SUPPORTING INFORMATION

Crystalline Cobalt Oxide Films for Sustained Electrocatalytic Oxygen Evolution under Strongly Acidic Conditions

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Calculation estimating the amount of O_2 released through dissolution of Co_3O_4

Molar Mass of Co: 58.9332 g/mol
Thickness of deposited Co film: 150 nm
Density: 8.90 g/cm^3
Area of Electrode: 1 cm^2

Volume of deposited Co film:

$$150\ nm \times \frac{1\times10^{-7} cm}{nm} \times 1\ cm^2 = 1.5\times10^{-5} cm^3$$

Loading density of Co deposited:

$$\frac{1.5\times10^{-5} cm^3}{cm^2} \times \frac{8.90\ g}{cm^3} \times \frac{1000\ mg}{g} = 0.1335\ \frac{mg}{cm^2}$$

Loading density of Co_3O_4 deposited:

$$\frac{0.1335\ mg\ Co}{cm^2} \times \frac{g\ Co}{1000\ mg\ Co} \times \frac{mol\ Co}{58.9332\ g\ Co} \times \frac{1\ mol\ Co_3O_4}{3\ mol\ Co} \times \frac{240.8\ g\ Co_3O_4}{1\ mol\ Co_3O_4} \times \frac{1000\ mg\ Co_3O_4}{1\ g\ Co_3O_4}$$

$$= 0.182\ \frac{mg\ Co_3O_4}{cm^2}$$

Moles of O_2 from Co_3O_4:

$$\frac{0.182\ mg\ Co_3O_4}{cm^2} \times \frac{mmol\ Co_3O_4}{240.8\ mg\ Co_3O_4} \times \frac{2\ mmol\ O_2}{1\ mmol\ Co_3O_4} \times \frac{1\ mol\ O_2}{1000\ mmol\ O_2} \times 1\ cm^2 = 1.51\times10^{-6}\ mol\ O_2$$

Volume of O_2 produced from dissolution of Co_3O_4:

$$\frac{1.51\times10^{-6}\ mol\ O_2 \times 0.0826\ \frac{atm\cdot L}{mol\cdot K} \times 298\ K}{1\ atm} \times \frac{1000\ mL}{1\ L} = 0.037\ mL\ of\ O_2$$

Before complete dissolution of the 300-nm Co_3O_4 film, 6.12 moles of O_2 can be produced per gram of Co_3O_4 and 1.47×10^3 moles of O_2 can be produced per mole of Co_3O_4.

Supplementary Figures

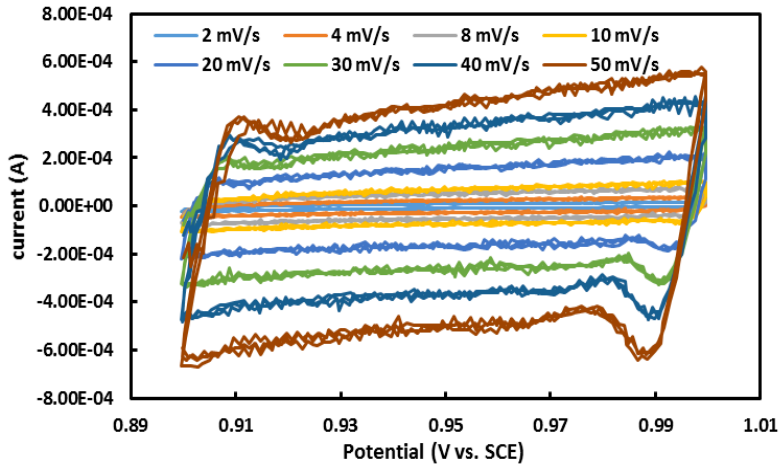

Figure S1. Cyclic voltammograms at different scan rates collected after 2 hours of electrolysis at 10 mA/cm^2 of a representative sample: the Co_3O_4 nanoparticle film that was prepared by annealing colloidally synthesized Co nanoparticles.

