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Iron Incorporation Affecting Structure and Boosting Catalytic Activity of β-$Co(OH)_2$: a Reaction Mechanism Exploring of Ultrathin Two-Dimensional Carbon-free Fe_3O_4-Decorated β-$Co(OH)_2$ Nanosheets as Efficient Oxygen Evolution Electrocatalysts

Fengzhan Sun[‡], Linbo Li[‡], Guo Wang*, and Yuqing Lin*

([‡] These authors contributed equally to this work)

Department of Chemistry, Capital Normal University, Beijing 100048, China

*E-mail: linyuqing@cnu.edu.cn; wangguo@mail.cnu.edu.cn

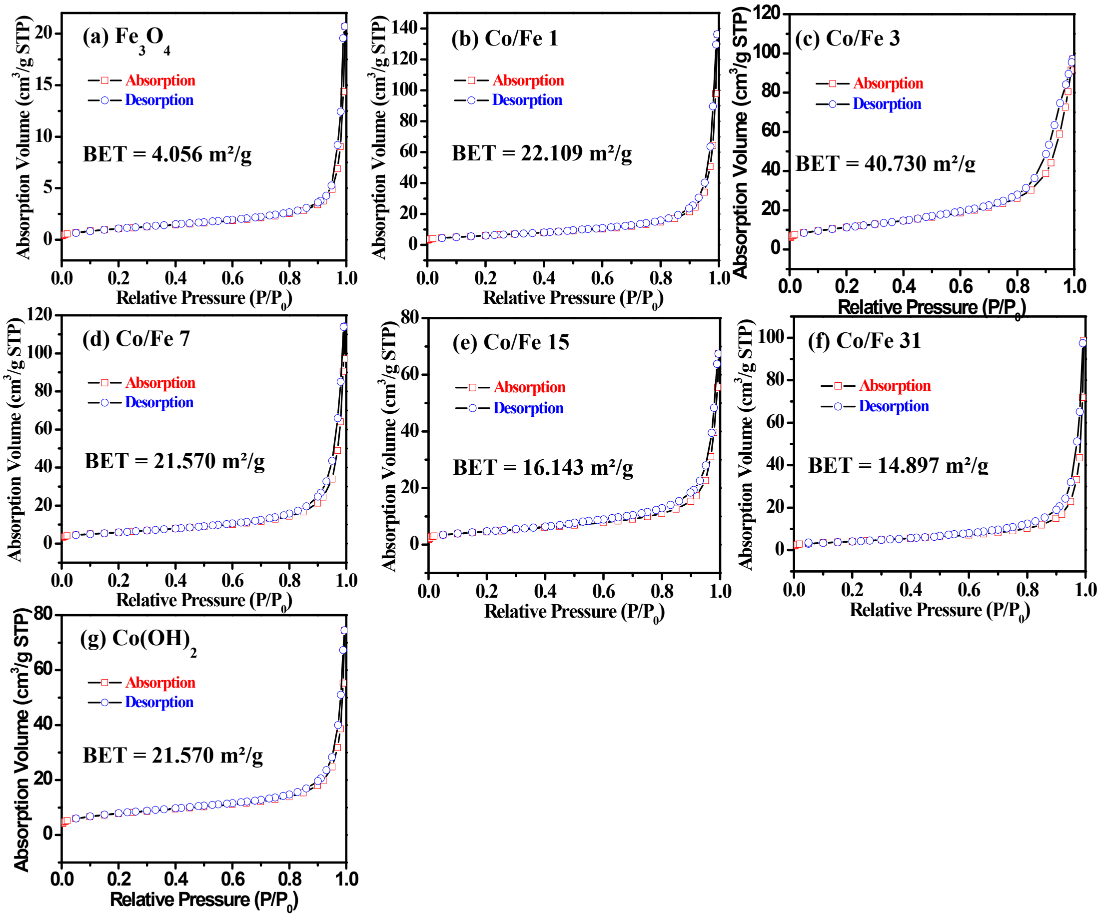

Fig. S1 N_2 adsorption/desorption isotherms of Fe_3O_4 NPs, $Co(OH)_2$ NSs, and $Fe_3O_4/Co(OH)_2$ NSs with different Co/Fe mole ratio (1, 3, 7, 15, and 31).

