Supporting Information：

Metal organic frameworks-derived yolk-shell structured cobalt-based bimetallic oxide polyhedron with high activity for electrocatalytic oxygen evolution

Zhou Yu,[†, ‡] Yu Bai, *[, ‡, #] Yuxuan Liu,[†] Shimin Zhang,[†] Dandan Chen,[†] Naiqing Zhang,[‡, §] and Kening Sun, *[, ‡, §]

[†]School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150090, PR China

[‡]Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150001, China

[#]Advanced Research Institute for Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, PR China

[§]State Key laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China

*E-mail: yubaiit@163.com (B Yu)

*E-mail: keningsunhit@126.com (KN Sun)

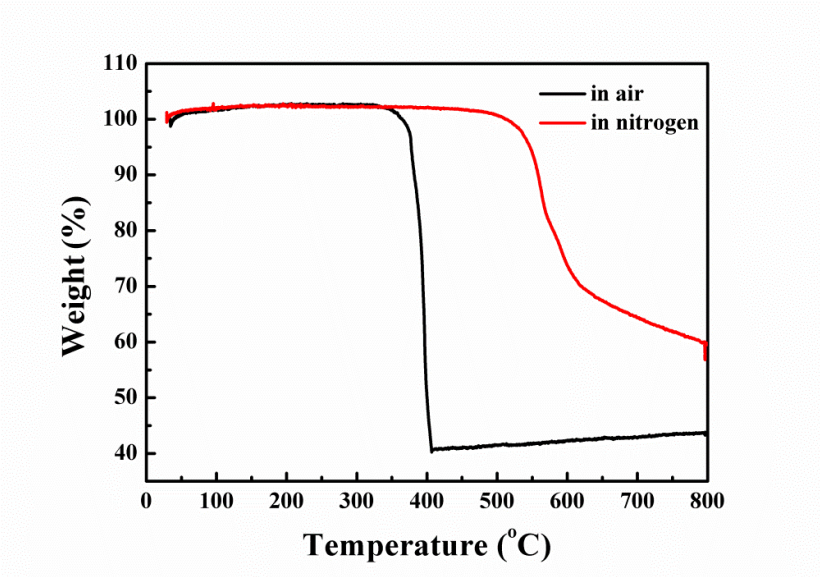

Fig. S1 TGA curves of ZnCo-ZIFs under air and nitrogen atmosphere with a ramp of 10 °C min^{-1}.

