Supporting Information

Homologous Metal-Free Electrocatalysts Grown on Three-Dimensional Carbon Networks for Overall Water Splitting in Acid and Alkaline Media

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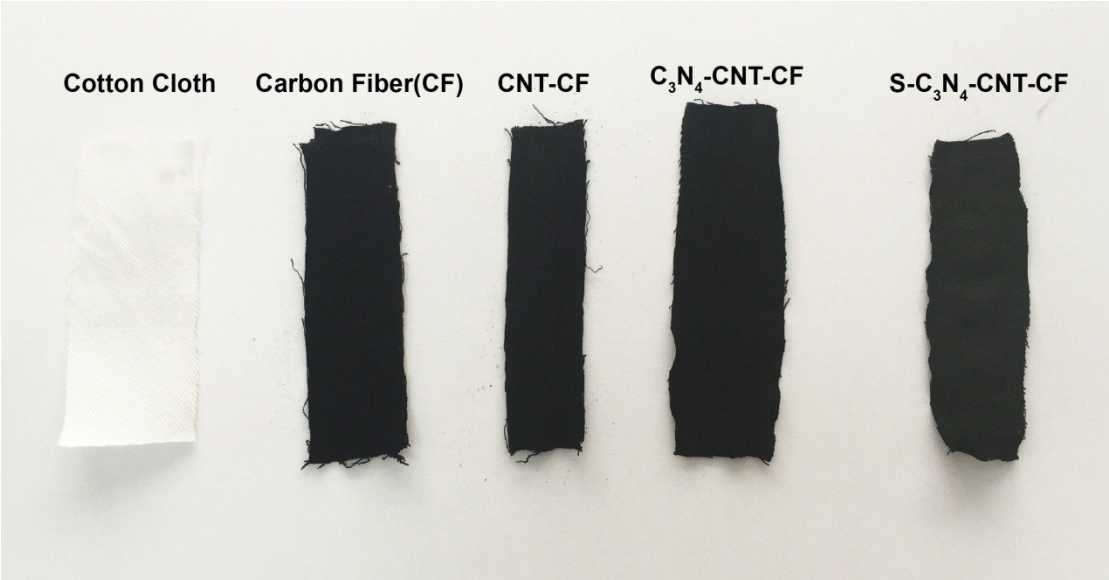

Figure S1. Photograph of the various electrodes during the synthsize porcedure.

