Supporting Information

Oxidatively Electrodeposited Thin-Film Transition Metal (Oxy)Hydroxides as Oxygen Evolution Catalysts

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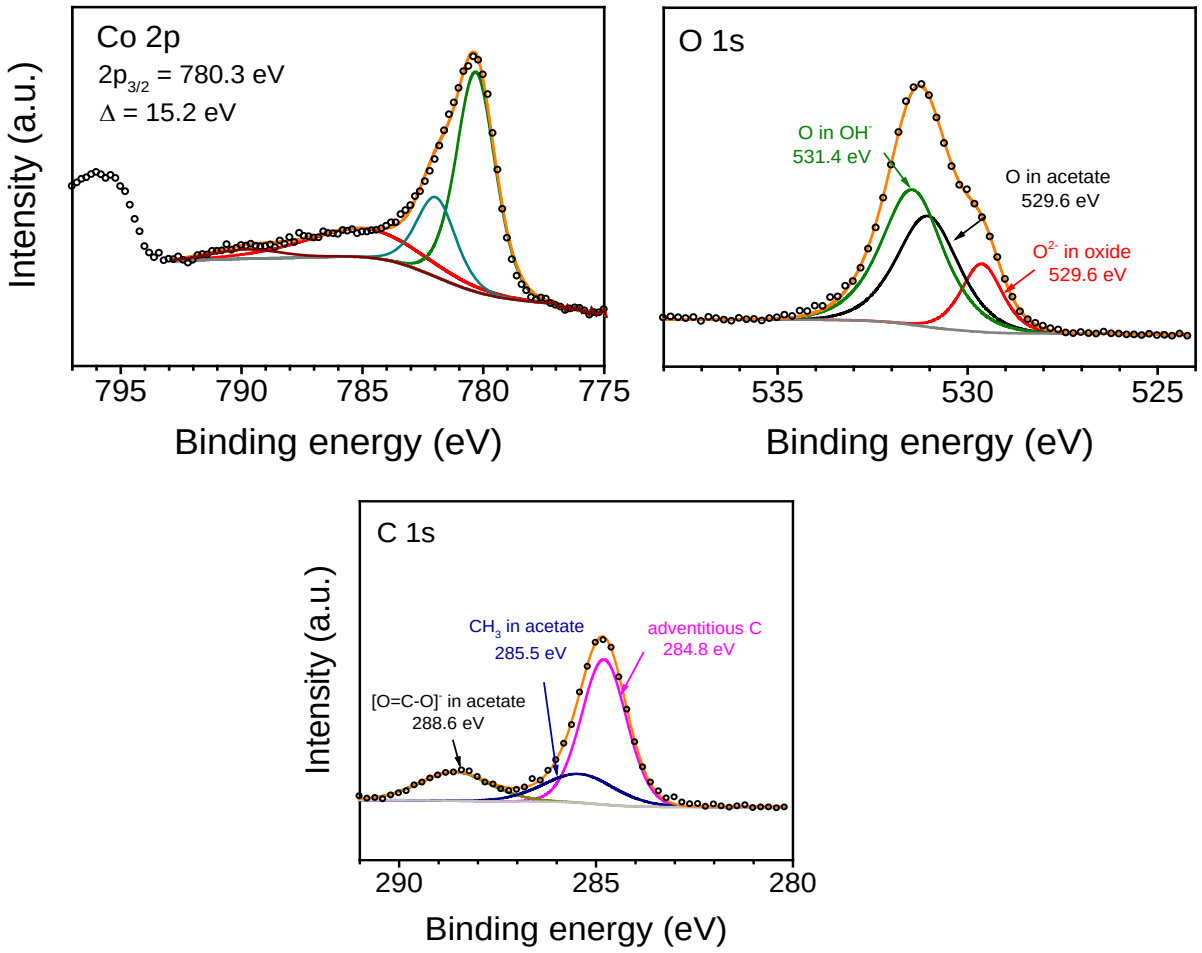

Figure S1| Co 2p, O 1s and C 1s regions of the XPS spectra of CoO_x.

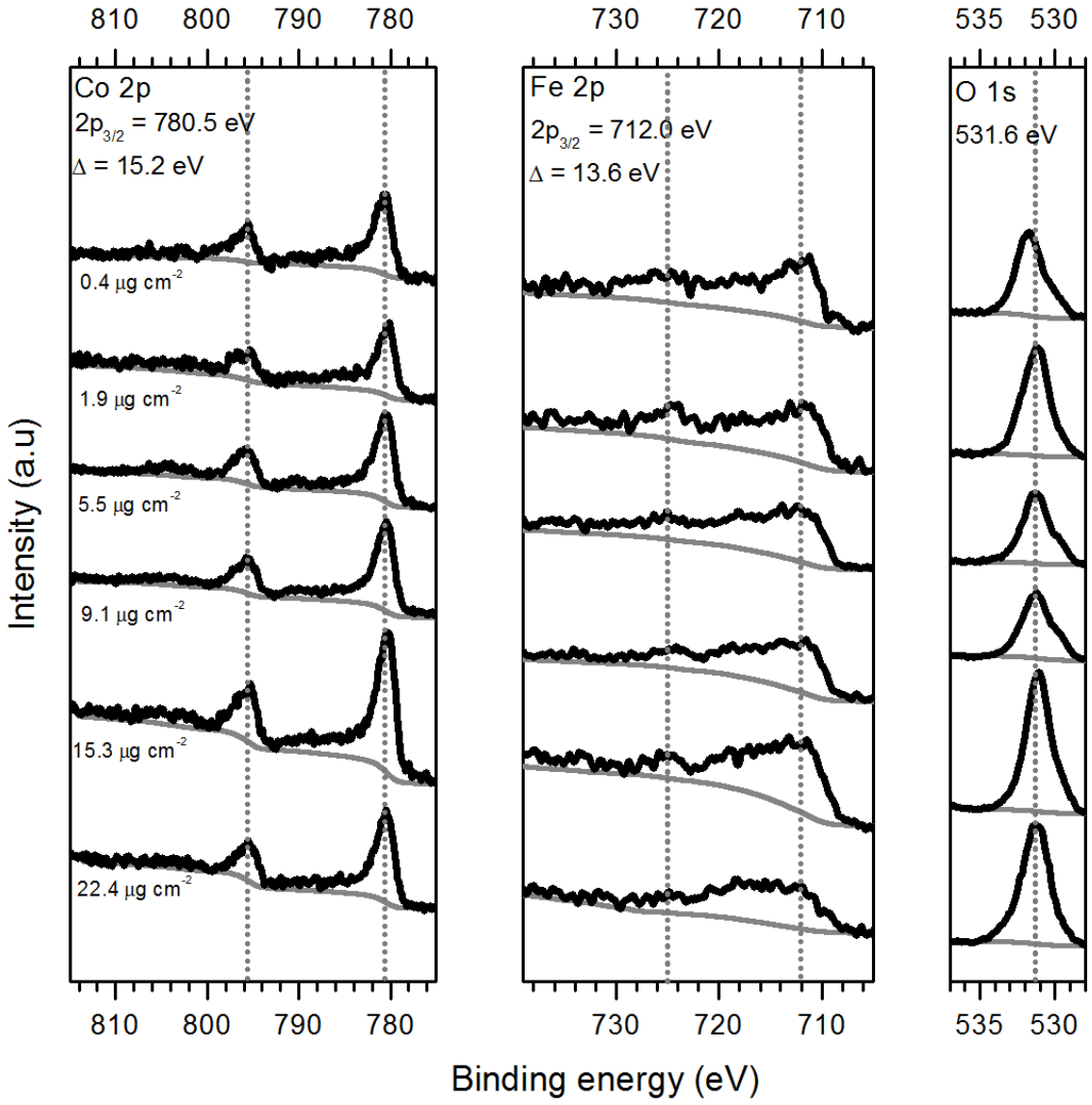

Figure S2| XPS spectra of $CoFeO_x$ films electrodeposited on Au.

