#### **Electronic Supplementary Information for**

# Efficient solar water oxidation using photovoltaic devices functionalized with earth-abundant oxygen evolving catalysts

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#### Functionalization of triple junction cells with OECs based on Ni(II) and Co(III) oxides

The cleaned ITO coating of the 3J cell was functionalized by immersion in 50 mM  $M^{n+}$  ( $M^{n+}$  = Ni<sup>2+</sup> or Co<sup>2+</sup>) (10 s) followed by dipping in 0.8 M NaClO (10 s) in analogy to what has been described in the Method section of the Article. The number of SILAR cycles was limited to just 1. In the case of nickel(II), or 2 in the case of cobalt(II). A final annealing at 300°C for 15 minutes completed the process. Heating at temperatures higher than 300°C resulted in cell degradation, independently by the presence of the OEC layer.

#### Cyclic Voltammetry of ITO electrodes modified with Fe(III) oxide



**Figure S1.** Cyclic voltammetry of an ITO electrode functionalized with Fe-OEC (10 SILAR cycles, NaOH route) recorded in 0.5 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution (pH 11.2) at 100 mV s<sup>-1</sup>. During the forward scan, no clear intermediate oxidation peaks are observed, due to the anodic discharge of the electrolyte, rising up at 0.6 V vs SCE. In the back sweep, however, a reduction peak is observed at *ca* 0.7 V vs SCE (black arrow), indicating the reduction to Fe(III) upon reversal of the potential scan.



**Figure S2.** Cyclic voltammetry of an ITO electrode functionalized with Fe-OEC (10 SILAR cycles, NaOH route) recorded in 0.1 M LiClO<sub>4</sub> in CH<sub>3</sub>CN at 100 mV s<sup>-1</sup>. The black arrow indicates the direction of the potential sweep. The cathodic peak at *ca.* -0.25 V vs SCE is attributed to the reduction of Fe(III) to Fe(II), while the anodic peak at *ca.* 1.2 V vs SCE is attributed to the reoxidation of Fe(II) to Fe(III). The latter peak was absent during the first anodic sweep and only appears after the scan at cathodic potentials. The direct evidence of the formation of highly valent oxidation states of iron (Fe(IV) or higher) was hidden by the solvent discharge.





**Figure S3.** X-ray diffractograms of Fe(III) oxide powders precipitated from 2.5 M NaClO annealed at different temperatures in air:  $150^{\circ}C$  (**a**);  $200^{\circ}C$  (**b**). X-ray diffractograms of Fe(III) oxide powders precipitated from 1 M NaOH annealed at different temperatures in air: RT =  $20^{\circ}C$  (**c**),  $150^{\circ}C$  (**d**);  $200^{\circ}C$  (**e**).



#### Infrared spectroscopy of Fe(III) oxide powders

**Figure S4.** IR spectra of ferric oxide powders precipitated by addition of 2.5 M NaClO solution (**a-c**) and of 1 M NaOH solution (**d-f**) recorded in transmission mode in KBr pellet. Samples annealed at various temperatures: 150°C (**a**, **d**); 200°C (**b**, **e**); 300°C (**c**, **f**).

500

500

500



# Density Functional Theory calculations on various minimal Fe(III) oxide fragments





**Figure S5.** Computed IR spectra (B3LYP 6311G +,d) of geometry optimized ferric oxide fragments (total charge = 0) terminated with water molecules (**a**),  $O^{-}$  (**a**) and OH (**b**, **c**) groups. The two iron atoms are singly (**a**, **b**) or doubly bridged (**c**) by oxygen atoms.

### X-ray Photoelectron Spectroscopy analyses of Fe(III) oxide powders and of Fe-OEC-ITO

Annealing Temp.	O <sub>1s</sub> (%)	Fe <sub>2p</sub> (%)	C <sub>1s</sub> (%)	Cl <sub>2p</sub> (%)
(°C)	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>
RT	45.9	25.7	20.9	7.5
	(531)	(712)	(285)	(199)
150	42.1	32.1	18.1	7.8
	(531)	(712)	(285)	(199)
200	42.6,	33.0	17.8	6.7
	(530.5)	(711.5)	(285)	(199)
300	44.8	40.6	12.6	2
	(530)	(712)	(285.5)	(199)

**Table S1.** Fe(III) oxide powder obtained by precipitation from 2.5 M NaClO. <sup>(1)</sup> Binding energies (BE) were measured within an approximation of 0.5 eV.

