Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information

Evaluating Spinel ferrites MFe_2O_4 (M = Cu, Mg, Zn) as Photoanodes for Solar Water Oxidation: Prospects and Limitations

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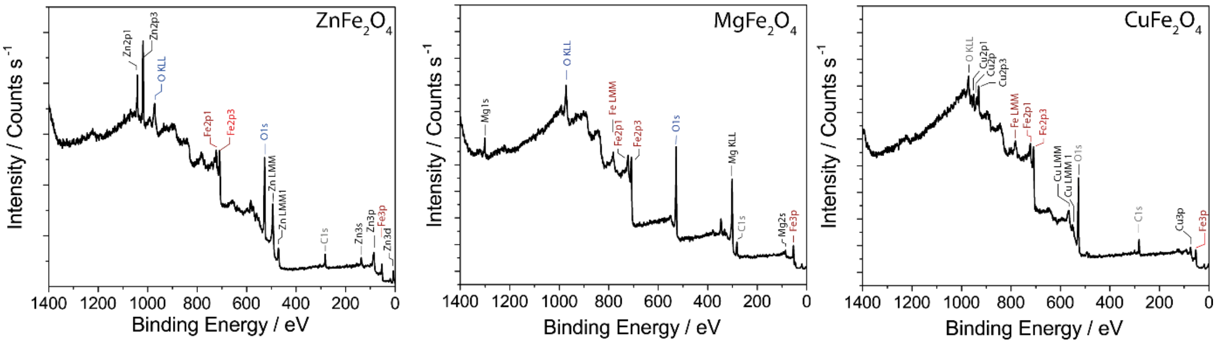


Figure S1. XPS survey for $ZnFe_2O_4$, $MgFe_2O_4$ and $CuFe_2O_4$, respectively, after the post-annealing treatments, labelling the main signals.

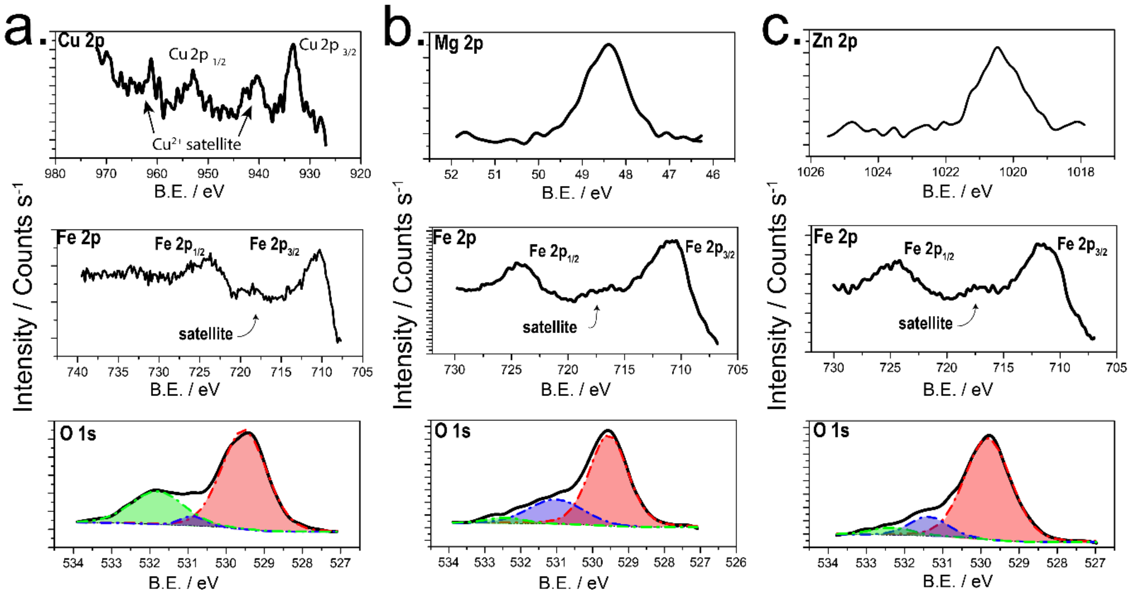


Figure S2. Narrow-scan XPS spectra of the as-prepared CFO (a), MFO (b) and ZFO (c) in the Cu 2p, Mg 2p or Zn 2p region (top), respectively, as well as in the Fe 2p (middle) and O 1s regions (bottom). The fitting and deconvolution of different contributions along with the background correction (Shirley method) were included.

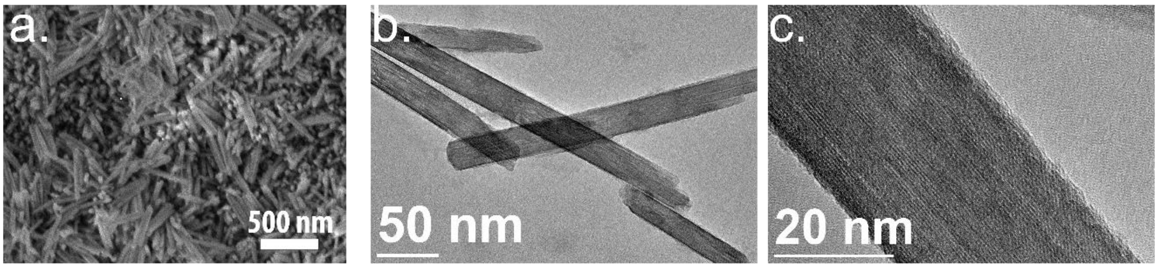


Figure S3. SEM top-view of as-grown β-FeOOH thin-film on FTO substrate (a) and TEM images (b,c) of the nanowires scratched from the film and deposited in a TEM grid.