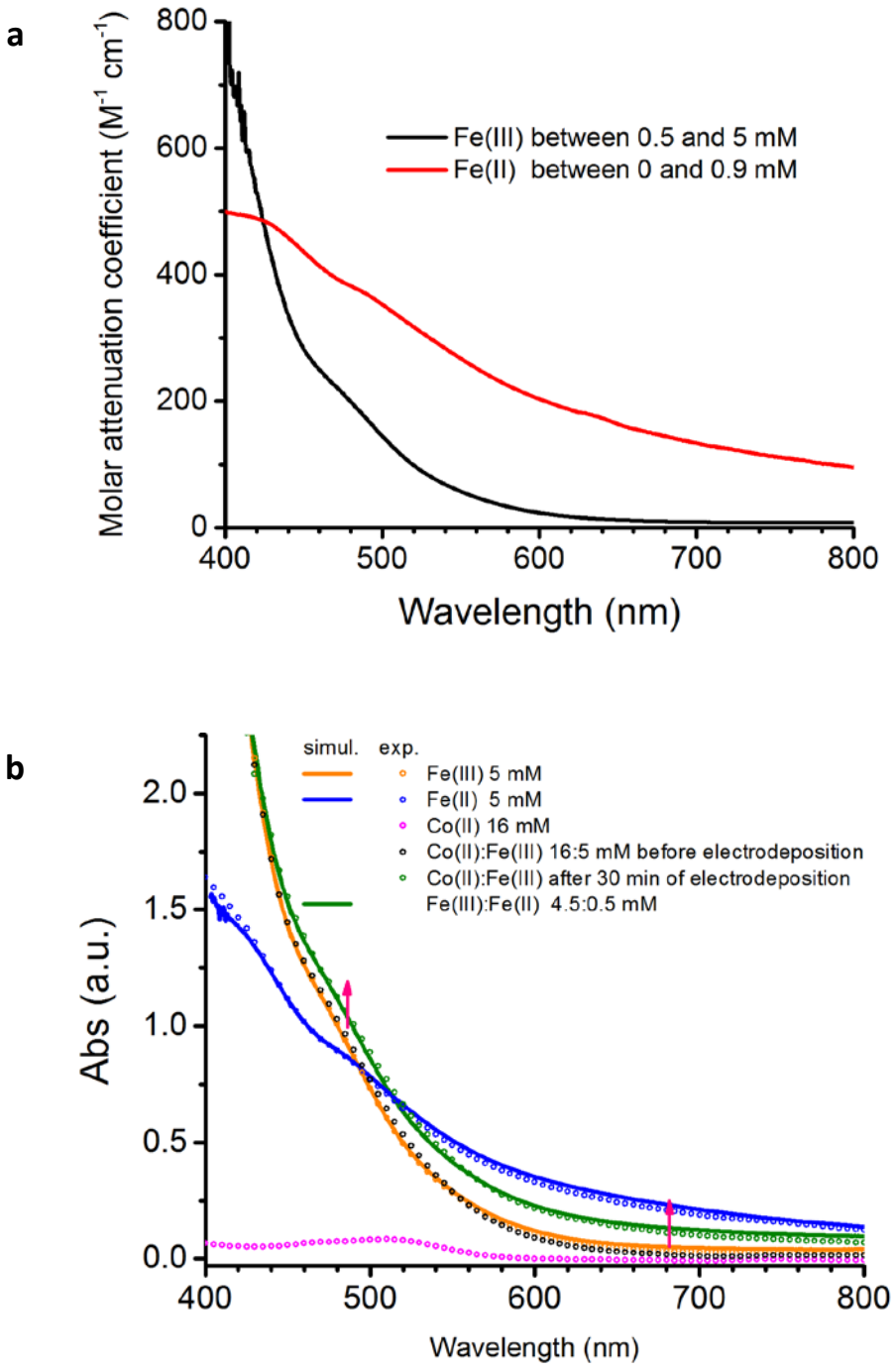

Figure S3| UV-vis absorbance. (a) Molar attenuation coefficients for Fe(III) and Fe(II) in 0.1M NaOAC at pH 5.3 in the range of concentrations relevant to in situ UV-vis measurements. **(b)** *In situ* UV-vis absorbance measurements during $CoFeO_x$ electrodeposition. Dotted lines correspond to experimental data while solid lines correspond to simulated absorbance using the molar attenuation coefficients in (a) for mixtures of Fe(III) and Fe(II).

