

**Supplementary information
For**

A Janus cobalt-based catalytic material for electro-splitting of water.

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Materials and Methods

Materials. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ were purchased from Aldrich. $[\text{Co}(\text{DO})(\text{DOH})\text{pnCl}_2]$ ¹ and $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ ($\text{dmgH}_2 = \text{dimethylglyoxime}$)² were prepared according to previously described procedure. Fluorine doped tin oxide (FTO) coated glass slides with 7-10 Ω/sq surface resistivity and a thickness of 6000 Å were purchased from Solems (France). KH_2PO_4 (98-100%) and K_2HPO_4 (99%) were purchased from Carlo Erba and Acros Organics respectively.

Methods

X-ray photoemission spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra DLD using a high-resolution monochromatic Al-K α line X-ray source at 1486.6 eV. Fixed analyzer pass energy of 20 eV was used for core level scans. Survey spectra were captured at pass energy of 160 eV. The photoelectron take-off angle was normal to the surface, which provided an integrated sampling depth of approximately 15 nm. All spectra were referenced with an external gold substrate with a binding energy of 84.0 eV for Au 4f. For quantification, relative sensitivity factors issued from Wagner's publication were used.³ The amount of carbon varies from samples and corresponds to carbon contamination from the atmosphere and or/ethanol washing after electrodeposition.

SEM images and EDX spectra were recorded with a FEG-SEM (Leo 1530) operating at 5 kV and equipped with a Princeton Gamma-Tech EDX system operating at 15 kV.

Surface morphologies were characterized using a Digital Instruments Veeco Dimension 3100 atomic force microscope operating in tapping mode. The RMS roughness values of the scans were calculated using the Gwyddion 2.19 program covered by GNU General Public License.

Electrochemical analysis was done using a Bio-logic SP300 potentiostat. FTO was preferred to graphite and ITO (indium-tin oxide) as the electrode material to minimize background H_2 evolution and avoid reductive degradation of the ITO substrate^{4,5} respectively. Cyclic voltammograms are shown using two different potential scales: first, potential is quoted against the Ag/AgCl reference electrode. Second, to ease reading the graphs in terms of overpotentials, potentials are also quoted against the Reversible Hydrogen Electrode (ie the

apparent standard potential of the H^+/H_2 couple at the given pH). The potential of the Reversible Hydrogen Electrode (RHE) is defined as $E^{RHE} = -0.059\text{pH}$. Thus potentials measured versus the Ag/AgCl electrode can be converted versus the RHE by using the following formula: $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + E^{\circ}\ Ag/AgCl + 0.059\text{pH}$. The $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple ($E^0 = 0.20\text{ V vs Ag/AgCl}$ in phosphate buffer at $\text{pH}=7$) has then been used for the standardisation of the measurements.⁶ The electrochemical experiments were carried out in a three electrode cell consisting of two compartments separated by a glass frit. The catalyst was assembled on a working electrode of FTO-coated glass of 1cm^2 and rinsed with acetone and deionized water prior to use. Connection of the FTO to the potentiostat was made via an alligator clip. The platinum-grid counter electrode was placed in a separate compartment connected by a glass-frit and filled with the electrolytic solution. The potential has been calibrated after each experiment by adding potassium ferrocyanide in the solution and measuring its half-wave potential.

Determination of the rate of H_2 production. During controlled-potential coulometry and linear sweep voltammetry experiments, we analysed H_2 and O_2 evolution with a Perkin-Elmer Clarus 500 gas chromatograph equipped with a porapak Q 80/100 column (6' 1/8") thermostated at $40\text{ }^\circ\text{C}$ and a TCD detector thermostated at $100\text{ }^\circ\text{C}$. The GC was mounted in the so called "continuous flow" mode, where a continuous stream of carrier gas flushes the electrochemical cell in permanence at a given rate D ($5\text{ mL}\cdot\text{min}^{-1}$). This stream fills an injection loop of a given volume V (here $100\mu\text{L}$) in the GC. The contents of the injection loop is fed at given intervals Δt (here 2 minutes) into the GC that measures the concentration of H_2 and O_2 contained within the sample. Assuming that the concentration of the species in the gas phase varies slowly during the interval Δt (which can be verified *a posteriori* by looking at successive samplings), the rate at which a given gas is extracted from the electrochemical cell is simply given by:

