Supplementary Information For:

Evaluation of Sputtered Nickel Oxide, Cobalt Oxide and Nickel-Cobalt Oxide on n-type Silicon Photoanodes for Solar-Driven O$_2$(g) Evolution from Water

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Experimental Procedures

Preparation of Electrodes

Ohmic contacts to Si samples were formed by scribing an In-Ga eutectic alloy (Alfa Aesar, 99.99%) onto the back surfaces. High-purity Ag paint (SPI supplies) was then used to mechanically attach a coiled, tin-plated Cu wire (McMaster-Carr) which was then threaded through a glass tube (Corning Incorporation, Pyrex tubing, 7740 glass). The sample was then encapsulated and sealed to the glass tube using a mixture of 2:1 grey epoxy (Hysol 9460F) or white epoxy (Hysol 1C). The epoxy was typically allowed to cure under ambient laboratory conditions for ≥ 8 h before the electrodes were put into aqueous solutions for measurements.   A high-resolution optical scanner (Epson

Perfection V370 with a resolution of 2400 psi) was used to image the exposed surface area of each electrode, and the geometric areas were determined by analyzing the images using ImageJ software. All of the electrodes used in this study were $0.1 - 0.2$ cm^2 in area unless otherwise specified.

X-ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy (XPS) data were obtained at base pressures $<1 \times 10^{-9}$ Torr using an M-Probe spectrometer. A monochromatic Al Kα source generated X-rays incident on the sample with a 300 µm spot. High-resolution spectra were acquired with a 100 mm hemispherical electron analyzer set to a 20 eV pass energy and controlled using the ESCA 2000 E Capture software (Service Physics). All XP spectra were energy corrected assuming an adventitious C 1s photoelectron binding energy peak of 284.6 eV, and fit using a Shirley baseline. For the study of Fe incorporation onto the sputtered films, Fe 2p high resolution XPS data were collected using a Kratos AXIS Ultra photoelectron spectrometer equipped with an achromatic Mg Kα X-ray source (1253.6 eV), a hybrid electrostatic and magnetic electron lens system, and a delay-line detector. The chamber pressure was maintained $<5 \times 10^{-9}$ Torr and the photoelectron ejection vector was 90° with respect to the surface plane. The electron lens aperture was set to collect a 700×300 µm spot. Survey spectra were collected with an analyzer pass energy of 80 eV, while high-resolution spectra were collected with an analyzer pass energy of 10 eV. The instrument was operated by Vision Manager Software v. 2.2.10, revision 5. The peak energies were calibrated against the binding energy of the adventitious C 1s peak at 284.8 eV. For quantitative analysis, the XPS peaks were fitted using CasaXPS software (CASA Ltd., Teignmouth, United Kingdom) to symmetric Voigt line shapes composed of

Gaussian (70%) and Lorentzian (30%) functions that employed a Shirley background. The atomic ratio between Ni and Co was obtained from eq 1:

$$\frac{N_{Ni}}{N_{Co}} = \frac{A_{Ni}/S_{Ni}}{A_{Co}/S_{Co}}$$

(1)

where N is the number of atoms, A is the total area of the photoemission peaks, and S is the sensitivity factor. Values for S (for M-Probe system, S_{Ni} is 14.61 and S_{Co} is 12.62; for Kratos system, S_{Ni} is 3.85 and S_{Co} is 3.51 and S_{Fe} is 2.95) were provided by the instrument manufacturer.

Electrochemical Impedance Spectroscopy and Mott-Schottky Analysis

Electrochemical impedance spectroscopy was carried out on n^+-Si|NiO$_x$, n^+-Si|CoO$_x$, n^+-Si|NiCoO$_x$ and n-Si|NiO$_x$, n-Si|CoO$_x$, n-Si|NiCoO$_x$, to determine the doping level of NiO$_x$, CoO$_x$, and NiCoO$_x$ and the barrier height of the n-Si|NiO$_x$, n-Si|CoO$_x$, n-Si|NiCoO$_x$ interface. Impedance spectra were acquired by a BioLogic SP-200 with built-in EIS analyser. A sinusoidal, 15 mV$_{RMS}$ AC signal that was scanned between 1 and 10^6 Hz was superimposed on each DC potential. The DC potentials were stepped in a sequence from -1.0 to 0.5 V for n^+-Si electrodes and 0.1 to 0.8 V for n-Si electrodes with a step of 0.05 V. All measurements were performed in the absence of illumination and in a quiescent solution of 50 mM $K_3Fe(CN)_6$, 350 mM $K_4Fe(CN)_6$, and 1.0 M Na_2SO_4 in 200 mL of H_2O. Both $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were sufficiently concentrated to prevent mass transport interference with the measurements and maintained a well-defined redox potential. The reverse bias dependence of the area-normalized semiconductor depletion-region capacitance is given by the Mott-Schottky eq 2:

$$A^2 C_{diff}^{-2} = \frac{2}{q\epsilon\epsilon_0 N_d}(E - E_{fb} - \frac{k_B T}{q})$$

(2)

where A is the area of the semiconductor-liquid junction, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of vacuum, N_d is the doping density of the sample, T is the absolute temperature, k_B is Boltzmann's constant, and q is the (unsigned) charge on an electron. A Mott-Schottky (M-S) plot of C^{-2} versus E should be linear with a slope related to N_d and an x-intercept related to E_{fb}.