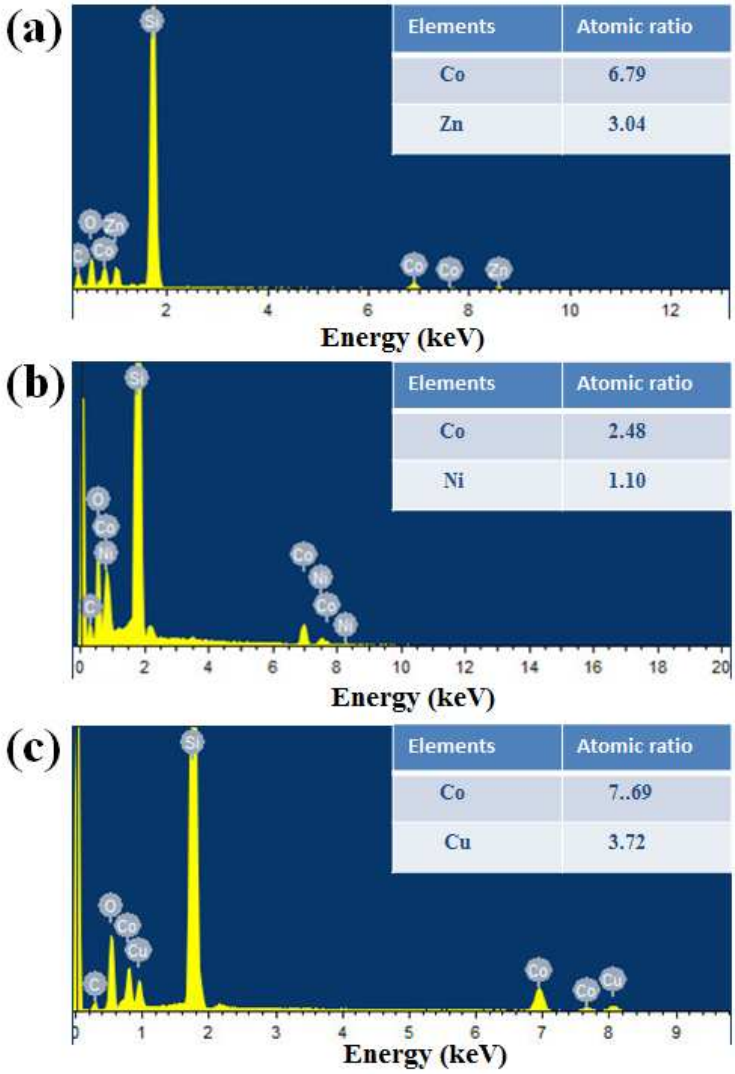

Fig. S2 EDS patterns of (a) $Zn_xCo_{3-x}O_4$ YSP, (b) $Ni_xCo_{3-x}O_4$ YSP and (c) $Cu_xCo_{3-x}O_4$ YSP.

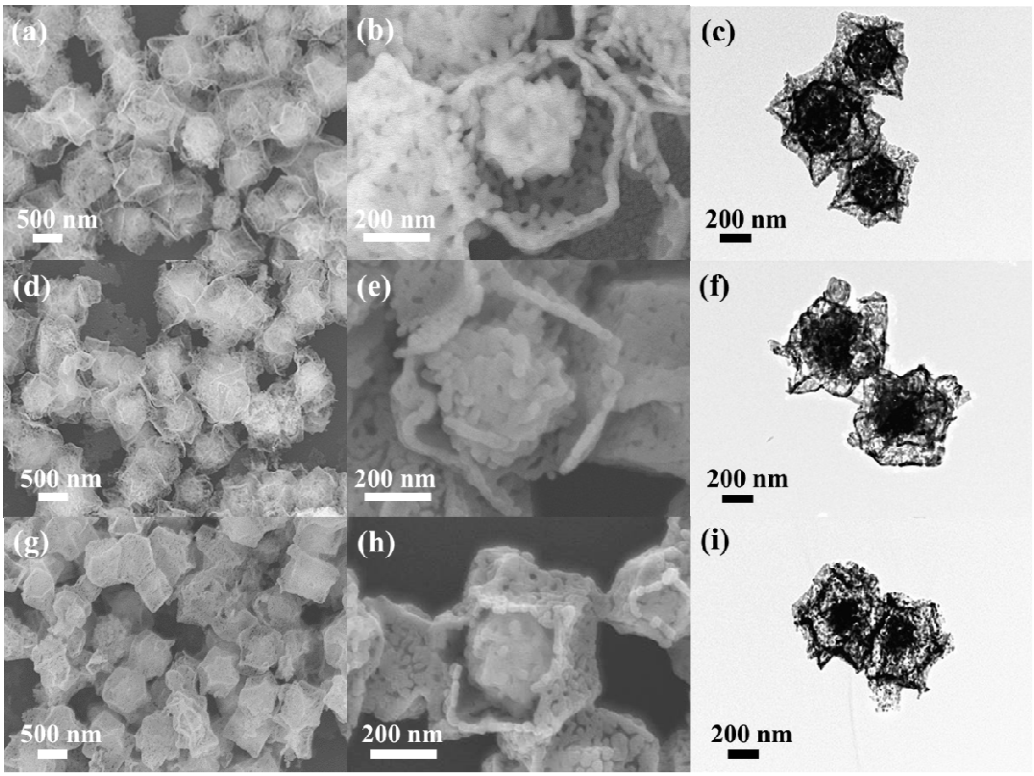

Fig. S3 FESEM and TEM images of (a-c) $Ni_xCo_{3-x}O_4$ YSP, (d-f) $Cu_xCo_{3-x}O_4$ YSP and (g-i) Co_3O_4 YSP.

