Supporting Information

Co Intake Mediated Formation of Ultrathin Nanosheets of Transition Metal LDH — an Advanced Electrocatalyst for Oxygen Evolution Reaction

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Experimental Section

Synthesis of FeNi$_{10-x}$Co$_x$ based layered hydroxides:

FeNi$_{10-x}$Co$_x$ LDHs were synthesized by one step hydrothermal method with different feed ratios. 0.145 ml of 1 M ferrous nitrate (Fe(NO$_3$)$_3$) aqueous solution, (1.45-0.145x) ml of 1 M nickel chloride (NiCl$_2$) aqueous solution, and 0.145x ml of 1 M cobalt chloride (CoCl$_2$) aqueous solution, were mixed in the beaker with 70.8 ml DI water. Then 5.6 ml of 0.5 M urea aqueous solution ad 2 ml of 0.01 M trisodium citrate (TSC) were added into the beaker in sequence with magnetic stirring.

The mixed solution was transferred to a 100 ml Teflon lined stainless steel autoclave for hydrothermal reaction at 150 ℃ for 2 days. The FeNi-CO$_3$ LDH was collected by centrifuge, washed with water three times and then dried.

Sample preparation for electrochemical characterizations:

Ni foam electrode: 1 mg catalyst was dispersed in 0.967 ml ethanol, then 33.33 μl of 60 wt% PTFE was added (containing 1 mg of catalyst). After sonication for 1 hour, 250 μl of catalyst ink was drop dried onto a 1 cm × 1 cm Ni foam (loading 0.25 mg/cm^2).

Rotating disc electrode (RDE): 1mg catalyst was dispersed in 192 ul DI water and 50 ul alcohol, then 8 ul of Nafion (5 wt%) was added into the suspension. 1 hour sonication was needed to form a homogeneous ink. Then, 10 ul of catalyst ink (containing 0.04 mg of catalyst) was loaded onto the glass carbon electrode with diameter of 5 mm (loading 0.2 mg/cm^2)

Electrochemical characterizations:

Electrochemical studies were carried out in a standard three electrode system controlled by a CHI 660D electrochemistry workstation. Catalysts loaded on Ni foam was used as the working electrode, coiled platinum wire as the counter electrode and Ag/AgCl electrode as the reference electrode. The reference was calibrated against and converted to revisable hydrogen electrode (RHE).

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were carried out at 5 mV/s for the polarization curves and 0.1 mV/s for Tafel plots. The catalysts was cycled about 5 times of cyclic voltammetry (CV) until a stable CV curve was developed before measuring polarization curves of catalysts. All LSV polarization curves were corrected with 95% iR-compensation before measurements 95% iR compensation is an optimal compensation level to achieve best curve shape as well as avoid curve distortion by over-compensation.

Chrompotentiometry (CP) was carried out under a constant current density of 5 mA/cm^2, 10 mA/cm^2, and 20 mA/cm^2.

Turnover frequency (TOF) calculation of the catalysts: The TOF values are calculated from the equation:

$$TOF = \frac{j \times A}{4 \times F \times m}$$

j is the current density at overpotential of 0.3 V. A is the area of the electrode. F is the faraday constant (96485 C/mol). m is the number of moles of active materials that are deposited onto the electrodes.

Structure and morphology characterization

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) samples were prepared by drop-dry the aqueous suspensions onto silicon wafer, and was characterized by a JSM-6700F and by a 6390 respectively.

Transmission electron microscopy (TEM) samples were prepared by drop dry the catalysts suspensions onto copper grids and was measured by JEM 2010 (JEOL) TEM.

Other characterizations

X-ray diffraction (XRD) sample were prepared by drop dry catalysts aqueous solution onto glass substrate to form a thin film and then measured by PW1830 (Philips);

X-ray photoelectron spectroscopy (XPS) samples were prepared by centrifuging the catalyst suspension at 13000 rpm for 30 min and washed wished with alcohol. The dried samples were measured by XPS on PHI 5600.

Energy dispersive X-ray spectroscopy (EDS) sample was prepared by drop dry catalysts suspension on Si wafer and then measure by JSM 6300 (JEOL).

Brunar-Emmett-Teller (BET) surface areas and N_2 absorbing-desorbing isotherms were recorded on a Coulter SA 3100 surface area analyzer.