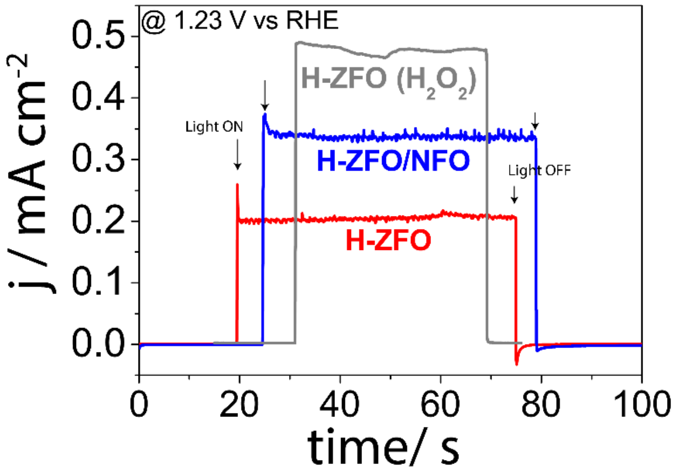


Figure S4. Current vs. time for H-ZFO (red), H-ZFO/NFO (blue) and H-ZFO (H_2O_2) (grey) obtained at 1.23 V vs RHE in 1 M NaOH or 0.5 M H_2O_2 + 1 M NaOH (grey line) as electrolyte.

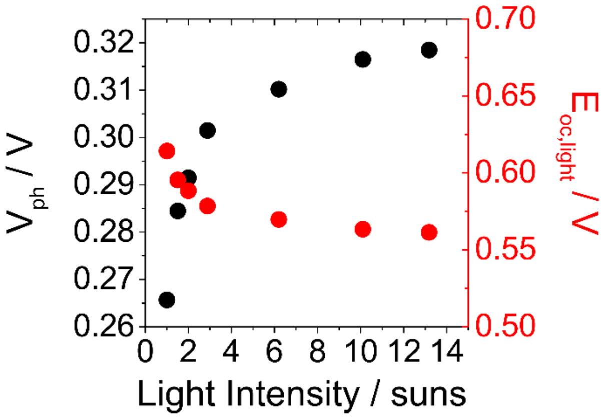


Figure S5. Evolution of the photovoltage (V_{ph}) and $E_{OC,light}$ as a function of the light intensity for the NFO-coated H-ZFO samples.