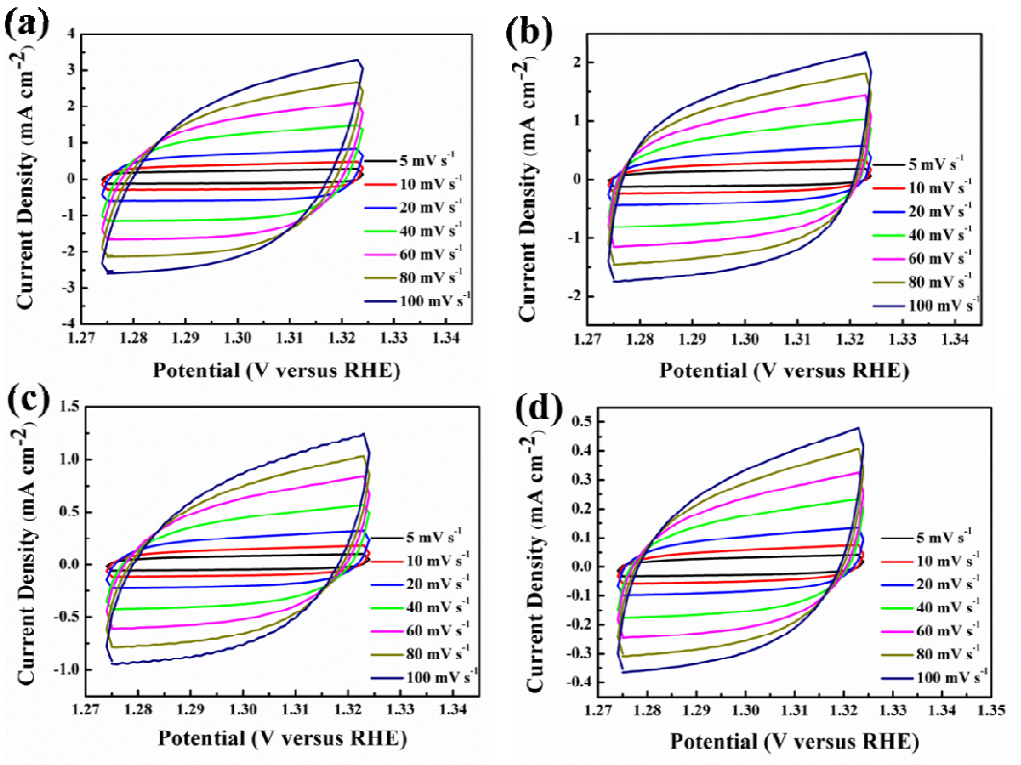

Fig. S4 Cyclic voltammograms in the double-layer region of the electrodes loaded with (a) $Zn_xCo_{3-x}O_4$ YSP, (b) $Ni_xCo_{3-x}O_4$ YSP, (c) $Cu_xCo_{3-x}O_4$ YSP, and (d) Co_3O_4 YSP.

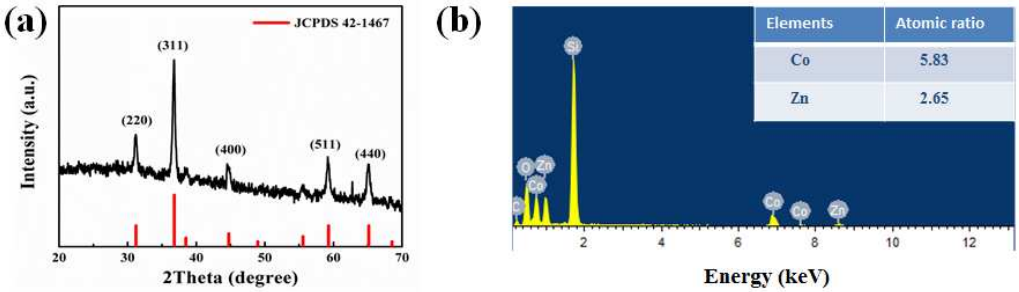

Fig. S5 (a) XRD and (b) EDS patterns of $Zn_xCo_{3-x}O_4$ HP.