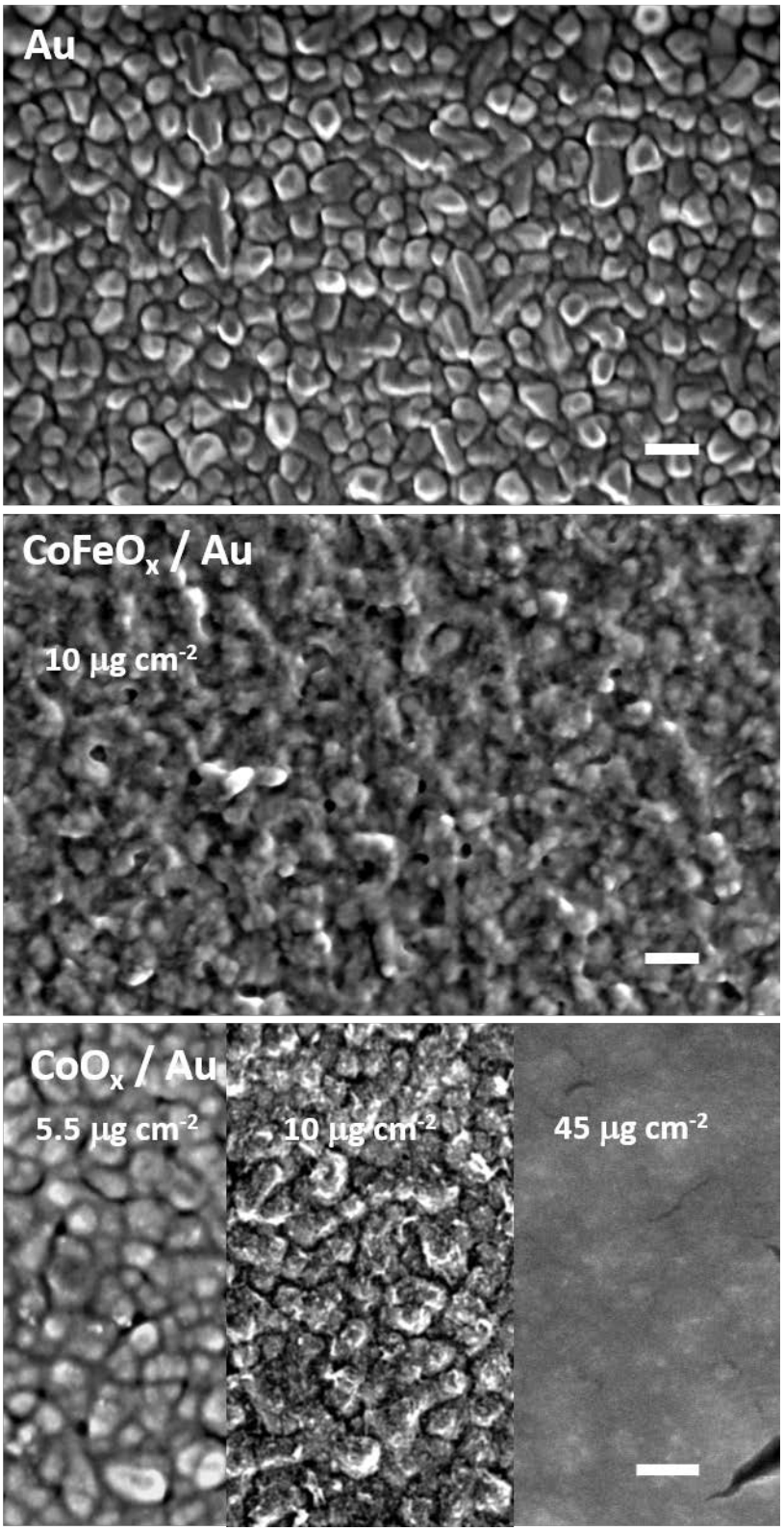

Figure S4| SEM images of $CoFeO_x$ and CoO_x films on Au. Scale bar size corresponds to 200 nm.

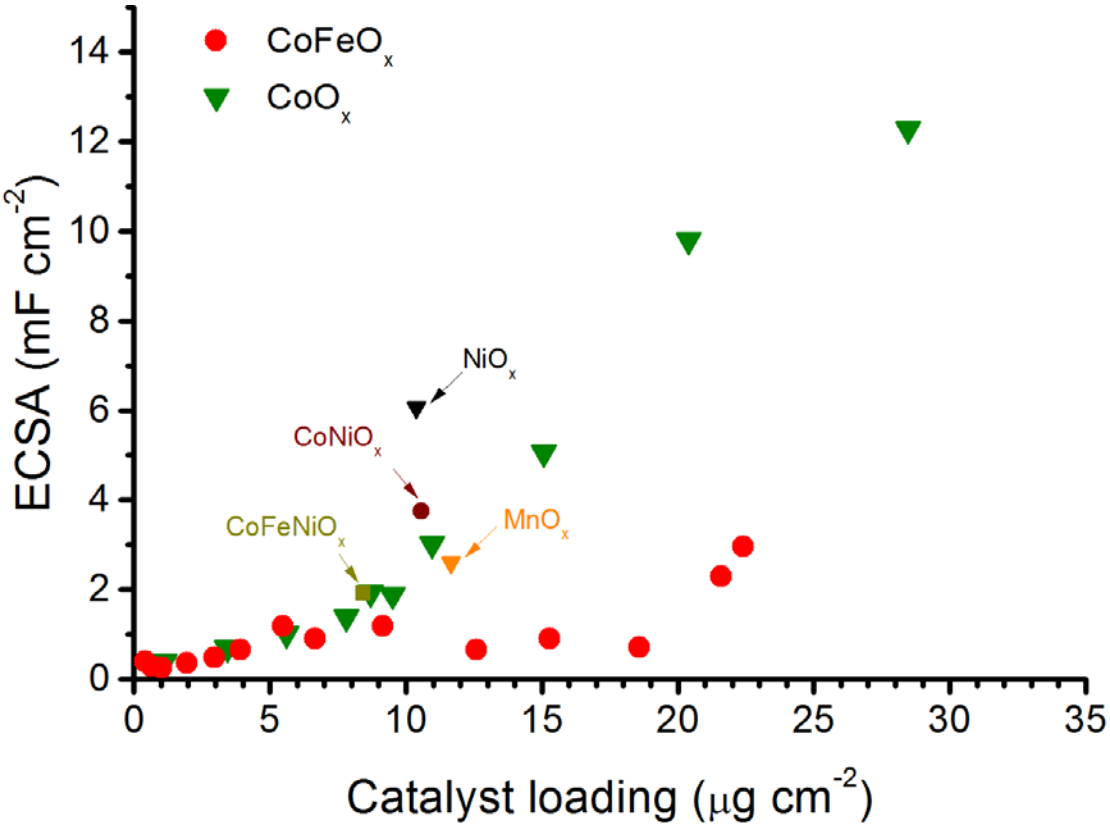

Figure S5| ECSA of $CoFeO_x$ and CoO_x at various catalyst loadings.