$$v_g^e = C_g \times D$$

where C_g is the concentration of gas g measured by the GC and v_g^e is the rate at which the gas is *extracted* from the cell. As the gas extraction system is linear, this extraction rate is related to the rate at which the gas is *produced* (v_g^p) in the electrochemical cell through the system response function, $g(t)$:

$$v_g^e(t) = \int_0^t v_g^p(t-t')g(t') dt'$$

To obtain v_g , one has to determine the response function, by injecting a determined quantity of gas in the cell at a given time and recording the response, and then use it to deconvolve the signal using FFT. In practice however, we found that the response function time scale (a few minutes) was significantly faster than the time scale of the variations of gas production, in which case one has $v_g^p \approx v_g^e$. This is why we plotted directly v_g^e (normalized by the electrode geometric surface in order to compare to the current density) on Figure 1.

Deposition procedure. Before starting the deposition, the FTO substrate is cycled hundreds of times between -1 V and $+1$ V in 0.5 M potassium phosphate buffer (KPi), pH 7.0 to ensure the stability and reproducibility of experiments. Catalyst films were grown by controlled potential electrolysis of freshly prepared 0.5 mM $\text{Co}(\text{NO}_3)_2$ solution and in 0.5 M KPi, pH 7.0. Performing the electrolysis at -1 V (vs Ag/AgCl) gives rise to a catalyst film of several micrometer thickness formed by nanoparticles after a course of around three hours. During this time, a film is formed on the working electrode surface. After the film formation is completed, the substrate is transferred to a cobalt-free 0.5 M KPi, pH 7.0, with potential switching between oxidative ($+1.16$ V vs. Ag/AgCl) and reductive conditions (-1 V vs. Ag/AgCl).

XAS sample preparation and data collection.

$\text{Co}^{\text{II}}(\text{OH}_2)_6(\text{NO}_3)_2$ (99.9% purity) was purchased from Sigma Aldrich. The glassy carbon substrates (SIGRADUR K, thickness $100\mu\text{m}$) had a surface resistivity of $2\text{-}15$ Ω/sq and were from HTW Hochtemperatur-Werkstoffe GmbH. KH_2PO_4 (99.5%) and K_2HPO_4 (99.5%) were purchased from AppliChem.

For preparing the XAS samples, we employed a single compartment, three electrode setup driven by an SP-200 potentiostat from BioLogic. The electrochemical cell consisted of a sample frame for XAS measurements glued (Momentive, SCNC silicone glue) on a glassy carbon substrate (working electrode) and a Pt wire (counter electrode) attached on the inner side of the frame. An Hg/HgSO₄ reference electrode (-440 mV vs Ag/AgCl) was approached close to the center of the frame.

Aqueous solutions of KH_2PO_4 (0.5 mol.L⁻¹) and K_2HPO_4 (0.5 mol.L⁻¹) were mixed until the KPi mixture reached a pH of 7.0. This electrolyte was pipetted into the sample frame until the liquid reached the reference electrode. The overall ohmic resistance of the electrochemical

cell was determined by impedance spectroscopy and then used as set value for the applied IR compensation. The electrochemical background of the glassy carbon substrate was low, as verified by cyclic voltammetry.

For the formation of the Co film, 0.5 mmol.L⁻¹ cobalt(II) nitrate was added and a voltage of –1.0 V vs Ag/AgCl was applied for 3h. Then the cobalt solution was replaced by (cobalt-free) KP_i via pipetting. Four CVs from –1.21 V to –0.56 V vs Ag/AgCl (scan rate: 20 mV/s) were performed to characterize the Co deposit.

Finally, the Co film was equilibrated either at –1V or at +1.16 V vs Ag/AgCl for 4 min and then rapidly frozen in a bath of liquid nitrogen. The reference electrode was removed before freezing to avoid any damage to the electrode by immersion in liquid nitrogen. However the potential between the working and the counter electrode was kept constant by applying the same voltage that had been present before removing the reference electrode (using a standard DC power supply connected to working and counter electrode). The power supply was disconnected after freezing in liquid nitrogen.