Raman spectroscopy was collected by MicroRaman (InVia Renishaw) with laser source of 633 nm and spectral range from 1100 cm^{-1} to 100 cm^{-1}.
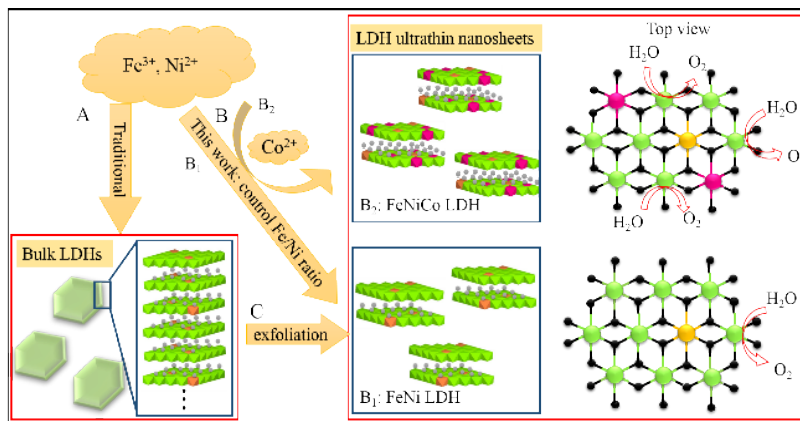
Scheme S1. Schematic description of FeNi LDH and FeNiCo LDH ultrathin nanosheets as efficient OER catalysts. (A) FeNi LDH with thickness of more than 10 nm previously reported. (B) FeNi LDH (B_1) and FeNiCo LDH (B_2) ultrathin nanosheets with thickness less than 2 nm (about two layer of octahedral $M(OH)_6$) synthesized in this work. (C) Exfoliation process is needed to get the ultrathin nanosheets from bulk LDHs. The FeNi LDH ultrathin nanosheets show advanced OER catalytic performances that is further improved by Co incorporation. Ni: green; Co: purple red; Fe: orange; OH: black; interlayer anions and water molecules: grey spheres.
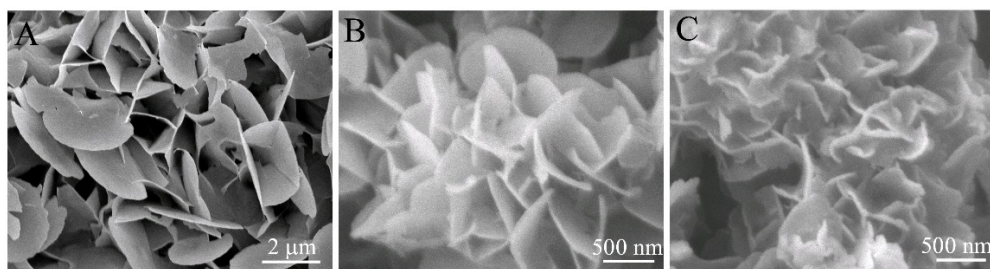
Figure S1. SEM images of Ni(OH)$_2$ nanosheets (A) and FeNi LDH formed in the mother solution with Fe/Ni=1/5 (B) and 1/8 (C), respectively.
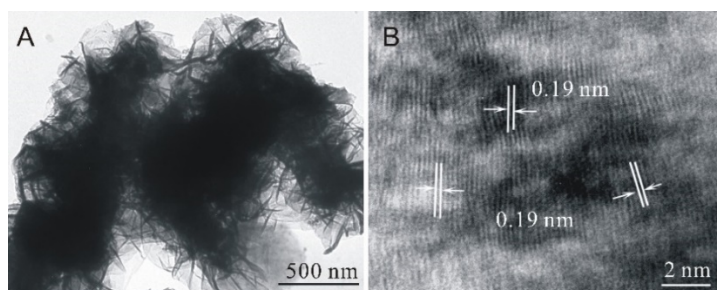

Figure S2. TEM (A) and HRTEM (B) images of FeNi$_{10}$ LDH nanosheets.
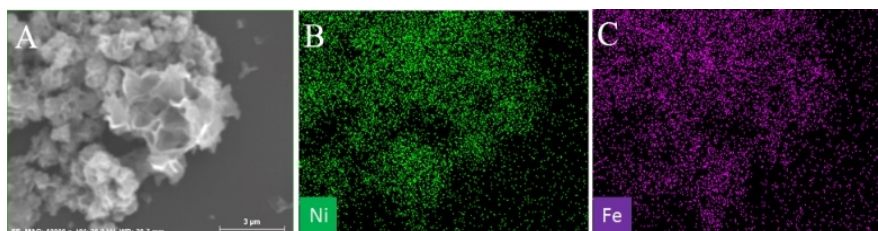