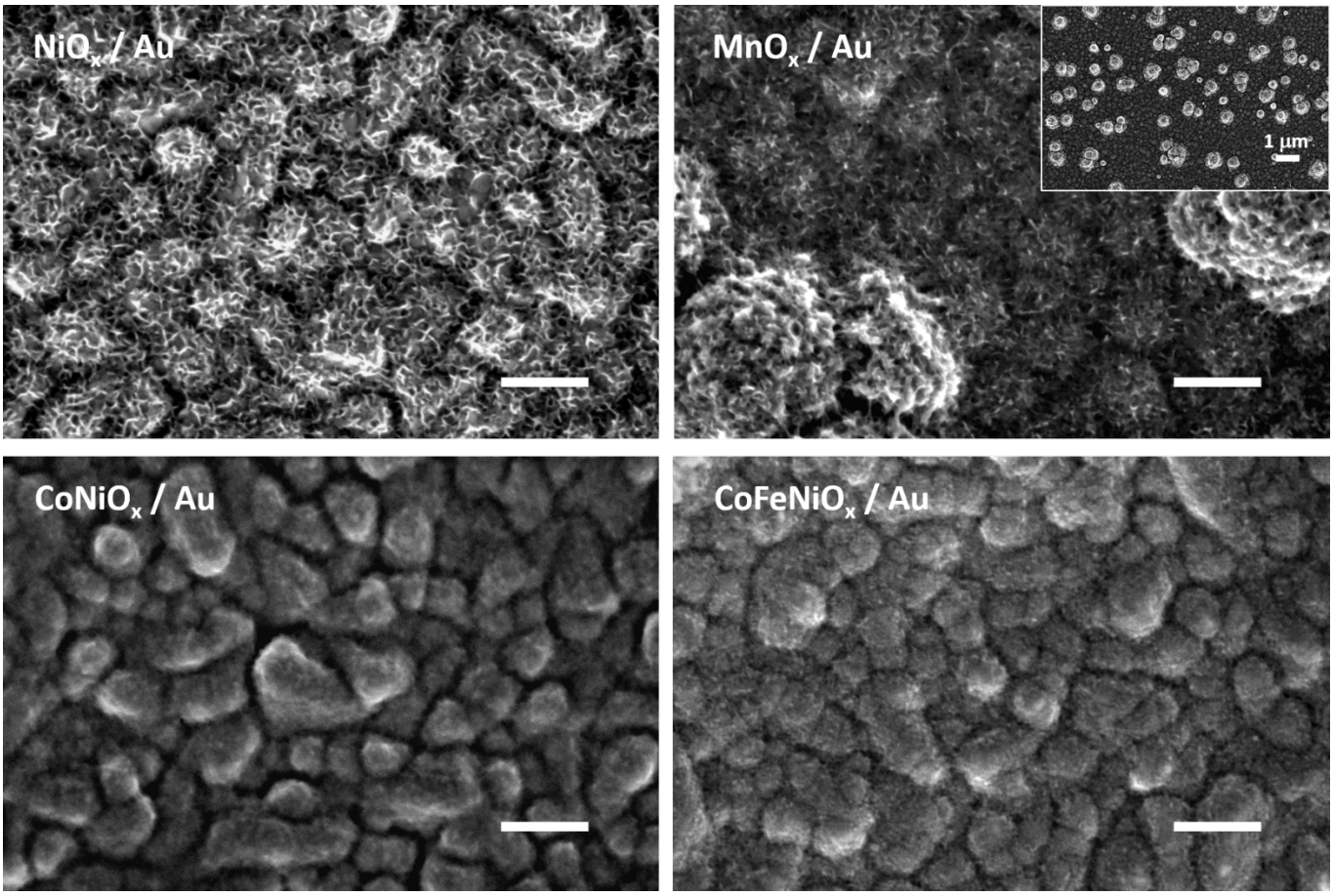

Figure S6| SEM images of NiO_x, MnO_x, $CoNiO_x$ and $CoFeNiO_x$ films on Au. The catalyst loading is ~10 μg cm^{-2}. Scale bar size corresponds to 200 nm.

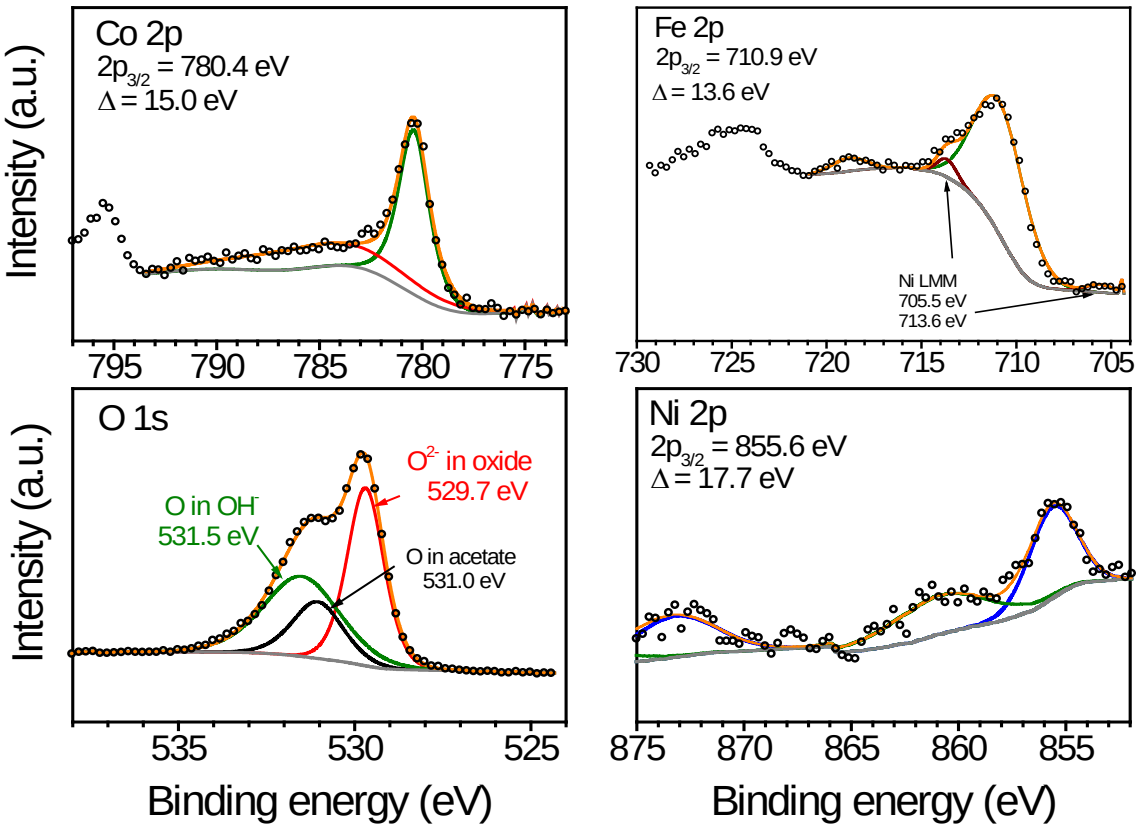

Figure S7| XPS spectra of $CoFeNiO_x$ films electrodeposited on Au substrates.

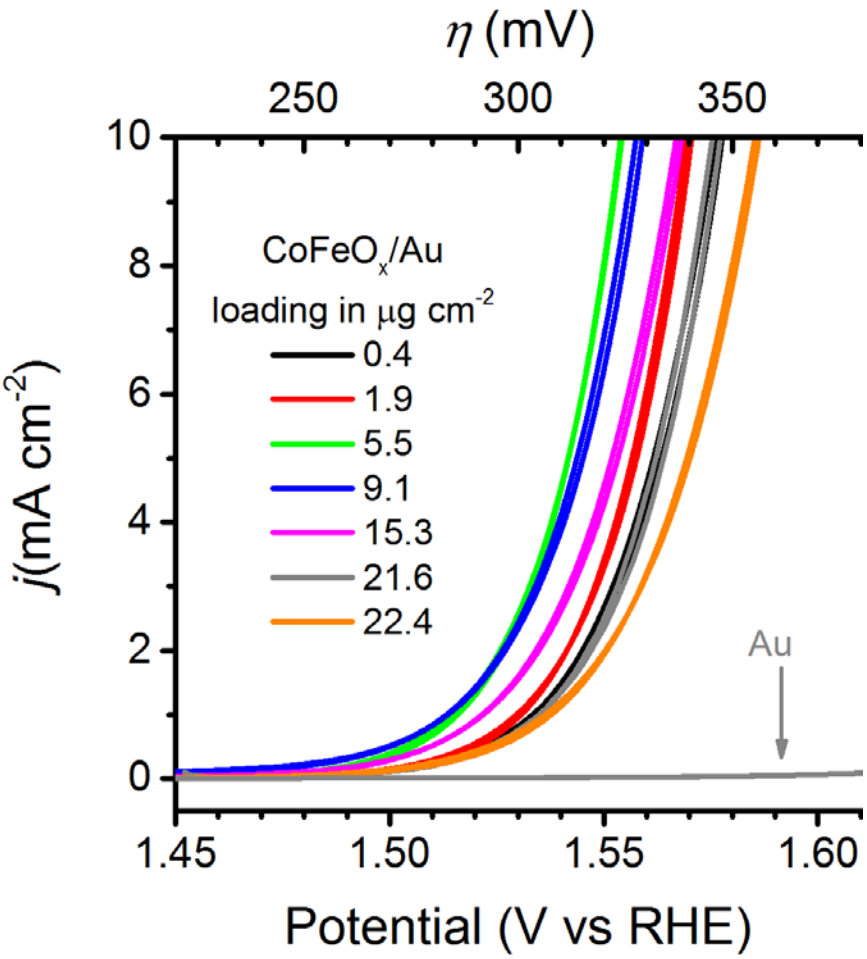

Figure S8| Current density-potential curves for $CoFeO_x$ films of different loadings electrodeposited on Au. Conditions: 1 M KOH, 5 mV s^{-1}.