XAS measurements at the cobalt *K*-edge were performed at beamline KMC-1⁴⁷ of the Helmholtz-Zentrum Berlin for Materials and Energy (formerly BESSY II). Spectra were collected at 20 K in absorption and fluorescence mode as described elsewhere⁴⁸. The scan range of the excitation energy was 7570-8740 eV. The energy windows of the single channel analyzers for the 13 elements of the fluorescence detector were set to the K_α-emission of Co. No filter foil was put between sample and detector. For energy calibration, the energy axis of the experimental data was shifted by an offset such that the first maximum in the derivative of the reference signal (Co foil, 5 μm thick) aligned with the value of 7709 eV reported by Bearden and Burr⁴⁶. The EXAFS oscillations were extracted by minimizing a “knot-spline” with 3 knots between 7718 and 8750eV, which then was subtracted from the data.

Table S1. Composition of Co species in the electro-deposited Co films as deduced from the XANES and EXAFS spectra (see also Figs. S3 and S9).

H ₂ -CoCat ^a	H ₂ -CoCat equilibrated at 1.16 V vs Ag/AgCl ^b
60% metallic Co ⁰ 40% non-metallic cobalt species	30% metallic Co ⁰ 20% non-metallic cobalt species 50% O ₂ -CoCat

^a H₂-CoCat was electro-deposited on a glassy carbon electrode at –1.0 V (vs. Ag/AgCl) for 3 h from an aqueous solution containing 0.5 M potassium phosphate (KP_i, pH 7) and 0.5 mmol.L⁻¹ Co²⁺, then equilibrated at –1.0 V for 4 min in a Co-free KP_i solution and rapidly frozen in liquid nitrogen.

^b H₂-CoCat was electro-deposited for 3 h at –1.0 V and then equilibrated at +1.16 V for 4 min, followed by rapid freezing in liquid nitrogen.

Figure S1. Cyclic voltammograms recorded at an FTO electrode (1 cm^2) of a solution (0.1 mmol.L^{-1}) of the water-soluble diimine dioxime cobalt(III) complex $[\text{Co}(\text{DO})(\text{DOH})\text{pnCl}_2]$ ($(\text{DOH})(\text{DOH})\text{pn} = \text{N}^2, \text{N}^{2'}$ -propanediylbis(2,3-butandione 2-imine 3-oxime)) in phosphate buffer (KPi, 0.5 mol.L^{-1} , pH 7). The first cathodic wave near -0.6 V vs Ag/AgCl produces the orange Co(II) complex.¹ The second cathodic wave with onset at -0.9 V vs Ag/AgCl, corresponds to both catalytic hydrogen evolution and coating of the electrode with a cobalt-based material. The cyclic voltammogram recorded under the same condition in the absence of Co complex is shown in grey.

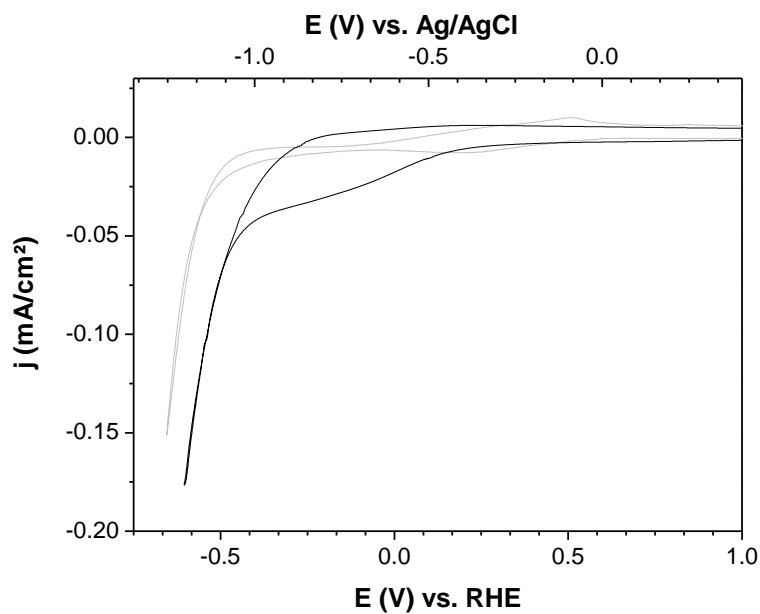


Figure S2. Characteristic EDX spectrum acquired at 15kV counts per second of FTO electrodes modified by (a) H_2 -CoCat and (b) H_2 -CoCat equilibrated for 90 min. at $+1.16 \text{ V}$ vs. Ag/AgCl in phosphate buffer (KPi, 0.5 mol.L^{-1} , pH 7).

