

## Supporting information:

### Fast and Persistent Electrocatalytic Water Oxidation by Co-Fe Prussian Blue Coordination Polymers

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**Materials.** All chemicals were commercially available (> 99.9 %, Sigma-Aldrich) and were used without further purification. Electrolyte solutions were prepared with Milli-Q water (typically 18.2 MΩ-cm resistivity). As fluorine-doped tin oxide coated glass slides (FTO) we used Pilkington NSG TEC 15A 2.2 mm slides with 12-14 Ω/sq surface resistivity, and 80.0-81.5 % transmittance. FTO slides were cleaned prior use by sonication for 10 minutes in basic soapy solution, deionized water and isopropanol, followed by annealing at 400 °C during 30 minutes.

**Electrochemical methods.** All electrochemical experiments were performed with a Biologic SP-150 potentiostat, a ALS Ag/AgCl (3.5 M KCl) reference electrode and a Pt wire or mesh counter electrode. All potentials reported in this manuscript were converted to the NHE reference scale using  $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.209 \text{ V}$ . Unless otherwise stated, the buffer electrolyte used for bulk water electrolysis was prepared at 50 mM KPi, and 1 M KNO<sub>3</sub>.

**Preparation of catalyst modified electrodes.** 1 x 2.5 cm FTO electrodes were used as working electrodes, but only a surface of 1 x 1.5 cm was immersed in the solution. The first step was the plating of the electrode with metallic cobalt by passing a total charge of  $66 \pm 1 \text{ mC cm}^{-2}$  at  $-0.695 \text{ V}$  (vs. NHE) in a KCl (0.1 M) water solution containing Co<sup>2+</sup> ions (10 mM). During this time (~ 1 minute), a dark covering was observed on the FTO surface as metallic cobalt is deposited. After deposition, the

slides were sonicated for 15 minutes in deionized water. The second step, namely derivatization, was also carried out with a potentiostatic method by passing a total charge of  $70 \pm 1 \text{ mC cm}^{-2}$  at 0.508 V (vs. NHE) with the metallic cobalt-covered electrode immersed in a KCl 0.1 M water solution containing 10 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$ . During this process, cobalt slowly dissolves under the oxidation potential to be trapped by the formation of the desired CoHCF. Derivatization time is usually 5-6 hours long. After derivatization, the electrodes were sonicated again for 15 minutes.

**Spectroscopy.** UV-Vis spectroscopy data was acquired with a Cary 50 (Varian) UV-Vis spectrometer. The modified FTO electrodes were placed in the standard cuvette holder, with the light beam perpendicular to the electrode, passing through the deposited CoHCF, the FTO coating and the glass substrate. IR spectroscopy data was acquired with an Alpha Bruker FTIR equipped with Attenuated Total Reflectance (ATR) sample holder.

**X-ray powder diffraction:** Crystallites from the surface of a CoHCF modified electrode were supported with paratone oil on a Kapton tip and mounted on a Bruker Kappa APEX II DUO diffractometer equipped with an APPEX 2 4K CCD area detector, a Microsource with  $\text{MoK}_\alpha$  radiation and an Oxford Cryostream 700 low temperature device. Data collection was performed at 100 K with the Apex2 V2012.2-0 program (Bruker AXS 2010), and integrated with Pilot plug-in from Apex2 V2012.2-0.

**Electrochemistry.** Cyclic voltammograms were collected in an electrochemical cell between 10 and 500 mV/s in KPi buffer (50 mM) electrolyte solution (1 M  $\text{KNO}_3$ ) at pH 7. The surface concentration of redox active Co centers was extracted from the slope of the linear relationship between the peak current of the reduction wave at 0.87 V and the scan rate ( $v$ ):

$$\text{slope} = \frac{n^2 F^2 A \Gamma_0}{4RT}$$

(eq. 1)

where  $n = 1$ ;  $F$  = Faraday's constant;  $A$  = surface area;  $\Gamma_0$  = surface concentration ( $\text{mol cm}^{-2}$ );  $R$  = ideal gas constant;  $T$  = temperature. This expression is derived from the Nerst equation:

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_{ox}(t)}{C_{red}(t)}$$

(eq. 2)

where  $E^{0'}$  = formal potential of the redox couple, and  $C(t)$  are the time-dependent concentrations of the oxidized and reduced forms, respectively. Since there is no bulk concentration, the current ( $i$ ) can be expressed in terms of the change of concentration of the oxidized species:

$$i = -n F V \left[ \frac{d C_{ox}(t)}{dt} \right]$$

(eq. 3)

where  $n$  = number of transferred electrons;  $V$  = volume and  $t$  = time. Since the total concentration is constant:

$$C_T = C_{ox}(t) + C_{red}(t)$$

(eq. 4)

And an expression for  $C_{ox}(t)$  can be obtained as a function of applied potential  $E$ :

$$C_{ox}(t) = \frac{C_T \exp \left[ \frac{nF(E - E^{0'})}{RT} \right]}{1 + \exp \left[ \frac{nF(E - E^{0'})}{RT} \right]}$$

(eq. 5)

Differentiating this equation with respect to  $t$ , and substituting in Eq. 3, we can obtain:

$$i = \frac{n^2 F^2 V C_T v}{RT} \frac{\exp \left[ \frac{nF(E - E^{0'})}{RT} \right]}{\left\{ 1 + \exp \left[ \frac{nF(E - E^{0'})}{RT} \right] \right\}^2} \quad (\text{eq. 6})$$

where the scan rate is  $v = -\frac{dE}{dt}$ . At peak current,  $E = E^{0'}$ , and then:

$$i = \frac{n^2 F^2 V C_T v}{4RT} \quad (\text{eq. 7})$$

Thus, Eq. 1 is the slope of the linear  $i$  vs  $v$  plot, simply replacing  $V C_T$  by  $A \Gamma_0$ .

In addition to the CoHCF redox activity, we observed a minor irreversible oxidation wave at 0.7 V in the first voltammetry cycles without an associated cathodic process. This irreversible oxidation disappears after several cycles, or after applying an oxidation potential for a few minutes. The cyclic voltammograms of used modified electrodes after bulk water electrolysis did not show this feature. Since CoHCF exhibits reversible redox chemistry, we assume this weak oxidation wave correspond to the FTO substrate. In any case, it cannot be involved in the catalytic process since it disappears after a few minutes.

**Bulk water electrolyses.** Bulk water electrolyses were carried out with stirring in a two-chamber cell, with a porous frit connecting both chambers. In one chamber we placed a Pt mesh counter electrode, and in the other chamber a 1 cm x 1.5 cm CoHCF modified FTO working electrode and a BASi Ag/AgCl (KCl 3.5 M) reference electrode. Electrolysis experiments were carried out in a 50 mM KPi buffer solution with KNO<sub>3</sub> as electrolyte (1 M). Ohmic drop was compensated using the positive feedback compensation implemented in the instrument. Oxygen evolution was determined

with an Ocean Optics NeoFOX oxygen sensing system equipped with a FOXY probe inserted into the head space of the anodic compartment. The solution head-space was purged with high purity nitrogen gas for 30 minutes with vigorous stirring. Once the nitrogen gas stream is stopped, the oxygen fluorescence signal was allowed to stabilize. The residual oxygen signal in the absence of an applied potential was recorded for one hour, although it becomes constant after ~5 minutes. This confirms the cell is gas-tight. Then the desired potential was applied. Oxygen evolution was monitored in multiple electrolyses at different potentials between 1.2 and 1.8 and for different times (up to 24 hours). The Faradaic oxygen evolution was calculated taking into account  $4e^-$  are needed to produce one molecule of  $O_2$ . The fluorescence data measured was transformed into  $\mu\text{mol}$ s of  $O_2$  after a five point calibration of the same electrochemical cell by addition of known quantities of high purity oxygen gas.