Figure S3. SEM and corresponding EDX maps of FeNi$_{10}$ LDH ultrathin nanosheets. (A) SEM image, (B) corresponding Ni mapping, (C) corresponding Fe mapping.
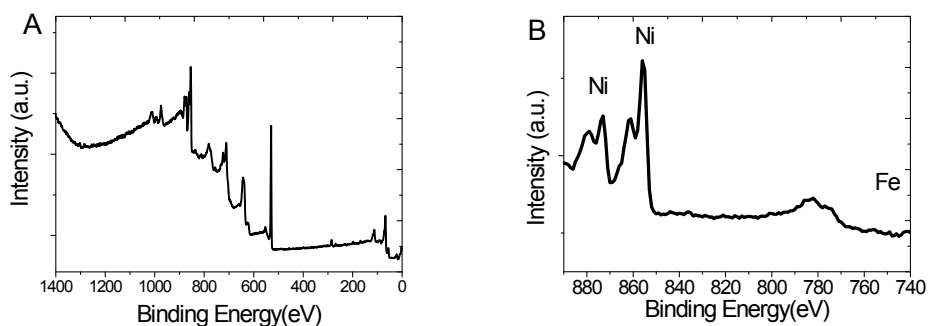

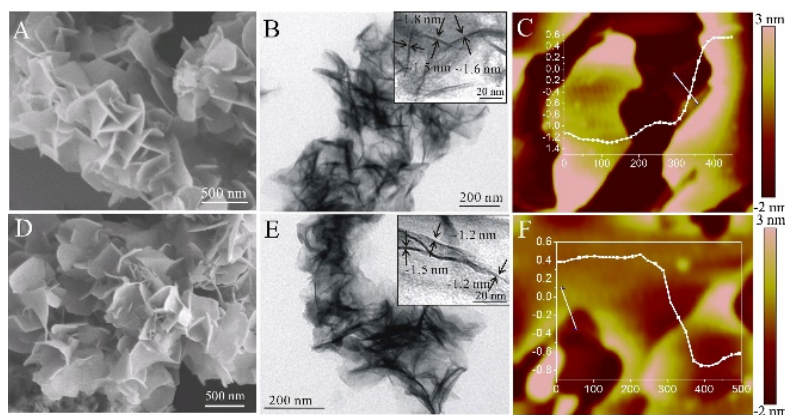**Figure S4.** XPS spectra of FeNi$_{10}$ LDH ultrathin nanosheets.

Figure S5. SEM (A, D), TEM (B, E) and AFM height (C, F) images of FeNiCo LDHs nanosheets with different Fe/Ni/Co ratios. (A-C) FeNi$_9$Co LDH, (D-F) FeNi$_8$Co$_2$ LDH. Inset images in B and E are enlarged TEM images of corresponding FeNiCo LDHs showing the thickness of LDH nanosheets.
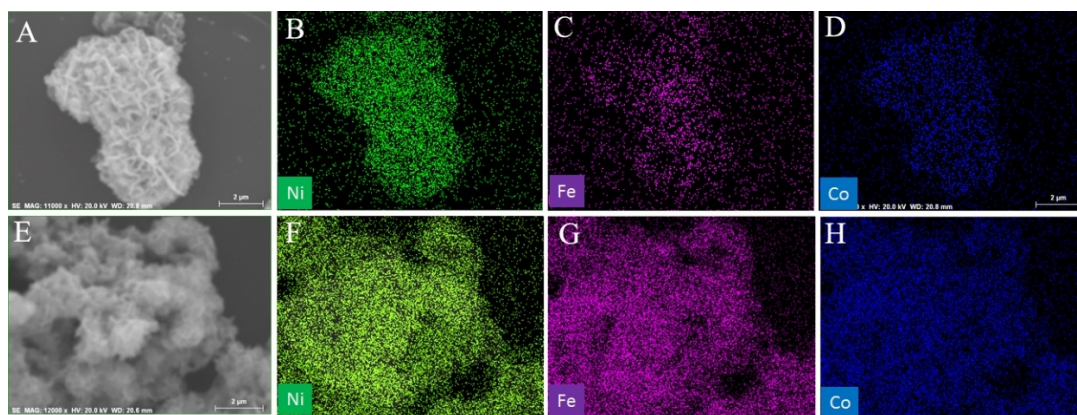