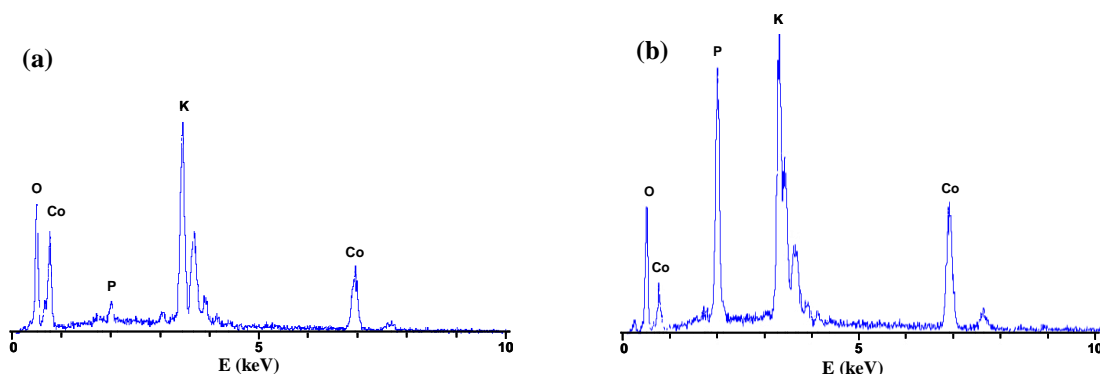


Figure S3. X-ray absorption spectra of H₂-CoCat (red lines) and of purely metallic Co⁰ (black lines). H₂-CoCat was electro-deposited on a glassy carbon electrode at -1.0 V (vs. Ag/AgCl) for 3 h from an aqueous solution containing 0.5 M potassium phosphate (KP_i, pH 7) and 0.5 mmol.L⁻¹ Co²⁺, then equilibrated at -1.0 V for 4 min in a Co-free KP_i solution and rapidly frozen in liquid nitrogen. In (a) and (b), XANES spectra; in (c) and (d), Fourier-transformed EXAFS spectra. The blue line in (d) was obtained by subtraction of the appropriately weighted metal spectrum from the spectrum of H₂-CoCat (and renormalisation of the resulting spectrum) assuming that 59% of film consisted of purely metallic cobalt. The resulting spectrum (blue line) is assignable to a non-metallic species with light atoms (O, N, C) in the first coordination sphere of cobalt. A more quantitative analysis is prevented by noise problems and the uncertainties in the used approach to correct for contributions of the metallic cobalt.