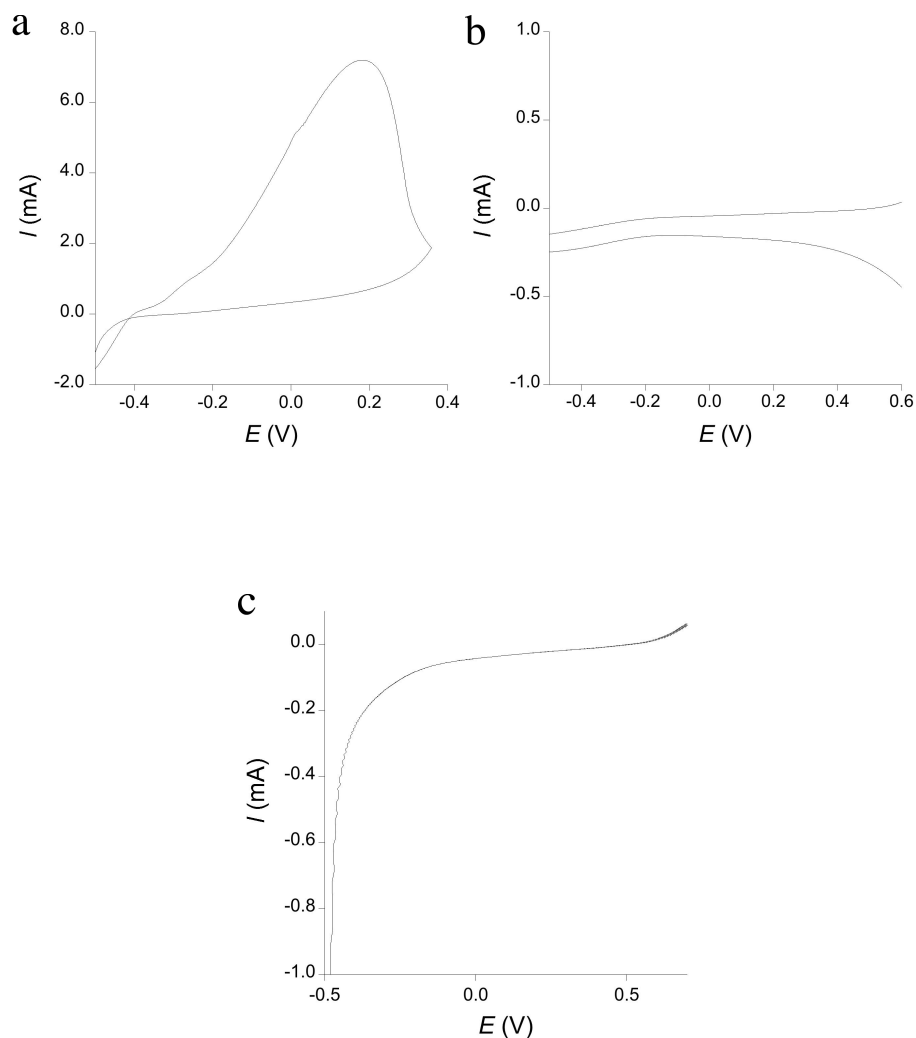
**Tafel analysis.** Steady current density data were obtained from bulk water electrolysis at different applied potentials in a well-stirred 50 mM  $KP_i$  buffer pH 7 solution with  $KNO_3$  as electrolyte (1 M) in a two-chamber cell, with a porous frit connecting both chambers. In one chamber we placed a Pt mesh counter electrode, and in the other chamber a 1 cm x 1.5 cm CoHCF modified FTO working electrode and a BASi Ag/AgCl (KCl 3.5 M) reference electrode. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument. The current values after 30 minutes of electrolysis were used as steady state data. All measurements were made three times and averaged. The variation found in different runs was always less than 5 %.