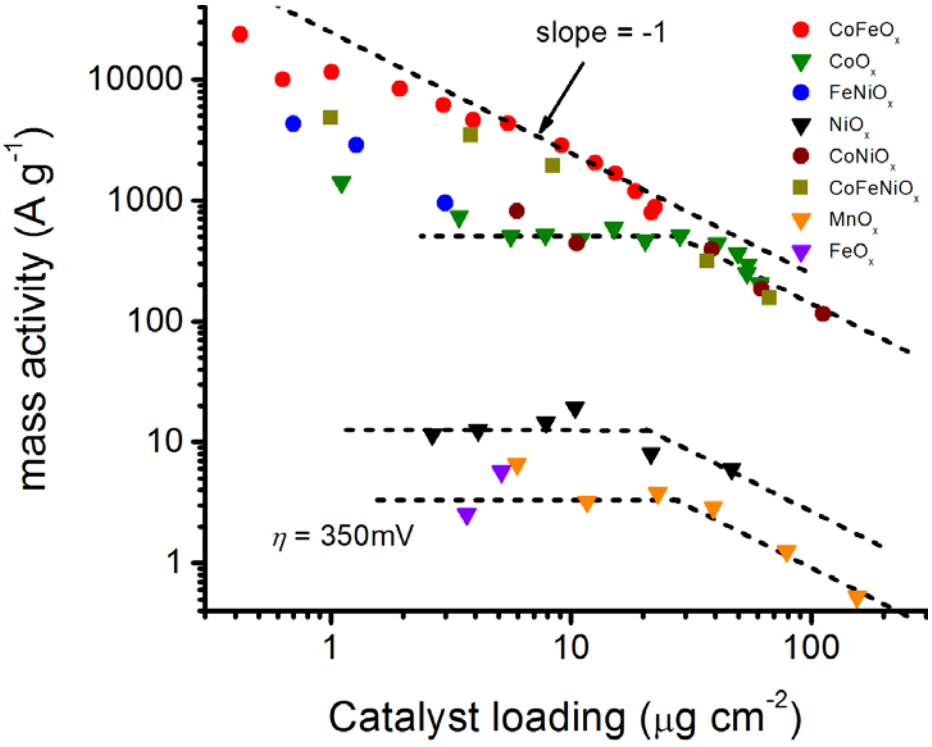

Figure S9|Activity-mass loading relation for various transition metal (oxy)hydroxides.

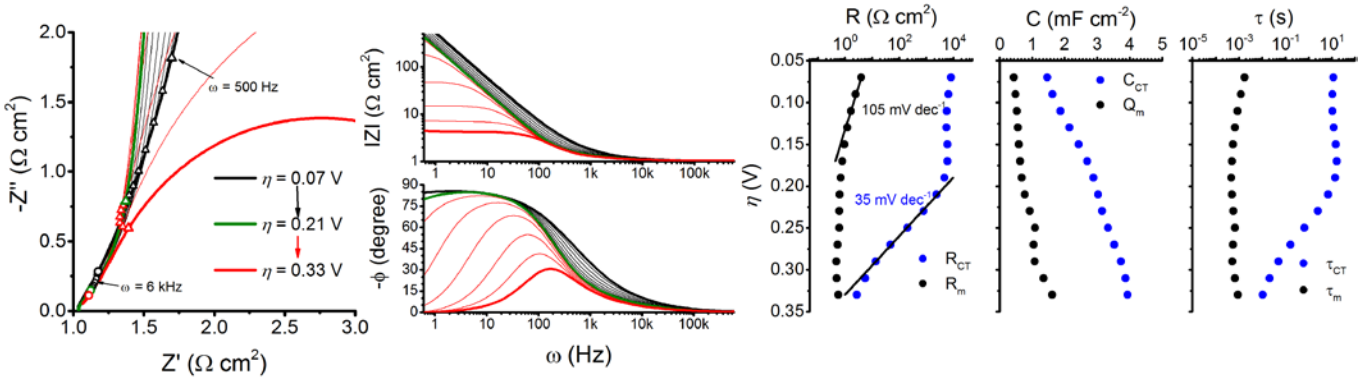

Figure S10| EIS response and fitting parameter of $CoFeO_x$ films at loadings of 15.3 μg cm^{-2}. Conditions: Au substrate, iron-free 1 M KOH. The EIS response was measured every 20 mV between 1.3 and 1.56 V vs. RHE.

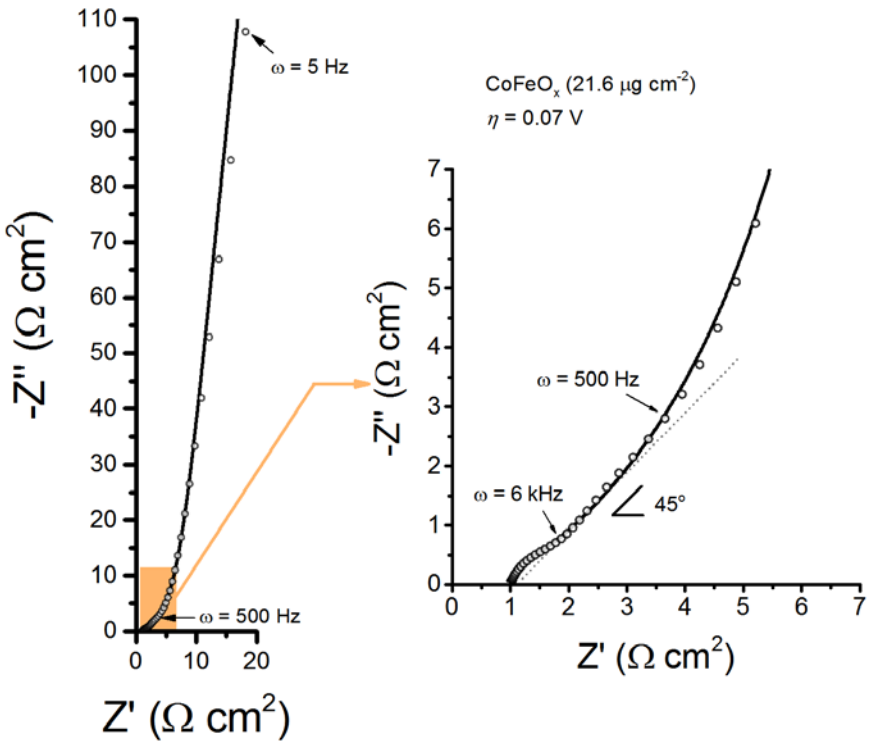

Figure S11| EIS response for the $CoFeO_x$ catalyst film at a loading of 21.6 μg cm^{-2} at η = 0.07 V. The transmission line components for charge transport for the thick catalyst film is indicated by a 45° component between 0.5 and 6 kHz. At ω > 6 kHz the EIS response corresponds to the fast electron transferat the back contact and electron transport through a thin inner (oxy)hydroxide layer as shown in model (b) in Scheme 1 of the main text. At ω < 500 Hz the EIS response approaches almost a vertical straigh line corresponding to the charging/discharging of the chemical capacitance of the $CoFeO_x$.[1]