**Table S2.** Fe(III) oxide powder obtained by precipitation from 1 M NaOH. <sup>(1)</sup> Binding energies (BE) were measured within an approximation of 0.5 eV.

Annealing Temp.	O <sub>1s</sub> (%)	Fe <sub>2p</sub> (%)	C <sub>1s</sub> (%)	Cl <sub>2p</sub> (%)
(°C)	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>
RT	46.2	31.4	16.5	4.7
	(530.5)	(711.5)	(285)	(198.5)
150	47	33.7	13.6	4.1
	(531)	(712)	(285)	(199)
200	47.2	40.9	6.1	3.9
	(530)	(711.5)	(285)	(199)
300	44.8	42.5	6.5	4.1
	(531)	(711.5)	(285.5)	(199)

Samples of ferric oxide powder precipitated from both NaClO and NaOH solutions exhibited overall similar surface compositions. As expected, iron and oxygen were the main surface constituents, showing analogous concentration and binding energies in both samples. The Fe and O binding energies were consistent with ferric oxide. Thermal annealing does not alter their binding energy but improves the relative surface percentage of iron. This is due to a concomitant decrease of the percentage of carbon that is present both as an environmental contaminant and as adsorbed carbonate. A minor fraction of chloride is also observed, due to conglomeration of chloride anions during the precipitation stage, which could not be completely removed during the repeated washings of the precipitate.

**Table S3.** Fe-OEC-ITO obtained by SILAR in 0.8 M NaClO. <sup>(1)</sup> Binding energies (BE) were measured within an approximation of 0.5 eV.

Annealing Temp.	O <sub>1s</sub> (%)	Fe <sub>2p</sub> (%)	C <sub>1s</sub> (%)	In <sub>3d</sub> +Sn <sub>3d</sub> (%)
(°C)	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE(eV)) <sup>1</sup>	(BE (eV)) <sup>1</sup>
RT	42.6	16.3	34.6	4.7
	(530.5) (532)	(711.5)	(285)	(444.5) (486.8)
300	47.4	9.7	20.6	20.2
	(531) (532)	(711)	(285.5)	(444.5) (486.8)

The XPS peaks from iron and oxygen at the surface of functionalized ITO electrodes show a binding energy similar to that found in the oxide powders (711.5 and 531 eV). A considerable fraction of carbon, partly present as adsorbed carbonate, is also observed, consistently with a secondary O1s peak at 532 eV. Upon annealing in air, the surface concentration of both Fe and C decreases, whereas the In and Sn signals (BE(In<sub>3d5/2</sub>) = 444.5 eV; BE(Sn<sub>3d5/2</sub>) = 486.8 eV) of the underlying ITO gain intensity (Table S3). This is consistent with the presence of a thin discontinuous iron oxide layer as also indicated by SEM imaging. Anodic response of ITO electrode functionalized with Fe-OEC in various electrolytes



**Figure S6.** JV curves of ITO electrodes modified with Fe-OEC (10 SILAR cycles, NaOH route), recorded in 0.5 M  $Na_2CO_3$  (black line),  $NaClO_4$  (blue line) and  $Na_2SO_4$  (red line) at pH 11.2, compared to bare ITO (green line).



**Figure S7.** JV curves of ITO electrodes modified with Fe-OEC (10 SILAR cycles, NaOH route), recorded in sodium carbonate (red lines), phosphate (green lines) and borate (blue lines) buffers at pH 9 (a), 10 (b), 11 (c) and 12 (d). All the solutions were adjusted to the same conductivity (26 mS cm<sup>-1</sup>) by addition of an electrochemically and hydrolytically inert salt (NaClO<sub>4</sub>).



#### Electrochemical Impedance Spectroscopy of Fe-OEC-ITO electrode

**Figure S8.** Nyquist plots of Fe-OEC-ITO electrode (10 SILAR cycles, NaOH route), recorded in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2), biased in the potential range between 1 and 1.5 V vs SCE. Continuous red lines: fitting curves as a function of the applied voltage.