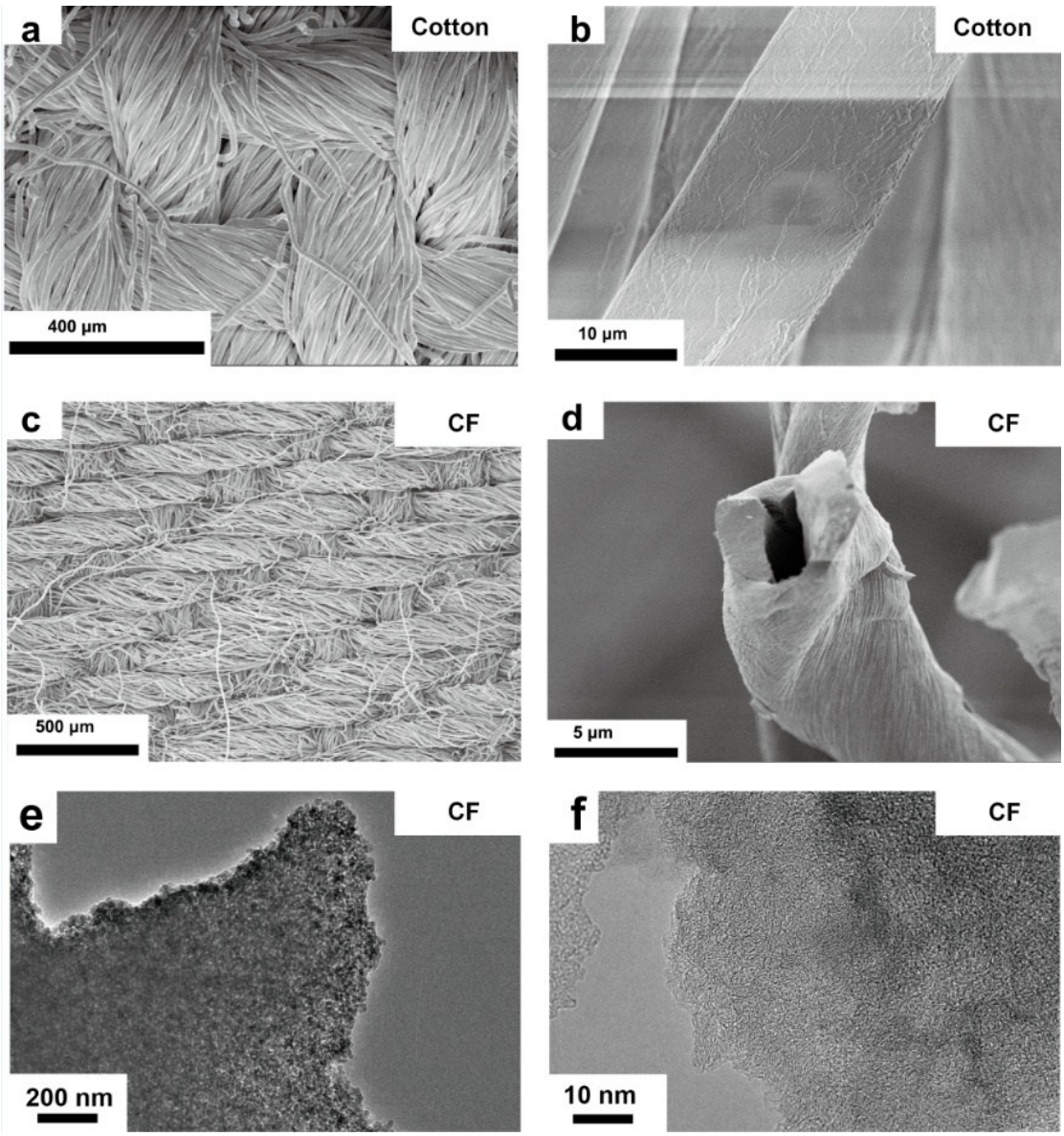

Figure S2. SEM images of (a) cotton and (b) carbon fiber. TEM images of (c) carbon fiber.