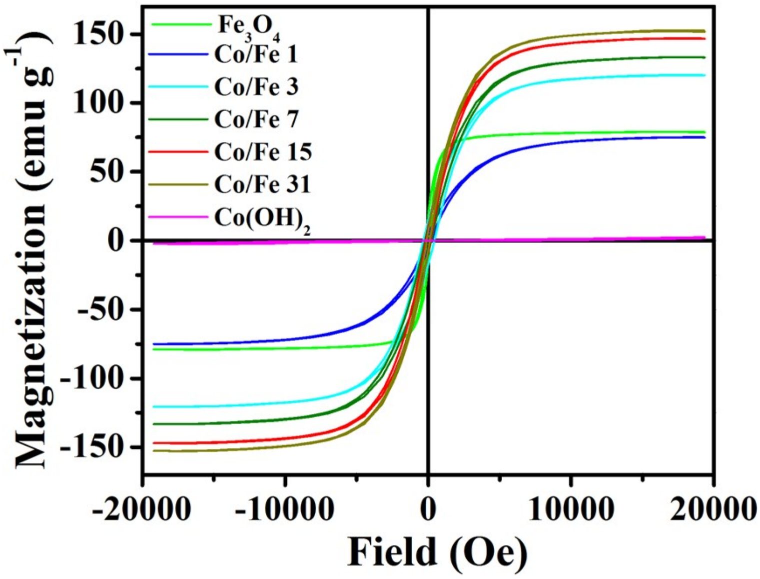

Fig. S2 Room temperature hysteresis loop of Fe_3O_4 NPs, $Co(OH)_2$ NSs, and $Fe_3O_4/Co(OH)_2$ NSs with different Co/Fe mole ratio (1, 3, 7, 15, and 31).

The hysteresis loop at room temperature of the as-prepared catalysts are shown in Fig. S2. The $Fe_3O_4/Co(OH)_2$ NSs and Fe_3O_4 NPs show ferromagnetism while $Co(OH)_2$ NSs show antiferromagnetic property. The saturation magnetization of the Fe_3O_4 nanoparticles is 78.8 emu/g. As for $Fe_3O_4/Co(OH)_2$ NSs, the saturation magnetizations are 75.0 emu g^{-1} (Co/Fe 1), 120.6 emu g^{-1} (Co/Fe 3), 133.2 emu g^{-1} (Co/Fe 7), 146.8 emu g^{-1} (Co/Fe 15) and 152.6 emu g^{-1} (Co/Fe 31), which increase with the iron content decreasing.