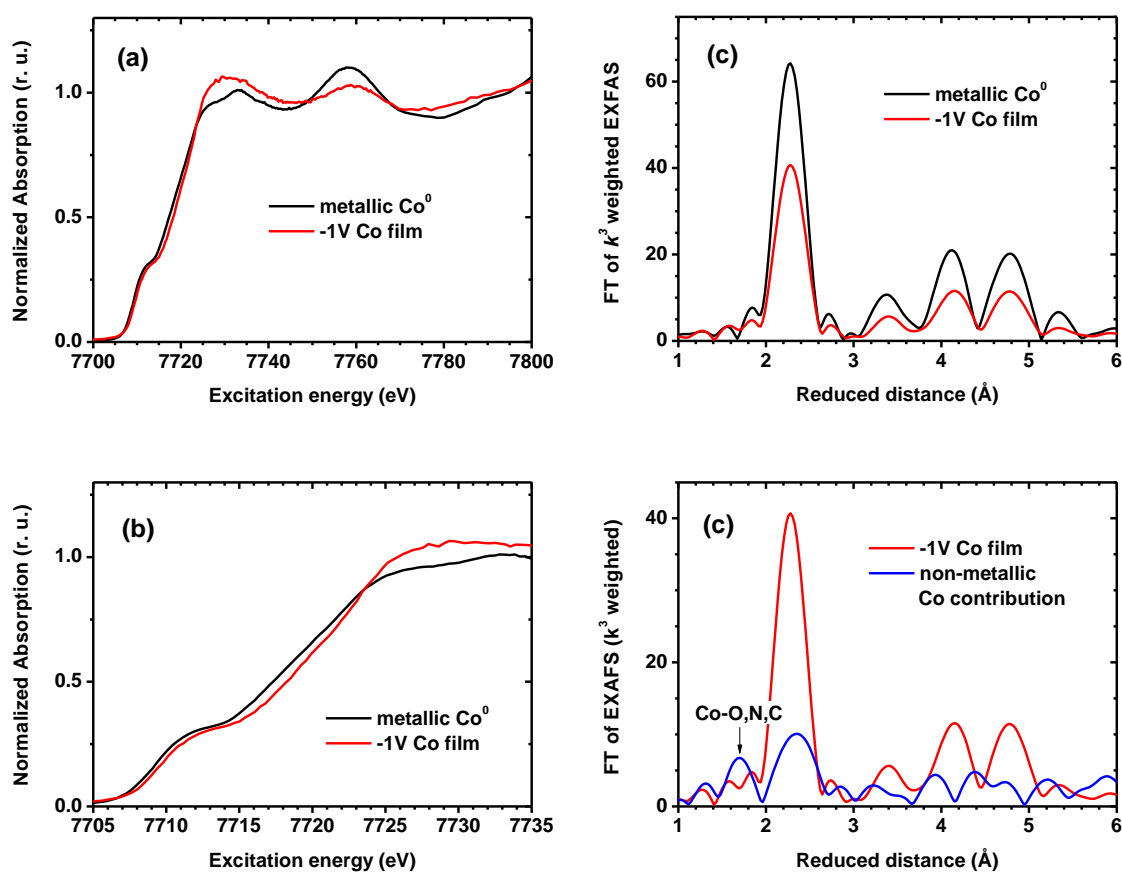


Figure S4. Linear voltammetry experiments recorded at a low scan rate ($0.05 \text{ mV}\cdot\text{s}^{-1}$) at a FTO electrode (1 cm^2): (\blacksquare) H_2CoCat in phosphate buffer (KPi, $0.5 \text{ mol}\cdot\text{L}^{-1}$, pH 7) solution, (\square) Co-coating obtained from a NH_4Cl ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($0.5 \text{ mmol}\cdot\text{L}^{-1}$) and recorded from a cobalt-free NH_4Cl ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution and (\blacktriangle) Co-coating obtained from a LiClO_4 ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($0.5 \text{ mmol}\cdot\text{L}^{-1}$) and recorded from a cobalt-free LiClO_4 ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution. Corresponding Tafel plots are shown in the inset.