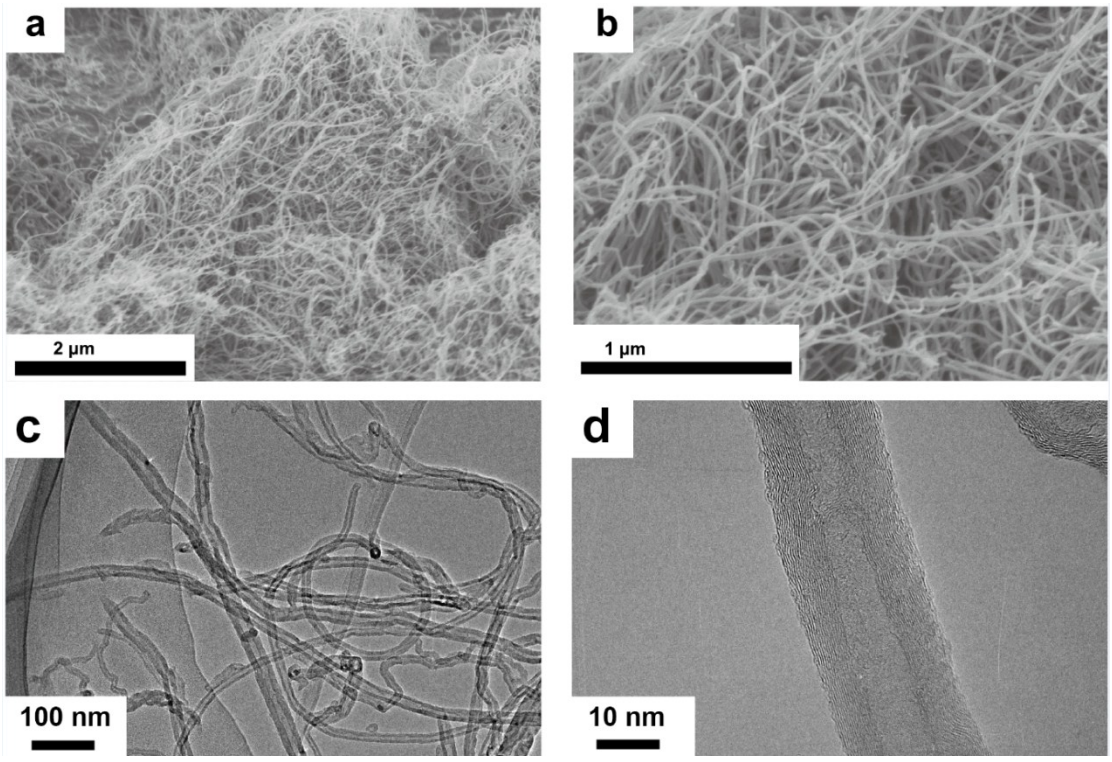

Figure S3. (a-b) SEM and (c-d) TEM images of CNTs.

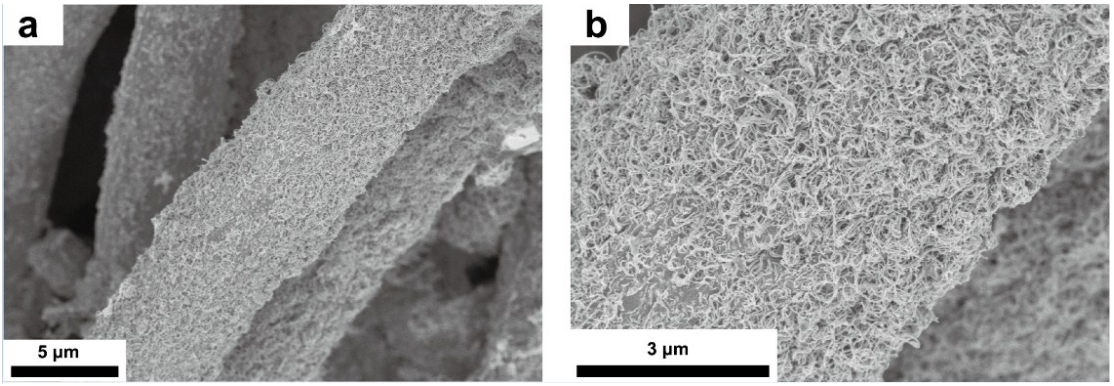

Figure S4. (a-b) SEM image of CNT-CF samples.

