Supporting Information:

Dual-doping of ruthenium and nickel into Co_3O_4 nanoparticles for improving oxygen evolution activity

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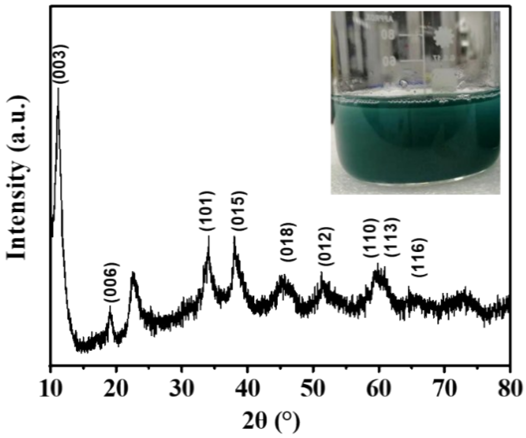

Figure S1. The XRD image of the as-prepared cobalt hydroxide nanoparticles by precipitation method without hydrothermal process. The inset is the photograph of the cobalt hydroxide nanosheets.

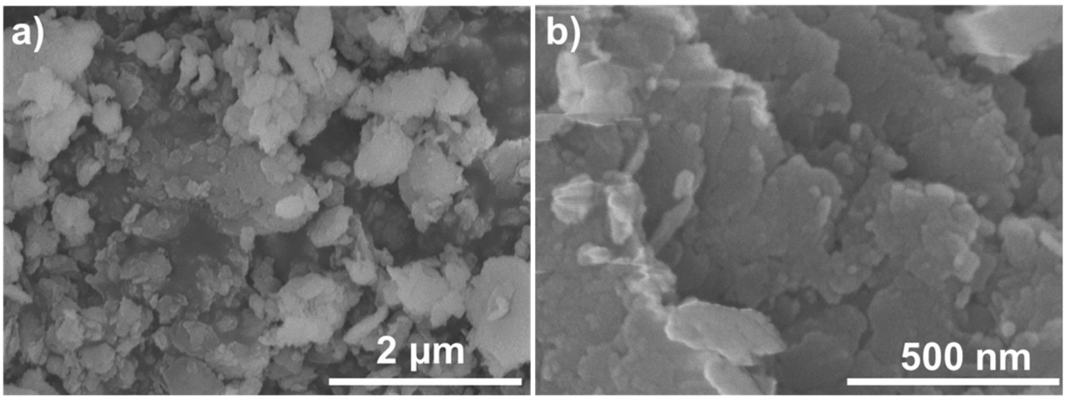

Figure S2. The SEM image of the as-prepared cobalt hydroxide nanoparticles by precipitation method without hydrothermal process.