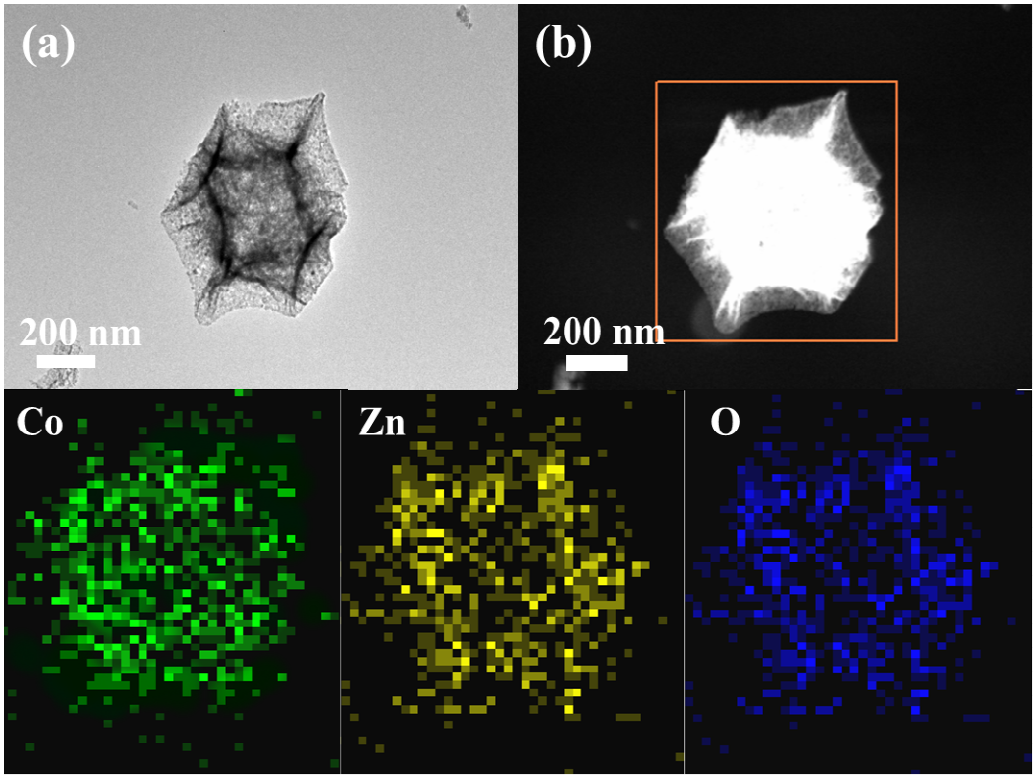

Fig. S6 (a) TEM image of an individual $Zn_xCo_{3-x}O_4$ HP and (b) EDX element mapping of $Zn_xCo_{3-x}O_4$ HP obtained by annealing ZnCo-ZIFs.