The electrochemical impedance data were fit with EC-Lab software (V10.37) EIS data analysis tool Zfit using a Randles circuit. The dielectric constant of NiO_x, CoO_x and $NiCoO_x$ are set at 12, 13 and 12.5 from previous report.[1] The average value of N_d extracted from the M-S slope of n^+-Si|NiO_x, n^+-Si|CoO_x and n^+-Si|$NiCoO_x$ were all in the range of $\sim 10^{19}$ cm^{-3}.

The average value of N_d extracted from the M-S slope of n-Si|NiO_x, n-Si|CoO_x and n-Si|$NiCoO_x$ were 0.8×10^{16}, 1.2×10^{16} and 1.0×10^{16} respectively, which were in excellent agreement with the range specified by the manufacturer ($8\times10^{16}\sim5\times10^{15}$ cm^{-3}), confirming that the measured capacitance was indeed the depletion-region capacitance at the n-Si|NiO_x, n-Si|CoO_x and n-Si|$NiCoO_x$ interface.

Electrochemical Measurements

All the electrochemical measurements were performed with a standard three-electrode setup. A home built electrochemical cell with a flat Pyrex glass bottom was used for all the electrochemical measurements. During electrochemical measurements, the electrolyte was constantly agitated with a magnetic stir bar driven by a model-train motor (Pittman)

with a Railpower 1370 speed controller (Model Rectifier Corporation). The illumination intensity was calibrated with a Si photodiode (Thor Labs, FDS-100Cal) by placing the photodiode at the same position as the working electrode. The Si photodiode was previously calibrated by measuring the short-circuit current under AM 1.5 simulated sunlight at 100 mW cm^{-2}. All the electrochemical measurements were performed with a Biological SP-200 potentiostat (Bio-Logic Science Instruments). Cyclic voltammetry was acquired at a scan rate of 50 mV s^{-1}.

An Hg/HgO (CH Instruments, CH152) electrode was used as the reference electrode, which has been calibrated to 0.92 V versus Reversible Hydrogen Electrode (RHE) in 1M KOH(aq) solution, and a carbon cloth that was sealed in a fritted glass tube (gas dispersion tube Pro-D, Aceglass, Inc.) was used as the counter electrode in 1M KOH(aq) solution.

A Pt wire (0.5 mm diameter, 99.99% trace metals basis, Alfa-Aesar) was used as a reference and a Pt gauze (100 mesh, 99.9% trace metal basis, Alfa-Aesar) was used as the counter electrode for electrochemical measurements in $Fe(CN)_6^{3-/4-}$ solution.

A Xenon arc lamp (Newport 67005 and 699111) equipped with an infrared filter (Newport 61945) and an AM 1.5G filter (Newport 81094 and 71260) was used for the spectral response measurements. The quantum yield was acquired with a Biological SP-200 potentiostat with its output connected to a lock-in amplifier (Stanford Research System, Model SR830) while the incident light was chopped at a frequency of 19 Hz.

For the long-term stability test in 1M KOH (aq, ACS grade) solution, ENH-type (EIKO) tungsten-halogen lamps in a custom housing with a ground glass diffuser (Thor Labs, DG20-1500) that are powered by a transformer (Staco Energy Products Co.) at 110 V

were used to provide simulated AM1.5 illumination at 100 mW cm^{-2}. Cyclic voltammetry were acquired consecutively between -0.4 to 1.1 V vs the Hg/HgO reference electrode at a scan rate of 50 mV s^{-1}. During each cyclic voltammetry, chronoamperometry was recorded at a bias voltage of 0.83 V vs Hg/HgO reference for 10 hours with a sampling rate of 1 point/10 second. The solution in photoelectrochemical cell was constantly stirred with a magnetic bar to remove the oxygen gas on electrode and the cell was maintained at room temperature by cooling with house airline.

