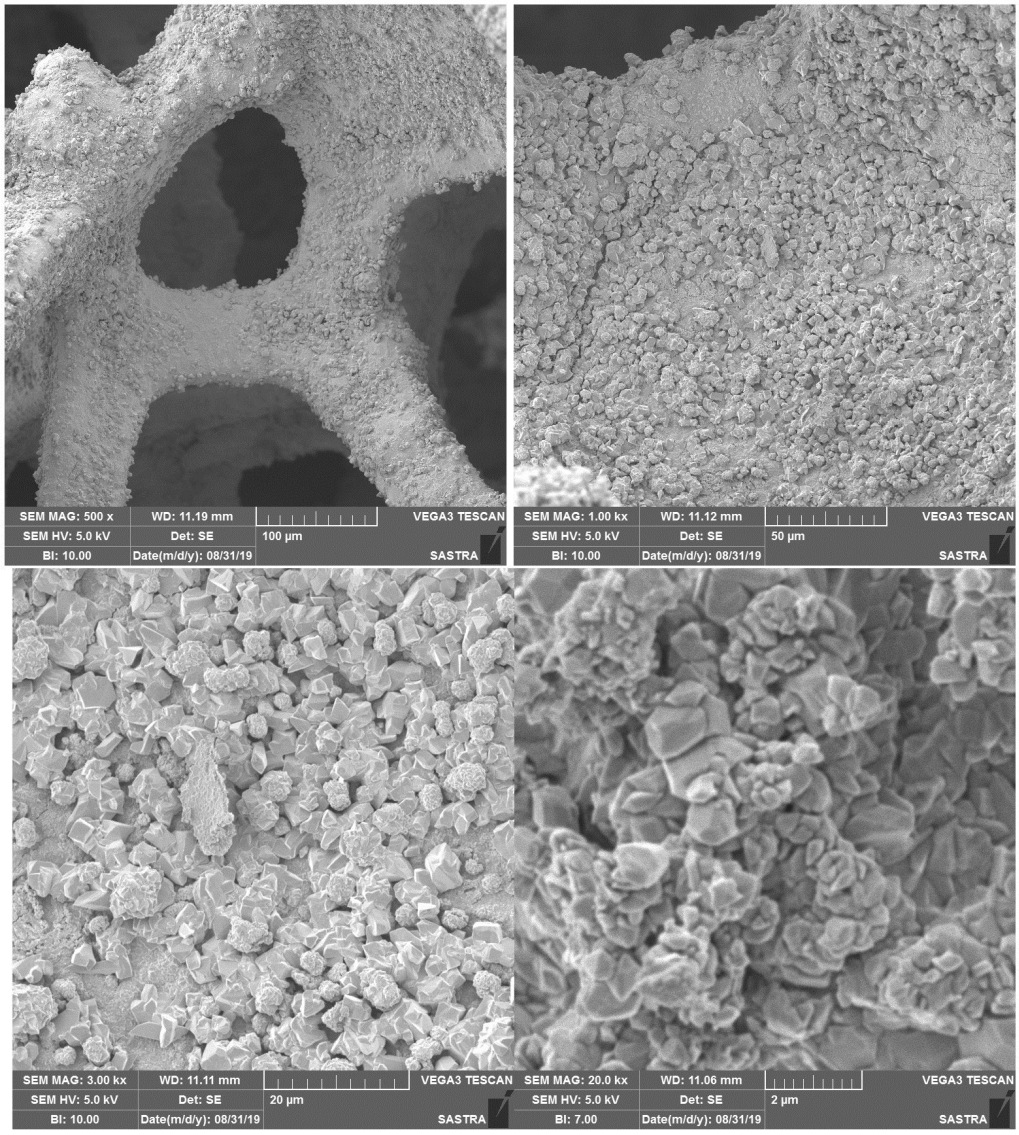

Figure S7. FE-SEM images of Cu-Cu_2O-CuO@NF..