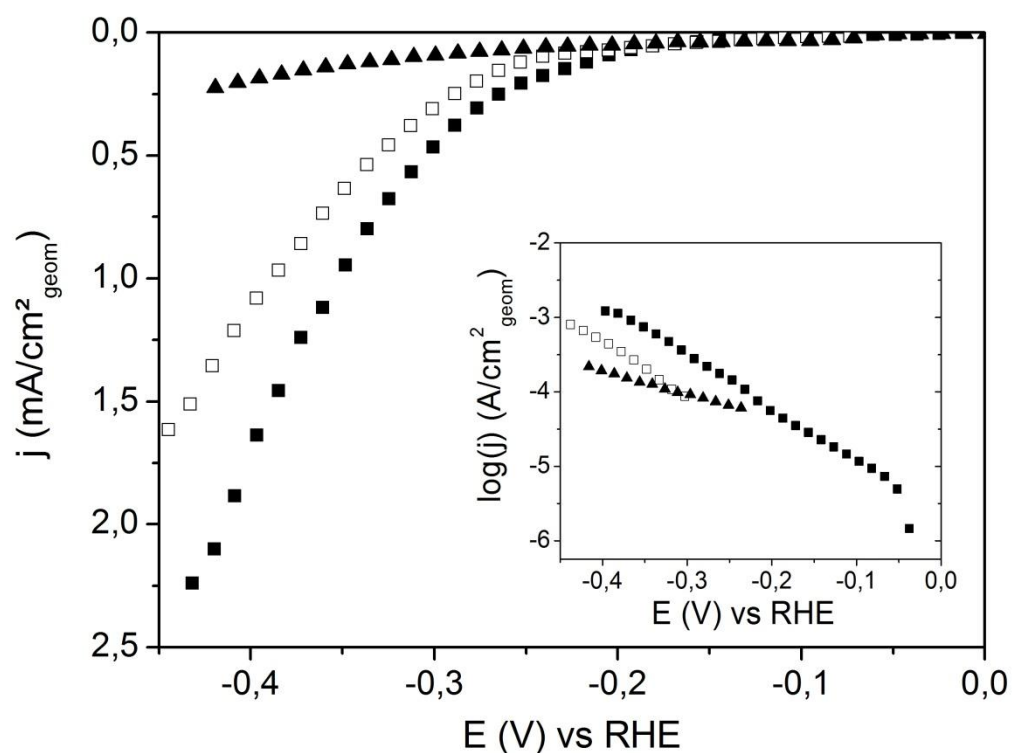


Figure S5. SEM images of modified FTO electrodes (1 cm^2): (a) H_2CoCat (b) Co-coating obtained from a NH_4Cl ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($0.5 \text{ mmol}\cdot\text{L}^{-1}$) (c) Co-coating obtained from a LiClO_4 ($1 \text{ mol}\cdot\text{L}^{-1}$, pH 5) solution containing $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($0.5 \text{ mmol}\cdot\text{L}^{-1}$).

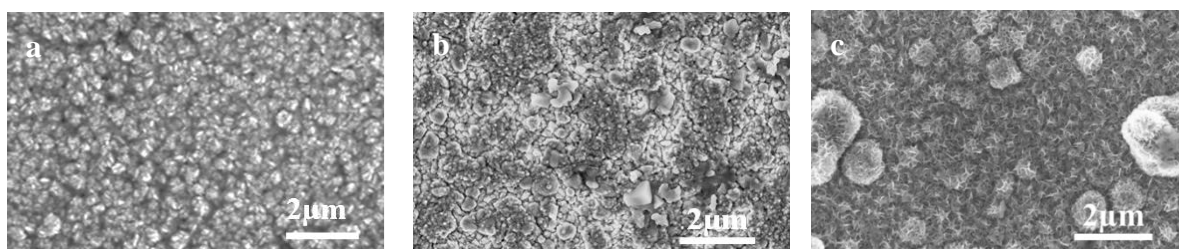


Figure S6. AFM images of modified FTO electrodes (1 cm^2): (a) H_2CoCat (b) Co-coating obtained from a NH_4Cl (1 mol.L^{-1} , pH 5) solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol.L^{-1}) and (c) Co-coating obtained from a LiClO_4 (1 mol.L^{-1} , pH 5) solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol.L^{-1}).