Load-line Analysis and Definition of Photovoltaic Properties

The load-line analysis has been performed following the procedures that have been published before.[2,3] The photoelectrochemical performance data were treated with a generalized equivalent circuit model, in which a photovoltaic cell is connected in series with a dark electrolysis cell. The photovoltaic properties including the open-circuit photovoltage (V_{oc}), the short-circuit current density (J_{sc}), the fill factor (*ff*) and the ideal regenerative cell energy-conversion efficiency (η_{IRC}) are evaluated by subtracting the dark electrolysis *J–E* data obtained from a p$^+$-Si electrode in dark from the *J–E* data obtained from n-Si electrode under illumination.
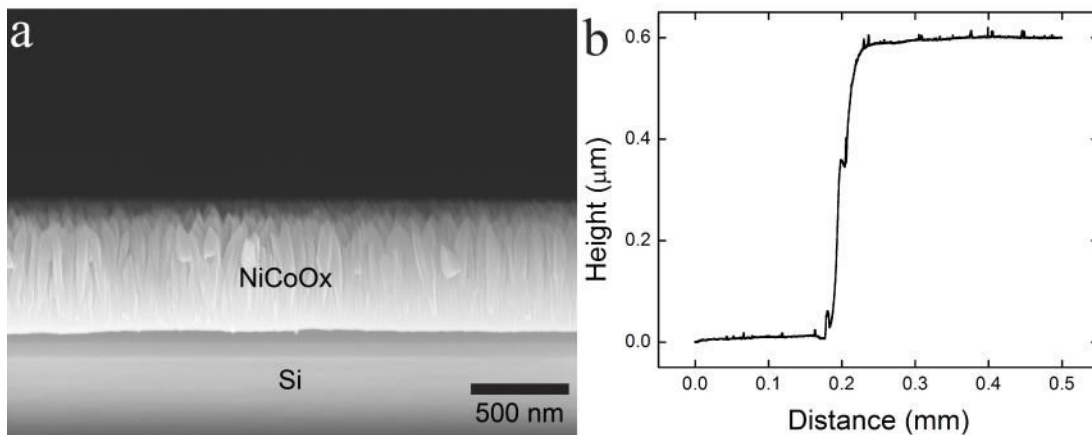
Figure S1. (a) Cross-section SEM image of a NiCoO$_x$ film that was sputtered for 120 min onto a p$^+$-Si substrate. (b) Profilometer measurement of the same sample as shown in (a).
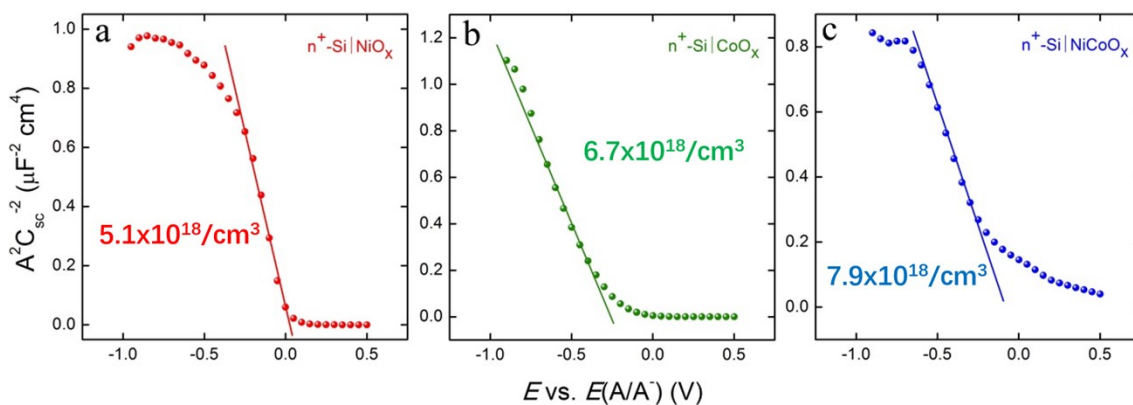