#### Functionalization of ITO with CoPi and elaboration of Tafel plots

Electrodepositions of CoPi on ITO substrates were performed by following two different literature procedures (references 27 and 28b in the main text) starting from a 0.5 mM Co<sup>2+</sup> solution in 0.1 M potassium phosphate buffer at pH 7.

JV curves of the resulting electrodes were collected in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2) at a scan rate of 2 mV s<sup>-1</sup>. Tafel plots of log J *vs* overpotential ( $\eta$ ) were graphed for all the CoPi electrodes and for a Fe-OEC-ITO (obtained from 10 SILAR cycles, NaOH route). Tafel slopes were reported in Table S4. The overpotentials were calculated as follows:

$$\eta = V_{appl} - iR - E_{(O2/H2O, pH 11.2)}$$

where  $V_{appl}$  is the applied potential, iR is the ohmic drop of the solution and  $E_{(O2/H2O, pH 11.2)}$  is the oxygen evolution potential at pH 11.2 (*i.e.* 0.569 V).

The solution resistance R was measured by means of electrochemical impedance spectroscopy at high frequencies (1000-100000 Hz).

**Table S4.** Tafel slopes of Fe-OEC-ITO compared to ITO electrodes functionalized with CoPi catalyst obtained at various electrodeposition potentials and times.

OEC on ITO	Deposition	Tafel slope	Photo
Fe-OEC	10 SILAR, NaOH route	(mv decade ) 37	
CoPi1	Potentiostatic deposition at 1.29 V vs NHE (ref. 27 in the main text); 5 min	93	
CoPi2	Potentiostatic deposition at 1.29 V vs NHE (ref. 27 in the main text); 15 min	108	
СоРіЗ	Potentiostatic deposition at 1.29 V vs NHE (ref. 27 in the main text); 8 h	230	
CoPi4	Potentiostatic deposition at 1.05 V vs NHE (ref. 28b in the main text); 25 min	100	
CoPi (ref. 28b in the main text)	Potentiostatic deposition at 1.05 V vs NHE	60	

# Dark JV characteristic of Fe-OEC-3J anode in two electrode configuration



**Figure S9.** JV curves of a Fe-OEC-3J anode (5 SILAR cycles, NaOH route) (red) and Fe-OEC-ITO (10 SILAR cycles, NaOH route) (black) in two electrode configuration. The counter electrode was a Pt wire. 0.5 M Na<sub>2</sub>CO<sub>3</sub> at pH 11.2.





**Figure S10.** Stability of the photoanodic response of Fe-OEC-3J photoanodes recorded in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH  $\approx$  11) under AM 1.5G illumination. (**a-c**): NaClO route, 1 SILAR cycle, annealed at 150°C (**a**), 200°C (**b**), 300°C (**c**); (**d-e**): NaOH route, 5 SILAR cycles: (**d**) 200°C, (**e**) 300°C. The 1<sup>st</sup>, 5<sup>th</sup> and 10<sup>th</sup> of 10 subsequent JV cycles are reported.

# Electrochemical Impedance Spectroscopy of 3J photoanodes under illumination

**Table S5.** Ohmic ( $R_1$ ) and Charge transfer resistances ( $R_{CT2}$  and  $R_{CT3}$ ) extracted from the fits of Figure 8, b.

Voltage (V vs SCE)	R <sub>1</sub> (Ω)	R <sub>CT2</sub> (Ω)	R <sub>CT3</sub> (Ω)
-1.44 (V <sub>oc</sub> )	3.3	15.6	3.4
-1.3	3.1	51.5	7.8
-1.2	3	57.5	4
-1.1	3	66.8	4.3
-0.9	3	96.5	48.6
-0.8	3.1	101.6	33
-0.7	3	111.4	38.9
-0.6	3	210	2.8

**Table S6.** Ohmic ( $R_1$ ) and charge transfer resistances ( $R_{CT2}$  and  $R_{CT3}$ ) extracted from the fits of Figure 8, c.