**Scanning Electron microscopy (SEM):** SEM images and EDX spectra were obtained with an Environmental Scanning Electron Microscope JEOL-JMS6400 equipped with an Oxford Instruments X-ray elemental analyzer. The peaks corresponding to K, Fe and Co were integrated. Each electrode surface was analyzed in multiple points and the mean value was calculated to determine the

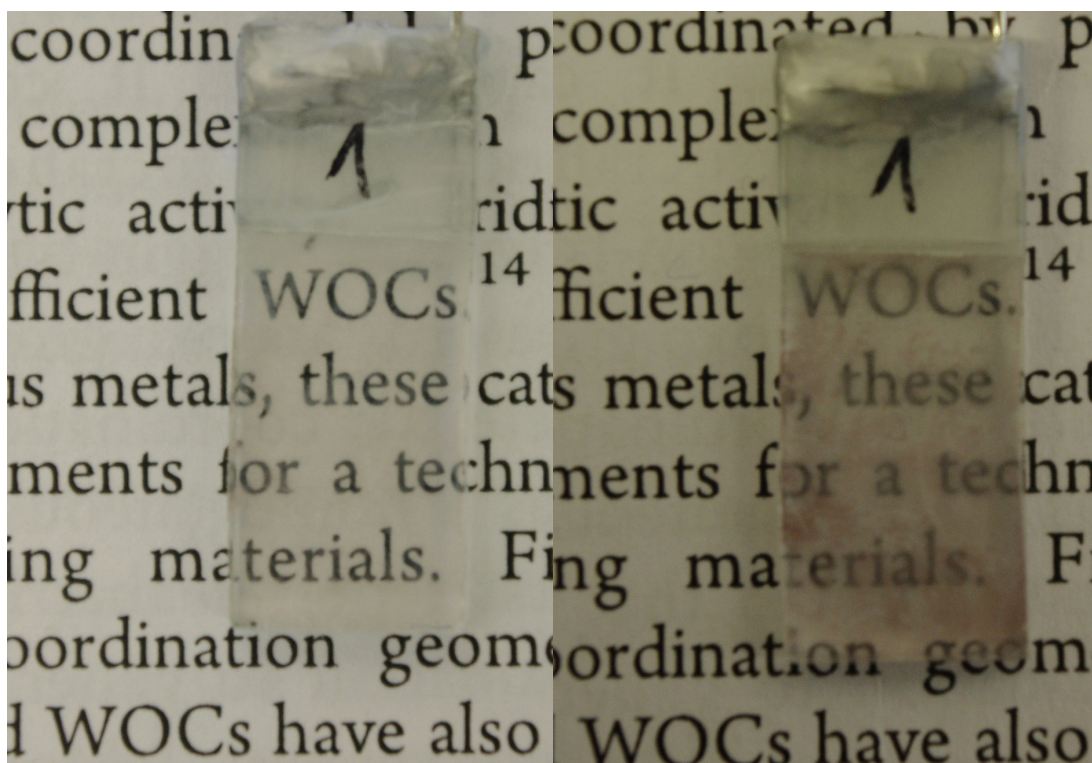
stoichiometry. The data from a batch of 10 electrodes prepared from the same solution is presented in Table 1.

**Table 1.** EDX analysis for a batch of 10 electrodes prepared from the same solutions following the procedure described in the preparation of catalyst modified electrodes section.

