Supporting Information for

Highly efficient oxygen evolution electrocatalysts prepared by reduction-engraved ferrites on reduced graphene oxides

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Faraday Tests

The detection of oxygen was performed in a one-compartment, three-electrode cell (the volume of the headspace was measured as 35 mL) with stirring. A 1×1 cm of nickel foam electrode with 1.0 mg cm⁻² catalyst loading was used as the working electrode. The counter electrode a 1×1 cm Pt foil and the reference electrode is an Ag/AgCl (saturated KCl solution) electrode. Before oxygen detection, the cell was firmly sealed to be gas-tight and subsequently purged with argon for 30 min. Before and after the electrolysis at a current density of 10 mA cm⁻² for 1 hour, the gas products were analyzed by gas chromatography (Agilent 7820A-GC, molecular sieve columns, thermal-conductivity detector, TCD). The theoretical amount of O₂ produced was calculated by the charge of electrolysis for 1 hour.

Samples	Co (mmol)	Ni (mmol)	Fe (mmol)	Molar ratio of Co : Ni : Fe
	0.301	0.329	1.451	
CNFg	0.320	0.344	1.525	1.000 : 1.083 : 4.788
	0.321	0.347	1.535	
	0.279	0.318	1.400	
r-	0.280	0.301	1.352	1.000 : 1.096 : 4.882
CNFg	0.280	0.302	1.350	

Table S1. ICP-AES results of CNFg and r-CNFg.



Figure S1. TGA curve for CNFg under an air atmosphere.



Figure S2. Size distribution of CNFg.



Figure S3. SEM images of a) NFg, b) r-NFg, c) CNFg, d) r-CNFg, e) CFg and f) r-CFg.



Figure S4. a) HAADF-STEM image of **CNFg**, b-f) elemental mappings of r-**CNFg**, revealing the elemental distribution of C, O, Co, Ni and Fe.



Figure S5. a) TEM and b) HRTEM images of **NFg**; c) SAED pattern and d) HAADF-STEM image of **NFg**; e-h) elemental mappings of **NFg**, revealing the elemental distribution of C, O, Ni and Fe.



Figure S6. a) TEM and b) HRTEM images of r-**NFg**; c) SAED pattern and d) HAADF-STEM image of r-**NFg**; e-h) elemental mappings of r-**NFg**, revealing the elemental distribution of C, O, Ni and Fe.



Figure S7. a) TEM and b) HRTEM images of **CFg**; c) SAED pattern and d) HAADF-STEM image of **CFg**; e-h) Elemental mappings of **CFg**, revealing the elemental distribution of C, O, Co and Fe.



Figure S8. a) TEM and b) HRTEM images of r-**CFg**; c) SAED pattern and d) HAADF-STEM image of r-**CFg**; e-h) Elemental mappings of r-**CFg**, revealing the elemental distribution of C, O, Co and Fe.



Figure S9. PXRD patterns of $Co_x Ni_{1-x} Fe_2 O_4 @GO$ with different Co : Ni stoichiometric ratios (x = 0.1, 0.3, 0.5, 0.7, 0.9) and their reduced counterparts.



Figure S10. FT-IR spectra of GO, spinel ferrite composites and their reduced composites.



Figure S11. LSVs of r-CNFg, GO, r-GO, CNF, r-CNF and CNFg on NF (catalyst loading of ~ 1.5 mg cm^{-2}) measured in 1.0 M KOH solution with the scan rate of 1.0 mV s⁻¹.



Figure S12. LSVs of r-Co_xNi_{1-x}Fe₂O₄@GO (x = 0.1, 0.3, 0.5, 0.7, 0.9) on the nickel foam (catalyst loading of ~ 1.5 mg cm⁻²) measured in 1.0 M KOH solution with the scan rate of 1.0 mV s⁻¹.



Figure S13. Chronopotentiometric curves obtained with different loading amount of r-CNFg ($0.25 \sim 2.00 \text{ mg cm}^{-2}$) on Ni foam with constant current densities of 10 mA cm⁻².



Figure S14. a) Chronopotentiometric curves of spinel composites (**CNFg**, **CFg** and **NFg**), their reduced forms (**r-CNFg**, **r-CFg** and **r-NFg**), and IrO₂ with constant current density of 10 mA cm⁻²; b) Chronopotentiometric curve obtained with **r-CNFg** on nickel foam with constant current density of 20 mA cm⁻².



Figure S15. XPS spectra of r-CNFg before and after electrolysis.