Figure S2. Mott-Schottky plots of 75 nm thick oxide overlayers forming (a) n$^+$-Si|NiO$_x$, (b) n$^+$-Si|CoO$_x$ and (c) n$^+$-Si|NiCoO$_x$ photoanodes in contact with 50 mM Fe(CN)$_6{}^{3-}$ and 350 mM Fe(CN)$_6{}^{4-}$ in 1.0 M Na$_2$SO$_4$(aq), at frequency of 10 kHz and in the absence of illumination.
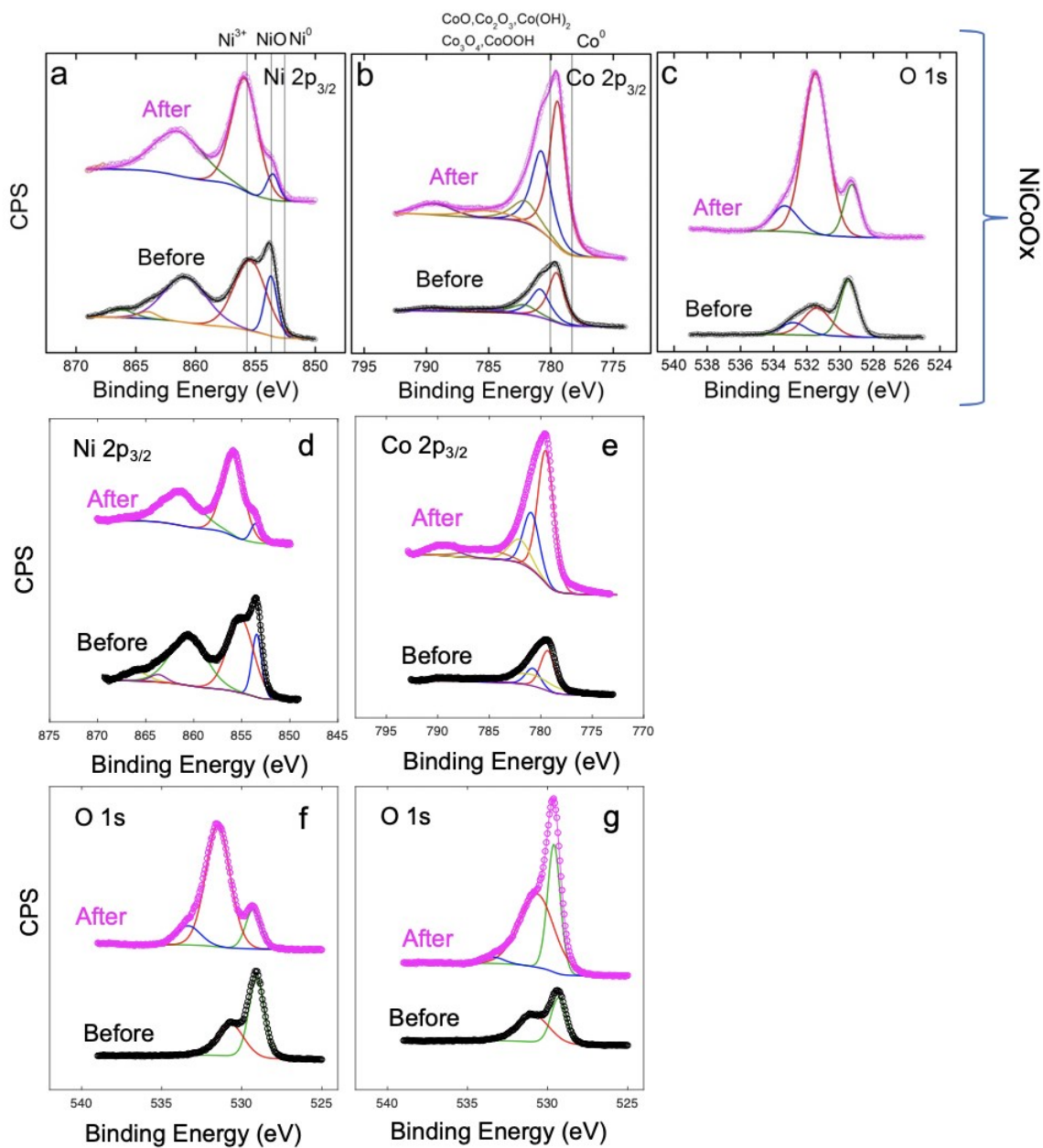