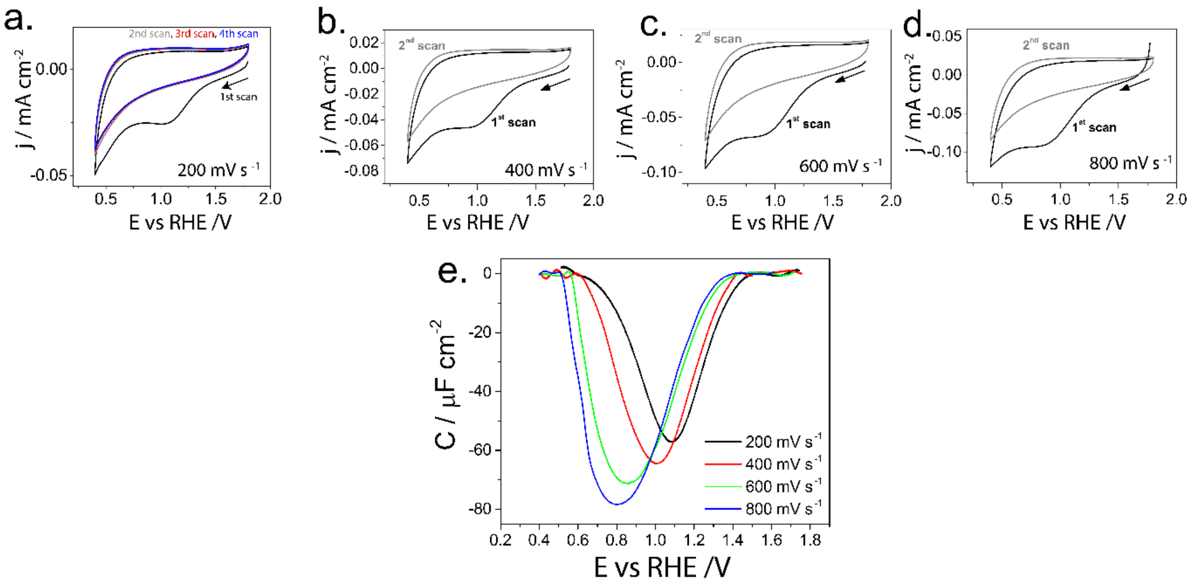


Figure S6. Rapid-scan cyclic voltammograms (RSVs) (first –black line- and second –grey line- cycle) (a-d) as a function of the scan rate (200-800 mVs^{-1}) for the H-ZFO photoanode. In (a) 4 scans are shown (3rd scan –red line- and 4th scan –blue line-) to show that the CV does not change after the second cycle, i.e. all the accumulated holes “sensitive” to this measurement were extracted during the first scan. Capacitance vs. potential plots (e) including baseline correction for the different scan rates. Note that the capacitance was obtained by dividing the current by the scan rate. It is worth emphasizing that the cathodic band related to surface-accumulated holes appear to shift to lower potentials with increasing scan rate which typically is a sign of a quasi-reversible charge transfer process (slow kinetics). Additionally, the fact that the capacitance changes only slightly with the scan rate suggests that the population of surface-holes does not change rapidly over time which is characteristic of holes trapped in intrinsic surface defects of the material.

RSVs were obtained by a two-step process with a minimum delay in-between them. First, the electrode was held at 1.8 V vs RHE under constant-illumination for 60 s recording the photocurrent (chronoamperometry) followed by the interruption of the light and recording the cyclic voltammograms (starting potential 1.8 V vs RHE and scanning in the negative direction). Measurements were done in 1M NaOH. *Note that all the trapped charges (susceptible to be extracted by this measurement) were indeed extracted with the 1st cathodic scan, since already the 1st anodic scan matches with that of the subsequent CVs.*

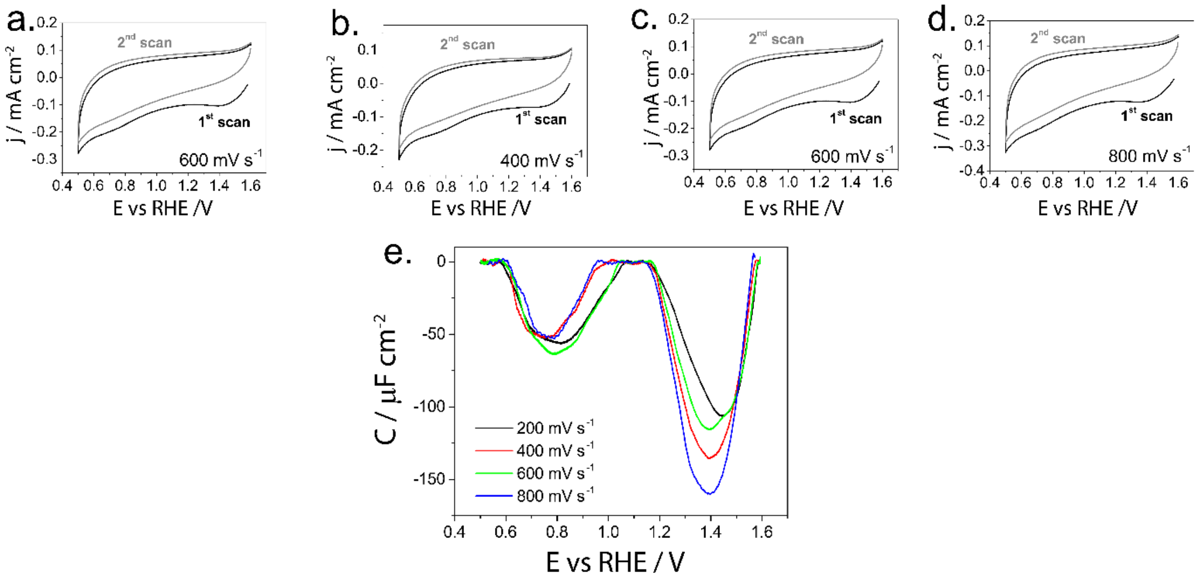


Figure S7. Rapid-scan cyclic voltammograms (RSVs) as a function of the scan rate (200-800 mVs^{-1}) for the 550-CFO samples (a-d). In this case the applied potential during the chronoamperometry that precedes the cyclic voltammetry was 1.6 V vs RHE. Capacitance vs. the applied potential (e) was obtained by substracting the current of the 2nd cathodic scan to the1st one and dividing this current by the scan rate, and correcting the baseline for the sake of the analysis. In all the cases the electrolyte was 1 M NaOH.

We can distinguish two bands around 0.8 and 1.4 V vs RHE. On the one hand, the first one changes very little in magnitude with the scan rate. Therefore we associate this capacitance to the signature of holes trapped in surface defects which are probably unable to participate in water oxidation reaction. On the other hand, the second changes more markedly with the scan rate, the faster the scan rate the higher the capacitance. This result, together with the fact that is located below 1.23 V vs RHE would lead to associate them with intermediates that rapidly decay over time due to their active participation in the water oxidation reaction.[s1]