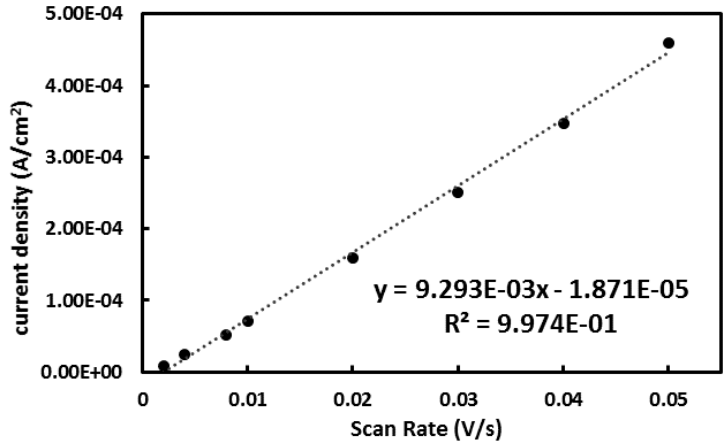

Figure S2. *j* - *v* plot of a 1 cm^2 Co_3O_4 nanoparticle film that was prepared from annealing Co nanoparticles. The slope of the plot (9.293 mF/cm^2) gives the capacitance of the catalyst film. When divided by the capacitance of bare FTO (0.008 mF/cm^2), the result can be interpreted as the Co_3O_4 nanoparticle film being 1162 times rougher than bare FTO.

EDS data (Figure S3) indicate that no noble metal contaminants, including Ir and Ru, are present. High-resolution X-ray photoelectron spectra of the Ir 4d and Ru 3p regions are consistent with the EDS data, revealing no signal above baseline (Figure S4). Additionally, the XPS data are consistent with the formation of Co_3O_4 and also reveal that minor residual sulfur contaminants are present on all surfaces, including the bare FTO substrate. Time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is typically considered to have a higher elemental sensitivity than XPS and EDS,[1] also indicates that Ir and Ru are not present.

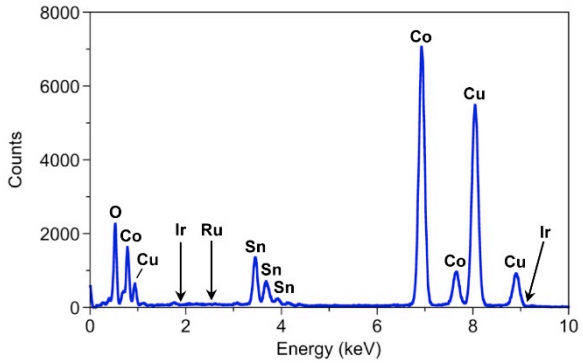

Figure S3. EDS spectrum of a Co_3O_4/FTO electrode showing the presence of oxygen, cobalt, and tin. No peaks corresponding to iridium or ruthenium were observed. The copper signal is from the copper TEM grid.