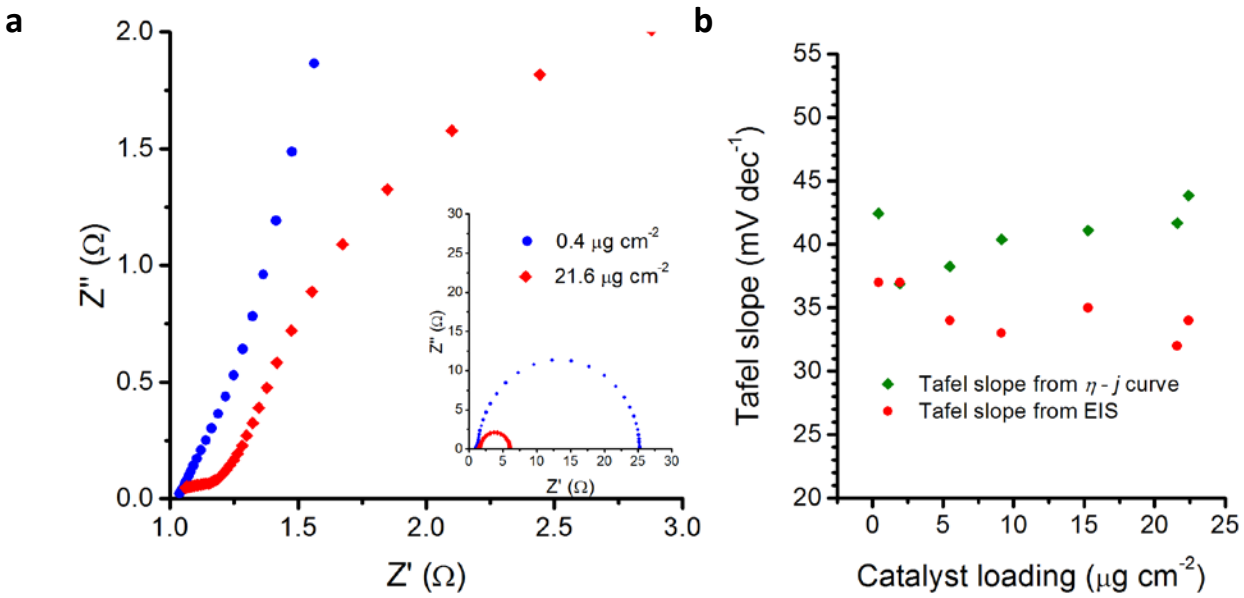

Figure S12| Characterization and OER activity of CoFeOx by EIS. (a) Nyquist plot (η = 310 mV) and **(b)** Tafel slopes determined from the η - j curve and EIS for the $CoFeO_x$ catalyst at different loadings.

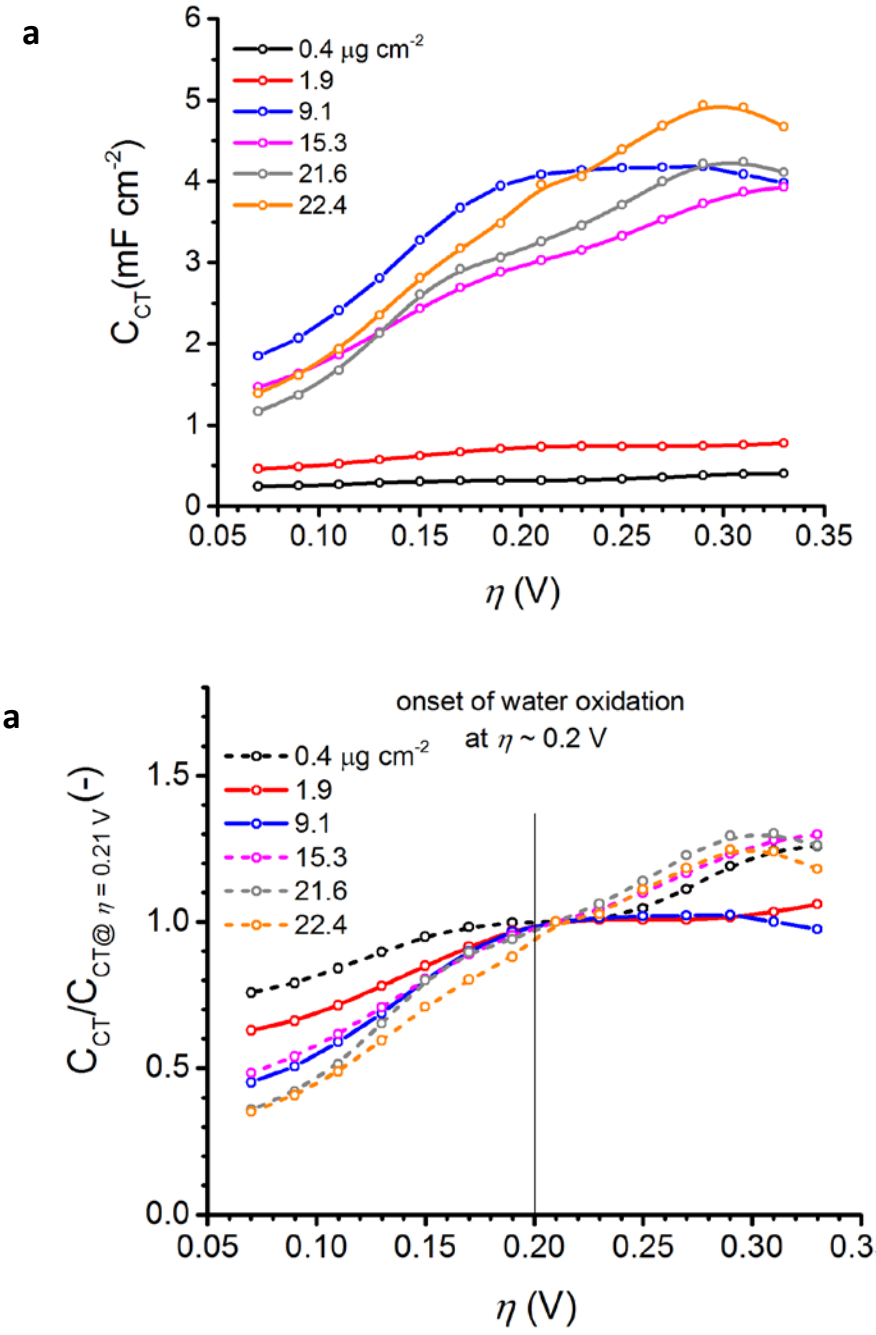

Figure S13| Charge transfer capacitance variation with overpotential for $CoFeO_x$ films determined by EIS. (a) Charge transfer capacitance. **(b)** charge transfer capacitance in (a) normalized to the capacitance value at the onset for water oxidation.

