Supporting Information

Design of 2D nanocrystalline Fe₂Ni₂N coated onto graphene nanohybrid sheets for efficient electrocatalytic oxygen evolution

Sung Hoon Kwag,^{a,§} Yang Soo lee,^{b,§} Jooyoung Lee,^b Dong In Jeong,^b Seok Bin Kwon,^b Jung Hyeon Yoo,^b Seongwon Woo,^b Byeong Seok Lim,^a Won Kyu Park,^c Min-Jun Kim,^d Jung Ho Kim,^{e,f} Byungkwon Lim,^b Bong Kyun Kang,^{*,a} Woo Seok Yang^{*,a} and Dae Ho Yoon^{*,b}

^aNano Materials and Components Research Center, Korea Electronics Technology Institute, 25, Saenari-ro, Bundang-gu, Seongnam-si, Gyeonggi-do 13509, Republic of Korea

^bSchool of Advanced Materials Science and Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 16419, Republic of Korea

^eNano Material Division, Cheorwon Plasma Research Institute, Cheorwon, Gangwon, 24047,

Republic of Korea

^dAdvanced Materials & Processing Center, Institute for Advanced Engineering (IAE), Yongin, 17180, Republic of Korea

^eAustralian Institute for Innovative Materials (AIIM), University of Wollongong, Squires Way, North Wollongong, NSW 2500, Australia

^fDepartment of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, 1732 Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do, 17104, Republic of

Korea

*Corresponding Author: B. K. K, W. S. Y, and D. H. Y, E-mail: <u>kangbk84@keti.re.kr</u>, <u>wsyang@keti.re.kr</u>, and dhyoon@skku.edu

Keywords: Transition metal nitride, 2D structures, Graphene, Oxygen evaluation reaction, Electrolysis

[§]These authors contributed equally to this work.



Figure S1. Wide angle PXRD pattern of the 2D-NC Fe_xNi_yN/rGO NHSs via 2D Ni_xFe_3 . $x[Fe(CN)_6]_2/rGO$ (x = 0 to 3) precursors at 450°C for 2 hours with co-atmosphere of N₂ (200 sccm) and NH₃ (50 sccm).



Figure S2. FTIR spectra of the as-prepared 2D-NC Fe₂Ni₂N/rGO NHSs and 2D Ni_{2.25}Fe_{0.75}[Fe(CN)₆]₂/rGO precursors.



Figure S3. XPS wide scan of the as-prepared 2D-NC Fe₂Ni₂N@rGO NHSs.



Figure S4. FESEM images of synthesized (a) $NiFe_2O_4$ and (b) $Fe_2Ni_2N NPs$. (c) PXRD pattern of the synthesized $NiFe_2O_4$ and $Fe_2Ni_2N NPs$ by LPP method.



Figure S5. CVs scanned at different rates from 2 to 10 mV s⁻¹ in the potential range of 1.0–1.12 V vs. RHE for the (a) 2D-NC Fe₂Ni₂N/rGO NHSs, (b) Fe₂Ni₂N, and (c) NiFe₂O₄ NPs electrodes.



Figure S6. (a) XPS wide scan and spectra of high-resolution (b) C 1s of the 2D-NC Fe₂Ni₂N/rGO NHSs after OER.

Matariala	Overpotential		Electrolyte	Pof
Materials	(at 10 mA cm ⁻²))	Electrolyte	Kel.
2D Fe₂Ni₂N/Graphene hybrid sheets	290 mV	49.1 mV dec ⁻¹	0.1 М КОН	Our research
Fe2Ni2N/CNTs	282 mV	38 mV dec ⁻¹	1 M KOH	1
Fe₂Ni₂N Nanoarrays	420 mV	34 mV dec ⁻¹	1 M KOH	2
Nanoparticles- stacked porous Ni₃FeN nanosheets	223 mV	40 mV dec ⁻¹	1 M KOH	3
Ni₃FeN microspheres	355 mV	70 mV dec ⁻¹	1 М КОН	4
[Ni,Fe]O nanoparticles	300 mV	50 mV dec ⁻¹	0.1 M KOH	5
Fe-doped NiO _x nanotubes	310 mV	49 mV dec ⁻¹	1 M KOH	6
Mesoporous NiO/NiFe ₂ O ₄ biphasic Nanorods	302 mV	42 mV dec ⁻¹	1 M KOH	7
nNiFe LDH/NGF	337 mV	73 mV dec ⁻¹	0.1 M KOH	8
Ni–P porous Nanoplates	300 mV	64 mV dec ⁻¹	1 M KOH	9
NiS _x films	353 mV	41 mV dec ⁻¹	1 M KOH	10