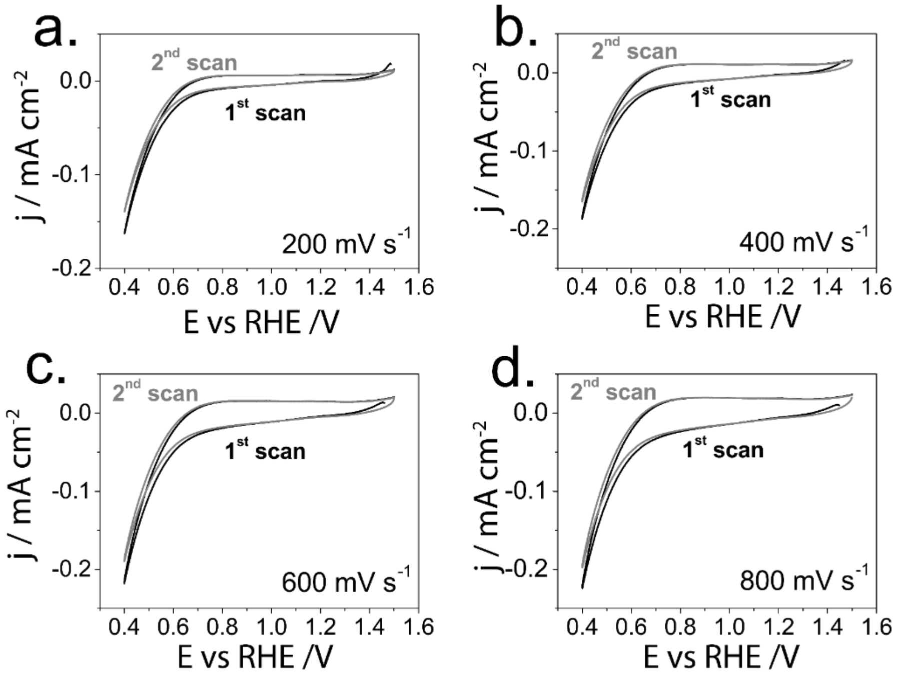


Figure S8. Rapid-scan cyclic voltammograms as a function of the scan rate (200-800 mV s^{-1}) obtained in 1 M NaOH + 0.5 M H_2O_2 for the H-ZFO. Chronoamperometry prior the cyclic voltammetry was performed at 1.5 V vs RHE.

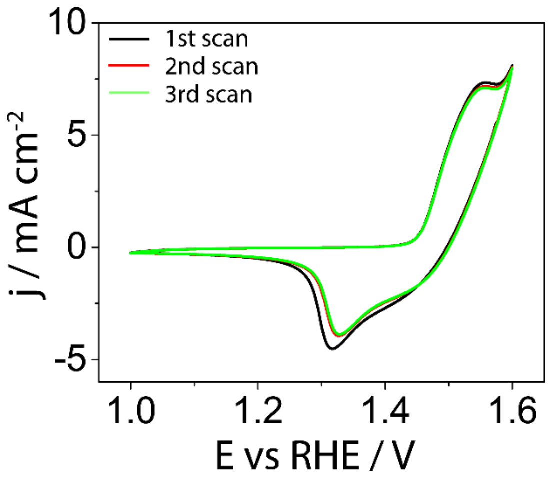
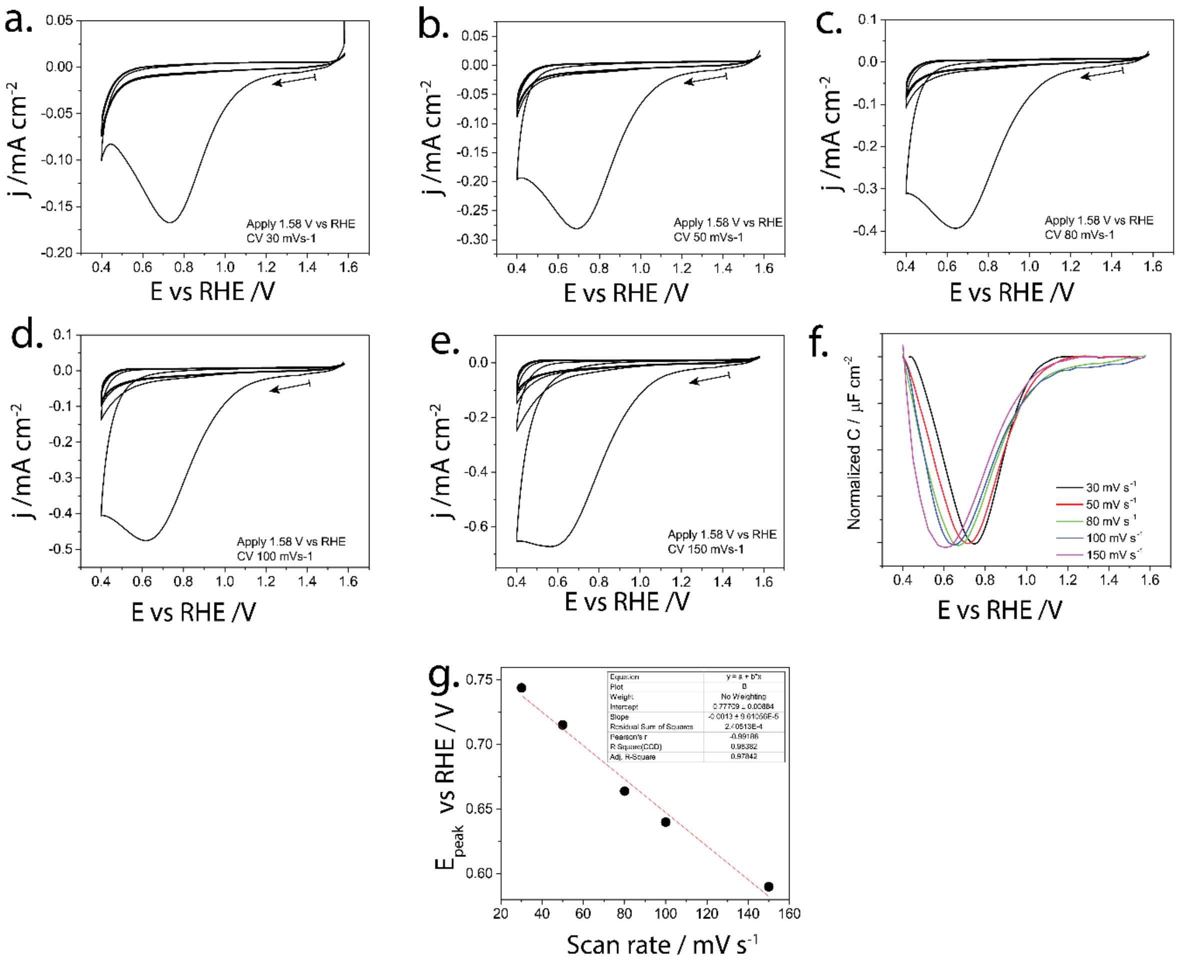