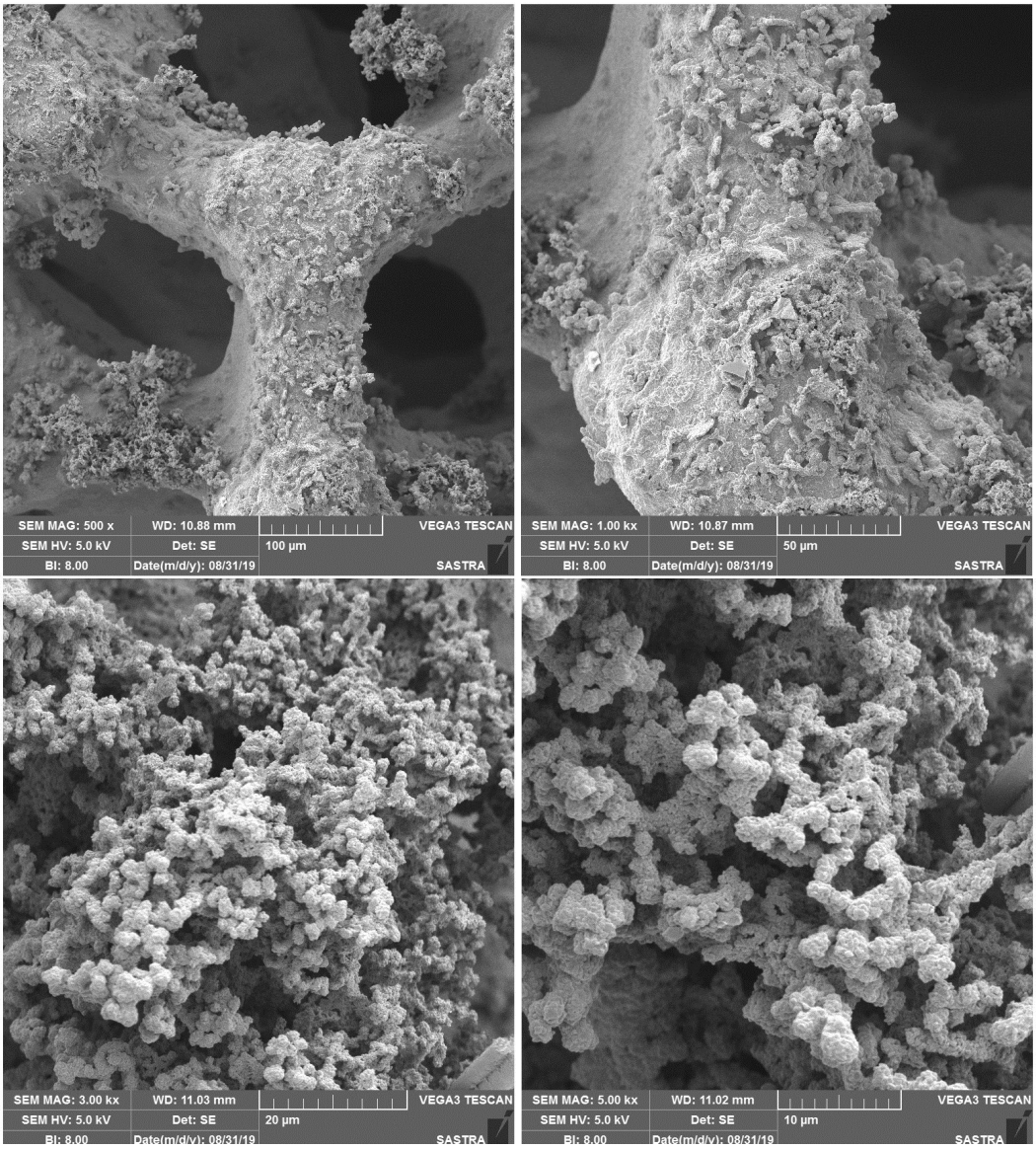

Figure S8. FE-SEM images of Cu_2O-CuO@NF.

