Tunable CoFe-Based Active Sites on 3D Heteroatom Doped Graphene Aerogel Electrocatalysts via Annealing Gas Regulation for

Efficient Water Splitting

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Figure S1 Digital Photograph (a), XRD patterns (b), SEM (c, d) and TEM (e, f) images of rGO-based (CoFe@rGO) precursor.



Figure S2 The SEM images of CoFeO@N/S-rGO (a) and CoFe@N-rGO (b).



Figure S3 Particle size distribution curves for the CoFeO@N/S-rGO and CoFe@N-rGO samples calculated from the TEM images. For the measurement of particle size, over 200 particles were measured using nanomeasurer.



Figure S4 (a) TEM and (b) SEM image, and (c) SEM image and the corresponding EDS mapping images of CoO@N/S-rGO.



Figure S5 (a) TEM and (b) SEM image, and (c) SEM image and the corresponding EDS mapping images of Co@N-rGO.



Figure S6 (a) TEM and (b) SEM image, and (c) SEM image and the corresponding EDS mapping images of CoNiO@N/S-rGO.



Figure S7 (a) TEM and (b) SEM image, and (c) SEM image and the corresponding EDS mapping images of CoNi@N-rGO.



Figure S8 XPS survey spectra (a, d), C 1S (b, e), and O 1s (c, f) CoFeO@N/S-rGO and CoFe@N-rGO,

respectively.

Sample	C (at. %)	O (at.	N (at. S(at.%)	Co (at.	Fe (at. %)
		%)	%)	%)	
CoFeO@N/S-	82.7	6.09	1.82 2.82	2.26	4.6
rGO					
CoFe@N-rGO	89.08	5.4	3.37 /	0.87	1.28

Table S1 Surface composition of the samples determined from XPS.

Table S2 Surface composition of N-based species determined from XPS.

Sample	pyridinic N	pyrrolic	graphitic N	oxidized
	(at. %)	Ν	(at. %)	Ν
		(at. %)		(at. %)
CoFeO@N/S-	0.84	0.80	0.08	0.1
rGO				
CoFe@N-rGO	1.2	0.78	0.89	0.5



Figure S9 (a) The XRD of CoFeO@N/S-rGO-700 and CoFeO@N/S-rGO-900. (b) The XRD of CoFe@N-rGO-700 and CoFe@N-rGO-900.

For comparison, the samples were also annealed at various temperatures of 700 and 900 °C, respectively. The obtained samples annealed in N₂ were named as CoFeO@N/S-rGO-700 and CoFeO@N/S-rGO-900 while the samples annealed in NH₃ were named as CoFe@N-rGO-700 and CoFe@N-rGO-900, respectively. For the XRD pattern of CoFeO@N/S-rGO-700 (Figure S9a), the typical diffraction peaks can be indexed to the diffraction of CoFe₂O₄ (JCPDS 22–1086) in addition to the broad peak for rGO, which are similar to that of the CoFeO@N/S-rGO. The CoFeO@N/S-rGO-900 sample exhibits the strongest diffraction peaks, suggesting improved crystallinity. The CoFe@N-rGO-700 sample exhibits the similar XRD pattern with that of CoFe@N-rGO (Figure S9b). However, in addition to the broad peak at around 24.5°, CoFe@N-rGO-900 also exhibits a diffraction peak at 43.1°, which is ascribed to the diffraction of the CoFe crystalline particles (JCPDS 65-6829). The results indicate that the increased temperature is beneficial to improve the crystallinity.



Figure S10 SEM images of (a, c) and TEM image (b, d) of CoFeO@N/S-rGO-700 and CoFe@N-rGO-700, respectively. SEM images of (e, g) and TEM images (f, h) of CoFeO@N/S-rGO-900 and CoFe@N-rGO-900, respectively.

As shown in Figure S10, the samples annealed in 700 °C exhibit porous structure composed with interconnected rGO sheets and lots of nanoparticles are dispersed on the rGO sheets. However, both CoFeO@N/S-rGO-900 and CoFe@N-rGO-900 exhibit much larger particles. The results suggest the obvious aggregation at the higher annealing temperature of 900 °C.



Figure 11 Linear sweep voltammetry (LSV) curves of CoFeO@N/S-rGO-700, CoFeO@N/S-rGO, CoFeO@N/S-rGO-900, CoFe@N-rGO-700, CoFe@N-rGO and CoFe@N-rGO-900 for OER (a) and HER (b) in 1.0 M KOH at a scan rate of 5 mV s⁻¹.

With increasing the annealing temperature from 700 to 800 °C, the samples obtained at 800 °C exhibit the enhanced catalytic activities to OER and HER, respectively. However, further increasing the temperature to 900 °C, CoFeO@N/S-rGO-900 and CoFe@N-rGO-900 exhibit the poorer catalytic activities in comparison with CoFeO@N/S-rGO and CoFe@N-rGO. The aggregation (Figure S10) is likely to decrease the active surface area and results in the poor catalytic activity. The results suggest that CoFeO@N/S-rGO and CoFe@N-rGO have superior catalytic activities.



Figure S12 Linear sweep voltammetry (LSV) curves of N/S-rGO, N–rGO for OER (a) and HER (b) in 1.0 M KOH at a scan rate of 5 mV s⁻¹.