Figure S9. Fast-scan cyclic voltammogram recorded at 200 mV s^{-1} for an NFO-coated FTO electrode. The electrode was held at 1.6 V vs RHE for 60 seconds (chronoamperometry) before starting the cyclic voltammetry. Measurement was performed in 1 M NaOH.



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	0.77709 ± 0.00884
Slope	-0.0013 ± 9.61050E-5
Residual Sum of Squares	2.40513E-4
Pearson's r	-0.99186
R-Square(COD)	0.98382
Adj. R-Square	0.97842

Figure S10. Rapid-scan cyclic voltammograms (RSVs) (a-e) corresponding to the NFO-coated H-ZFO as a function of the scan rate (30-150 mVs^{-1}) showing the first four scans. For all the measurement, the initial chronoamperometry was performed at 1.58 V vs RHE (for 1 min) followed by the RSV.Normalized capacitance (f) was obtained by substracting the current of the 4th cathodic scan to the 1st cathodic scan, correcting the baseline and dividing by the scan rate. Peak position (E_{peak}) of the capacitance extracted from RSV vs. the scan rate (g). All the experiments were performed in 1 M NaOH as electrolyte.

We note that the scan rate employed for NFO-coated samples is lower than that use in bare samples, When recorded the RSV at faster scan rates (150 mVs^{-1} or higher) we observe a non-negligible cathodic current associated to the discharge of trapped holes during 2nd and 3rd scan. Likely, the kinetic for the charge-transfer process from the back contact to the NFO in the surface is so slow that only sufficiently slow scan rates are able to complete the reaction (withdrawal of surface holes) in the 1st scan. Additionally, we observe that the capacitance peak is shifting with the scan rate (g) which evidences the slow kinetics of the charge transfer process.