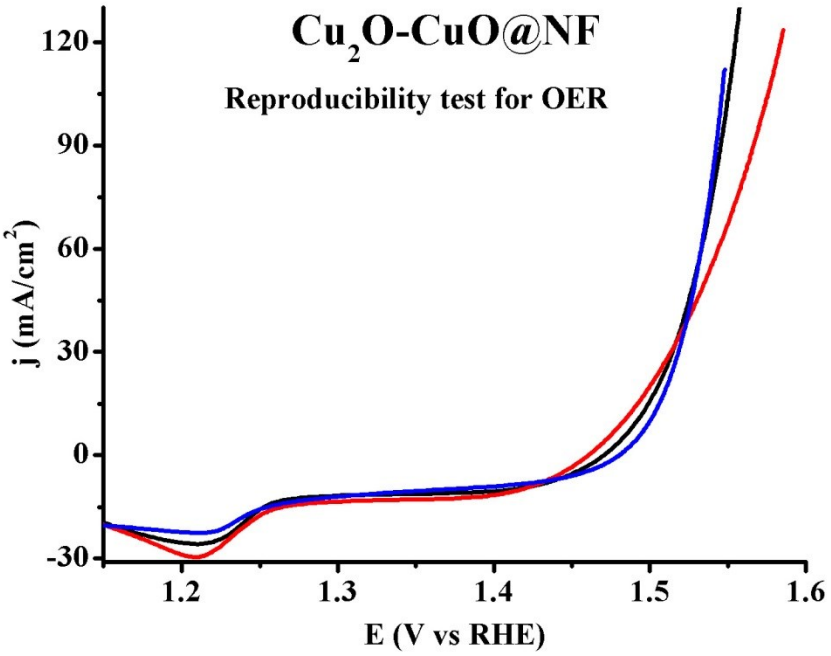

Figure S9. OER reproducibility of Cu_2O-CuO@NF.

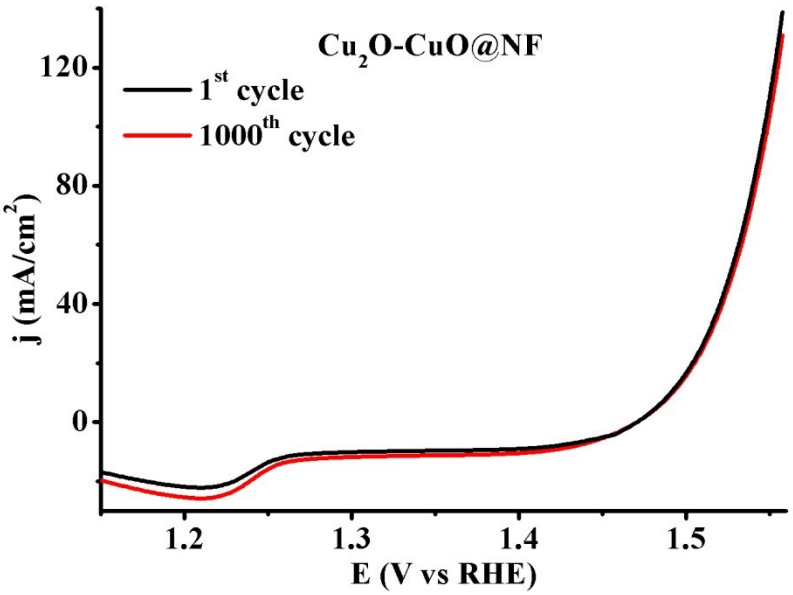

Figure S10. LSV OER curve of OER Cu_2O-CuO@NF.

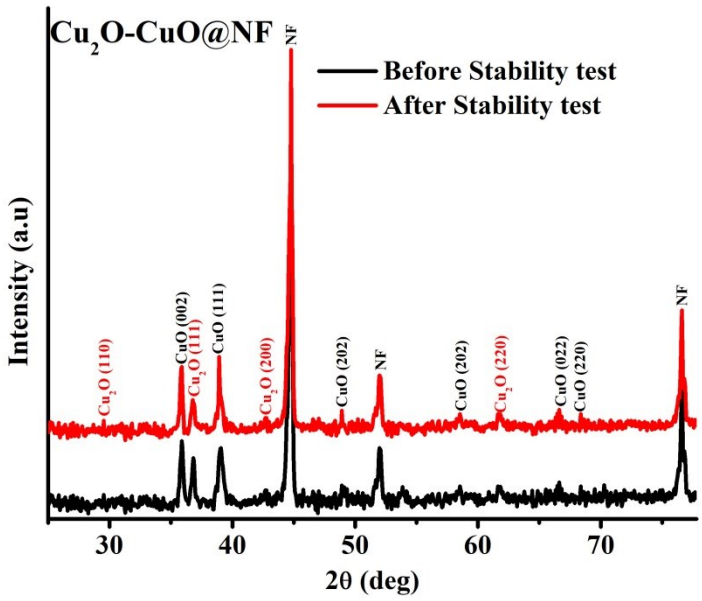

Figure S11. Comparison of PXRD pattern of Cu_2O-CuO@NF before and after the reaction.