Table S1. Comparison of OER performance of different non-noble transition metal based electrocatalysts.

References

- Chen, X.; Gao, P.; Liu, H.; Xu, J.; Zhang, B.; Zhang, Y.; Tang, Y.; Xiao, C. In situ growth of iron-nickel nitrides on carbon nanotubes with enhanced stability and activity for oxygen evolution reaction. *Electrochim. Acta* 2018, 267, 8-14.
- Jiang, M.; Li, Y.; Lu, Z.; Sun, X.; Duan, X. Binary nickel–iron nitride nanoarrays as bifunctional electrocatalysts for overall water splitting. *Inorg. Chem. Front.* 2016, *3*, 630-634.
- Wang, Y.; Xie, C.; Liu, D.; Huang, X.; Huo, J.; Wang, S. Nanoparticle-Stacked Porous Nickel–Iron Nitride Nanosheet: A Highly Efficient Bifunctional Electrocatalyst for Overall Water Splitting. ACS Appl. Mater. Interfaces 2016, 8, 18652-18657.
- Fu, G.; Cui, Z.; Chen, Y.; Xu, L.; Tang, Y.; Goodenough, J. B. Hierarchically mesoporous nickel-iron nitride as a cost-efficient and highly durable electrocatalyst for Zn-air battery. *Nano Energy* 2017, *39*, 77-85.
- Bau, J. A.; Luber, E. J.; Buriak, J. M. Oxygen Evolution Catalyzed by Nickel–Iron Oxide Nanocrystals with a Nonequilibrium Phase. *ACS Appl. Mater. Interfaces*, 2015, 7, 19755-19763.
- Wu, G.; Chen, W.; Zheng, X.; He, D.; Luo, Y.; Wang, X.; Yang, J.; Wu, Y.; Yan, W.; Zhuang, Z.; Hong, X.; Li, Y. Hierarchical Fe-doped NiO_x nanotubes assembled from ultrathin nanosheets containing trivalent nickel for oxygen evolution reaction *Nano Energy* 2017, *38*, 167-174.

- Liu, G.; Gao, X.; Wang, K.; He, D.; Li, J. Uniformly mesoporous NiO/NiFe₂O₄ biphasic nanorods as efficient oxygen evolving catalyst for water splitting. *Int. J. Hydrog. Energy* 2016, *41*, 17976-17986.
- Tang, C.; Wang, H. S.; Wang, H. F.; Zhang, Q.; Tian, G. L.; Nie, J. Q.; Wei, F. Spatially Confined Hybridization of Nanometer-Sized NiFe Hydroxides into Nitrogen-Doped Graphene Frameworks Leading to Superior Oxygen Evolution Reactivity. *Adv. Mater.* 2015, 27, 4516-4522.
- Yu, X. Y.; Feng, Y.; Guan, B.; Lou, X. W.; Paik, U. Carbon coated porous nickel phosphides nanoplates for highly efficient oxygen evolution reaction. *Energy Environ. Sci.* 2016, 9, 1246-1250.
- Li, H.; Shao, Y.; Su, Y.; Gao, Y.; Wang, X. Vapor-Phase Atomic Layer Deposition of Nickel Sulfide and Its Application for Efficient Oxygen-Evolution Electrocatalysis. *Chem. Mater.* 2016, 28, 1155-1164.