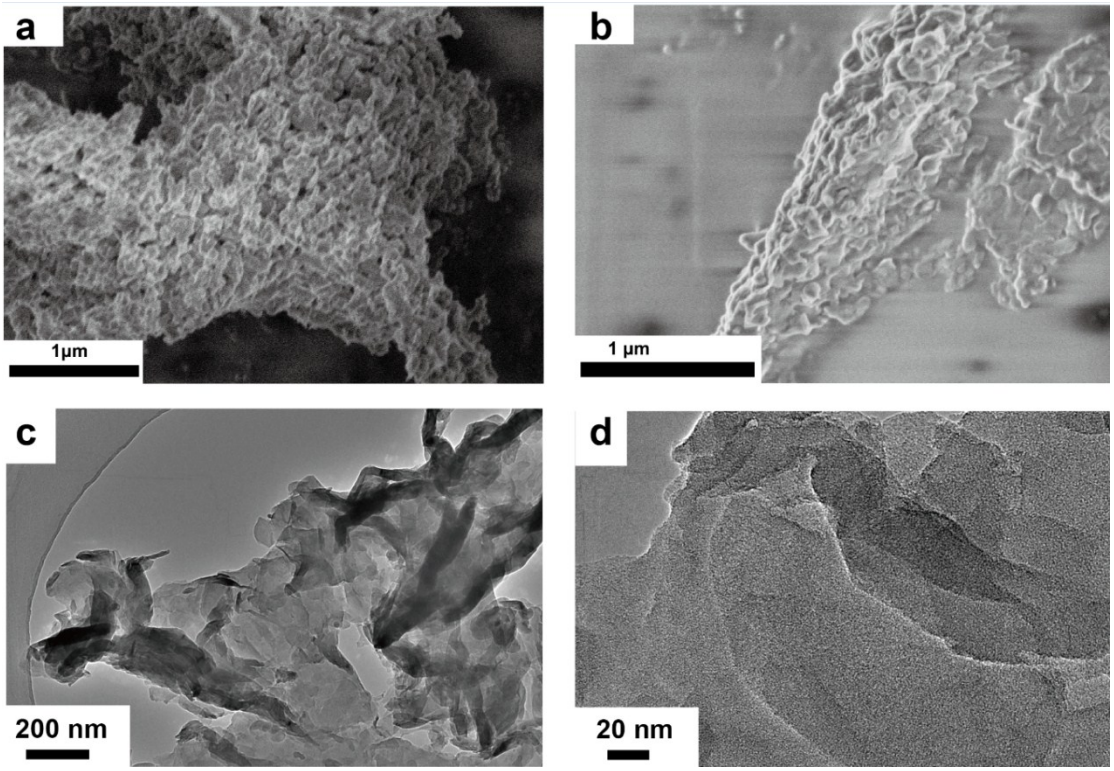

Figure S5. (a-b) SEM and (c-d) TEM images of C_3N_4 samples.

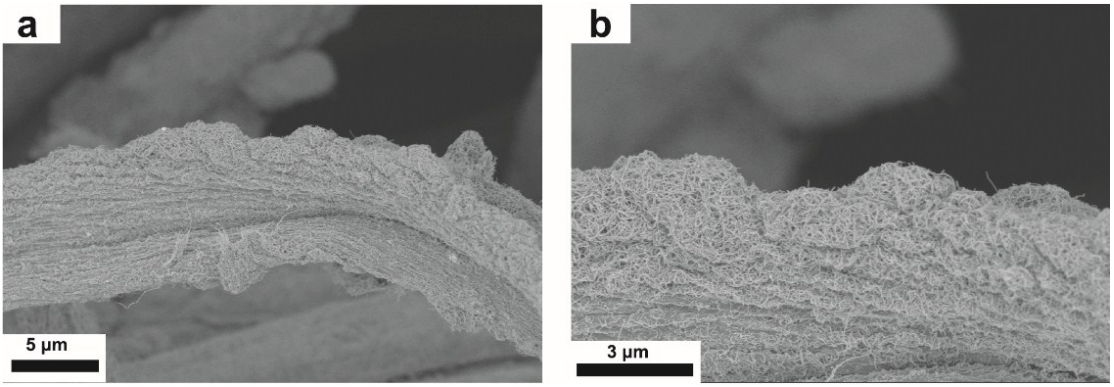

Figure S6. SEM images of S-C_3N_4-CNT-CF electrode.

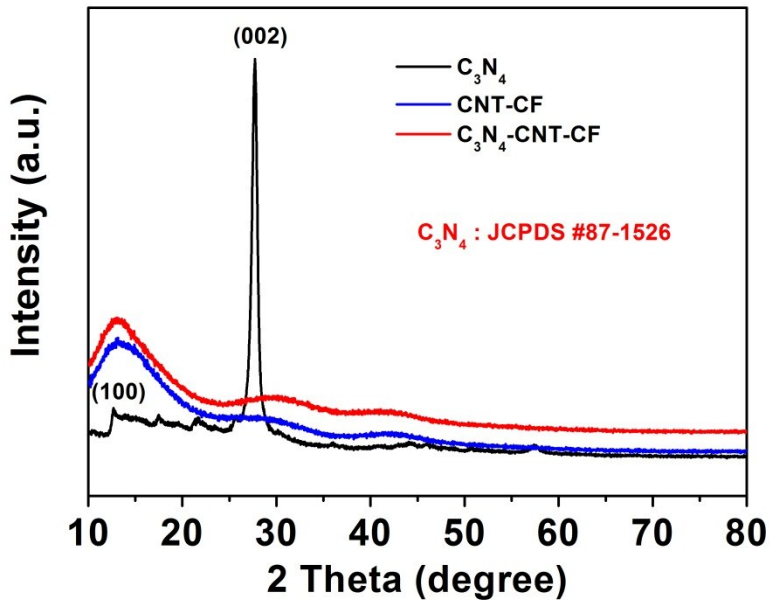

Figure S7. X-ray diffraction (XRD) patterns of C_3N_4, CNT-CF and C_3N_4-CNT-CF. Seen in Figure S7, the pure C_3N_4 presents two typical diffraction peaks of (100) and (002), belongs to the PDF No. 87-1526.