Figure S6. SEM (A, E) and corresponding EDX mapping (B-D, F-H) of FeNiCo LDH ultrathin nanosheets. (A-D) FeNi$_9$Co LDHs, (B-H) FeNi$_8$Co$_2$ LDHs. Green: Ni, purple: Fe, blue: Co.
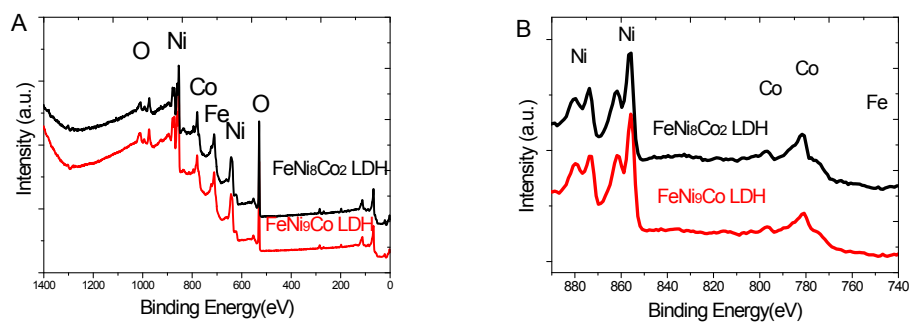

Figure S7. XPS spectra of FeNiCo LDHs with different Fe/Ni/Co ratios. Black curves: FeNi$_8$Co$_2$ LDHs; red curves: FeNi$_9$Co LDHs.
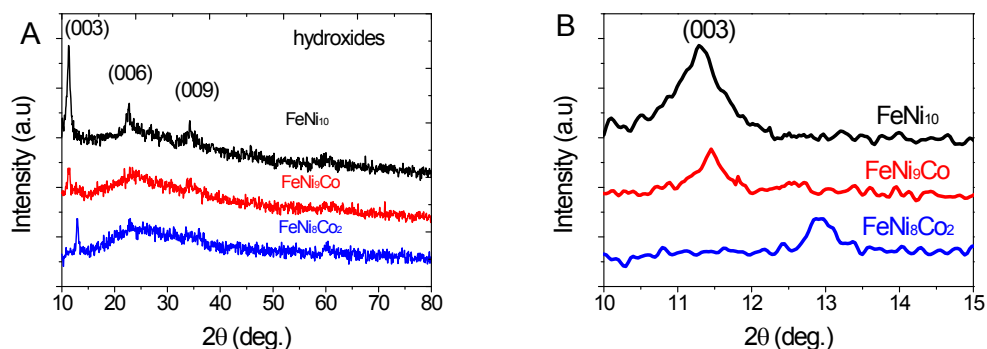
Figure S8. XRD spectra of FeNi LDHs and FeNiCo LDHs (black curve), FeNi$_9$Co LDHs (red curves) and FeNi$_8$Co$_2$ LDHs (blue curves) with the scan range from 10 to 80 degree (A) and 10 to 15 degree (B).

The XRD of FeNiCo LDHs (Fig. S8, ESI†) showed that only the (003) diffraction peak remains pronounced whereas the (006) and (009) peaks become ambiguous due most likely to the ultrathin structure of the LDHs (only about two layers).This is consistent with the report of Hu et al., which showed that the (00n) diffraction peaks disappear once the bulk LDH is exfoliated into single layers.[3a] Moreover, the (003) diffraction peak is positively shifted with Co incorporation (Fig.S8B, ESI†) from 11.281for FeNi10LDH to 11.451and 12.91for FeNi$_9$Co LDH and FeNi$_8$Co$_2$ LDH, respectively, suggesting a decrease in the d-spacing along the c axis from 0.78 nm to 0.77 nm an 0.68 nm due to the substitution of Ni^{2+} with Co^{2+}.
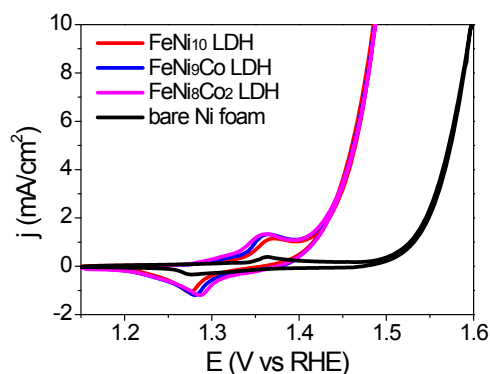