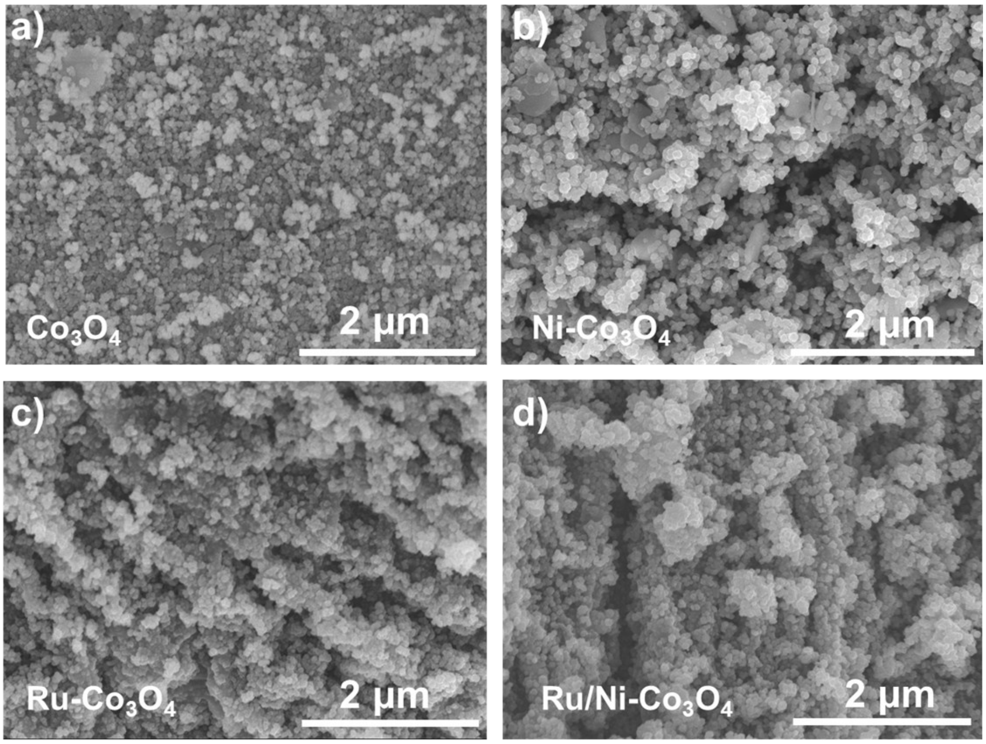

Figure S3. SEM image of (a) Co_3O_4, (b) Ni-Co_3O_4, (c) Ru-Co_3O_4 and (d) Ru/Ni-Co_3O_4 nanoparticles by hydrothermal process.

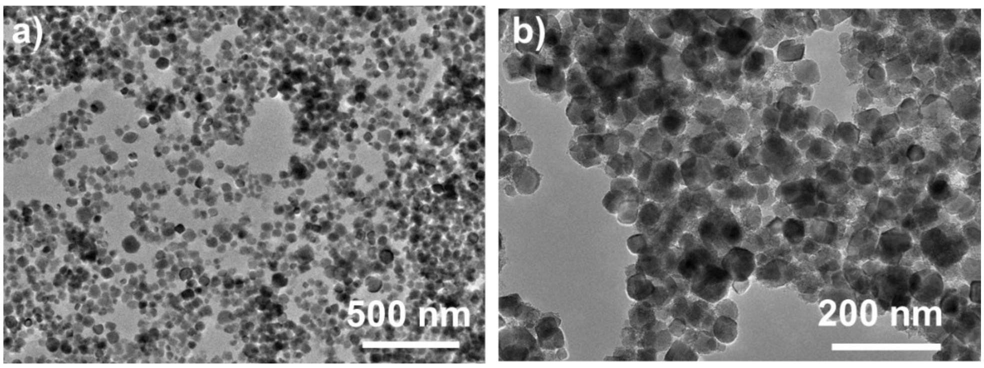

Figure S4. TEM image of Ru/Ni-Co_3O_4 nanoparticles at different magnifications.

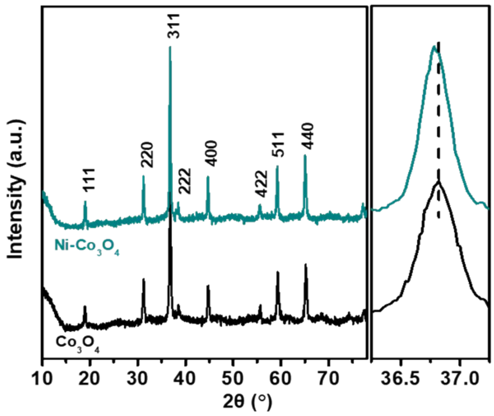

Figure S5. XRD patterns of Co_3O_4 and Ni-Co_3O_4.