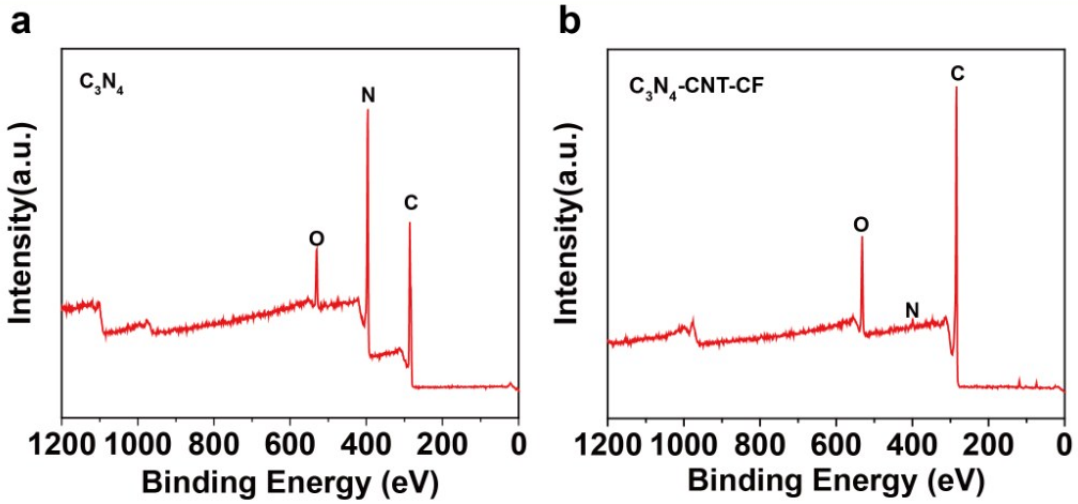

Figure S8. XPS survey spectra of (a) C_3N_4 and (b) C_3N_4-CNT-CF. The whole XPS survey spectrum of these two sample shows the main elements (C and N), with a small amount of adsorbed oxygen.