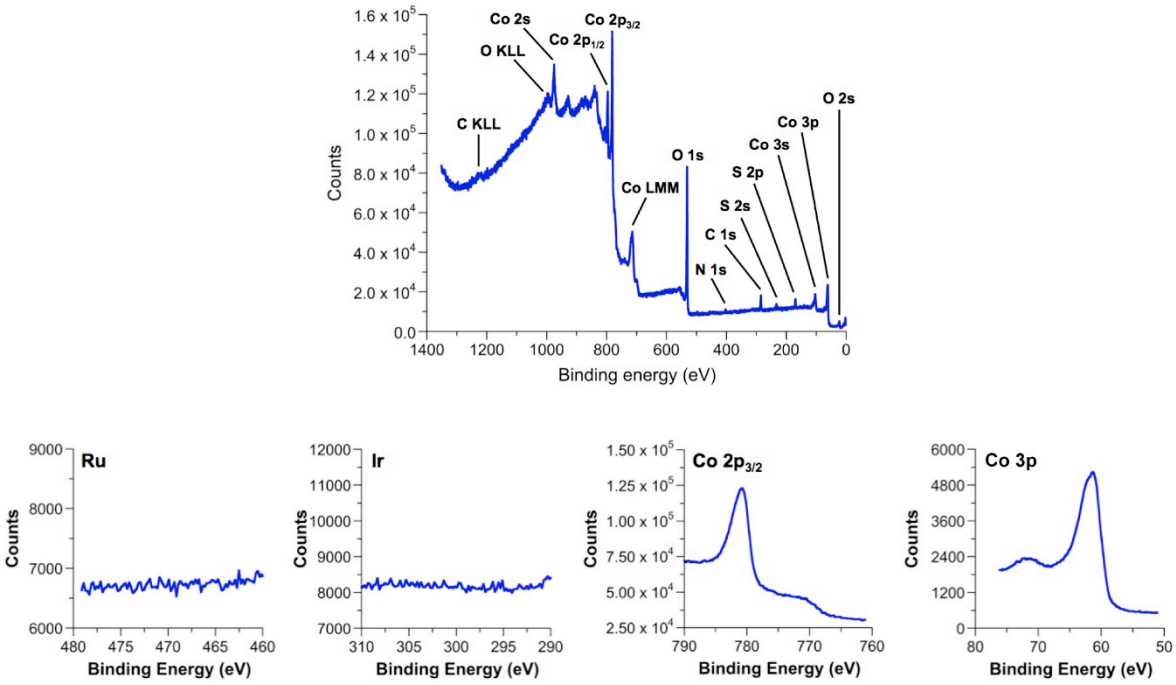

Figure S4. XPS spectra of a Co_3O_4/FTO electrode: (top) Survey scan showing the spectra obtained before electrochemical testing. (bottom) High-resolution scans of the Ru 3p, Ir 4d, Co 2p, and Co 3p regions.