Figure S9: Cyclic voltammograms of FeNi LDH and FeNiCo LDH catalyzed OER. Data were collected at a scan rate of 5 mV/s in 1 M KOH.
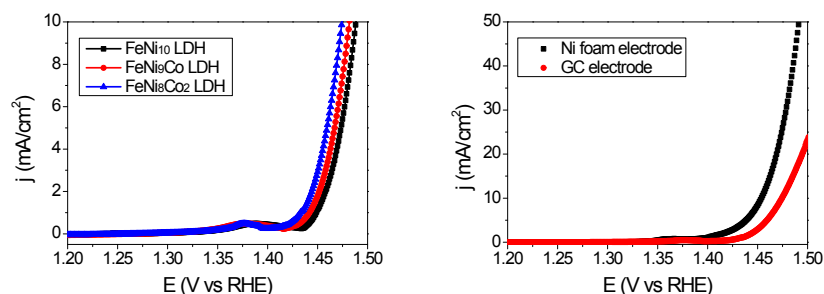
Figure S10. LSV curves of LDHs catalyzed OER. (A) FeNiCo LDHs loaded glass carbon as working electrode (black: FeNi$_{10}$ LDH, red: FeNi$_9$Co LDH, blue: FeNi$_8$Co$_2$ LDH), (B) FeNi$_8$Co$_2$ LDH loaded glass carbon electrode (black curve) and Ni foam (red curve) as working electrodes.
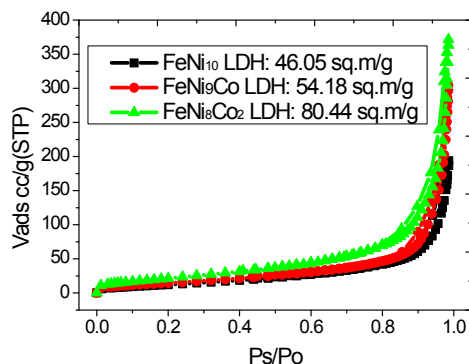

Figure S11. N$_2$ adsorbing-desorbing isotherm curves of FeNi$_{10}$ and FeNiCo LDH ultrathin nanosheets. Black curve: FeNi$_{10}$ LDH; red: FeNi$_9$Co LDH; green: FeNi FeNi$_8$Co$_2$ LDH.
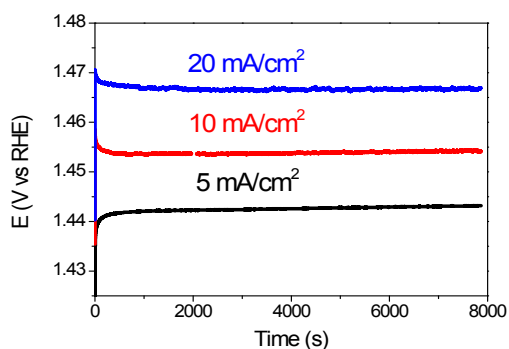

Figure S12. Chronopotentiometry test of FeNi$_8$Co$_2$ LDH at the current density of 5 mA/cm^2, 10 mA/cm^2 and 20 mA/cm^2.
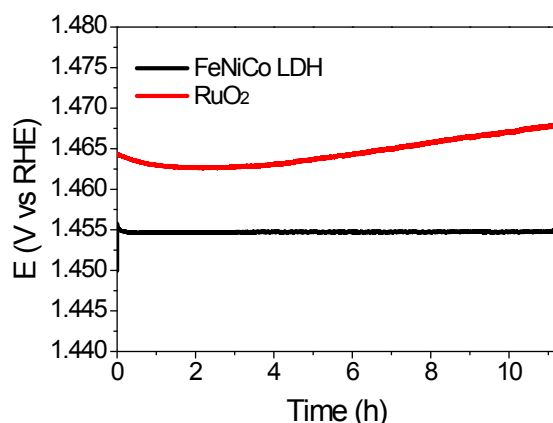
Figure S13. Chronopotentiometry spectra of $FeNi_8Co_2$ LDH and RuO_2 at the current density of 10 mA/cm^2.
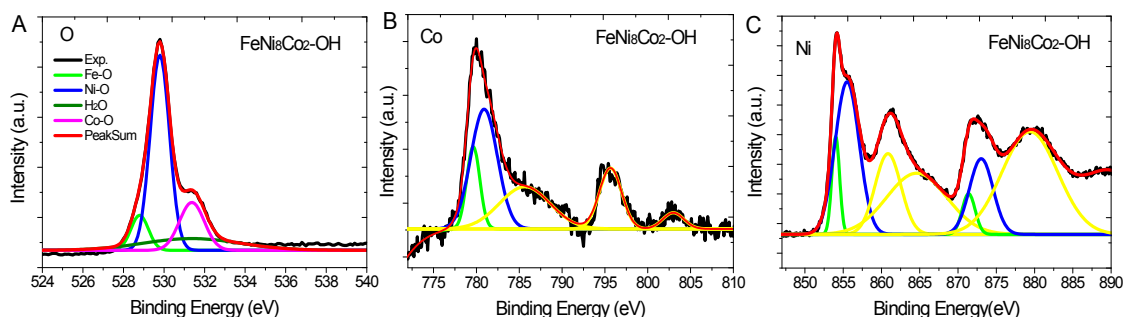