Figure S3. High-resolution XPS data for NiCoO$_x$ (a-c), NiO$_x$ (d,f), and CoO$_x$ (e,g), before and after potential cycling on crystalline Si in 1.0 M KOH (aq, ACS grade) in the (a,d) Ni 2p$_{3/2}$, (b,e) Co 2p$_{3/2}$ and (c, f, g) O 1s signal regions, with CPS representing counts per second.
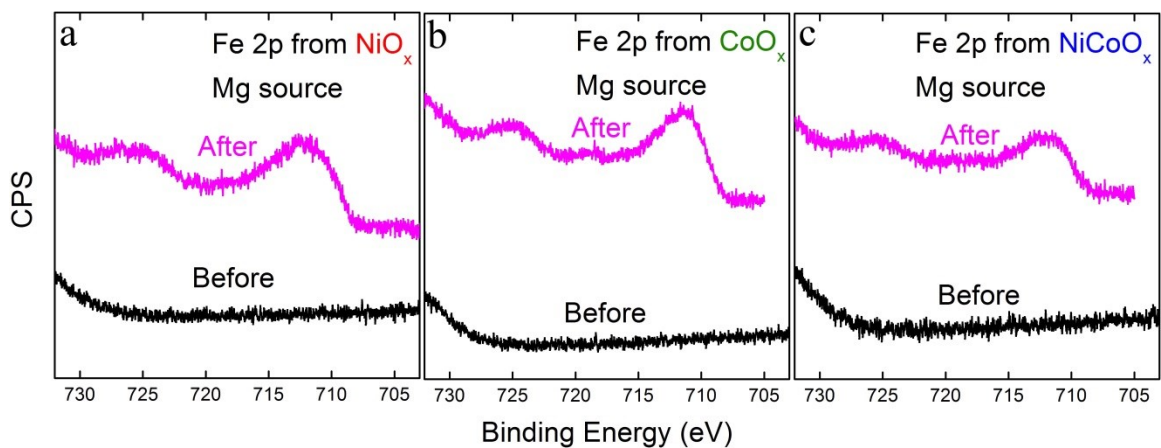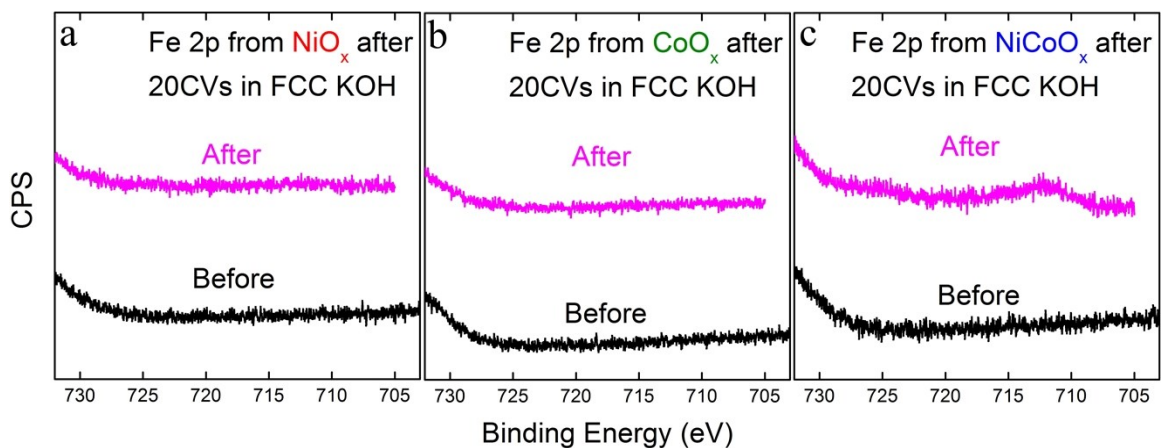