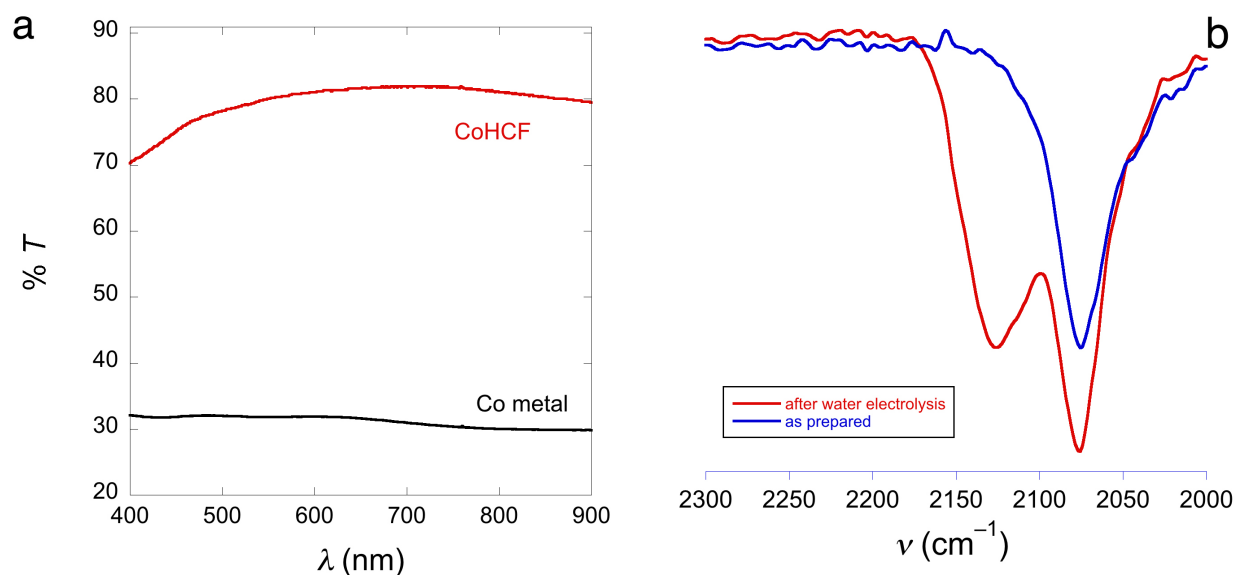
Electrode	Fe:Co:K ratio			$K_{2x}Co_{(2-x)}[Fe(CN)_6]$
	Fe	Co	K	x
<b>1</b>	1	1.06	1.88	0.94
<b>2</b>	1	1.14	1.75	0.86
<b>3</b>	1	1.05	1.90	0.95
<b>4</b>	1	1.15	1.74	0.90
<b>5</b>	1	1.05	1.93	0.95
<b>6</b>	1	1.09	1.82	0.91
<b>7</b>	1	1.04	1.90	0.96
<b>8</b>	1	1.14	1.78	0.86
<b>9</b>	1	1.11	1.70	0.88
<b>10</b>	1	1.08	1.86	0.92



**Figure 1.** (a) Cyclic voltammogram of a FTO electrode plated with metallic cobalt in a neutral 50 mM KPi buffer solution with  $\text{KNO}_3$  as electrolyte (1 M) showing the strong  $\text{Co}/\text{Co}^{2+}$  oxidation band. (b) Detail of the cyclic voltammogram of a CoHCF modified FTO electrode in the same conditions. (c) Differential pulse voltammogram of a CoHCF modified FTO electrode in the same condition showing the absence of any redox process in the region of the  $\text{Co}/\text{Co}^{2+}$  oxidation band. All potentials are reported vs NHE.

