

Supporting Information

Observation of charge transfer cascades in α -Fe₂O₃/IrO_x photoanodes by operando X-rays absorption spectroscopy

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EXPERIMENTAL SECTION

Preparation of α -Fe₂O₃ / IrO_x photoanodes. α -Fe₂O₃ films were grown on conductive FTO coated glass slides (Aldrich) by using PE-CVD. Ferrocene vapors were injected by a pulsed Ar flow into the core of a cold tubular plasma (power 30 W) fed by an Ar/O₂ 4.5% gas mixture. The FTO target was placed orthogonally with respect to the gas flow, plunged in the plasma plume at 5 cm from the core. All α -Fe₂O₃ films were thermally treated in air at 500°C for 1 h and thereafter at 750°C for 10 min.

IrO_x film deposition was achieved as described in previous works^{1,2} briefly, 0.0151 g of IrCl₃•3H₂O (Alfa Aesar) are dissolved in Milli-Q water (10 ml). After 30 min stirring, 100 μ l of H₂O₂ (30%) are added and the resulting solution is kept under stirring for 30 min. Then, 0.0518 g of oxalic acid are added. The solution is stirred for 10 min. Finally, dried K₂CO₃ is added until pH is about 10.5. The procedure leads to the formation of a yellow solution that turns blue/violet after 3 days at room temperature. The blue colloid is used as a deposition bath, from which IrO_x is easily deposited onto a conductive support (a carbon disk deposited onto a 175 μ m thick Polyethylene terephthalate lamina, supplied by Dropsens) at constant current density. We obtained durable and XAS suitable deposits by applying 0.1 mA cm⁻² for 800 s, using a Pt plate as the counter electrode.

Photo-Spectroelectrochemical cell. The experimental scheme was designed in order to perform in situ and in operando measurements for investigating light-driven electrochemical processes. Thanks to a 400 nm LED it was possible to acquire spectra both in Uv-vis light and dark conditions, thus allowing to study the role of the electrocatalyst when coupled to a semiconductor. In the three-electrodes assembly employed, the working electrode was a photoanode composed of an electrocatalytic domain (IrO_x) in contact with a semiconductor domain (Fe₂O₃) supported onto Fluorine-doped Tin Oxide film (FTO). A Pt foil was used as a counter electrode and the reference was a Ag/AgCl. The electrochemical cell is made of a polyacrylate and was obtained by means of a 3D printer.³ The structure of the Spectro-electrochemical cell is such that the thickness of the HK₂PO₄ 1 M aqueous solution contained is less than 1 mm. The need to fulfil this requirement lies in the fact that one side of the electrocatalyst is in contact with Fe₂O₃ (which prevents from measuring X-ray fluorescence) and the other with the electrode solution: having in mind that the absorption length of water is 0.363 cm at 11215 eV (Ir-L_{III} edge), the width of the solution layer should not be more than 1 mm to allow to collect spectra with sufficient signal-to-noise ratio. The reference electrode is separated from the solution by a salt bridge

consisting of a glass pipet filled with agar containing 0.2 M aqueous KClO_4 . One side of the cell includes a hole that matches with the working electrode area.

X-ray absorption spectroscopy set-up. XAS measurements were acquired in fluorescence mode at the GILDA beamline⁴ (European Synchrotron Radiation Facility) at the Ir-L_{III} edge. The main characteristics of the beamline are a Si(311) sagittally focusing double crystal monochromator, harmonic rejection was achieved using Pd mirrors with a cut-off energy of 18 keV whereas a 12-element Ge fluorescence detector to detect the X-ray fluorescence from the sample. The energy calibration was performed by measuring the Absorption Spectrum of a metallic Hafnium foil at the Hf-L_I edge (Hf-L_I: 11271 eV; Ir-L_{III}: 11215 eV). The sample was illuminated with a Light Emitting Diode (LED) with a peak wavelength of 400 nm (LEDengine, 5mW, width of the emission $\approx 15\text{nm}$) focalized using BK7 glass spherical lenses. The radiant flux from the diode was about 0.25 W. All data were obtained at room temperature. In order to check for the reproducibility of the results here presented, the experiment has been repeated with three electrode materials prepared in different ways, at four different applied potentials, obtaining identical results. X-ray signal extraction and normalization was performed by means of ATHENA, belonging to the set of interactive programs IFEFFIT.⁵ Furthermore, this software allows to carry out preliminary analysis such as removing glitches and calculating the derivative spectra.

PEC measurements. The electrodes were electrochemically characterized in a three electrodes system: the RE (reference electrode) was a silver chloride electrode ($\text{Ag}/\text{AgCl}/1\text{M KCl}$), while a high surface area Pt mesh was the CE. The potential (E) was referred to the reversible hydrogen electrode (RHE) scaled through the Nernst equation:

$$E_{\text{RHE}} = E_{\text{AgCl}} + 0.23 \text{ V} + 0.059 \text{ pH}$$

where E_{AgCl} is the measured electrode potential vs. the used reference electrode and 0.23 V is the reference electrode standard potential vs. the normal hydrogen electrode. Mott-Schottky measurements were performed in NaOH (1 M) aqueous solution (pH 13.6) in the dark at various frequencies between 1 and 1000 Hz with a PGSTAT204 Autolab potentiostat. In particular, the values reported in Figure S3 were obtained at 1000 Hz.