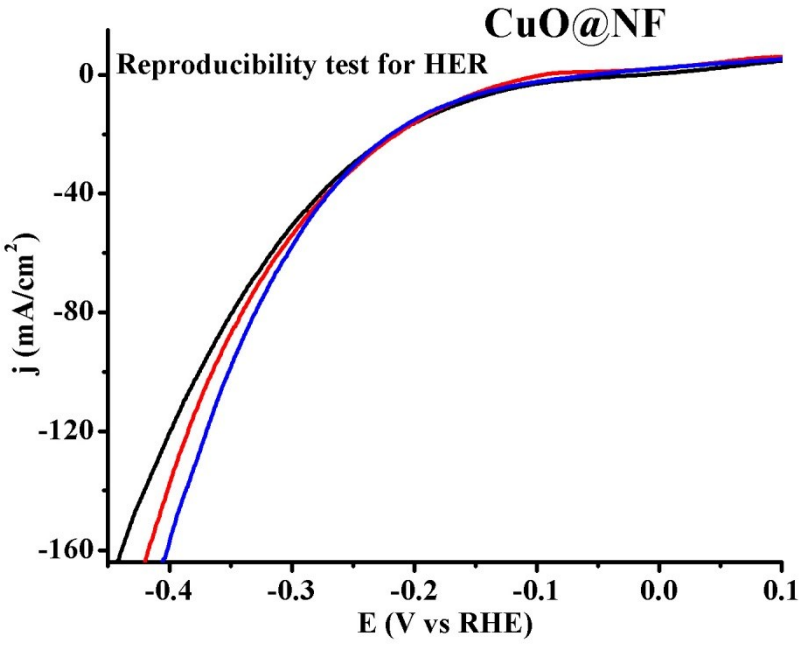

Figure S12. HER reproducibility of CuO@NF.

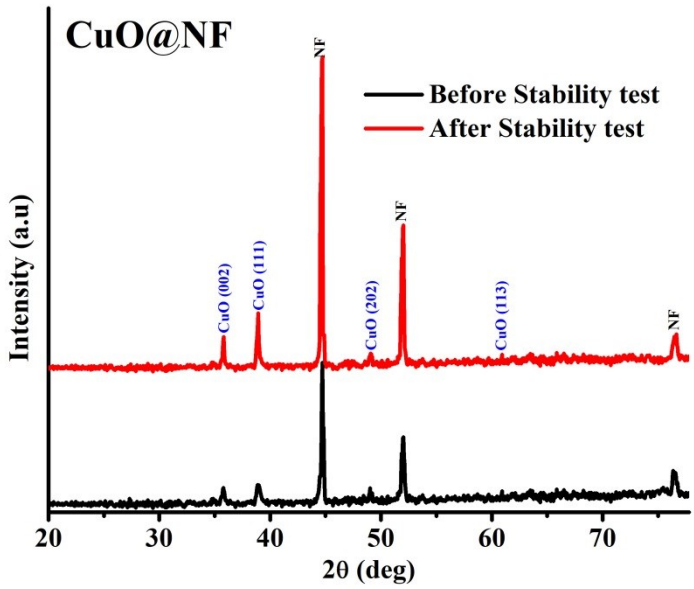

Figure S13. Comparison of PXRD pattern of CuO@NF before and after the reaction.

Table S1. Comparison of OER activities of different copper catalysts.

Catalyst	**η_{10j} (mV)**	**Stability**	**Ref**
Cu_2O-CuO/NF	**262**	**1000 cycle & 24 h**	**Present work**
$Cu_{1-x}Ni_xS$/NF	350 (20 j)	NA	1
$Cu(OH)_2$-Ni_2O_3H/NF	319	10 h	2
Pt-Cu@Cu_xO NWs/ 3DF	250	NA	3
$CuCo_2O_4$	260	25 h	4
Cu_3P-300	310	20 h	5
CuO/Ni@400	364	500 cycle 24 h	6
Cu_2S@Cu	345 (20 j)	10 h	7
CuO-$Co_{0.2}$/GCE	394	NA	8
CuO NSDs/CF	371	24 h	9
CuO@NiP NA/CF	275 (30 j)	1000 cycle & 24 h	10
HS-CuO/C NDs	308	50 h	11

Cu_3P-450	290	1000 cycle & 18 h	12
Cu_3P NB/Cu	380	1000 cycle & 10 h	13
Cu@CuO-C	340		14
NiFe-LDH/CuO NRs	290 (50 j)	35 h	15
$CuCu_3P$/CuO	315	50 h	16
Co-CuO NA/CF	299 (50 j)	1000 cycle &15 h	17
Fe_2Cu_5Ni	280	1000 cycle & 25 h	18
CuO	350	10 h	19
Cu/Cu_2O/CuO on CuO	290	100 h	20
Cu_2S/CF	336 (20 j)	1000 cycle & 10 h	21
$CuCo_2O_4$	290 (20 j)	25 h	22
Cu_2O@C	330	1000 cycle & 100 h	23
$CoFe_2O_4$	410 (5 j)	20000 sec	24
$CuFe_2O_4$	450 (5 j)	NA	24
Cu_2O−Cu foam	350	50 h	25

Table S2. Comparison of HER activities of different copper catalysts.