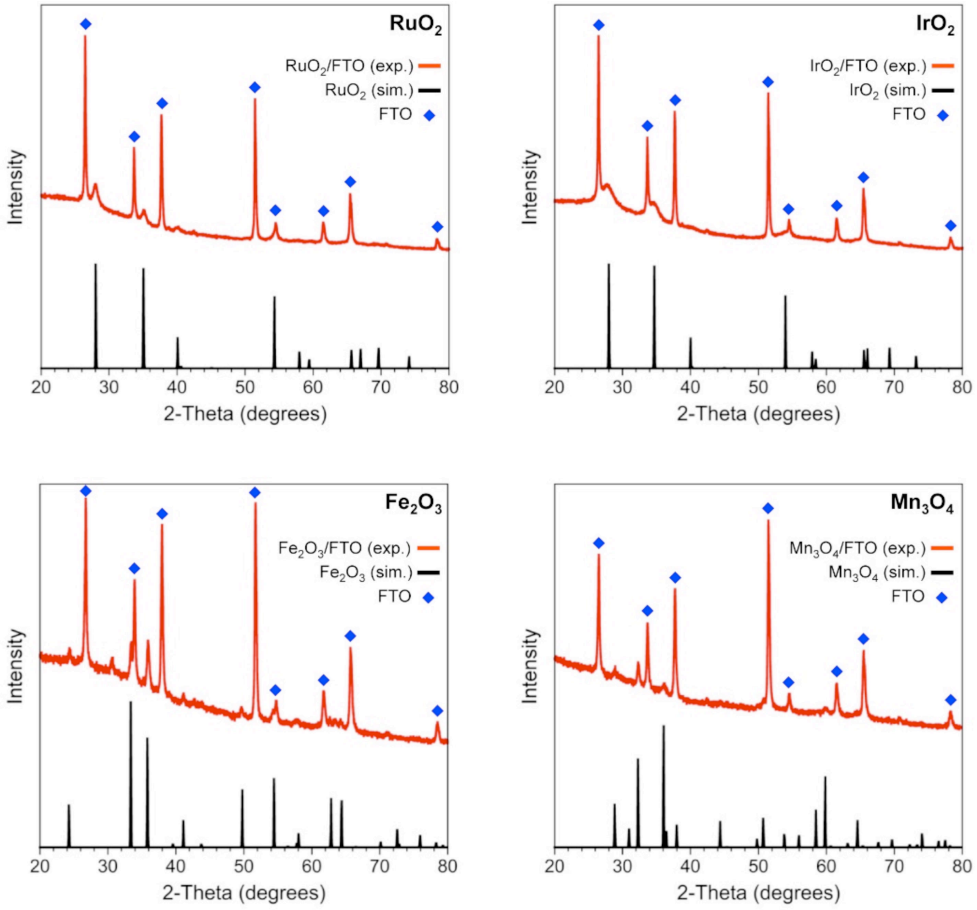

Figure S5. XRD patterns corresponding to the RuO_2/FTO, IrO_2/FTO, Fe_2O_3/FTO, and Mn_3O_4/FTO electrodes used for benchmarking and comparison.

Table S1. Summary of relative roughness of three different Co_3O_4 catalyst films collected at 2, 4, and 8 hours during a 10 mA/cm^2 electrolysis experiment.

	150 nm Co_3O_4 Film	**Co_3O_4 nanoparticle Film**	**Bulk Co_3O_4 Film**
0 hr	4	728	38
2 hr	15	1153	100
4 hr	19	1204	109
8hr	14	1185	147

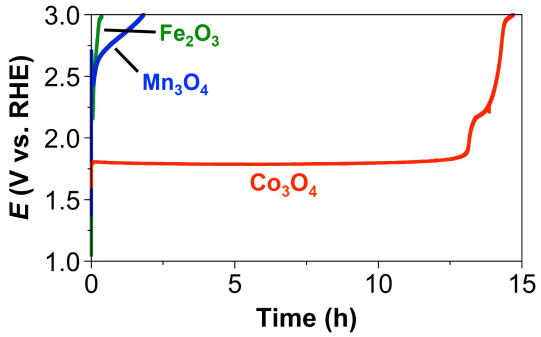

Figure S6. Galvanostatic measurements at 10 mA/cm^2 for Co_3O_4/FTO from Figure 5B extended out to 15 h to show the electrode's failure after complete film dissolution. The iron and manganese analogues, which dissolve rapidly, are also shown for comparison.

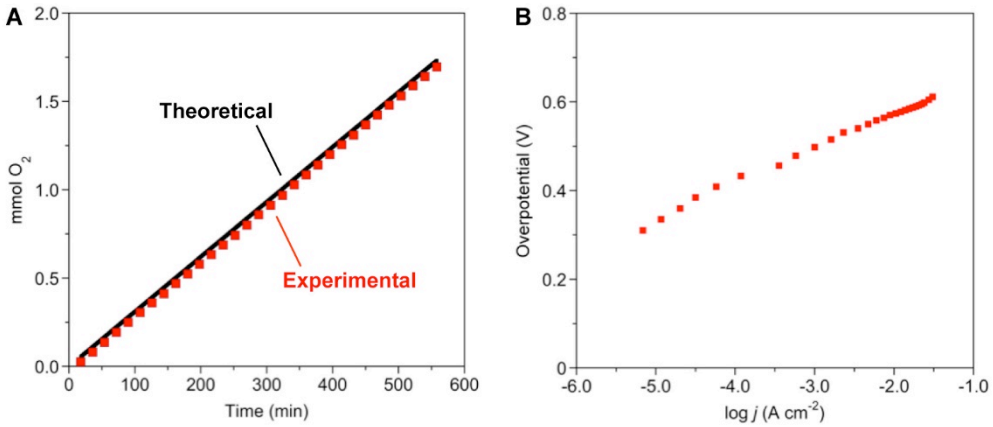

Figure S7. (A) Faradaic yield and (B) Tafel plot of a Co_3O_4/FTO electrode.