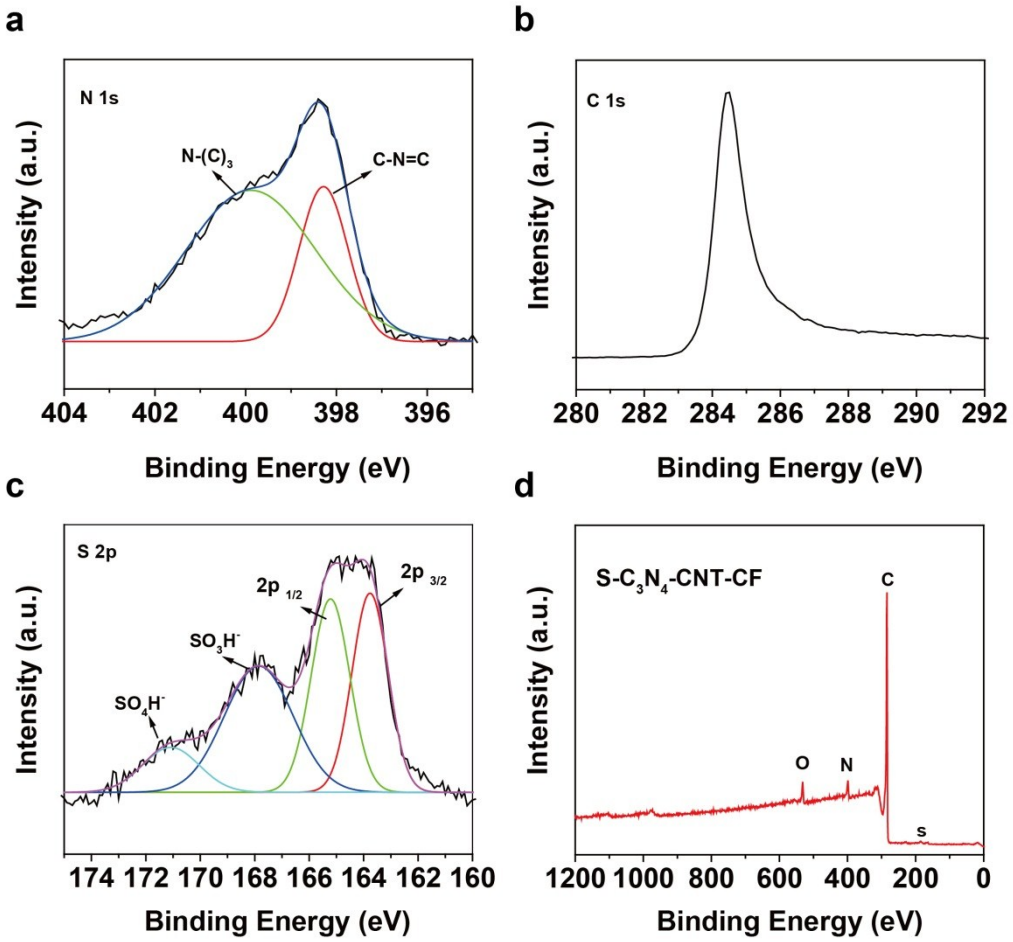

Figure S9. High-resolution XPS spectra of (a) N 1s , (b) C 1s and (c) S 2p core levels and (d) XPS survey spectrum of S-C_3N_4-CNT-CF.

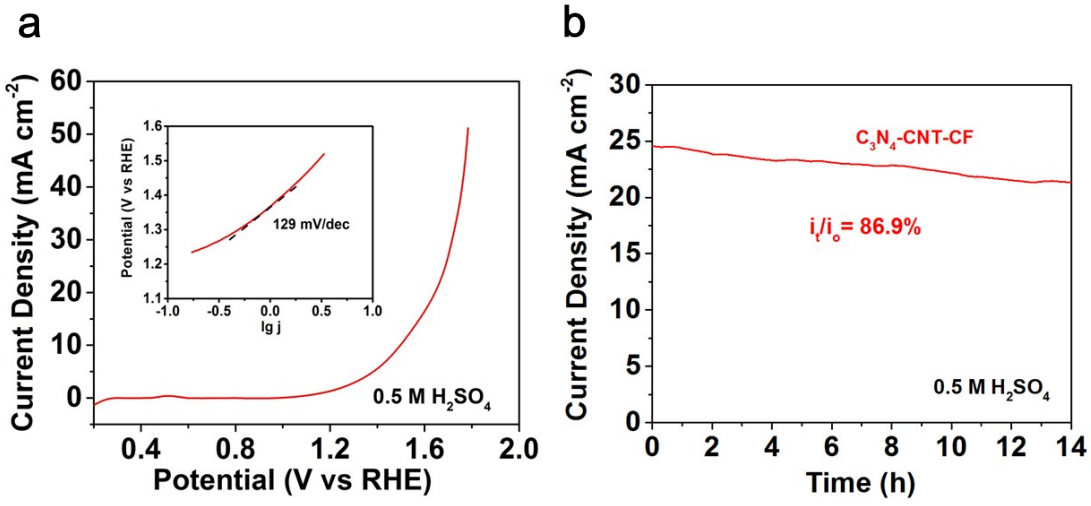

Figure S10. (a) LSV curves and (b) duration tests at 1.63 V of C_3N_4-CNT-CF in 0.5 M H_2SO_4 solution at 5 mV s^{-1}.

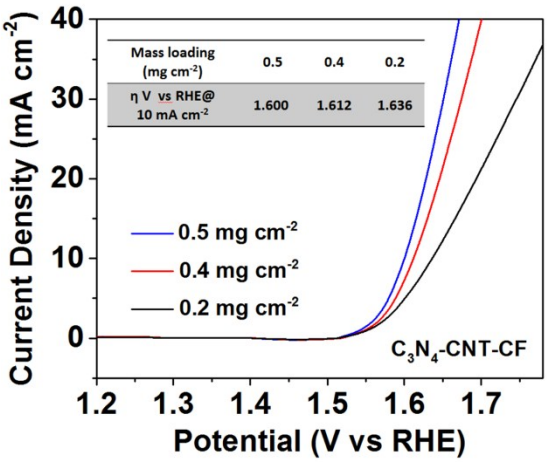

Figure S11. The OER acitivites of C_3N_4-CNT-CF with various mass loading including 0.5, 0.4 and 0.2 mg cm^{-2}, in 1 M KOH solution.Inste: applied potential to achieve the current density of 10 mA cm^{-2} at different loding masses.