Voltage (V vs SCE)	R <sub>1</sub> (Ω)	R <sub>CT2</sub> (Ω)	R <sub>CT3</sub> (Ω)
-1.2 (V <sub>oc</sub> )	7.8	6822	22
-0.9	7.8	3408	19
-0.8	6.8	1085	79
-0.7	6.7	740	80
-0.6	7	1659	118
-0.5	6.9	1619	142

#### Photoanodic stability of the Fe-OEC-3J photoanodes under continuous illumination



**Figure S11.** Chronoamperograms of the Fe-OEC-3J photoanode (5 SILAR cycles, NaOH route) recorded in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2) under AM 1.5G illumination biased at 0 (**a**) and at -1 V vs SCE (**b**). The experiment at -1 V vs SCE was performed immediately after the experiment a 0 V vs SCE.

#### Restoration of the photoanodic response after chronoamperometries



**Figure S12.** JV curves of the Fe-OEC-3J photoanode (5 SILAR cycles, NaOH route) recorded in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2), under AM 1.5G illumination, before (black) and after chronoamperometry at 0 V vs SCE (red) and at -1 V vs SCE (blue), when 120 minutes of continuous illumination were sustained. Green line: same photoanode after regeneration consisting in an additional SILAR cycle in NaOH, followed by annealing at 200°C.

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Determination of photoproduced O<sub>2</sub> and H<sub>2</sub>



**Figure S13.** Concentration (mg/L) of photoproduced molecular oxygen dissolved in the argon purged electrolyte (0.5 M Na<sub>2</sub>CO<sub>3</sub>, pH 11.2, Volume = 30 mL) during 60 minutes of photoelectrolysis employing a Fe-OEC-3J (5 SILAR cycles, NaOH route) photoanode under AM 1.5G illumination. Oxygen concentration was measured by means of a calibrated polarographic electrode.



**Figure S14.** Molar amount of photoproduced oxygen collected in the head-space of the 3 electrodes electrochemical cell (Fe-OEC-3J/Pt/SCE) under AM 1.5G illumination at 0 V vs SCE for 1 hour, in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2). The red line is the dark control measurement. The shallow slope of the red curve is due to slow leak of atmospheric oxygen into the sealed cell. The faradic yield for oxygen production in this experiment was 75  $\pm$  3 %.



**Figure S15.** Rate of hydrogen evolution at the Pt cathode of a Fe-OEC-3J/Pt/SCE cell under AM 1.5G illumination at 0 V vs SCE, in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2). Linear fitting of the curve led to a hydrogen production rate of 0.056  $\mu$ M s<sup>-1</sup>. A Faradic yield of 81 ± 2 % was determined.

# *iV curves of Pt counter electrodes*



Figure S16. iV curve of Pt wire in 0.5 M  $Na_2CO_3$  (pH 11.2) at a scan rate of 10 mV s<sup>-1</sup>.



Figure S17. iV curve of Pt grid in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2) at a scan rate of 10 mV s<sup>-1</sup>.



**Figure S18.** iV curve of the Pt grid in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2) at a scan rate of 10 mV s<sup>-1</sup>. Magnification of the curve in the potential range between -0.5 and 0 V vs SCE.

# JV curve of the Fe-OEC-3J photoanode under pulsed illumination in two electrode configuration



**Figure S19.** JV curve of Fe-OEC-3J photoanode (cell 2 of Figure 11) wired to a large area Pt grid in a two electrode configuration under pulsed AM 1.5 G illumination (0.1 W cm<sup>-2</sup>), recorded in 0.5 M Na<sub>2</sub>CO<sub>3</sub> (pH 11.2). Scan rate = 10 mV s<sup>-1</sup>.

# Anodic and Photoanodic response of ITO and 3J photoanodes modified with Ni and Co based



**Figure S20.** (a) JV curve of an ITO electrode modified with Ni-OEC catalyst, recorded in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH  $\approx$  11). The wave preceding the water oxidation process in ascribed to Ni<sup>2+</sup>  $\rightarrow$  Ni<sup>3+</sup> oxidation. (b) JV curve of Ni-OEC-3J photoanode (1 SILAR cycle) in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH  $\approx$  11) under 0.1 W cm<sup>-2</sup> AM 1.5G illumination.



**Figure S21.** (a) JV curves of an ITO electrode modified with Co-OEC catalyst, recorded in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH  $\approx$  11). (b) JV curve of Co-OEC-3J photoanode (1 SILAR cycle) in 0.1 M Na<sub>2</sub>CO<sub>3</sub> (pH  $\approx$  11) under 0.1 W cm<sup>-2</sup> AM 1.5G illumination.