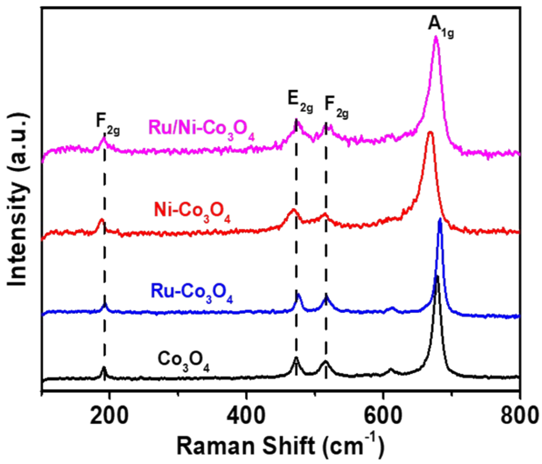

Figure S6. Raman spectra of the as-prepared spinel oxides.

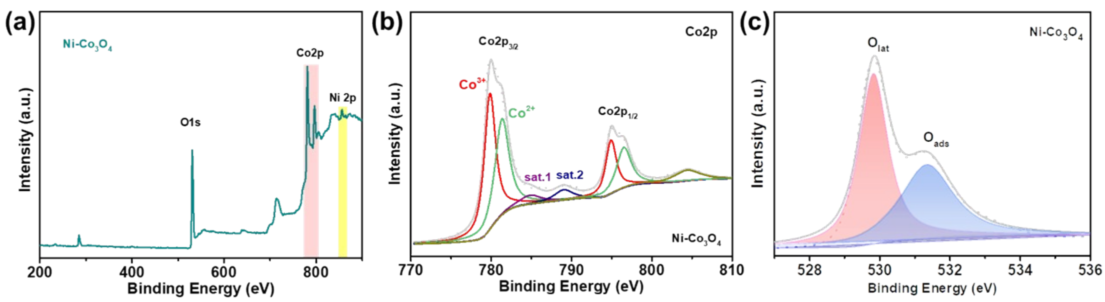

Figure S7. a) XPS survey spectra, and (b-c) high-resolution XPS b) Co2p, c) O1s spectra of Ni-Co_3O_4.

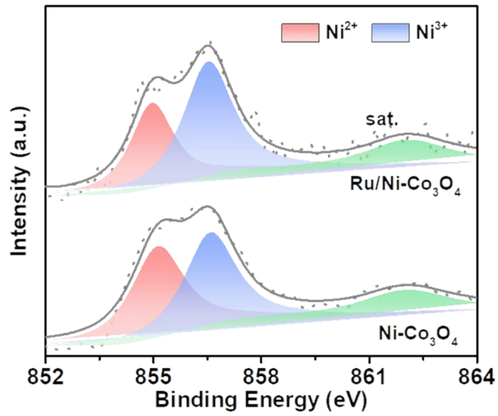

Figure S8. High-resolution Ni2p spectra of Ni-Co_3O_4 and Ru/Ni-Co_3O_4.