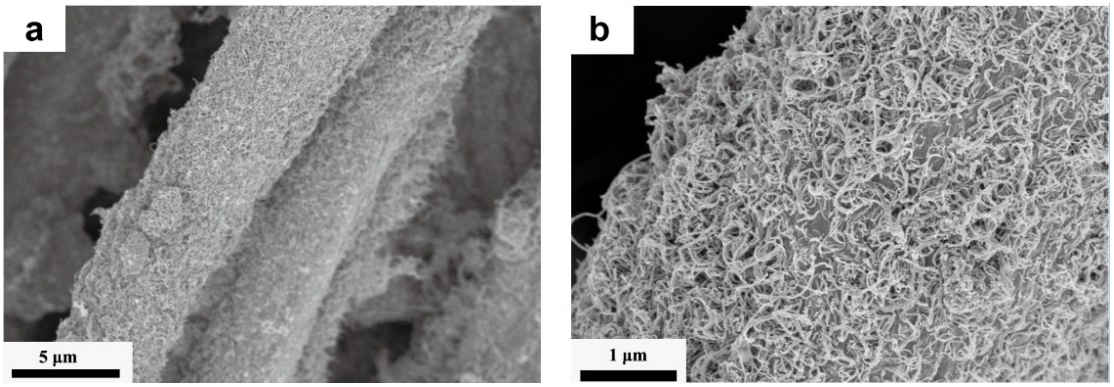

Figure S12. The morphologh of C_3N_4-CNT-CF electrode after long-time duration test in 1M KOH solution.

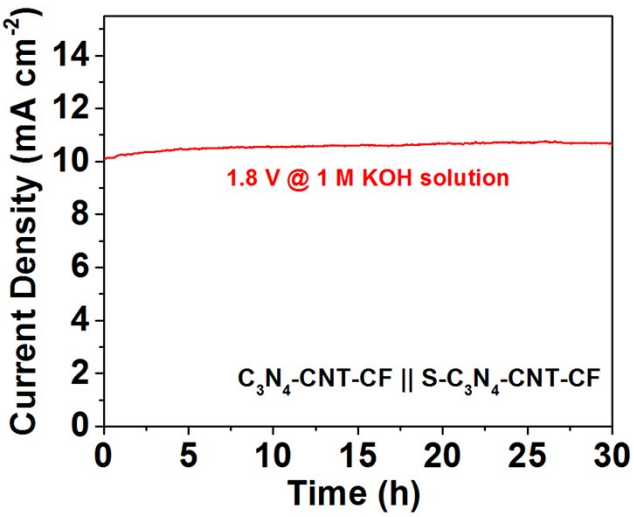

Figure S13. The long-time duration tests of C_3N_4-CNT-CF ‖ S-C_3N_4-CNT-CF system in 1 M KOH solution at 1.8 V.

Table S1. The texture properties of all carbon electrodes

Sample	BET surface area (m^2/g)	Pore size (nm)	Pore Volume (cm^3/g)
C_3N_4	21.4	21.6	0.16
CF	8.3	36.6	0.031
CNT-CF	45.6	28.4	0.19
C_3N_4-CF	34.6	25.4	0.15
C_3N_4-CNT-CF	53.7	35.2	0.21