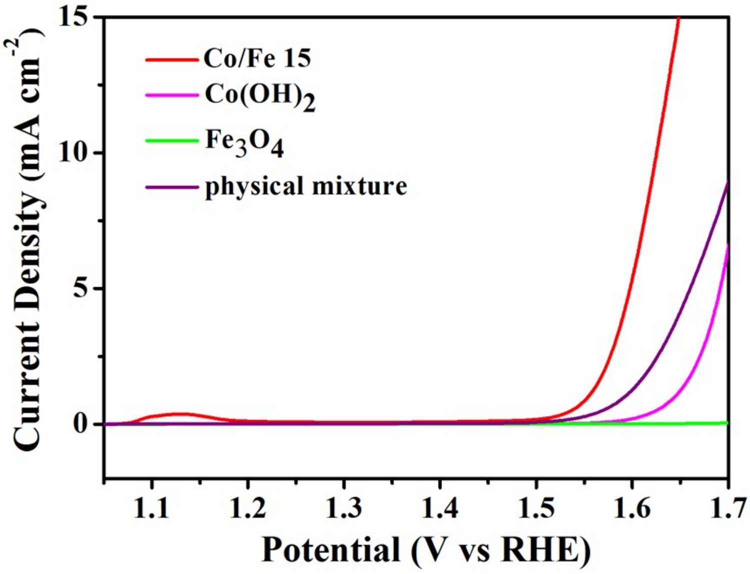

Fig. S3 Polarization curves for OER of Fe_3O_4/$Co(OH)_2$ NSs (Co/Fe 15), Fe_3O_4 NPs, $Co(OH)_2$ NSs and the physical mixture of Fe_3O_4 and $Co(OH)_2$ by grinding.

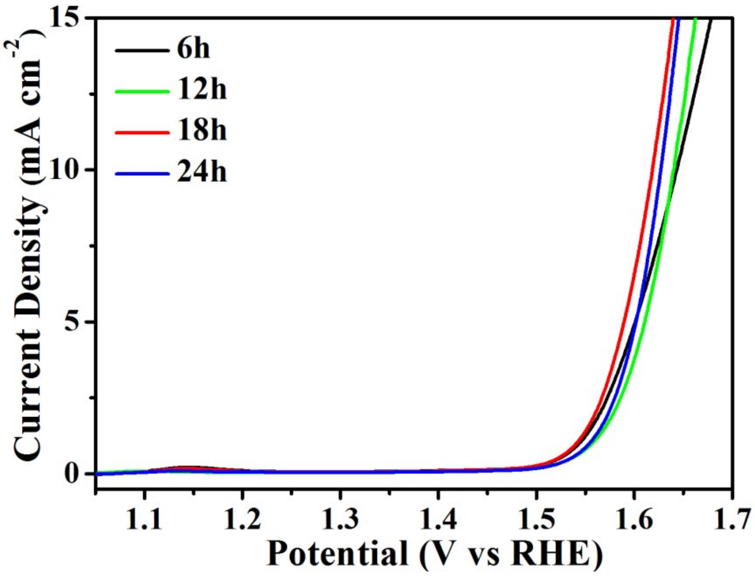

Fig. S4 Polarization curves for OER of $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) obtained at different hydrothermal reaction time of 6, 12, 18, and 24 h.

Different hydrothermal reaction time were changed to study the influence of time on the electrocatalytic activity of $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) (Fig. S4). $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) at different time show little differences, with 1.643 V (6 h), 1.639 V (12 h), 1.619 V (18 h) and 1.627 V (24 h) at the current density of 10 mA cm^{-2}. The electrocatalytic activity change a little with different time, but for more precise, $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) with 18 h heating time have a better electrocatalytic performance.

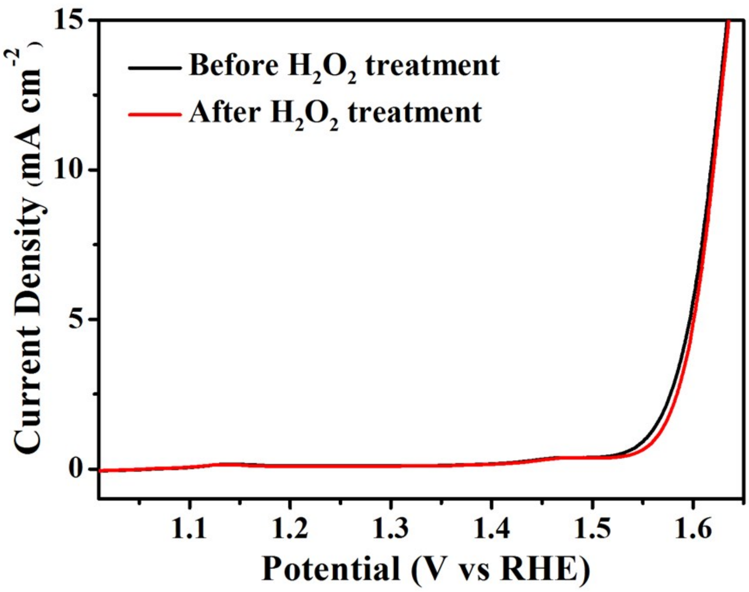

Fig. S5 Polarization curves for OER of $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) obtained with or without H_2O_2 treatment.

$Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) were treated with H_2O_2 to remove the extra hydrazine hydrate. To understand whether H_2O_2 will affect catalytic activity, $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) were examined without H_2O_2 treating for comparison. As is shown in Fig. S5, $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) afford current density of 10 mA cm^{-2} in 0.39 V when the samples were treated with or without H_2O_2. It is to say that H_2O_2 will pure the samples by removing organic impurities without reducing catalytic properties.

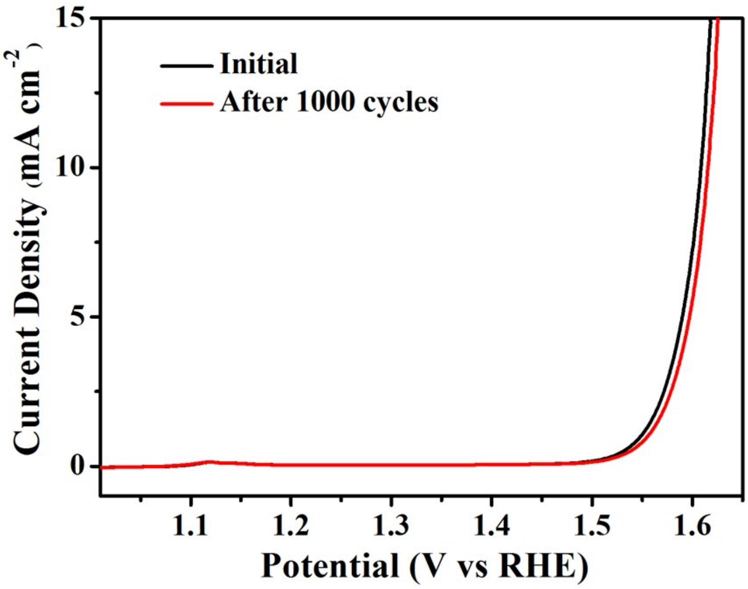

Fig. S6 Polarization curves of $Fe_3O_4/Co(OH)_2$ (Co/Fe 15) before and after CV testing of 1000 cycles in 0.1 M KOH solution.