Figure S13 (a) Polarization curves of CoNiO@N/S-rGO and CoNi@N-rGO for OER in 1.0 M KOH at a scan rate of 5 mV s⁻¹. (b) Corresponding Tafel plots. (c) Polarization curves of CoNiO@N/S-rGO and CoNi@N-rGO for HER in 1.0 M KOH at a scan rate of 5 mV s⁻¹. (d) Corresponding Tafel plots.

Catalysts	Mass loading	electrolyte	E j ₁₀ ^[a]	Durability	References
Anode Cathode	(mg·cm⁻²)		(V)	(h)	
CoFe@N-rGO // CoFeO@N/S-rGO	0.5	1 M KOH	1.63	100	This work
SNCF-NR	3	1 M KOH	1.68	30	Ref. 1
NESSP // NESS	/	1 M KOH	1.74	139	Ref. 2
Ni₃FeN/r-GO-20	0.5	1 M KOH	1.60	100	Ref. 3
CoP/NCNHP	0.4	1 M KOH	1.64	36	Ref. 4
Ni ₃ S ₂ nanosheet	1.6	1 M KOH	>1.7	150	Ref. 5
MoS_2/Ni_3S_2 Heterostructures	9.7	1 M KOH	1.56	10	Ref. 6
NiFe/NiCo ₂ O ₄	/	1 M KOH	1.67	10	Ref. 7
Ni ₂ P//NiO	/	1 M KOH	1.65	30	Ref. 8
cobalt selenide/NiFe	4	1 M KOH	1.67	10	Ref. 9
NiCo ₂ O ₄ //Ni _{0.33} Co _{0.67} S ₂	0.3	1 M KOH	` 1.73	20	Ref. 10
Co ₂ B-500//Co ₂ B-500/NG	5	3 М КОН	1.81	30	Ref. 11
Mo ₂ C/CS	0.4	1 M KOH	1.73	100	Ref. 12
CoFe/NF film	/	1 M KOH	1.64	50	Ref. 13
Co _{5.47} N NP@N-PC	4.5	1 M KOH	1.62	/	Ref. 14
NiNx//CoNi(OH)x	/	1 M KOH	1.64	0.17	Ref. 15
NiFe-P//NiFeOx	/	1 M KOH	< 1.60	24	Ref. 16

 Table S3 Summary of overall-water-splitting performance in 1 M KOH of some recently welldeveloped non-noble electrocatalysts.

[a] E j_{10} indicates the voltage required to afford an water-splitting current density of 10 mA cm⁻².

References

- S1 Y. Zhu, W. Zhou, Y. Zhong, Y. Bu, X. Chen, Q. Zhong, M. Liu and Z. Shao, *Adv. Energy Mater.*, 2017, **7**, 1602122.
- S2 M. S. Balogun, W. Qiu, Y. Huang, H. Yang, R. Xu, W. Zhao, G. R. Li, H. Ji and Y. Tong, *Adv. Mater.*, 2017, **29**, 1702095.
- S3 Y. Gu, S. Chen, J. Ren, Y. A. Jia, C. Chen, S. Komarneni, D. Yang and X. Yao, *ACS Nano*, 2018, **12**, 245-253.
- S4 Y. Pan, K. Sun, S. Liu, X. Cao, K. Wu, W. C. Cheong, Z. Chen, Y. Wang, Y. Li, Y. Liu, D. Wang, Q. Peng,
 C. Chen and Y. Li, *J. Am. Chem. Soc*, 2018, **140**, 2610-2618.
- S5 L. L. Feng, G. Yu, Y. Wu, G. D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, J. Am. Chem. Soc., 2015,

137, 14023-14026.

- S6 J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. Dong, S. Liu, X. Zhuang and X. Feng, *Angew. Chem. Int. Ed.*, 2016, **55**, 6702-6707.
- S7 C. Xiao, Y. Li, X. Lu and C. Zhao, Adv. Funct. Mater., 2016, 26, 3515-3523.
- S8 J. Zheng, W. Zhou, T. Liu, S. Liu, C. Wang and L. Guo, Nanoscale, 2017, 9, 4409-4418.
- S9 Y. Hou, M. R. Lohe, J. Zhang, S. Liu, X. Zhuang and X. Feng, *Energ. Environ. Sci.*, 2016, 9, 478-483.
- S10 Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, Adv. Energy Mater., 2015, 5, 1402031.
- S11 J. Masa, P. Weide, D. Peeters, I. Sinev, W. Xia, Z. Sun, C. Somsen, M. Muhler and W. Schuhmann, *Adv. Energy Mater.*, 2016, **6**, 1502313.
- S12 H. Wang, C. Sun, G. F. Zou, J. W. Huang, X. X. Kuai, J. Q. Zhao and L. J. Gao, *ChemSusChem*, 2017, 10, 3540–3546.
- S13 P. Babar, A. Lokhande, H. H. Shin, B. Pawar, M. G. Gang, S. Pawar and J. H. Kim, *Small*, 2018, **14**, 1702568.
- S14 Z. Chen, Y. Ha, Y. Liu, H. Wang, H. Yang, H. Xu, Y. Li and R. Wu, ACS Appl. Mater. Interfaces, 2018, 10, 7134-7144.
- S15 S. Li, Y. Wang, S. Peng, L. Zhang, A. M. Al-Enizi, H. Zhang, X. Sun and G. Zheng, Adv. Energy Mater., 2016, 6, 1501661.
- S16 J. Wang, L. Ji, S. Zuo and Z. Chen, Adv. Energy Mater., 2017, 7, 1700107.