UV-Visible spectrum was recorded in transmittance using a Shimadzu UV-Vis-NIR UV3600 Spectrophotometer on a IrO_x layer electrodeposited onto a fresh FTO (SigmaAldrich) substrate by application of 0.1 mA cm^{-2} for 800 s (vs a Pt counter electrode) in the deposition bath described above.

FEXRAV and XANES

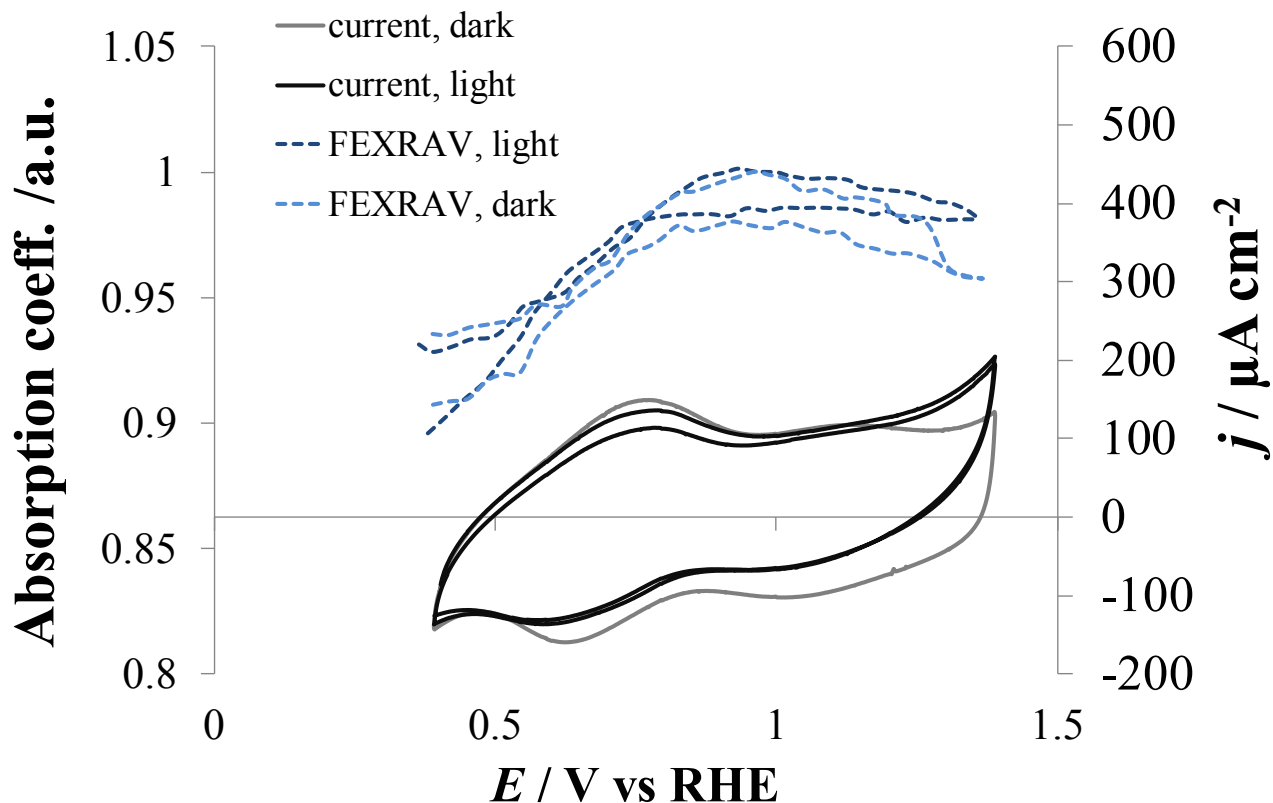


Figure S1: FEXRAV (second cycle) of Ir at 11221 eV in 1 M HK_2PO_4 . Hydrous IrO_x is deposited onto hematite, which is kept in the dark (dark blue, full line) or illuminated with a 410 nm LED (light blue, dashed line). Scan rate was set at 2 mV s^{-1} . In the figure, the data are normalized to absorption coefficient equal to 1 at an applied potential of 1 V_{RHE} for the sake of better comparison. The corresponding values of current densities are reported in the secondary scale both as recorded under illumination (black line) and in the dark (grey line).

As our previous electrochemical study on EIROF,¹ Ir clearly undergoes oxidation/reduction phenomena induced by the application of a potential, here referred to the reversible hydrogen electrode (RHE). In

Figure S1 both signals are normalized with respect to the value of μ at 1.0 V (i.e. at the highest concentration of Ir(IV)).

The shape of these FEXRAV scans is similar to that observed previously on EIROF.² However, in the present case, for $E > 0.8$ V the signal does not follow the dramatic decrease bound to the formation of Ir(V).