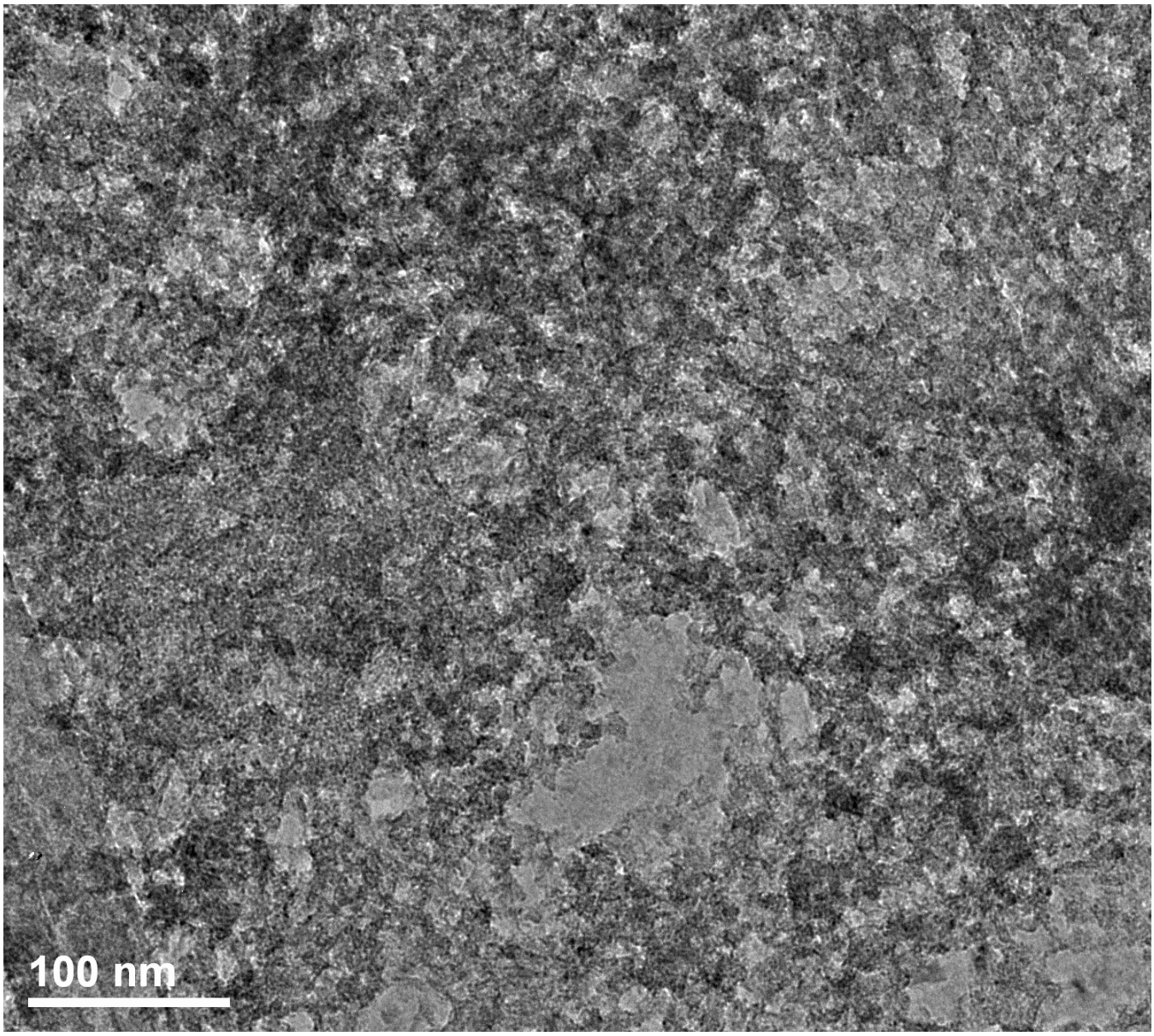

Figure S14| TEM of detached $CoFeO_x$ film.

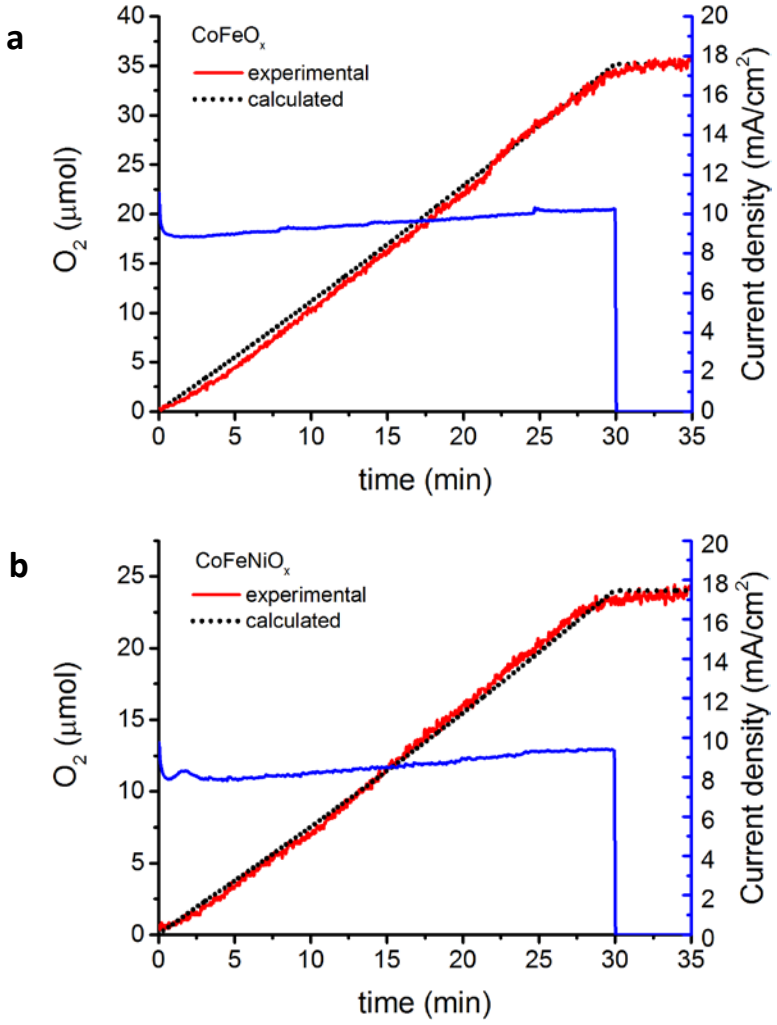

Figure S15| O_2 quantification during water oxidation in 1M KOH. (a) $CoFeO_x$ and (b) $CoFeNiO_x$. The potential was fixed to pass a current density of ~10 mA cm^{-2}.