Figure S4. High-resolution XPS data of the Fe 2p region on 75 nm-thick (a) p^+-Si|NiO_x , (b) p^+-Si|CoO_x and (c) p^+-Si|$NiCoO_x$ before and after, respectively, 20 *J-E* scans in 1.0 M KOH (aq, ACS grade).
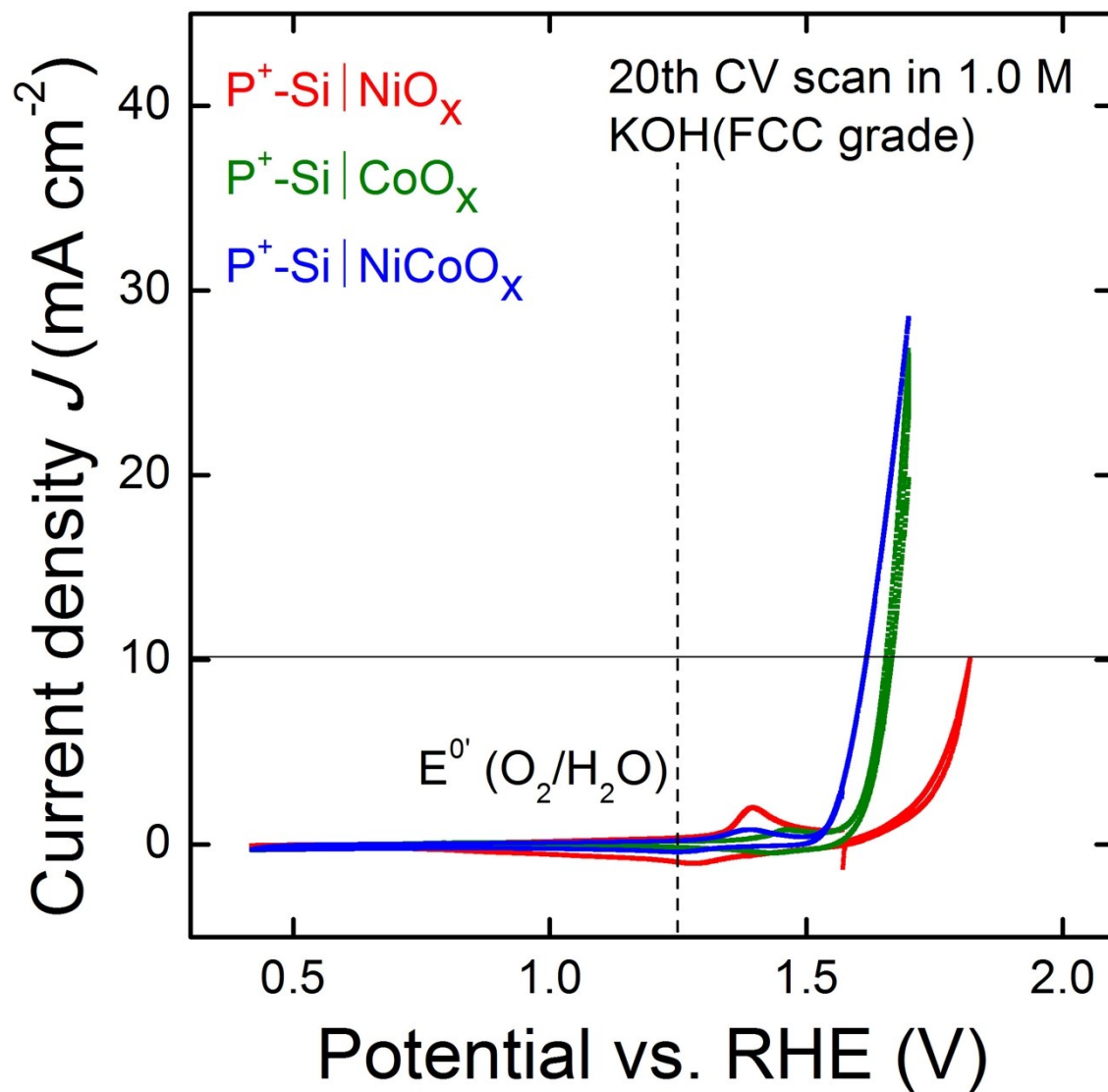
Figure S5. 20th *J-E* scans of NiO_x, CoO_x and $NiCoO_x$ in 1.0 M KOH (aq, FCC grade).