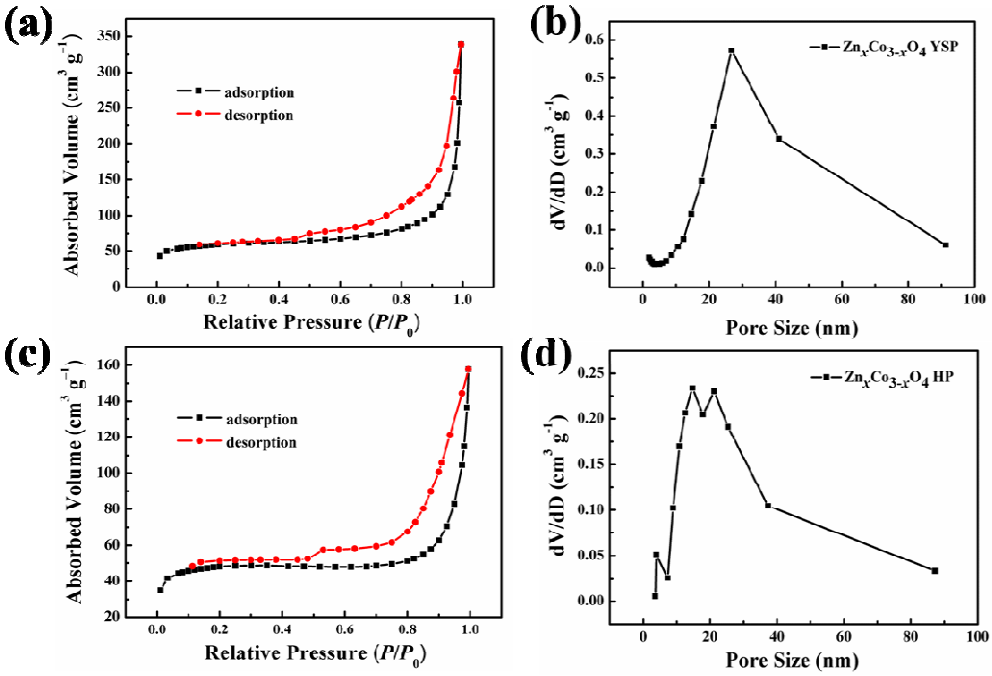

Fig. S7 (a) N_2 adsorption–desorption isotherms and (b) pore size distribution of the $Zn_xCo_{3-x}O_4$ YSP, (c) N_2 adsorption–desorption isotherms and (d) pore size distribution of the $Zn_xCo_{3-x}O_4$ HP.

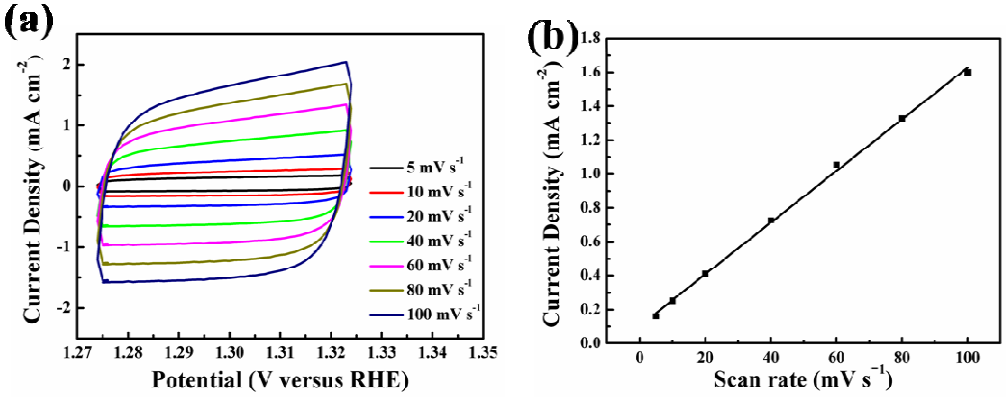

Fig. S8 (a) Cyclic voltammograms in the double-layer region of the electrodes loaded with $Zn_xCo_{3-x}O_4$ HP, (b) Scan rate dependence of the current density of electrode loaded with $Zn_xCo_{3-x}O_4$ HP at 1.3 V *vs* RHE.

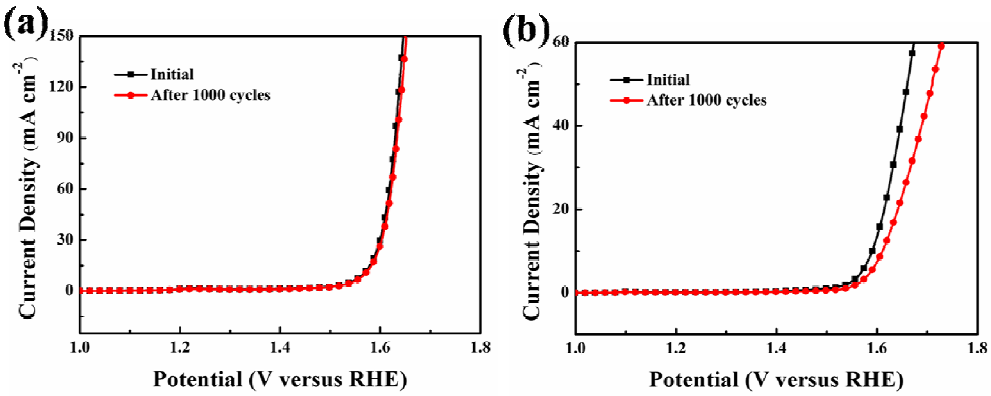

Fig. S9 LSV curves of $Zn_xCo_{3-x}O_4$ YSP (a) and $Zn_xCo_{3-x}O_4$ HP (b) before and after 1000 cycles.