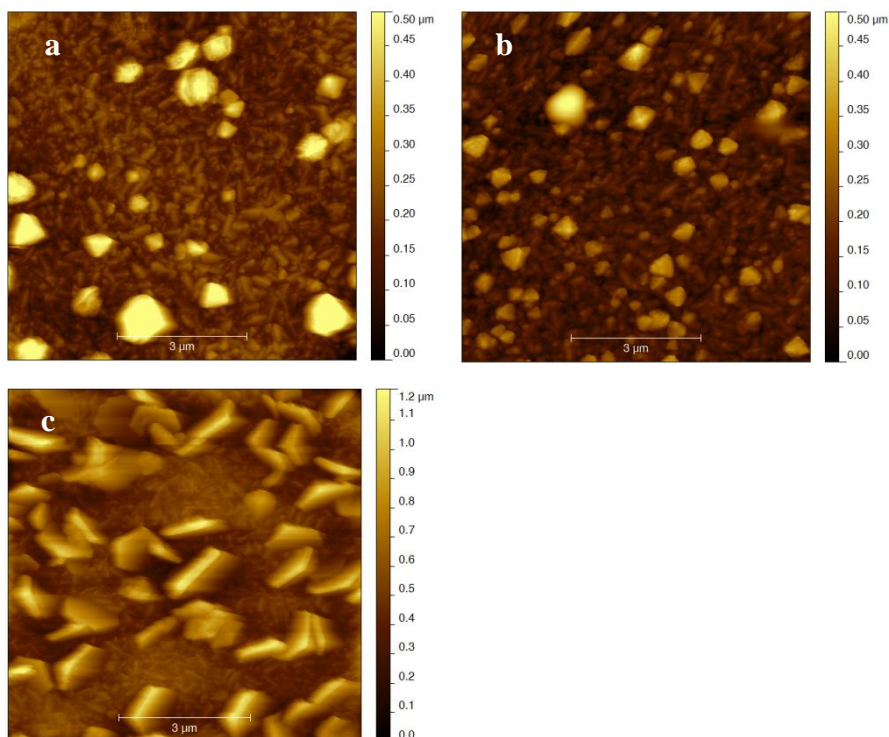


Figure S7. Evolution of the current density at a FTO electrode (1 cm^2) coated with $\text{H}_2\text{-CoCat}$ in 0.5 mmol.L^{-1} KPi, pH 7 electrolyte when the potential is switched from reductive conditions (red, -1 V vs. Ag/AgCl) to oxidative (blue, 1.16 V vs. Ag/AgCl) conditions.

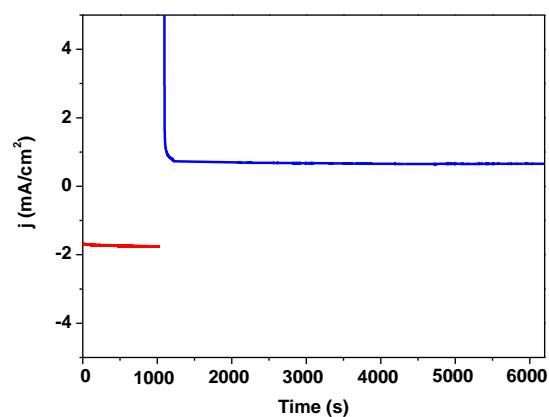


Figure S8. XPS survey of H₂-CoCat film after anodic equilibration at +1.16 V vs Ag/AgCl for 1 h in KPi (pH 7 0.5 mol.L⁻¹).