**Figure S6.** XPS high-resolution scan of the Fe 2p region on 75 nm-thick (a) p$^+$-Si|NiO$_x$, (b) p$^+$-Si|CoO$_x$ and (c) p$^+$-Si|NiCoO$_x$ film before and after, respectively, 20 *J-E* scans in 1.0 M KOH (aq, FCC grade).
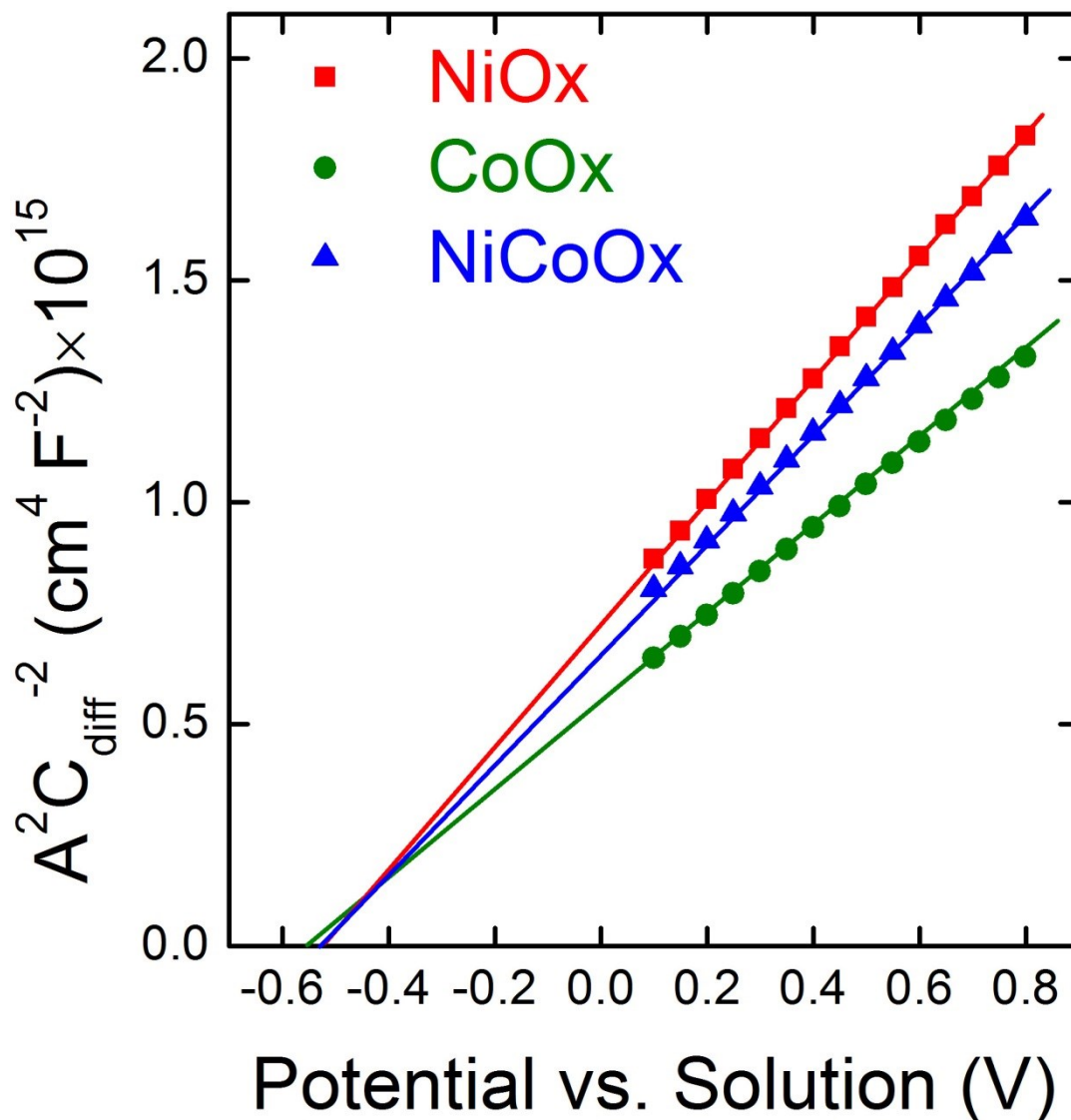
Figure S7. Area-corrected Mott-Schottky plots of the inverse of the differential capacitance of the electrode vs the Nernstian potential of the solution for 75 nm-thick TCO-coated n-Si|NiO$_x$ (red square), n-Si|CoO$_x$ (green circle) and n-Si|NiCoO$_x$ (blue triangle) photoanodes in contact with 50 mM Fe(CN)$_6^{3-}$ and 350 mM Fe(CN)$_6^{4-}$ in 1.0 M Na$_2$SO$_4$(aq) in the dark.
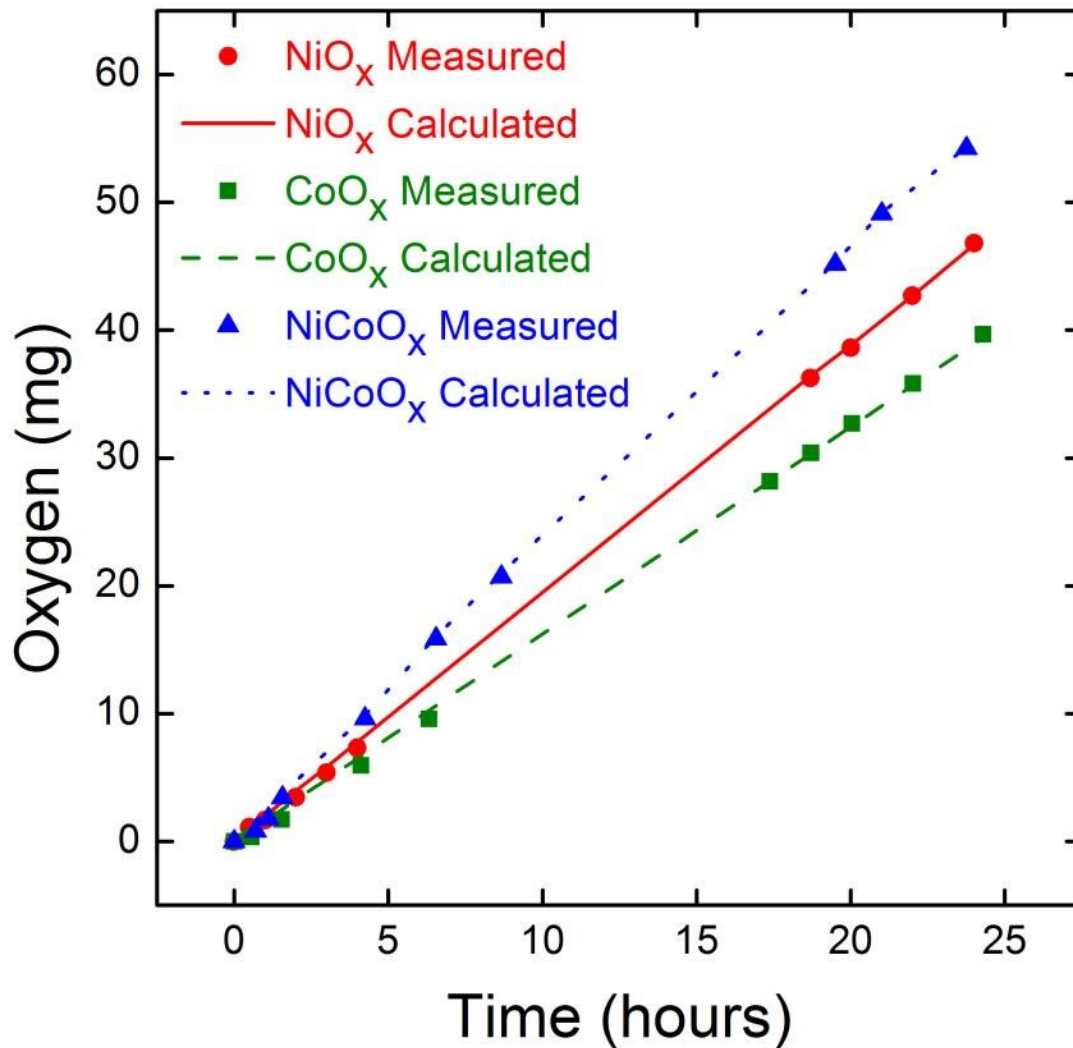