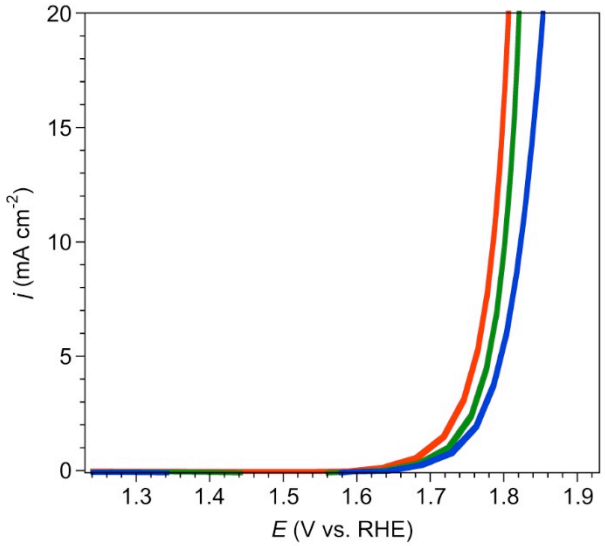

Figure S8. Plot of current density *vs*. potential for Co_3O_4/FTO electrodes in 0.5 M H_2SO_4 initially (red) and also after 100 (green) and 500 (blue) CV sweeps between 1.86 and 1.24 V *vs*. RHE.

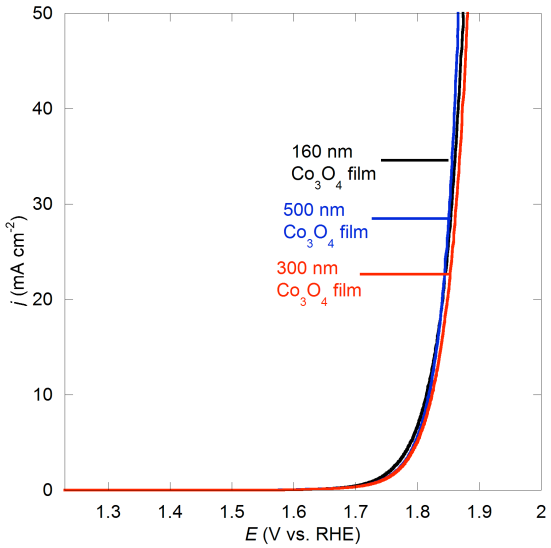

Figure S9. Linear sweep voltammagrams of 160-500 nm thick Co_3O_4 films in 0.5 M H_2SO_4.

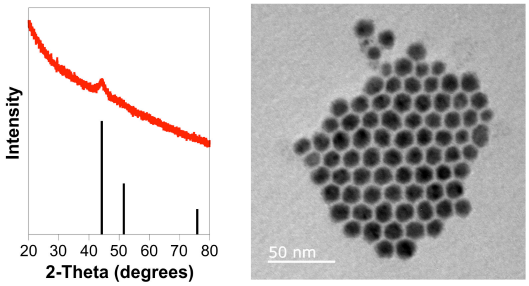

Figure S10. Powder XRD pattern (top: experimental, bottom: simulated) and TEM image for the colloidal Co nanoparticles.

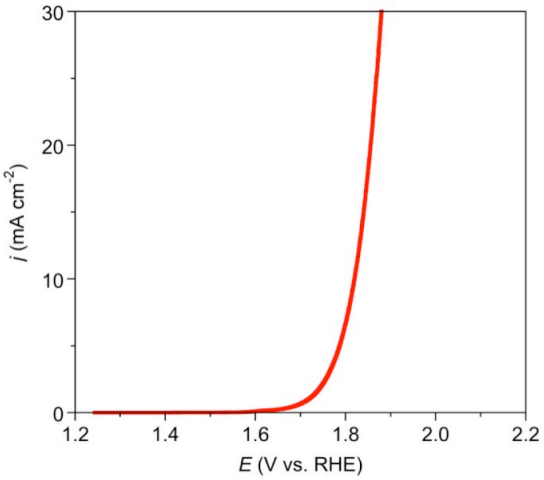

Figure S11. Linear sweep voltammogram of a Co_3O_4/Au/FTO electrode showing similar activity to a Co_3O_4/FTO electrode. The Co_3O_4/Au/FTO electrode was prepared by first depositing a ~150-nm Au film on FTO, then depositing a ~150-nm Co film on top of the Au, then oxidizing Co to Co_3O_4 by heating to 400 °C for 2 h.