Table S1. Comparison of OER activities for noble-metal-free catalysts.

Electrocatalysts	Overpotential (mV *vs*. RHE) at10 mA·cm^{-2}	Tafel slope	Electrolyte	Ref
$Zn_xCo_{3-x}O_4$ YSP	332 mV	59.3mV dec^{-1}	1 M KOH	This work
$Ni_3ZnC_{0.7}$-550	320 mV	52 mV dec^{-1}	1 M KOH	1
CP/CTs/Co-S	306 mV	72 mV dec^{-1}	1 M KOH	2
$ZnCo_2O_4$ spindle	389 mV	57.3mV dec^{-1}	1 M KOH	3
$Co_3O_4/NiCo_2O_4$	340 mV	88 mV dec^{-1}	1 M KOH	4
Zn_xCo_{3-x}O4 nanoarray	320 mV	51 mV dec^{-1}	1M KOH	5
rGO–Co_3O_4 nanocage	410 mV	84.9mV dec^{-1}	0.1 M KOH	6
MnO_x/S-GC hybrid	390 mV	67 mV dec^{-1}	0.1 M KOH	7
Au/$NiCo_2O_4$ arrays	360 mV	63 mV dec^{-1}	1 M KOH	8

REFERENCES

(1) Xiao, C.; Lu, X.; Zhao, C. Unusual Synergistic Effects upon Incorporation of Fe and/or Ni into Mesoporous Co_3O_4 for Enhanced Oxygen Evolution. *Chem. Commun.* 2014, 50, 10122-10125.

(2) Yu, X.; Sun, Z.; Yan, Z.; Xiang, B.; Liu, X.; Du, P. Direct Growth of Porous Crystalline $NiCo_2O_4$ Nanowire Arrays on a Conductive Electrode for High-Performance Electrocatalytic Water Oxidation. *J. Mater. Chem. A* 2014, 2, 20823-20831.

(3) Zhang, J.; Zhang, D.; Yang, Y.; Ma, J.; Cui, S.; Li, Y.; Yuan, B. Facile Synthesis of $ZnCo_2O_4$ Mesoporous Structures with Enhanced Electrocatalytic Oxygen Evolution Reaction Properties. *RSC Adv.* 2016, 6, 92699-92704.

(4) Hu, H.; Guan, B.; Xia, B.; Lou, X. W. 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.

(5) Liu, X.; Chang, Z.; Luo, L.; Xu, T.; Lei, X.; Liu, J.; Sun, X. Hierarchical $Zn_xCo_{3-x}O_4$ Nanoarrays with High Activity for Electrocatalytic Oxygen Evolution. *Chem. Mater.* 2014, 26, 1889-1895.

(6) Wu, Z.; Sun, L. P.; Yang, M.; Huo, L. H.; Zhao, H.; Grenier, J. C. Facile Synthesis and Excellent Electrochemical Performance of Reduced Graphene

Oxide-Co_3O_4 Yolk-Shell Nanocages as a Catalyst for Oxygen Evolution Reaction. *J. Mater. Chem. A* 2016, 4, 13534-13542.

(7) Gao, Y.; Zhao, H.; Chen, D.; Chen, C.; Ciucci, F. In Situ Synthesis of Mesoporous Manganese Oxide/Sulfur-Doped Graphitized Carbon as a Bifunctional Catalyst for Oxygen Evolution/Reduction Reactions. *Carbon* 2015, 94, 1028-1036.

(8) Liu, X.; Liu, J.; Li, Y.; Li, Y.; Sun, X. Au/$NiCo_2O_4$ Arrays with High Activity for Water Oxidation. *Chemcatchem* 2014, 6, 2501-2506.