Figure S16. O_2 production measured by GC (black line) and the theoretical amount of O_2 produced (red line) for r-CNFg, assuming a Faradic efficiency of ca. 100%.



Figure S17. GC results of the gas products after electrolysis of with r-CNFg catalysts. There are no peaks at 6 min and 44 min, which appeared as the existence of CO and CO₂, respectively.

		η (mV) @	Tafel slope	References	
Catalysts	Electrolyte	10 mA cm ⁻²	(mV dec ⁻¹)		
CNFg	1.0 M KOH	290	58	This work	
r-CNFg	1.0 M KOH	210	35	This work	
CFg	1.0 M KOH	290	57	This work	
r-CFg	1.0 M KOH	220	31	This work	
NFg	1.0 M KOH	300	62	This work	
r-NFg	1.0 M KOH	220	37	This work	
NiFe ₂ O ₄	1.0 M KOH	381	46.4	Ref 1	
amorphous CoFe ₂ O ₄	0.1 M KOH	490	48	Ref 2	
crystalline CoFe ₂ O ₄	0.1 M KOH	560	61	Ref 2	
CoFe ₂ O ₄ NPs-on-CFP	1.0 M KOH	378	73	Ref 3	
NiO-NiFe ₂ O ₄ /rGO	1.0 M KOH	296	42.8	Ref 4	
CoFe ₂ O ₄ /PANI-MWCNTs	1.0 M KOH	314	30.69	Ref 5	
CoFe ₂ O ₄ /C NRAs	1.0 M KOH	240	45	Ref 6	
rGO/NiMnCo spinel oxides	0.1 M KOH	320	58	Ref 7	
NiCo ₂ O ₄ nanosheet	1.0 M KOH	320	30	Ref 8	
NiCo ₂ O ₄ Hollow Microcuboids	1.0 M KOH	290	53	Ref 9	
CoMn ₂ O ₄	0.1 M KOH	~600	64	Ref 10	
MnCo ₂ O ₄	0.1 M KOH	~510	55	Ref 10	

Table S2. A comparison of the OER overpotentials for the reported spinel oxide catalysts in basic solution.



Figure S18. CVs of (a, b) **NFg** and **CFg**; (c, d) r-**NFg** and r-**CFg** in 1.0 M KOH solution at varying scan rates, with the plots of the capacitive current density as a function of scan rates (e, f).



Figure S19. N₂ absorption isotherms of GO, CNFg and r-CNFg at 77 K.



Figure S20. Water vapor absorption isotherms of CNF and r-CNF at 298 K.



Figure S21. TGA curves for CNF and r-CNF under an air atmosphere.



Figure S22. XPS spectra of O 1s of CNF and r-CNF.

Reference

- 1 V. Maruthapandian, M. Mathankumar, V. Saraswathy, B. Subramanian and S. Muralidharan, ACS Appl Mater Interfaces, 2017, **9**, 13132-13141.
- A. Indra, P. W. Menezes, N. R. Sahraie, A. Bergmann, C. Das, M. Tallarida, D. Schmeisser, P. Strasser and M. Driess, J. Am. Chem. Soc., 2014, 136, 17530-17536.
- A. Kargar, S. Yavuz, T. K. Kim, C. H. Liu, C. Kuru, C. S. Rustomji, S. Jin and P. R. Bandaru, ACS Appl Mater Interfaces, 2015, **7**, 17851-17856.
- 4 G. Q. Zhang, Y. F. Li, Y. F. Zhou and F. L. Yang, *Chemelectrochem*, 2016, **3**, 1927-1936.
- 5 Y. Liu, J. Li, F. Li, W. Z. Li, H. D. Yang, X. Y. Zhang, Y. S. Liu and J. T. Ma, *J. Mater. Chem. A*, 2016, **4**, 4472-4478.
- 6 X. F. Lu, L. F. Gu, J. W. Wang, J. X. Wu, P. Q. Liao and G. R. Li, *Adv. Mater.*, 2017, **29**, 1604437.
- 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.*, 2017, 7, 819-832.
- 8 J. Bao, X. Zhang, B. Fan, J. Zhang, M. Zhou, W. Yang, X. Hu, H. Wang, B. Pan and Y. Xie, Angew. Chem. Int. Ed., 2015, 54, 7399-7404.
- X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang and Z. Lin, *Angew. Chem. Int. Ed.*, 2016, 55, 6290-6294.
- 10 P. W. Menezes, A. Indra, N. R. Sahraie, A. Bergmann, P. Strasser and M. Driess, *ChemSusChem*, 2015, **8**, 164-171.