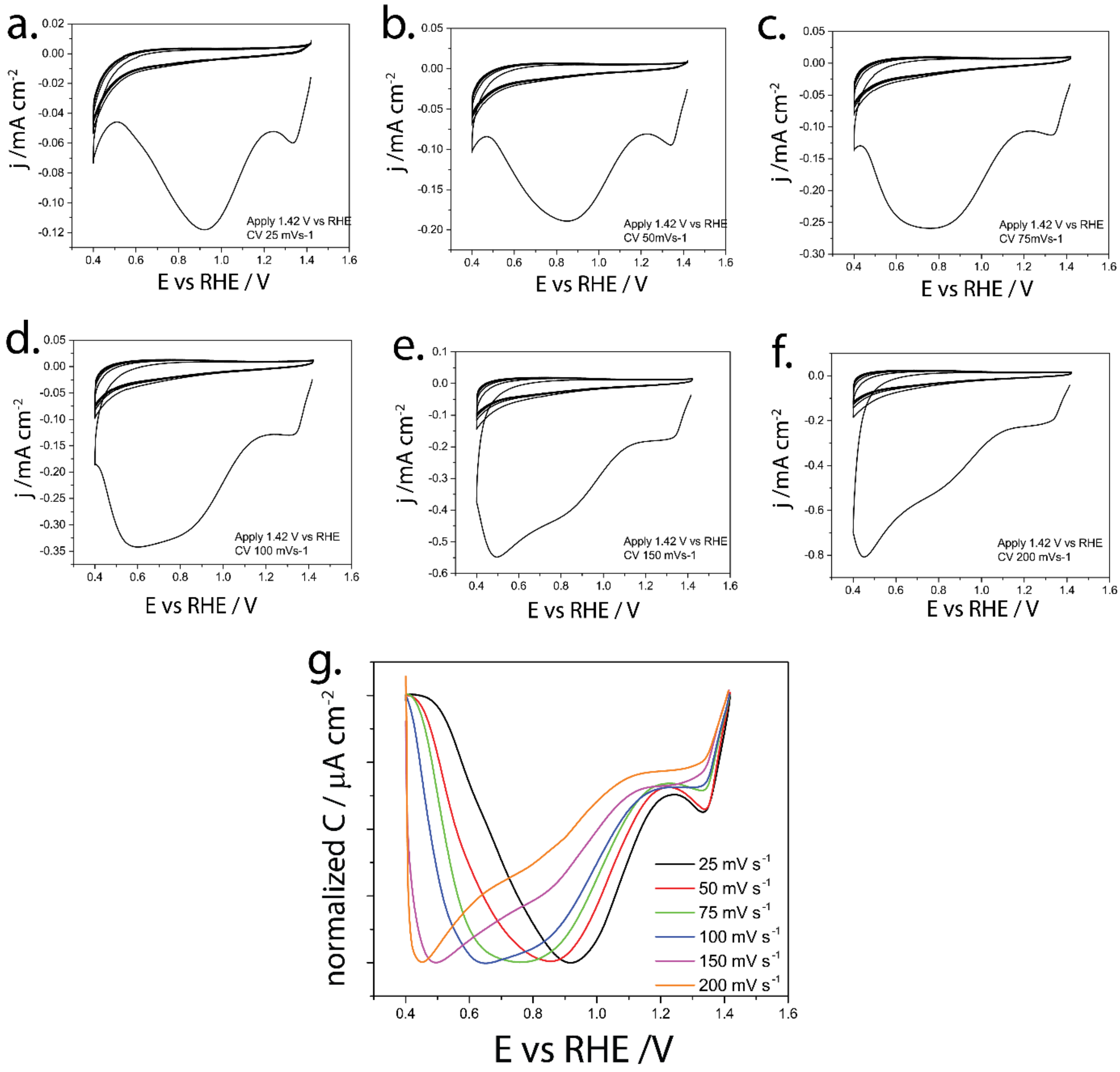


Figure S11. Rapid-scan cyclic voltammetry (RSV) performed on NFO-coated 550-CFO photoanodes as a function of the scan rate (25-200 mVs^{-1}) (a-f). All the RSVs were collected after applying 1.42 V vs RHE under illumination in 1 M NaOH. Normalized capacitance vs. potential plot (g) was obtained by subtracting the 2nd cathodic scan to the 1st one, converting the obtained current in capacitance by dividing by the scan rate and finally correcting the baseline.