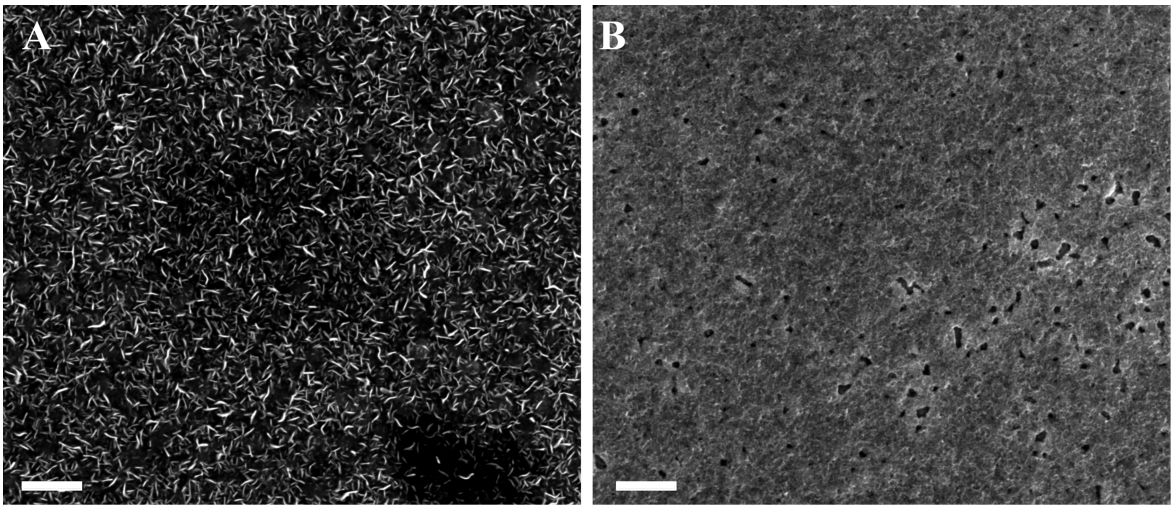

Figure S12. Scanning electron micrographs of a 300 nm Co_3O_4 film held galvanostatically at 10 mA/cm^2 in 0.5 M H_2SO_4 after (A) 10 minutes and (B) 4 hours. Scale bar is 1 μm.

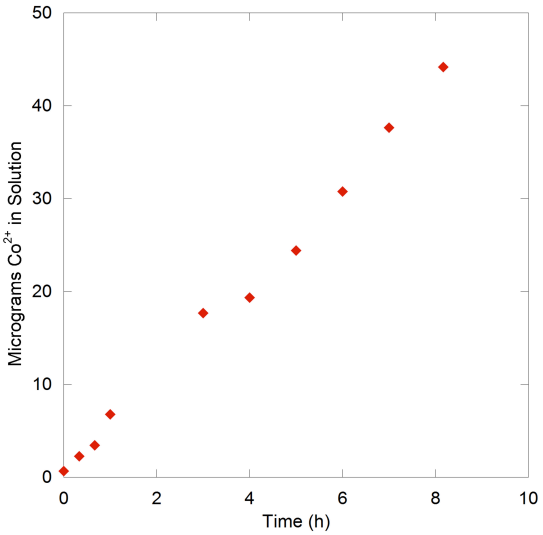

Figure S13. Time-dependent dissolution data of a 160 nm Co_3O_4 film.