Table S2. Comparasion for OER catalysts

Catalyst	Loading [$mgcm^{-2}$]	Electrolyte pH	Onset [V vs RHE]	j [$mAcm^{-2}$] @ η [V vs RHE]	Tafel slope [mV/dec]
C_3N_4-CNT-CF *	**~0.5**	**14**	**1.52**	**10 @ 1.60**	**45**
C_3N_4/CNT[1]	**0.2**	**14**	**1.53**	**10 @ 1.60**	**44.1**
P-doped C_3N_4/CFP[2]	**~0.2**	**13**	**1.53**	**10 @ 1.63**	**61.6**
N-doped graphene/CNT[3]	**0.2548**	**13**	**1.50**	**10 @ 1.63**	**83**
Reduced Co_3O_4[4]	**0.136**	**14**	**~1.52**		**72**
N-graphene /$NiCo_2O_4$[5]		**14**	**1.54**	**5 @ 1.603**	**156**
CoMnO@CN[6]	**~2.0**	**14**	**1.46**	**308 @ 1.65**	**97**
CoNi $(OH)_x$ [7]		**14**	**1.48**	**10 @ 1.51**	**77**
TiN@Ni_3N[8]	**~0.6**	**14**	**1.52**	**10 @ 1.58**	**93.7**
IrO_x[4]		**14**	**1.42**		**85**

* This work

Table S3. Comparasion for HER catalysts

Catalyst	Loading [mgcm^{-2}]	Electrolyte pH	Onset [mV]	j [mAcm^{-2}] @ η [mV]	Tafel slope [mV/dec]	j_0 [mAcm^{-2}]
S-C_3N_4-CNT-CF	~0.5	0	150	10 @ 236	81.6	0.0184
*		14	50	10 @ 131	79	0.2767
C_3N_4-graphite[9]	0.102	0		10 @ 240	51.5	3.5×10^{-7}
C_3N_4-TiO_2[10]		13.1	100	1.3 @ 300	120	
MoS_2/CNT[11]	0.136	0	90	10@180	44.6	
CoS_2 nanowire[12]	1.7 ± 0.3	0	75	10 @145	51.6	0.0188
MoB nanoparticle[13]	2.5	0	≧100	20 @ 210	55	1.4×10^{-3}
Mo_2C nanoparticle[13]	1.4	0	≧100	20 @ 240	56	1.3×10^{-3}
CoNiNx[7]		0	100		130	
TiN@Ni_3N[8]	~0.6	14	15	10 @ 21	42.1	
CoO_x@CN[14]	2.1	14	85	20 @ 134		
Pt[15]	1	0	0	2 @ 5	30	2.7

*this work

Reference:

1. T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *Angew. Chem., Int. Ed.*, 2014, **53**, 7281-7285.
2. T. Y. Ma, J. Ran, S. Dai, M. Jaroniec and S. Z. Qiao, *Angew. Chem., Int. Ed.*, 2015, **54**, 4646-4650.
3. G. L. Tian, M. Q. Zhao, D. Yu, X. Y. Kong, J. Q. Huang, Q. Zhang and F. Wei, *Small*, 2014, **10**, 2251-2259.

4. Y. Wang, T. Zhou, K. Jiang, P. Da, Z. Peng, J. Tang, B. Kong, W.-B. Cai, Z. Yang and G. Zheng, *Adv. Energy Mater.*, 2014, **4**, 1400696.
5. S. Chen and S.-Z. Qiao, *ACS Nano*, 2013, **7**, 10190-10196.
6. J. Li, Y. Wang, T. Zhou, H. Zhang, X. Sun, J. Tang, L. Zhang, A. M. Al-Enizi, Z. Yang and G. Zheng, *J. Am. Chem. Soc.*, 2015, **137**, 14305-14312.
7. S. Li, Y. Wang, S. Peng, L. Zhang, A. M. Al-Enizi, H. Zhang, X. Sun and G. Zheng, *Adv. Energy Mater.*, 2015, 1501661.
8. Q. Zhang, *J. Mater. Chem. A*, 2016, **4**, 5713.
9. Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec and S. Z. Qiao, *Nat. Commun.*, 2014, **5**, 3783.
10. M. Shalom, S. Gimenez, F. Schipper, I. Herraiz-Cardona, J. Bisquert and M. Antonietti, *Angew. Chem. Int. Ed.*, 2014, **53**, 3654-3658.
11. Y. Yan, X. Ge, Z. Liu, J.-Y. Wang, J.-M. Lee and X. Wang, *Nanoscale*, 2013, **5**, 7768-7771.
12. M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding and S. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 10053-10061.
13. H. Vrubel and X. Hu, *Angew. Chem., Int. Ed.*, 2012, **51**, 12703-12706.
14. H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694.
15. E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *J. Am. Chem. Soc.*, 2013, **135**, 9267-9270.