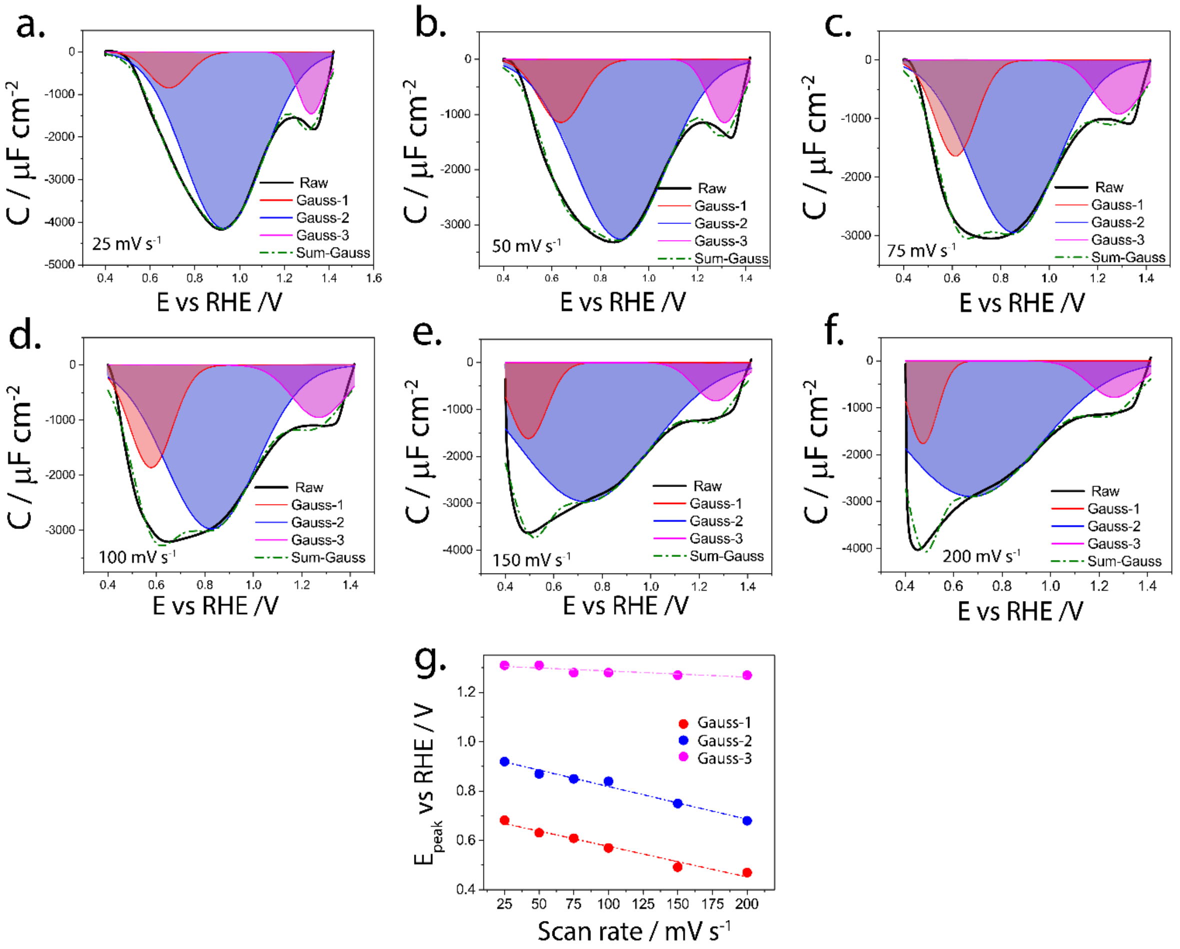


Figure S12. Capacitance vs. potential plots extracted from the RSV measurements as a function of the scan rate including deconvolution with 3 gaussian components (a-f). Shift of E_{peak} of the different gaussian components as a function of the scan rate (g). By using three gaussian components the RSV curves could be fitted with minor deviations. Interestingly, two bands (Gauss-1 and -2) appear to be very sensitive to the scan rate, whereas the third one (Gauss-3) seems to remain unaltered. The slow kinetics of the process tracked by Gauss-1 and -2 suggests that the capacitance is linked to surface-intermediates for water oxidation within NFO, whereas the fast kinetics of Gauss-3 suggest that either corresponds to intermediates on the bare CFO (matching with that observed in Figure S7) or a minor contribution of NFO in direct contact with the substrate.

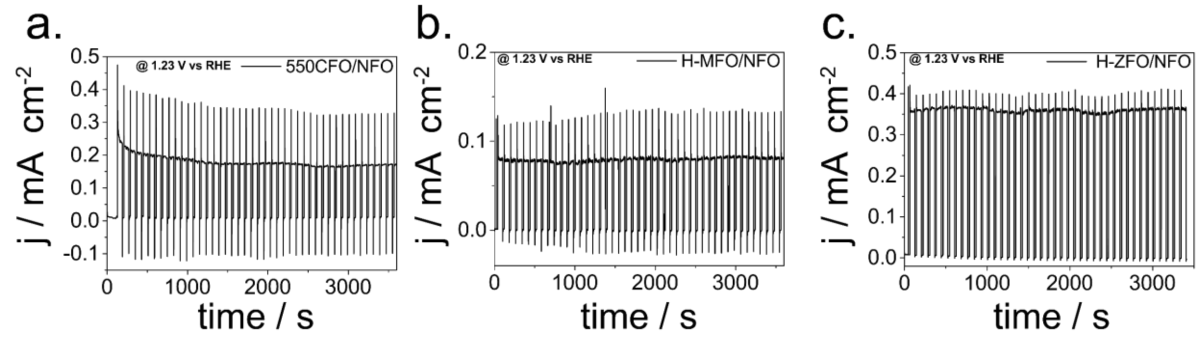


Figure S13. Current vs. time plot under chopped-light illumination (simulated 1 sun AM 1.5G) for NFO-coated 550-CFO (a), H-MFO (b) and H-ZFO (c) under an applied potential of 1.23 V vs RHE. In all the cases, the electrolyte used was 1 M NaOH.

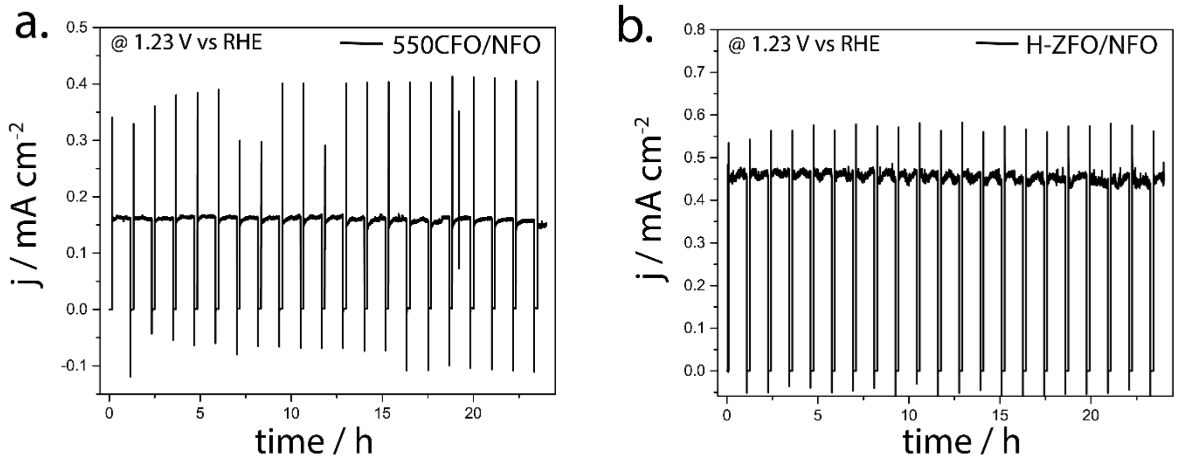


Figure S14. Extended current vs. time plot under chopped-light illumination (simulated 1 sun AM 1.5G) for NFO-coated 550CFO (a) and H-ZFO (b) recorded with an applied bias of 1.23 V vs RHE and using 1 M NaOH as electrolyte.