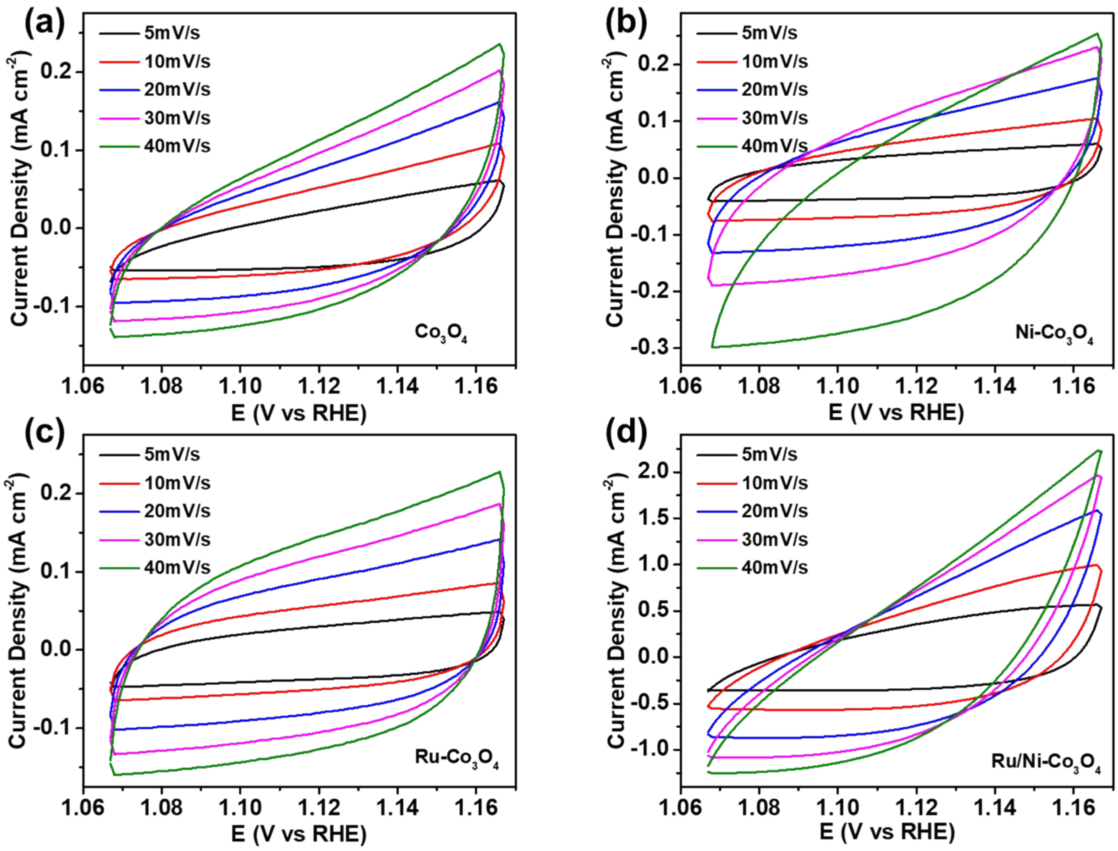

Figure S9. CVs at different scan rates in a potential window range from 0 to 0.1 V versus RHE for (a) Co_3O_4, (b) Ni-Co_3O_4, (c) Ru-Co_3O_4 and (d) Ru/Ni-Co_3O_4.

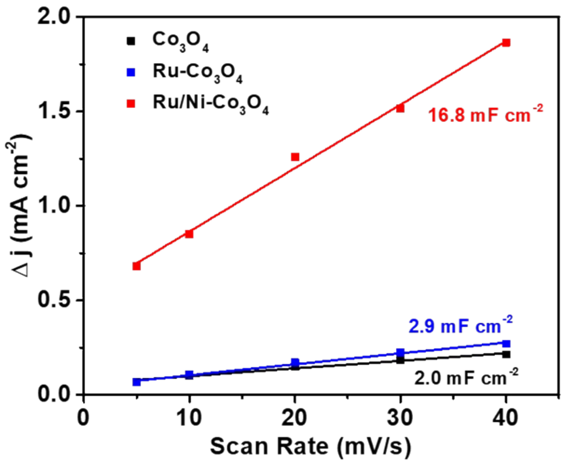

Figure S10. Current density as a function of the scan rate for the different electrodes.

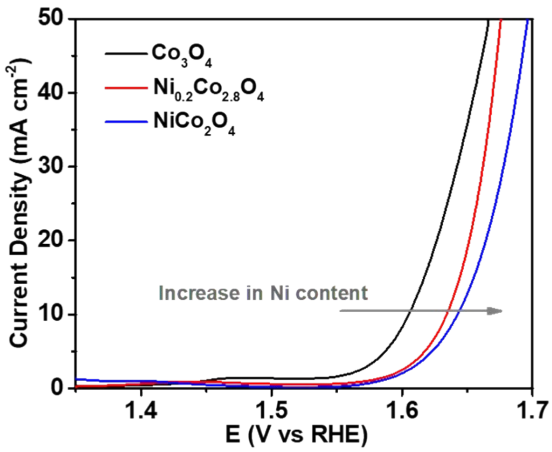

Figure S11. Polarization curves of Ni-Co_3O_4.