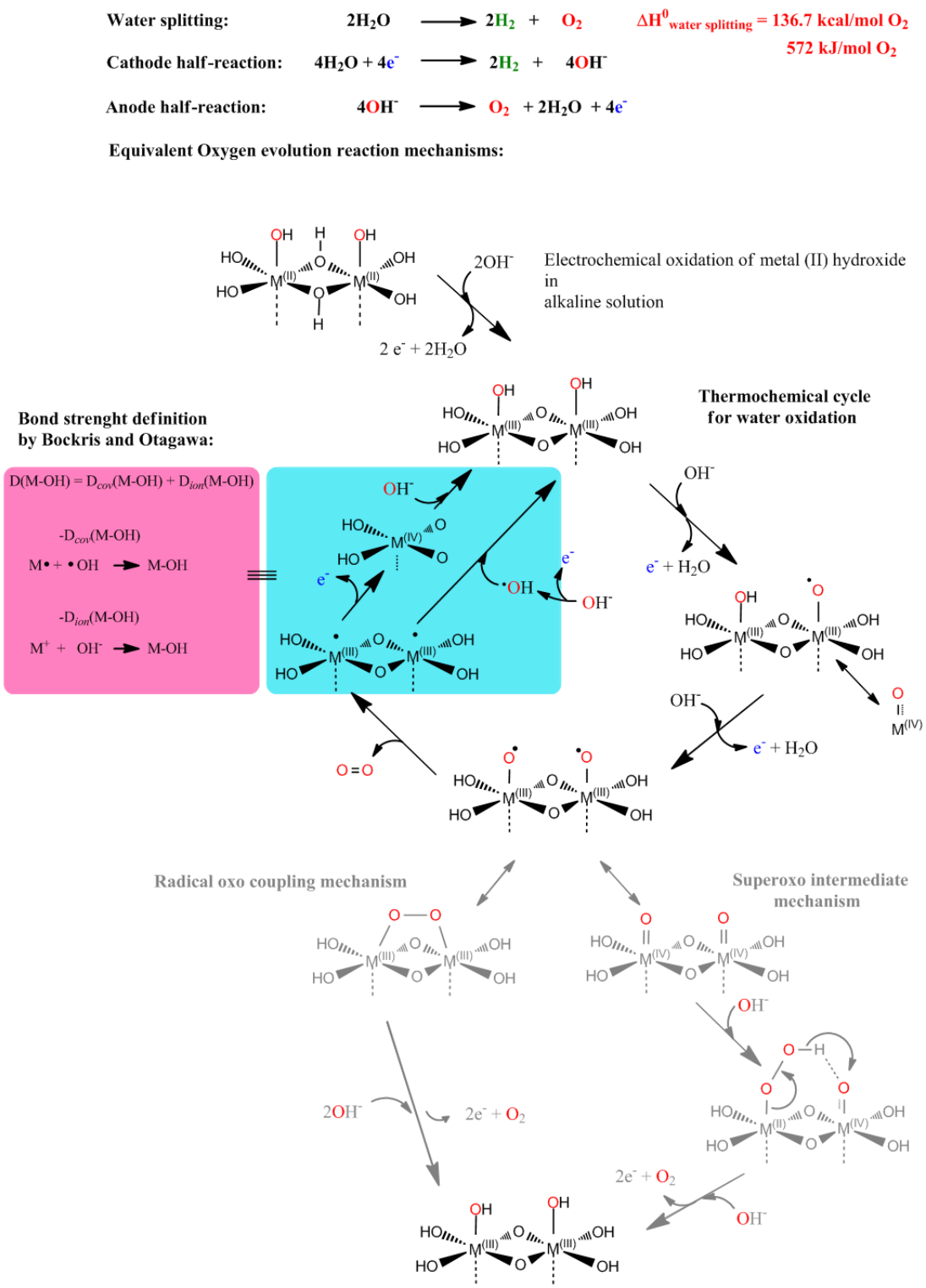

Figure S16| Thermochemical cycle (298 K) in support of the optimum M-OH bond strength. The total energy to split water in a thermochemical cycle is independent of the reaction mechanism.

Table S1. Summary of performance of representative anodes for water oxidation in 1M and 25wt% KOH.

Material/substrate	Electrolyte	Current density/ mA cm^{-2}	Overpotential /mV	Reference
$CoFeO_x$/Ni foam	1M KOH	10 100	270 299	This work
$CoFeNiO_x$/Ni foam	1M KOH	10 100	240 272	This work
NiFe/Ni foam	1M KOH	10	245	*Nat. Commun.* **2015**, (6), 6616
Co_3O_4/Ni foam	1M KOH	10	328	*J. Phys. Chem. C*, **2009**, 113, 15068
Co_3O_4/N-rmGO/Ni foam	1M KOH	10	310	*Nat. Mater*. **2011**, 10, 780.
$Ni_{0.9}Fe_{0.1}O_x$/Au	1M KOH	10	336	*J. Am. Chem. Soc.* **2012**, 134, 17253
Ni-Fe/Au	1M KOH	10	280	*J. Am. Chem. Soc.* **2013**, 135, 12329
[Ni-Fe]-LDH/HOPG	1M KOH	10	260	*J. Am. Chem. Soc.* **2014**, 136, 13118
CoMn LDH/CFP	1M KOH	10	293	*J. Am. Chem. Soc.* **2014**, 136, 16481
NiFe-LDH/CNT/CFP	1M KOH	10	247	*J. Am. Chem. Soc.* **2013**, 135, 8452
NiFe-NS/Ni foam	1M KOH	10	302	*Nat. Commun.* **2014**, (5), 4477

Table S2. Summary of intrinsic mass activity of various transition metal (oxy)hydroxides for OER in 1M KOH at η = 350 mV.

Metal (oxy)hydroxide	Mass activity (A g^{-1} at η = 350 mV)
MnO_x	3
FeO_x	6
CoO_x	510
NiO_x	12
$Fe_{0.8}Ni_{0.2}O_x$	4301
$Co_{0.6}Fe_{0.4}O_x$	4727
$Co_{0.5}Fe_{0.4}Ni_{0.1}O_x$	3438
$Co_{0.96}Ni_{0.04}O_x$	442

Table S3. Bond strength of various transition metal (oxy)hydroxides and average values for physical mixtures calculated using the method proposed by Bockris and Otagawa[2].

Mixture of metal (oxy)hydroxide	M-OH bond strength (Kcal mol^{-1})
Mn-OH	150
Fe-OH	141.8
Co-OH	130.4
Ni-OH	122.1
0.8Fe-OH + 0.2Ni-OH	137.9
0.6Co-OH + 0.4Fe-OH	135.0
0.5Co-OH + 0.4Fe-OH + 0.1Ni-OH	134.1
0.96Co-OH + 0.04Ni-OH	130.1

References

1 Bisquert, J., Grätzel, M., Wang, Q. & Fabregat-Santiago, F. Three-Channel Transmission Line Impedance Model for Mesoscopic Oxide Electrodes Functionalized with a Conductive Coating. *J. Phys. Chem. B* **110**, 11284-11290, (2006).

2 Bockris, J. O. M. & Otagawa, T. The Electrocatalysis of Oxygen Evolution on Perovskites. *J. Electrochem. Soc.* **131**, 290-302, (1984).