Catalyst	**η_{10j} (mV)**	**Stability**	**Electrolyte**	**Ref**
CuO/NF	165	16 h	1.0 M KOH	This work
Cu_3P	130	1000 cycle & 20 h	1.0 M KOH	26
N-enriched porous carbon containing Cu/CuO	470 (50 j)	NA	1.0 M KOH	27
C-Cu-DI	390	10000 sec	0.5 M H_2SO_4	28
Cu/Cu_2O/Ni el (5 min)	424	100 cycles	0.1 M H2SO4	29
Cu@Cu_3P/NF	218	48 h	1.0 M KOH	30
CFE-Cu_2O-TiO_2	114	24 h	1.0 M KOH	31
Cu/Cu_2O-CuO/rGO	105	15 h	1.0 M KOH	32
Ni-doped $CuCo_2S_4$	249	10 h	0.5 M H_2SO_4	33
Ag@Cu_2O	108	20 h	1.0 M KOH	34
Co-Cu-W Oxide	103	10 h	0.1 M KOH	35
Ni_3Cu_1@NG-NC	122	80 h	1.0 M KOH	36
($Cu_3(PO_4)_2$/Cu-	145	1000 cycle	1.0 M KOH	37

BDC-150-6 foam		& 50 h		
$Cu/Cu_2O/Cu_2S$ NT	~86	40000 sec	0.5 M H_2SO_4	38

References:

1 Y. Li, H. Su, J. Fu and X. Du, *Int. J. Hyd. Energy*, 2019, **44,** 11744-11753.
2 C. Li, B. Zhang, Y. Li, S. Hao, X. Cao, G. Yang, J. Wu and Y. Huang, *App. Cat. B,* 2019, **244**, 56-62.
3 D. T. Tran, H. T. Le, T. L. L. Doan, N. H. Kim and J. H. Lee, *Nano Energy,* 2019, **59**, 216-228.
4 S. M. Pawar, B. S. Pawar, P. T. Babar, A. T. A. Ahmed, H. S. Chavan, Y. Jo, S. Cho, J. Kim, B. Hou, A. I. Inamdar, S. Cha, J. H. Kim, T. G. Kim, H. Kim and H. Im, *App. Surf. Sci.,* 2019, **470**, 360-367.
5 S. M. Pawar, B. S. Pawar, P. T. Babar, A. T. A. Ahmed, H. S. Chavan, Y. Jo, S. Cho, J. Kim, A. I. Inamdar, J. H. Kim, H. Kim and H. Im, *Mater. Lett.,* 2019, **241**, 243-247.
6 A. Roy, H. S. Jadhav, M. Cho and J. G. Seo, *J. Industr. Eng. Chem.,* 2019, **76**, 515-523.
7 B. Ma, Z. Yang, Z. Yuan and Y. Chen, *Int. J. Hyd. Energy,* 2019, **44**, 1620-1626.
8 H. Xu, W. Liu, Y. Zhao, D. Wang and J. Zhao, *J. Coll. Inter. Sci,* 2019, **540,** 585-592.
9 Q. Zhou, T.-T. Li, W. Xu, H.- L. Zhu and Y. -Q. Zheng, *J. Mater. Sci*., 2018, **53**, 8141-8150.
10 B. Zhang, S. Hao, Z. Ye and, Y. Yang, *Chem. Commun.,* 2018, **54**, 2393-2396.
11 B. Zhang, C. Li, G. Yang, K. Huang, J. Wu, Z. Li, X. Cao, D. Peng, S. Hao and Y. Huang, *ACS App. Mater. Interfaces,* 2018, **10**, 23807-23812.
12 J. Hao, W. Yang, Z. Huang and C. Zhang, *Adv. Mater. Interfaces,* 2016, **3**, 1600236.
13 S. Wei, K. Qi, Z. Jin, J. Cao, W. Zheng, H. Chen and X. Cui, *ACS Omega,* 2016, **6**, 1367-1373.
14 J.- X. Wu, C.- T. He, G.- R. Li and J.- P. Zhang, *J. Mater. Chem. A*, 2018, **6**, 19176-19181.
15 Q. Zhou, T.- T. Li, J. Qian, W. Xu, Y. Hu and Y.- Q. Zheng, *ACS App. Energy Mater.,* 2018, **1**, 1364-1373.
16 J. Du, F. Li, Y. Wang, Y. Zhu and L. Sun, *ChemElectroChem*, 2018, *5,* 2064-2068.
17 X. Xiong, C. You, Z. Liu, A. M. Asiri and X. Sun, *ACS Sus. Chem. Eng.,* 2018, **6**, 2883-2887.
18 Y. Dong, F. Sun, X. Li, M. Chu, N. Li, X. Li, L. Wang, D. Qu, Y. Dong, Z. Xie, Y. Lin and C. Zhang, *J. Electrochem. Soc.,* 2018, **165,** F1127-F1132.
19 S. M. Pawar, B. S. Pawar, B. Hou, J. Kim, A. T. A. Ahmed, H. S. Chavan, Y. Jo, S. Cho, A. I. Inamdar, J. L. Gunjakar, H. Kim, S. Cha and H. Im, *J. Mater. Chem. A,* 2017, **5**, 12747-12751.
20 T. N. Huan. G. Rousse, S. Zanna, I. T. Lucs, X. Xu, N. Menguy, V. Mougel and M. Fontecave, *Angew. Chem. Inter. Ed.,* 2017, **56**, 4792-4796.
21 L. He, D. Zhou, Y. Lin, R. Ge, X. Hou, X. Sun and C. Zheng, *ACS Cat.,* 2018, **8,** 3859-3864.
22 A. T. A. Ahmed, B. Hou, H. S. Chavan, Y. Jo, S. Cho, J. Kim, S. M. Pawar, S. Cha, A. I. Inamdar, H. Kim and H. Im, *Small,* 2018, **14,** 1800742.
23 H. Zhang, Z. Zhang, N. Li, W. Yan and Z. Zhu, *J. Catal.,* 2017, **352,** 239-245.
24 M. Li, Y. Xiong, X. Liu, X. Bo, Y. Zhang, C. Han and L. Guo, *Nanoscale,* 2015, **7**, 8920-8930.
25 H. Xu, J. -X. Feng, Y.- X. Tong and G.- R. Li, *ACS Catl.,* 2017, **7,** 986-991.
26 J. Hao, W. Yang, Z. Huang and C. Zhang, *Adv. Mater. Interfaces*, 2016, **3**, 1600236.
27 S. Cui, M. Qian, X. Liu, Z. Sun and P. Du, *ChemSusChem*, 2016, **9**, 1-10.
28 X. Wei, N. Li and X. Zhang, *App. Surf. Sci.,* 2017, **425**, 663–673.
29 N. Farahbakhsh and S. Sanjabi, *J. Industr. Eng. Chem*., 2019, **70**, 211-225.
30 H. Zheng, X. Huang, H. Gao, G. Lu, W. Dong and G. Wang, *Chem. Eur. J*., 2019, **25**, 1083-1089.
31 B. Long, H. Yang, M. Li, M.-S. Balogun, W. Mai, G. Ouyang, Y. Tong, P. Tsiakaras, S. Song, *App. Cat. B,* 2019, **243,** 365-372.
32 L. Ye and Z. Wen, *Chem. Commun.,* 2018, **54**, 6388-6391.
33 Y. Sun, D. Li, J. Lu, Y. Zhang, L. Li and J. Liang, *Cryst. Res. Technol*., 2019, **54**, 1800248.
34 C. Song, Z. Zhao, X. Sun, Y. Zhou, Y. Wang and D. Wang, *Small,* 2019, **15**, 1804268.
35 D. Gao, R. Liu, J. Biskupek, U. Kaiser, Y.-F. Song, C. Streb, *Angew. Chem. Int. Ed.,* 2019, **58**, 4644-4648.
36 B. Liu, H.-Q. Peng, J. Cheng, K. Zhang, D. Chen, D. Shen, S. Wu, T. Jiao, X. Kong, Q. Gao, S. Bu, C.-S. Lee and W. Zhang, *Small,* 2019, 1901545.
37 J. Rong, F. Qiu, T. Zhang, Y. Fang, J. Xu and Y. Zhu, *Electrochimica Acta*, 2019, **313**, 179-188.
38 Y. Wei, W. He, P. Sun, J. Yin, X. Deng and X. Xu, *App. Surf. Sci.* 2019, **476,** 966–971.