Supporting Information

Multi-Shelled Cobalt-Nickel Oxide/Phosphide Hollow Spheres for Efficient Oxygen Evolution Reaction

Yaru Yang,^a Hao Wan,^a Gen Chen,^a Ning Zhang,^a Junhui Li,^a Wei Ma,^b Xiaohe Liu^{a,b,*} & Renzhi Ma^{c,*}

^aSchool of Materials Science and Engineering, Central South University, Changsha, Hunan

410083, P. R. China. E-mail: liuxh@csu.edu.cn

^b School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, P.R. China.

^cInternational Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan. E-mail: <u>MA.Renzhi@nims.go.jp</u>



Figure S1. The energy dispersive X-ray spectrum for the multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide. The signal of Al in the EDX spectrum was derived from the conductive aluminum foil substrate used for the FESEM measurement.



Figure S2. FESEM images of (a) $Co_{0.5}Ni_{0.5}$ CPS, (b) multi-shelled $Co_{0.5}Ni_{0.5}$ oxide and (c) multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide. (d) XPS spectrum of elements surveys for multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide.



Figure S3. XPS high-resolution spectra of (a) Co 2p, (b) Ni 2p, (c) O 1s and (d) P 2p for multi-shelled $Co_{0.9}Ni_{0.1}$ oxide/phosphide (upper), and multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide (bottom).



Figure S4. Cyclic voltammetry (CV) curves for (a) $Co_{0.9}Ni_{0.1}$ oxide/phosphide, (b) $Co_{0.6}Ni_{0.4}$ oxide/phosphide, (c) $Co_{0.5}Ni_{0.5}$ oxide/phosphide, (d) $Co_{0.4}Ni_{0.6}$ oxide/phosphide, (e) $Co_{0.1}Ni_{0.9}$ oxide/phosphide and (f) bare carbon paper at incremental scan rates in the potential range of 1.3 - 1.4 V vs RHE.



Figure S5. Polarization curves after being normalized by ECSA for multi-shelled Co_xNi_{1-x} oxide/phosphide electrocatalysts. (i) $Co_{0.9}Ni_{0.1}$ oxide/phosphide, (ii) $Co_{0.6}Ni_{0.4}$ oxide/phosphide, (iii) $Co_{0.5}Ni_{0.5}$ oxide/phosphide, (iv) $Co_{0.4}Ni_{0.6}$ oxide/phosphide and (v) $Co_{0.1}Ni_{0.9}$ oxide/phosphide.



Figure S6. (a) Nyquist plots obtained at overpotentials@10 mA cm⁻² and (b) Chronopotentiometric curve of multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide catalyst at a constant current density of 10 mA cm⁻². (i) $Co_{0.9}Ni_{0.1}$ oxide/phosphide, (ii) $Co_{0.6}Ni_{0.4}$ oxide/phosphide, (iii) $Co_{0.5}Ni_{0.5}$ oxide/phosphide, (iv) $Co_{0.4}Ni_{0.6}$ oxide/phosphide and (v) $Co_{0.1}Ni_{0.9}$ oxide/phosphide.



Figure S7. FESEM images of multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide after OER test under different magnifications.



Figure S8. XPS high-resolution spectra of (a) Co 2p, (b) Ni 2p, (c) O 1s and (d) P 2p for multi-shelled $Co_{0.5}Ni_{0.5}$ oxide/phosphide before (upper) and after (bottom) OER test.

Materials	$R_{s}\left(\Omega ight)$	$R_{ct}(\Omega)$
Co _{0.9} Ni _{0.1} oxide/phosphide	6.2	210.9
Co _{0.6} Ni _{0.4} oxide/phosphide	5.2	96.5
Co _{0.5} Ni _{0.5} oxide/phosphide	3.7	4.7
Co _{0.4} Ni _{0.6} oxide/phosphide	3.2	100.2
Co _{0.1} Ni _{0.9} oxide/phosphide	3.9	27.4

Table S1. The estimated values of R_s , and R_{ct} .

Table S2. Comparison of electrocatalytic performance of different typical materials (in 1 MKOH).

Materials	Overpotentials (mV)	Tafel slopes (mV dec ⁻¹)	References
NiCoP Film	275	87	References ¹
Co _{0.9} Ni _{0.1} P@NNCS hierarchical nanostructure	221	54	References ²
Ni/Co-P-1/1 nanoparticles	360	60	Reference ³
Ni-Co-P hollow nanobricks	270	76	Reference ⁴
Ni-Co-P nanosheets	290	88	Reference ⁴
NiFeO _x @NiFe-P core- shell metal oxides/phosphides	477	75	Reference ⁵
Multi-shelled Co _{0.5} Ni _{0.5} oxide/phosphide hollow spheres	268	41.4	This work

Table S3. Comparison of EDS test results for the multi-shelled $Co_x Ni_{1-x}$ oxide/phosphide.

Materials	Co (wt%)	Ni (wt%)
Co _{0.9} Ni _{0.1} oxide/phosphide	35.18	4.38
Co _{0.6} Ni _{0.4} oxide/phosphide	18.29	10.84
Co _{0.5} Ni _{0.5} oxide/phosphide	32.47	30.79
Co _{0.4} Ni _{0.6} oxide/phosphide	18.25	26.23
Co _{0.1} Ni _{0.9} oxide/phosphide	7.17	63.13

REFERENCES

- 1 T. Wang, X. Liu, Z. Yan, Y. Teng, R. Li, J. Zhang and T. Peng, ACS Sustainable Chem. Eng., 2020, 8, 1240.
- 2 G. B. Darband, M. Aliofkhazraei, S. Hyun, A. S. Rouhaghdam and S. Shanmugam, *J. Power Sources*, 2019, **429**, 156.

- H. Zheng, X. Huang, H. Gao, G. Lu, A. Li, W. Dong and G. Wang, *Appl. Surf. Sci.*, 2019, 479, 1254.
- E. Hu, Y. Feng, J. Nai, D. Zhao, Y. Hu and X. W. Lou, *Energy Environ. Sci.*, 2018, 11, 872.
- 5 Q. Hu, X. Liu, C. Tang, L. Fan, X. Chai, Q. Zhang, J. Liu and C. He, *Sustainable Energy Fuels*, 2018, **2**, 1085.