Figure S8. O_2(mg) detected vs O_2(mg) calculated based on the total charge passed, assuming 100% faradaic efficiency, for n-Si|NiO$_x$ (red), n-Si|CoO$_x$ (green) and n-Si|NiCoO$_x$ (blue) photoanodes a constant current density of ~8 mA cm^{-2}.
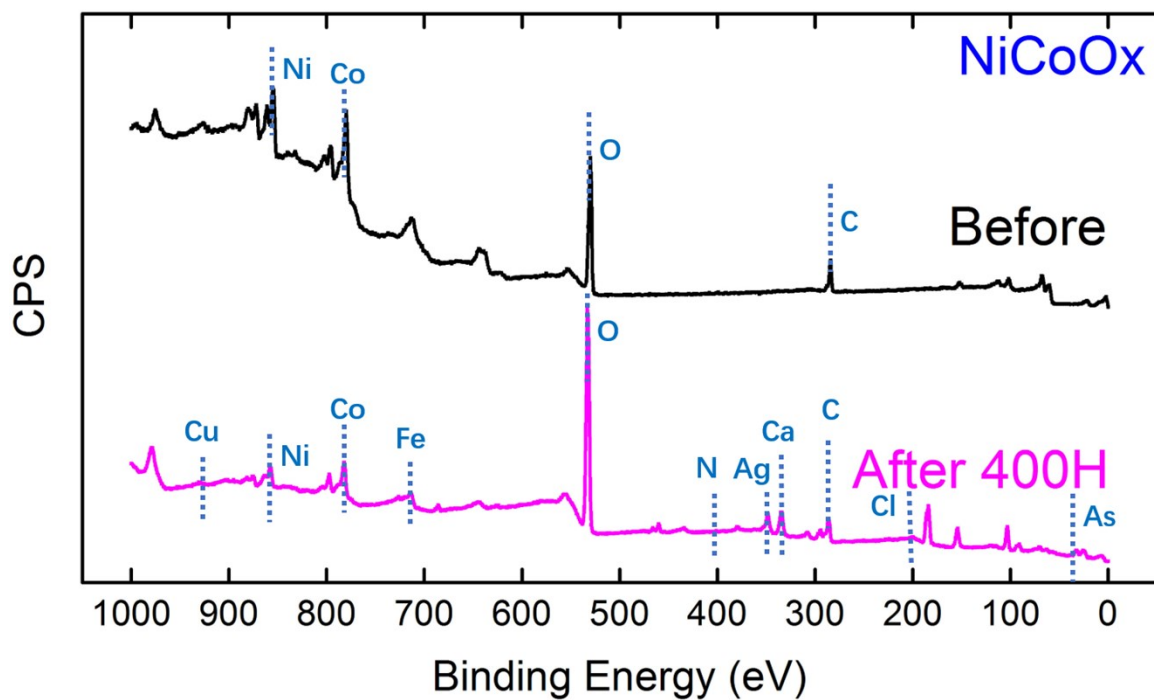
Figure S9. XPS survey scans on 75 nm-thick TCO-coated n-Si|NiCoO$_x$ photoelectrodes before and after a 400 h stability test in 1.0 M KOH (aq, ACS grade).

References

(1)   Rao, K. V.; Smakula, A. *Journal of Applied Physics* **1965**, *36*, 2031.

(2)   Shaner, M. R.; Fountaine, K. T.; Lewerenz, H.-J. *Applied Physics Letters* **2013**, *103*, 143905.

(3)   Mills, T. J.; Lin, F.; Boettcher, S. W. *Physical Review Letters* **2014**, *112*, 148304.