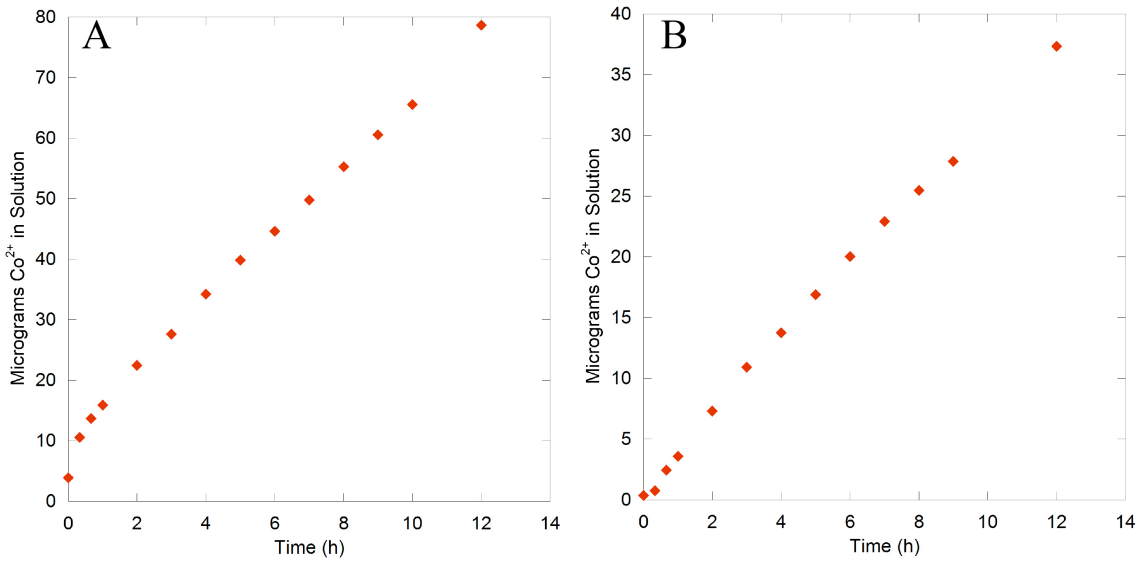

Figure S14. Time-dependent dissolution data of a 300 nm Co_3O_4 film held galvanostatically at 10 mA/cm^2 in (A) pH 1 and (B) pH 2 electrolyte.

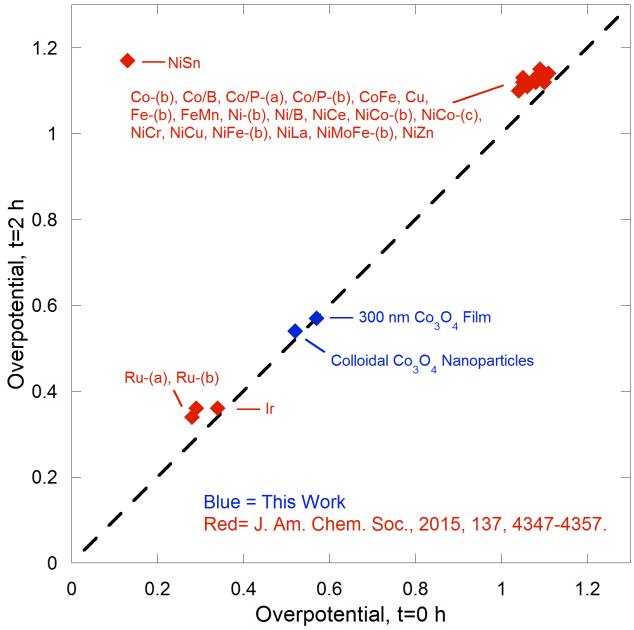

Figure S15. Plot overpotential at 2 h vs initial overpotential for the Co/FTO → Co_3O_4/FTO nanoparticle and film electrodes reported in this manuscript, along with OER catalysts reported in a recent benchmarking paper (ref. 28 of the main manuscript), in 0.5 M H_2SO_4. This plot shows how the Co_3O_4/FTO electrodes compare to other reported OER catalysts and also their short-term stability after 2 h of operation.

Reference

[1] Benninghoven, A. Chemical Analysis of Inorganic and Organic Surfaces and Thin Films by Static Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). *Angew. Chem., Int. Ed.* **1994**, *33*, 1023-1043.