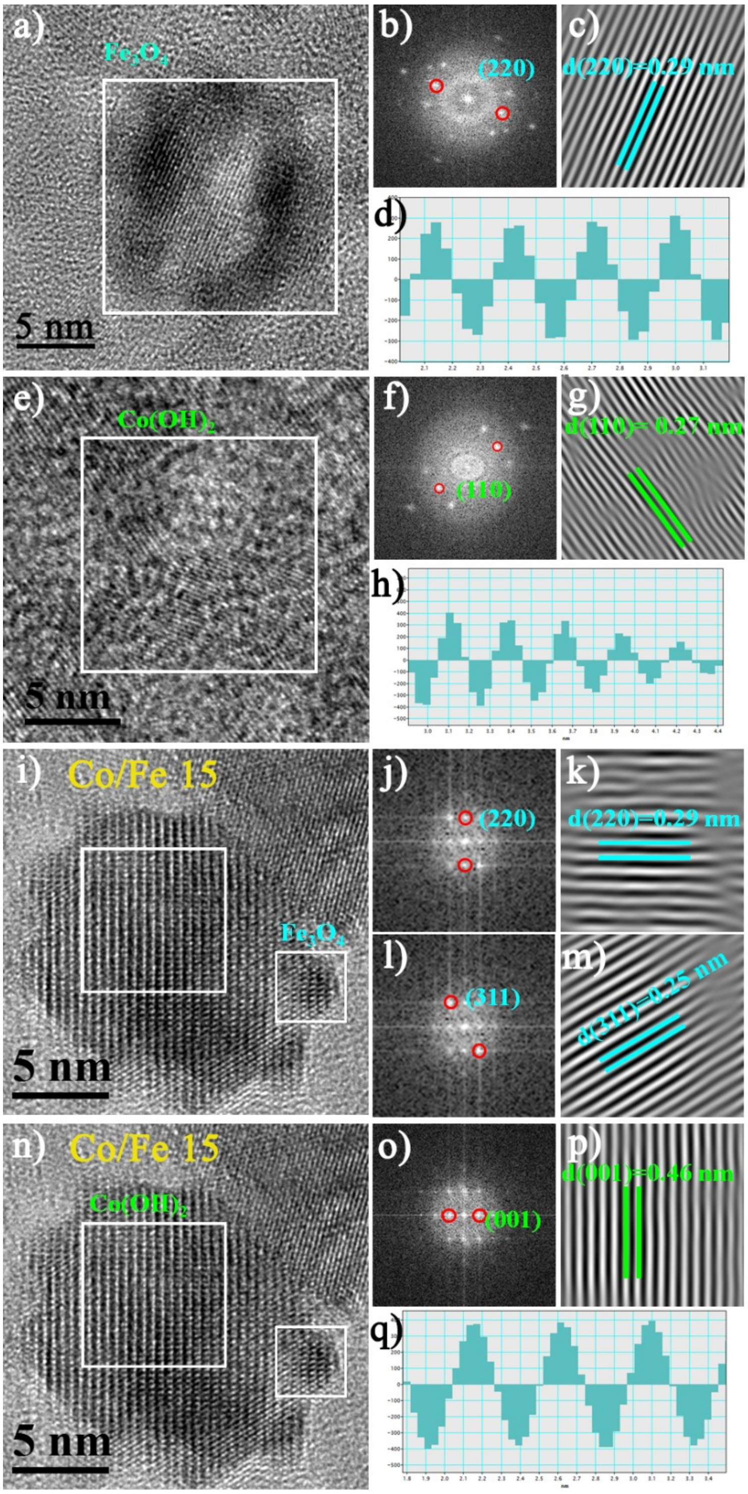

Fig. S7 Analysis of the HRTEM image of the Fe_3O_4 NPs, $Co(OH)_2$ NSs and $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15) with the assistance of DigitalMicrograph software. (a)(e)(i)(n) The original HRTEM image; (b)(f)(j)(l)(o) the corresponding fast Fourier transform images; (c)(g)(k)(m)(p) the enhanced lattice fringes; and (d)(h)(q) profile of IFFT.

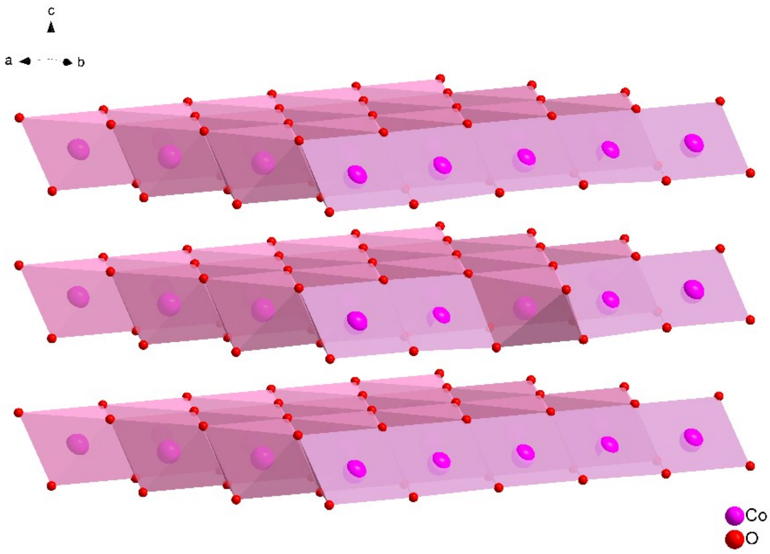

Fig. S8 The structure with stacking of synthesized $Co(OH)_2$ NSs.