Figure S14. X-ray photoelectron spectra of the $FeNi_8Co_2$ LDH nanosheets with multi-peak fitting deconvolution. (A) high resolution O 1s XPS spectra, (B) high resolution Co 2p XPS spectra, (C) high resolution Ni 2p XPS spectra. The black curves are experimental spectra; red curves are the peak sum of deconvoluted peaks; the yellow, blue and green curves in (B) and (C) are satellite shakeups, M^{2+} (Ni^{2+} in B, Co^{2+} in C) and M^{3+} (Ni^{3+} in B, Co^{3+} in C), respectively.

In the O 1s region, the spectra of $FeNi_8Co_2$LDH could be deconvoluted tofour oxygen peaks, which correspond to Fe–O (531.4 eV), Ni–O (531.7 eV), Co–O (532.7 eV),[20] and physi- and chemi-sorbed wateratornearthesurface (533.9 eV).[20a,b,S1]

Table 1. Summary of the specific surface area (A) and comparison the electrocatalytic performances on OER (η: overpotential, b: Tafel slope, TOF: turnover frequency) of FeNi and FeNiCo LDHs with different Fe/Ni/Co ratios to reported metal oxides/hydroxides catalysts in alkali solution.

Ref.		A (m^2/g)	η (V)	b (mV/dec)	TOF (η=0.3V, s^{-1})
	FeNi$_{10}$ LDH	46.05	0.22	55	0.53

This work	FeNi$_9$Co LDH	54.18	0.21	52	0.56
	FeNi$_8$Co$_2$ LDH	80.44	0.20	42	0.70
2h	IrO$_2$		0.427	49	---
3a	Exfoliated CoCo LDH		0.353	45	---
	Exfoliated NiCo LDH		0.334	41	---
	Exfoliated NiFe LDH		0.302	40	0.24
5a	NiFeO$_x$		0.35	---	---
	NiCoO$_x$		0.38	---	---
4b	NiFe LDH/CNT		0.25	31	0.56
2h	Ni$_{0.9}$Fe$_{0.1}$O$_x$		0.297 (1mA/cm^2)	30	0.21
	Ni$_{0.5}$Co$_{0.5}$O$_x$		0.32 (1mA/cm^2)	35	0.056
	Ni$_{0.25}$Co$_{0.75}$O$_x$		0.34 (1mA/cm^2)	36	0.0099
	Ni$_{0.75}$Co$_{0.25}$O$_x$		0.312 (1mA/cm^2)	33	0.089
S2	ZNNRAs		0.64	275	---
	NNTAs		0.64	145	---
	NNCNTAs		0.58	65	---
S3	NG-CoSe$_2$		0.29	40	0.03565 (η=366 mV)
	CoSe$_2$		0.37	66	0.00773 (η=366 mV)
	RuO$_2$		0.25	69	0.01724 (η=366 mV)
S4	NiCoO$_x$		0.325 (10 mA)	39	---

Additional references:

[S1]. J. Marco, J. Gancedo, M. Gracia, J. Gautier, E. Rıos and F. Berry, *J. Solid State Chem.,* **2000**, *153*, 74–81.

[S2]. Zhao, Z.; Wu, H.; He, H.; Xu, X.; Jin Y.; *Adv. Funct. Mater.* **2014**, *24*, 4698-4705.

[S3]. Gao, M.R.; Cao, X.; Gao, Q.; Xu, Y.F.; Zheng, Y.R.; Jiang, J.; Yu, S. H.; *ACS Nano*, **2014**, *8*, 3970-3978.

[S4]. Yang, Y.; Fei, H.; Ruan, G.; Xiang, C.; Tour, J. M.; *ACS Nano*, **2014**, *8*, 9518-9523.