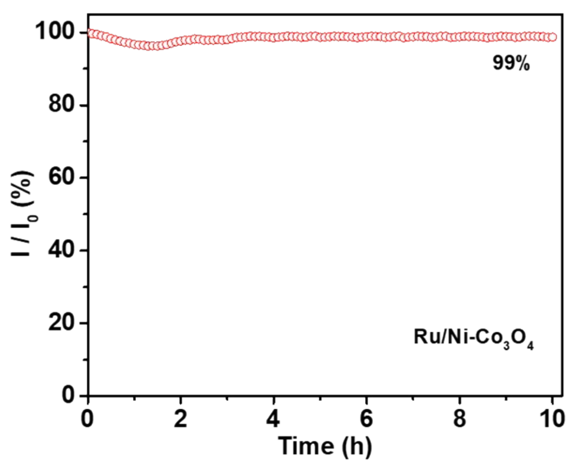

Figure S12. Chronoamperometric durability test of Ru/Ni-Co_3O_4.

Table S1. The composition analysis of XPS spectra.

Catalyst	Co (at%)	O (at%)	Ni (at%)	Ru (at%)
Co_3O_4	34.77	65.23	/	/
Ru-Co_3O_4	28.66	67.13	/	4.21
Ni-Co_3O_4	27.41	70.77	1.82	/
Ru/Ni-Co_3O_4	25.06	69.42	1.05	4.47

Table S2. Cobalt contents in the as-prepared spinel oxides.

Catalyst	Co^{3+} (%)	Co^{2+} (%)	Co^{3+} / Co^{2+}
Co_3O_4	60.9	39.1	1.5
Ru-Co_3O_4	59.0	41.0	1.4
Ni-Co_3O_4	53.4	46.6	1.2
Ru/Ni-Co_3O_4	52.0	48.0	1.1

Table S3. Nickel contents in the as-prepared spinel oxides.

Catalyst	Ni^{2+} (%)	Ni^{3+} (%)	Ni^{3+} / Ni^{2+}
Co_3O_4	71.7	28.3	2.5
Ru-Co_3O_4	54.1	45.9	1.2
Ni-Co_3O_4	56.3	43.7	1.3
Ru/Ni-Co_3O_4	44.7	55.3	0.8

Table S4. Oxygen contents in the as-prepared spinel oxides.

Catalyst	O_{latt} (%)	O_{ads} (%)	O_{latt} / O_{ads}
Ni-Co_3O_4	56.3	43.7	1.3
Ru/Ni-Co_3O_4	44.7	55.3	0.8

Table S5. Comparison of catalytic performance of the as-prepared spinel oxides to some reported spinel oxide catalysts.

Catalysts	η (mV) @ 10 mA cm^{-2}	Electrolyte	Substrate	Reference
Ru/Ni-Co_3O_4	290	1 M KOH	Glassy carbon	**This work**
Hierarchical $NiCo_2O_4$ hollow	290	1 M KOH	Ni foam	1
Co_3O_4/$NiCo_2O_4$ DSNCs	340	1 M KOH	Ni foam	2
$CoV_{1.5}Fe_{0.5}O_4$ spinel	300	1 M KOH	Glassy carbon	3
$NiCo_2O_4$ nanoneedles	323	1 M KOH	FTO	4
$ZnCo_2O_4$	389	1 M KOH	Glassy carbon	5
$NiCo_2O_4$@MnO_2 core-shell	337	1 M KOH	Carbon	6
Fe-$NiCo_2O_4$ nanowire	350	1 M KOH	Ni foam	7
Zn-$NiCo_2O_4$ particles	560	0.1 M KOH	Glassy carbon	8
MoS_2/rFe-NiCo2O4	270	1 M NaOH	Carbon paper	9
$CoFe_2O_4$	300	0.1 M KOH	Glassy carbon	10
NiCoFe@NiCoFeO NTAs/CFC	201	1 M NaOH	Carbon fiber	11
IrO_2	300	1 M KOH	Glassy carbon	**This work**

References for Supporting Information:

[1] X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang and Z. Lin, Hierarchical $NiCo_2O_4$ Hollow Microcuboids as Bifunctional Electrocatalysts for Overall Water-Splitting, *Angew. Chem. Int. Ed.*, 2016, **55**, 6290-6294.