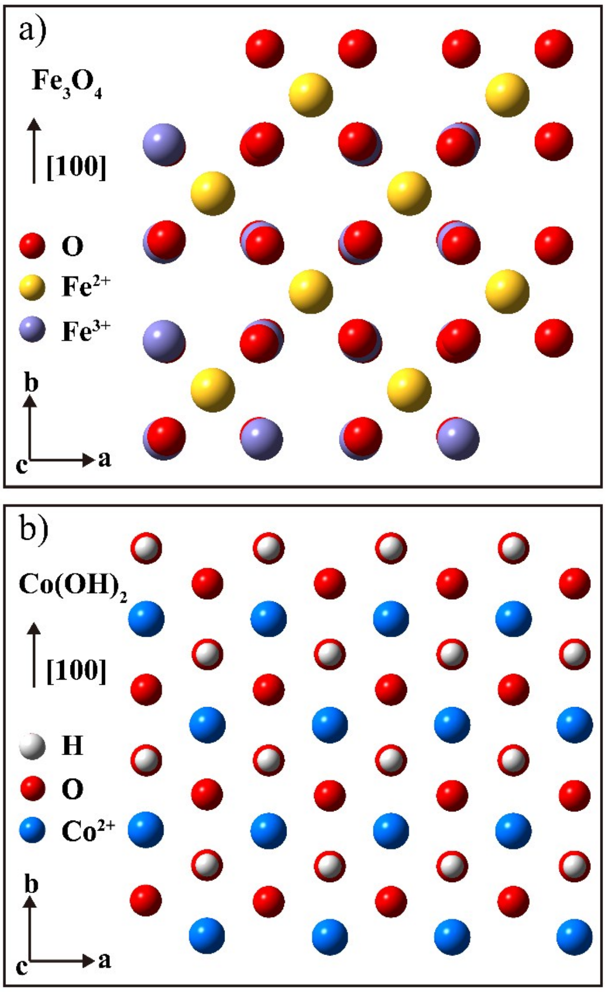

Fig. S9 Crystal structure illustration of cubic Fe_3O_4 and hexagonal $Co(OH)_2$.

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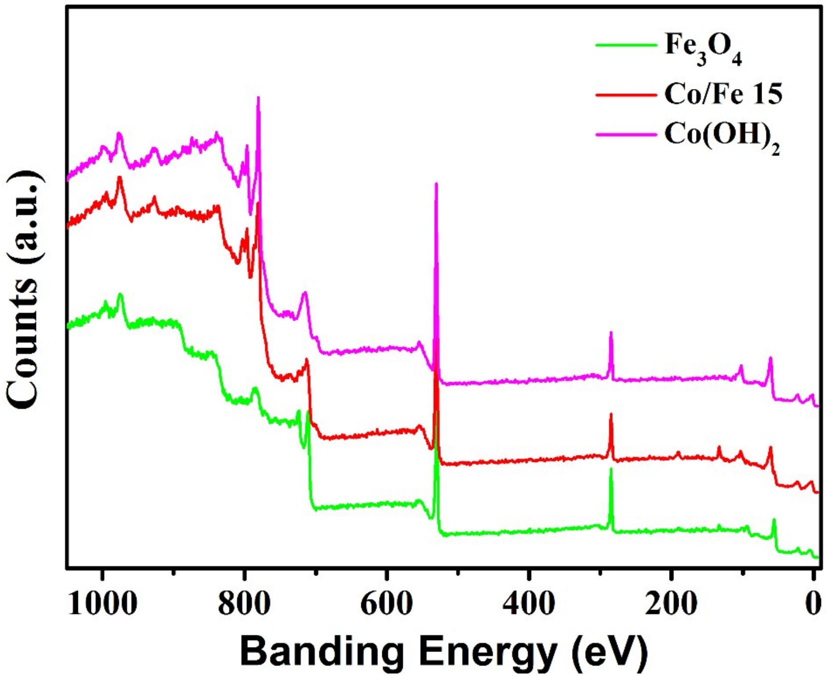