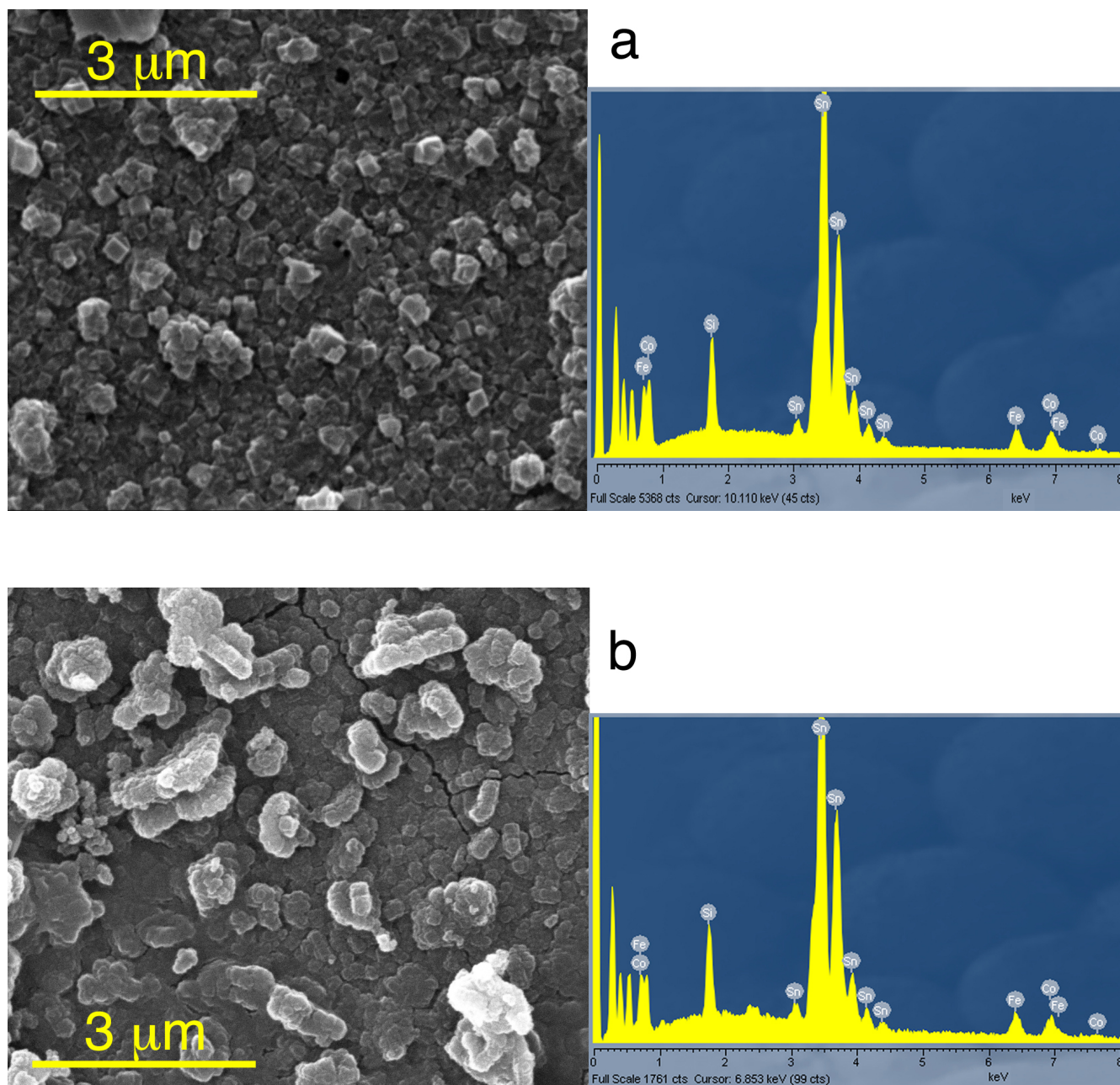


**Figure 2.** CoHCF modified FTO electrode before (left) and after 1 day water electrolysis at 1.41 V vs NHE (right).

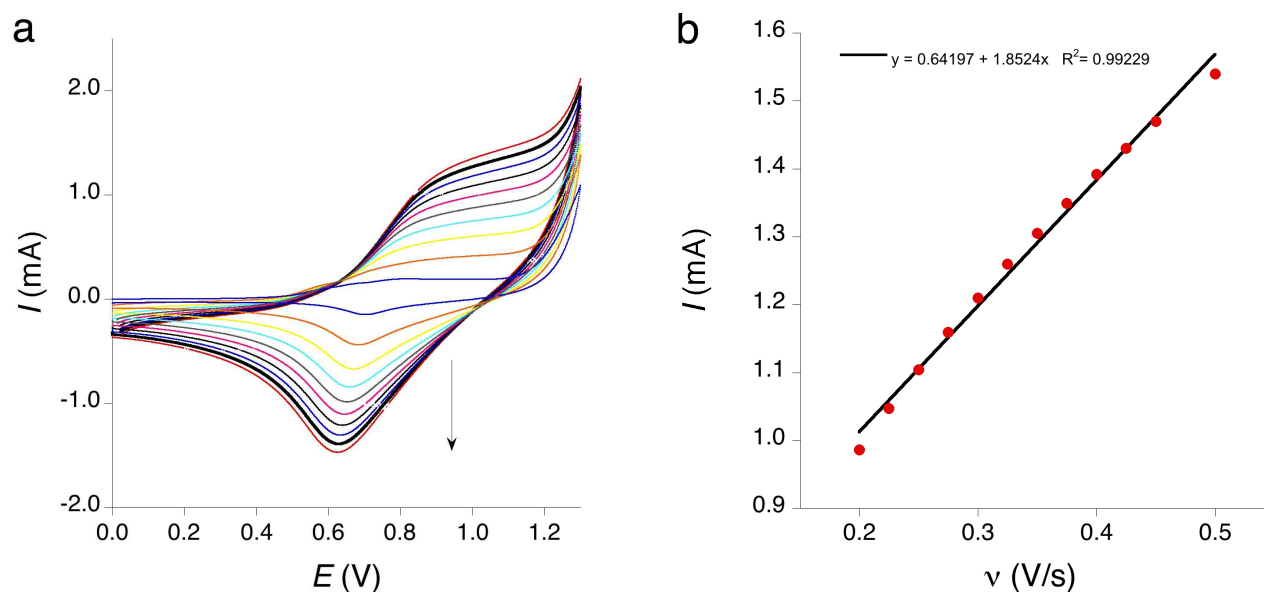


**Figure 3.** (a) Transmittance of FTO electrodes coated with metallic Co (after plating) and CoHCF (after derivatization). Nominal 81.5% transmittance of the FTP glass electrodes has been corrected. (b) IR spectra of CoHCF grown on a FTO electrode, before and after 12 h water electrolysis

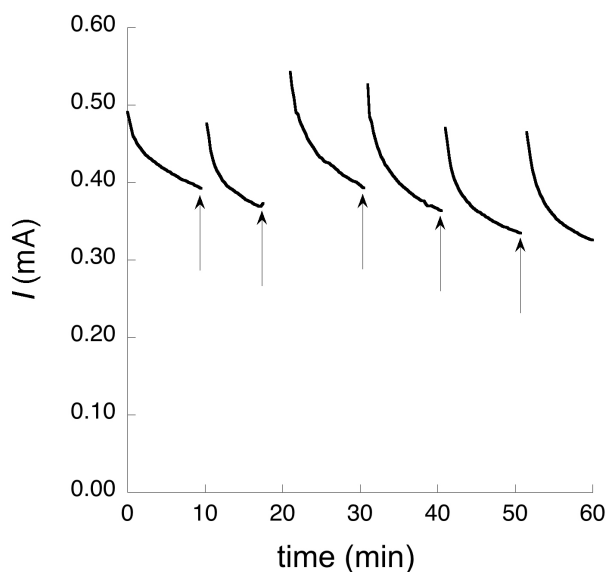




**Figure 4.** (a) SEM image and EDX analysis of “*as prepared*” CoHCF grown on a FTO electrode. (b) SEM image and EDX analysis of “*as used*” CoHCF grown on a FTO electrode after 12 h bulk water electrolysis.



**Figure 5.** (a) Cyclic voltammograms of a CoHCF modified FTO electrode in a neutral 50 mM KPi buffer solution with  $\text{KNO}_3$  as electrolyte (1 M) at different scan rates: the arrow indicates from 10 to 500 mV/s. (b) Linear dependence of the peak current of the  $\text{Co}^{3+}/\text{Co}^{2+}$  reduction wave vs scan rate. The concentration of redox active centers was calculated from the slope as described in the electrochemistry section.



**Figure 6.** Successive bulk water electrolyses with a CoHCF modified FTO electrode at 1.41 V applied potential in a 50 mM KPi buffer pH 7 solution with  $\text{KNO}_3$  as electrolyte (1 M). This plot shows that the induction period is not related to any decomposition or change in the catalyst since the same spike appears in multiple successive cycles. The arrows indicate when the circuit was opened to re-start the electrolytic current.