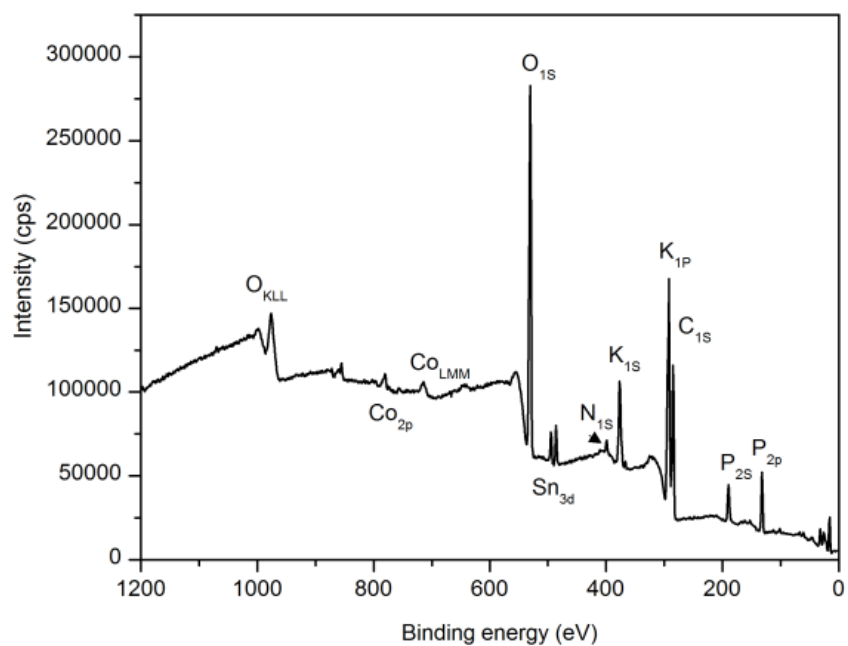
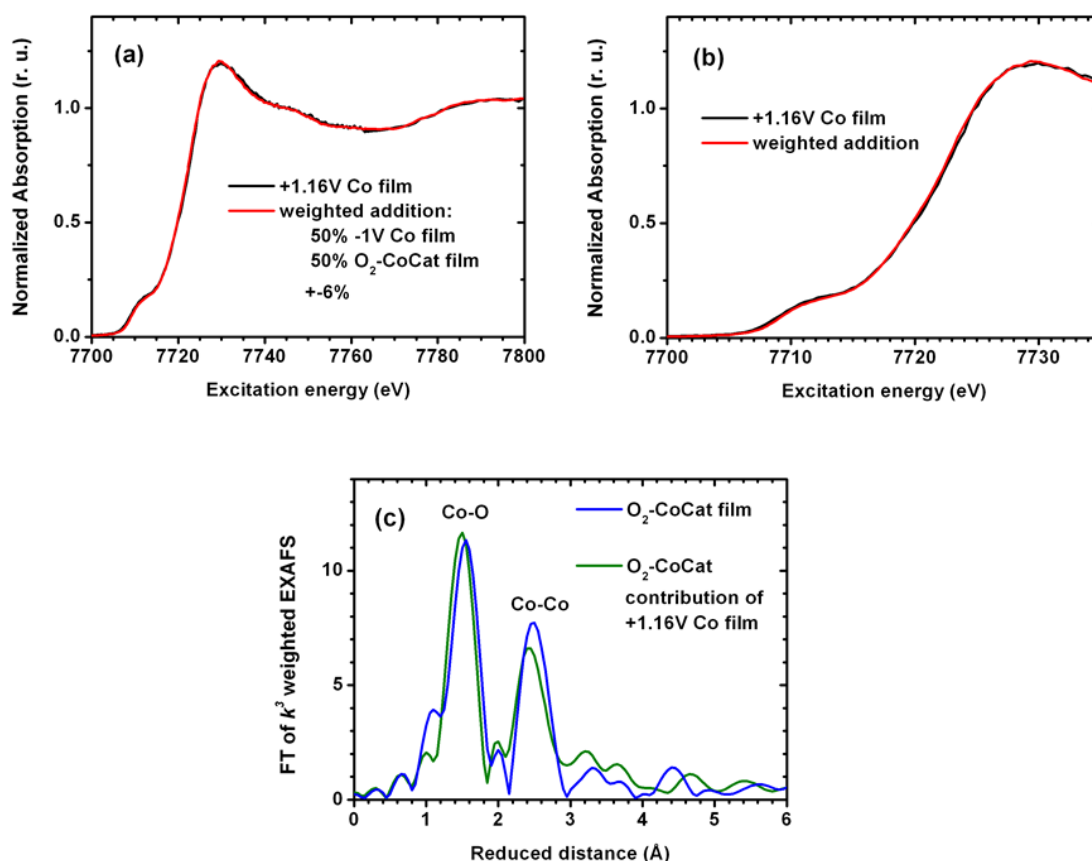


Figure S9. X-ray absorption spectrum of H₂-CoCat equilibrated at +1.16V for 4 min (black lines) compared to a weighted addition (red lines) of spectra from the H₂-CoCat (Fig. S5) and “O₂-CoCat initially described by Kanan and Nocera⁷ corresponding XAS data by Dau and coworkers” (blue line).⁸ In (a) and (b), XANES spectra; in (c), Fourier-transformed EXAFS spectra. The weighting coefficients in (a) and (b) suggest that about 50% of the Co ions of the +1.16V equilibrated CoCat film stay in the state present in H₂-CoCat before application of the positive voltage, whereas 50% of the deposit restructured resulting in the same Co oxide (consisting of clusters of edge-sharing Co^{III}O₆ octahedra^{8,9}) that is obtained by electro-deposition at positive potentials. The green line in (c) was determined by the subtraction of the XANES/EXAFS spectrum of H₂-CoCat weighted by a factor of 0.5 from the spectrum of the +1.16V equilibrated CoCat film. The resulting spectrum was renormalized and Fourier-transformed. It is assumed that this spectrum corresponds to the “O₂-CoCat” contribution of the +1.16V equilibrated CoCat film”.

The "+1.16V equilibrated CoCat film" was obtained from H₂-CoCat equilibrated at +1.16 V for 4 min in a Co-free KP_i solution and rapidly frozen in liquid nitrogen. The O₂-CoCat film was electro-deposited on a indium tin oxide electrode at +1.19V vs Ag/AgCl for 70 min from an aqueous solution containing 0.1 mol.L⁻¹ potassium phosphate (KP_i, pH 7) and 0.5 mmol.L⁻¹ Co²⁺ and rapidly frozen in liquid nitrogen.



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