Fig. S10 XPS spectra of Fe_3O_4 NPs, $Co(OH)_2$ NSs and $Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15).

Table S1. Analysis results of as-prepared $Fe_3O_4/Co(OH)_2$ NSs with different Co/Fe mole ratio from EDX.

Samples	Co Atom%	Fe Atom%	Co/Fe mole ratio
Co/Fe 1	14.27	13.49	1.1
Co/Fe 3	21.12	7.45	2.8
Co/Fe 7	24.48	3.79	6.5
Co/Fe 15	26.19	1.96	13.4
Co/Fe 31	27.81	1.08	25.8

Table S2 Comparison of OER catalytic performances for well-developed Co-based electrocatalysts in alkaline condition

Catalyst	Overpotential (V) @10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Electrolyte	Reference
$Fe_3O_4/Co(OH)_2$ NSs (Co/Fe 15)	0.390	61.1	0.1M KOH	This work
	0.370	50.6	1M KOH	This work
Mesoporous $Cu_xCo_yO_4$	0.471	/	0.1M KOH	S1
Fe-Co_3O_4 nanocast	0.486	/	0.1M KOH	S2
Co-MnHCF	0.450	80.0	0.1M KOH	S3
Hollow Co_3O_4 microspheres	0.400	/	0.1M KOH	S4
Co_3O_4/NPGC	0.450	/	0.1M KOH	S5
$Mn_3O_4/CoSe_2$ composite	0.450	49.0	0.1M KOH	S6
Fe–mCo_3O_4	0.380	60.0	0.1M KOH	S7
Co_3O_4/G	0.402	67.0	0.1M KOH	S8
Ni–Co mixed oxide cages	0.380	50.0	1M KOH	S9
$NiCo_2O_4$ nanowires	0.460	90.0	1M KOH	S10

References

(S1) T. Grewe, X. Deng, C. Weidenthaler, F. Schüth and H. Tüysüz, *Chem. Mater.*, 2013, **25**, 4926-4935.

(S2) T. Grewe, X. Deng and H. Tüysüz, *Chem. Mater.*, 2014, **26**, 3162-3168.

(S3) N. K. A. Venugopal and J. Joseph, *J. Power Sources*, 2016, **305**, 249-258.

(S4) 1.J. Zhao, Y. Zou, X. Zou, T. Bai, Y. Liu, R. Gao, D. Wang and G.-D. Li, *Nanoscale*, 2014, **6**, 7255-7262.

(S5) G. Li, X. Wang, J. Fu, J. Li, M. G. Park, Y. Zhang, G. Lui and Z. Chen, *Angew. Chem., Int. Ed.*, 2016, **55**, 4977-4982.

(S6) M.-R. Gao, Y.-F. Xu, J. Jiang, Y.-R. Zheng and S.-H. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 2930-2933.

(S7) C. Xiao, X. Lu and C. Zhao, *Chem. Commun.*, 2014, **50**, 10122-10125.

(S8) P. Zhang, X. Han, H. Hu, J. Gui, M. Li and J. Qiu, *Catal. Commun.*, 2017, **88**, 81-84.

(S9) L. Han, X. Y. Yu and X. W. D. Lou, *Adv. Mater.*, 2016, **28**, 4601-4605.

(S10) X. Yu, Z. Sun, Z. Yan, B. Xiang, X. Liu and P. Du, *J. Mater. Chem. A*, 2014, **2**, 20823-20831.