[2] H. Hu, B. Guan, B. Xia and X.W. Lou, Designed Formation of Co_3O_4/$NiCo_2O_4$ Double-Shelled Nanocages with Enhanced Pseudocapacitive and Electrocatalytic Properties, *J. Am. Chem. Soc.*, 2015, **137**, 5590-5595.

[3] K. Chakrapani, G. Bendt, H. Hajiyani, T. Lunkenbein, M.T. Greiner, L. Masliuk, S. Salamon, J. Landers, R. Schlögl, H. Wende, R. Pentcheva, S. Schulz and M. Behrens, The Role of Composition of Uniform and Highly Dispersed Cobalt Vanadium Iron Spinel Nanocrystals for Oxygen Electrocatalysis, *ACS Catal.*, 2018, **8**, 1259-1267.

[4] H. Shi and G. Zhao, Water Oxidation on Spinel $NiCo_2O_4$ Nanoneedles Anode: Microstructures, Specific Surface Character, and the Enhanced Electrocatalytic Performance, *J. Phys. Chem. C*, 2014, **118**, 25939-25946.

[5] J. Zhang, D. Zhang, Y. Yang, J. Ma, S. Cui, Y. Li and B. Yuan, Facile synthesis of $ZnCo_2O_4$ mesoporous structures with enhanced electrocatalytic oxygen evolution reaction properties, *RSC Adv.*, 2016, **6**, 92699-92704.

[6] H. Xue, H. Yu, Y. Li, K. Deng, Y. Xu, X. Li, H. Wang and L. Wang, Spatially-controlled $NiCo_2O_4$@MnO_2 core-shell nanoarray with hollow $NiCo_2O_4$ cores and MnO_2 flake shells: an efficient catalyst for oxygen evolution reaction, *Nanotechnol.*2018, **29**, 285401.

[7] K.L. Yan, X. Shang, Z. Li, B. Dong, X. Li, W.K. Gao, J.Q. Chi, Y.M. Chai and C.G. Liu, Ternary mixed metal Fe-doped $NiCo_2O_4$ nanowires as efficient electrocatalysts for oxygen evolution reaction, *Appl. Surf. Sci.*, 2017, **416**,

371-378.
[8] M. Yang, Y. Li, Y. Yu, X. Liu, Z. Shi and Y. Xing, Self-Assembly of Three-Dimensional Zinc-Doped $NiCo_2O_4$ as Efficient Electrocatalysts for Oxygen Evolution Reaction, *Chem.*, 2018, **24**, 13002-13008.
[9] J. Li, D. Chu, H. Dong, D.R. Baker and R. Jiang, Boosted Oxygen Evolution Reactivity by Igniting Double Exchange Interaction in Spinel Oxides, *J. Am. Chem. Soc.*, 2020, **142**, 50-54.
[10] S. Pal, U.P. Azad, A.K. Singh, D. Kumar and R. Prakash, Studies on some spinel oxides based electrocatalysts for oxygen evolution and capacitive applications, *Electrochim. Acta*, 2019, **320**, 134584.
[11] Y. Liu, Y. Ying, L. Fei, Y. Liu, Q. Hu, G. Zhang, S.Y. Pang, W. Lu, C.L. Mak, X. Luo, L. Zhou, M. Wei and H. Huang, Valence Engineering via Selective Atomic Substitution on Tetrahedral Sites in Spinel Oxide for Highly Enhanced Oxygen Evolution Catalysis, *J. Am. Chem. Soc.*, 2019, **141**, 8136-8145.