Determination of oxygen production and Faradaic Efficiency

Measurement of the oxygen production linked to the photo-assisted water oxidation reaction was performed by coupling a Gas Chromatograph Clarus 480 (Perkin Elmer) equipped with a molecular sieved column (5A, held at 50 °C) and a plasma emission detector (PlasmaDetek) to a three-electrode Cappuccino-type cell tighly closed. As working electrodes, NFO-coated 550-CFO, H-MFO and H-ZFO were used, whereas Pt foil was used as counter electrode and a Ag/AgCl/KCl (sat) as reference electrode. In all the cases, the electrolyte employed was 1 M NaOH. Prior the measurement the cell was purged for 1 h with argon to remove initial oxygen dissolved, and the argon-bubbling (10 mL min^{-1}) was kept during all the measurements acting as a carrier gas to conduct the gas produced in the cell to the gas chromatograph. To determine the faradaic efficiency the electrodes were submitted to 1.23 V vs RHE under an irradiance of 5 suns (higher light intensity increases the photocurrent response and hence facilitate to track the oxygen production) while the argon was continuously carrying the gases into the gas chromatograph. Figure S15 shows the photocurrent recorded over time for each one of the electrodes, and the red arrows indicate when the gas was indeed injected into the column of the gas chromatograph to analyze the gas mixture. The corresponding calibration line was obtained by using a Pt foil as a working electrode, considering that water oxidation occurs with a 100% faradaic efficiency. In this case, chronopotentiometry measurements at different currents were performed, recording the oxygen production at least 5 times at each current (Figure S15, d,e).

In the case of CFO, an average current of 0.046 mA was obtained with an average O_2 signal of 0.057. This, according to the calibration line corresponds to approx. 97 ± 3 % faradaic efficiency for oxygen production. The MFO, shows an average current of 0.030 mA with an average O_2 signal of 0.037 that corresponds, according to the calibration line, to around 97 ± 3 %. The ZFO, displays an average current of around 0.49 mA with a signal of O_2 of 0.59 which leads to a faradaic efficiency of ca. 99 %. Given the proven long-term stability of the electrodes we consider that the slight deviations on faradaic efficiency are not due to corrosion but experimental errors.

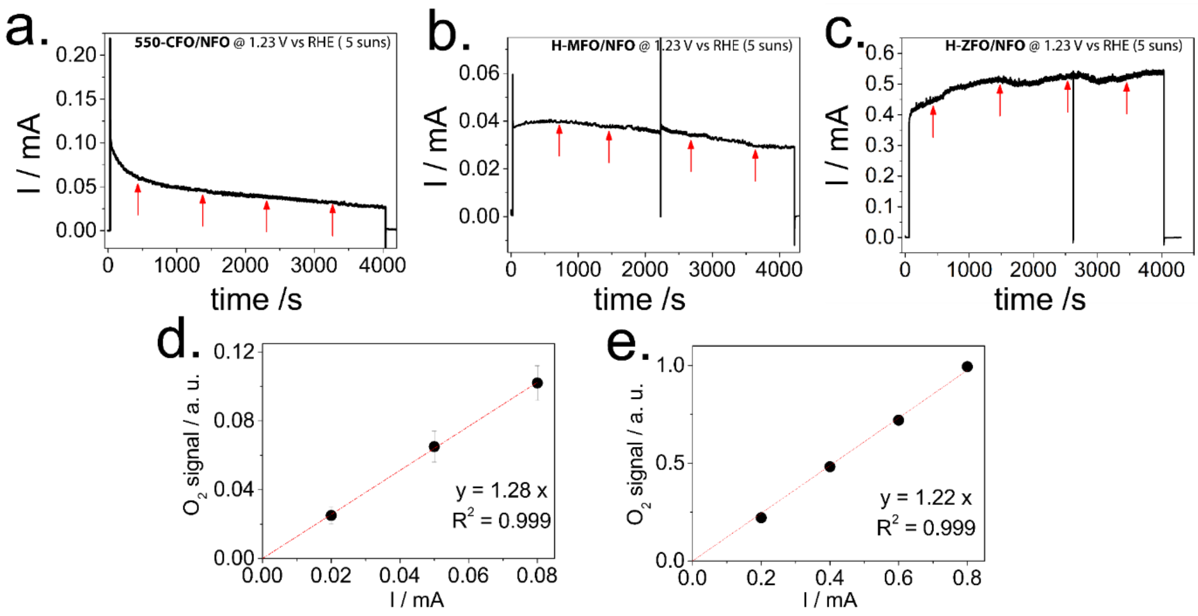


Figure S15. Constant-illumination chronoamperometry of NFO-coated 550-CFO (a), H-MFO (b) and H-ZFO (c) electrodes at 1.23 V vs RHE under 5 suns irradiance. The red arrows indicate when the O_2 measurement was performed. Calibration lines for the O_2 detection by the gas chromatograph using Pt as working electrode at two different ranges of current (d,e). In all cases 1 M NaOH aqueous solutions were employed as electrolyte.

Supporting References

(s1) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. *Energy Environ. Sci.* **2012**, *5* (6), 7626.