Control experiments for differential XAS

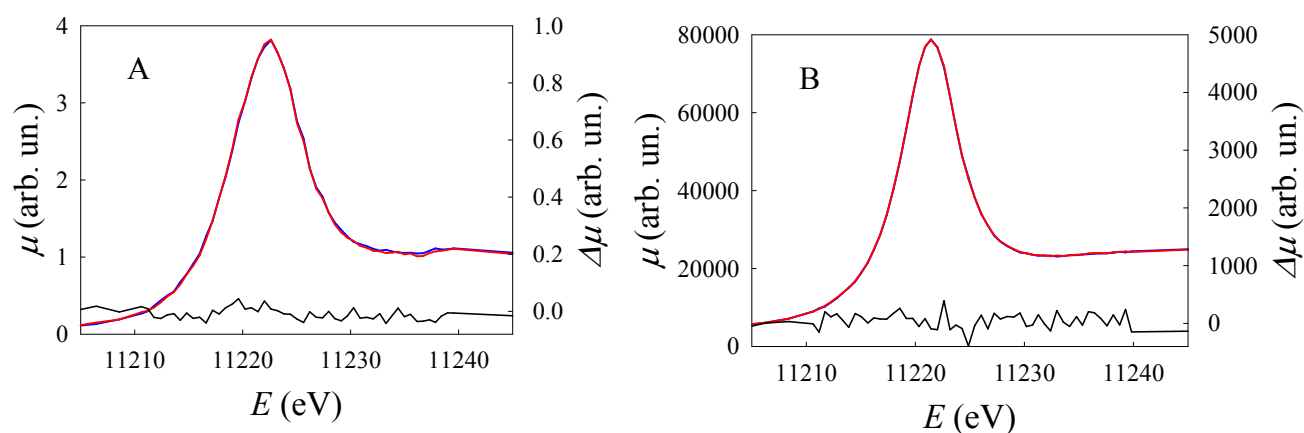


Figure S2. (A) Simultaneously recorded spectra of an electrodeposited IrO_x layer on a carbon support (Dropsens[®]) in the dark (blue line), under illumination at 400 nm (red line) and the difference of the two (black line, right axis). (B) Simultaneously recorded spectra of a hematite/IrO_x photoelectrode in the dark (blue and red curves) and their difference (black curve, right axis).

Determination of the flat band potential

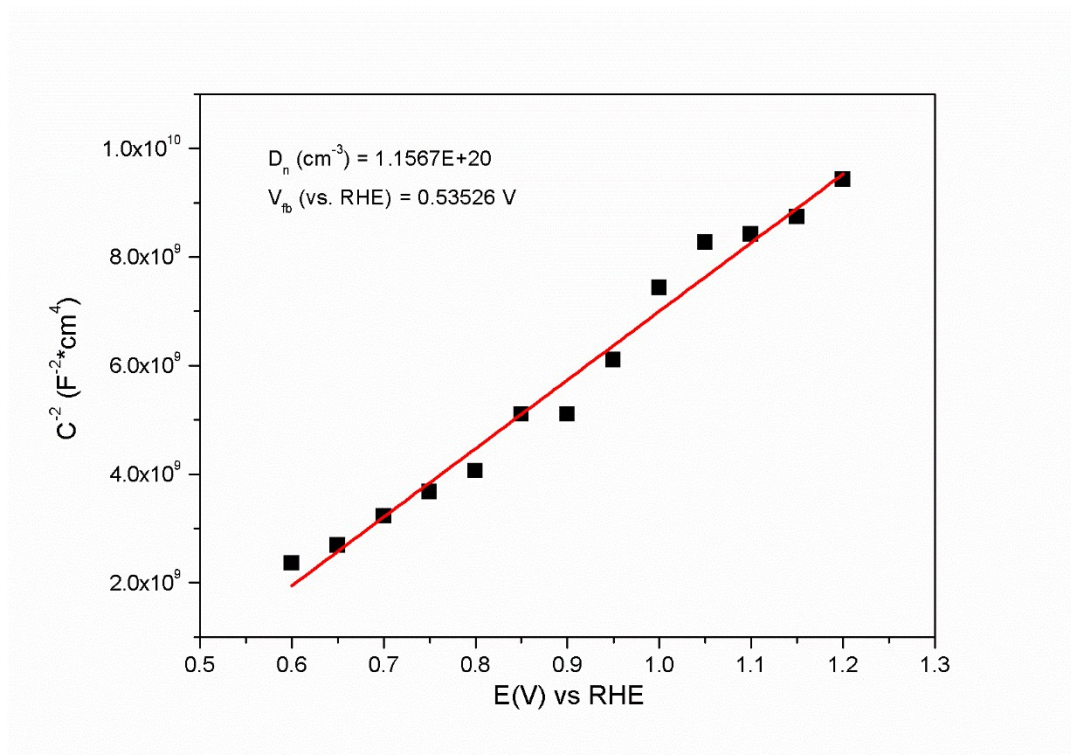


Figure S3. Mott-Schottky plot of α -Fe₂O₃ photoelectrodes performed at 1000 Hz in NaOH (1 M) solution.

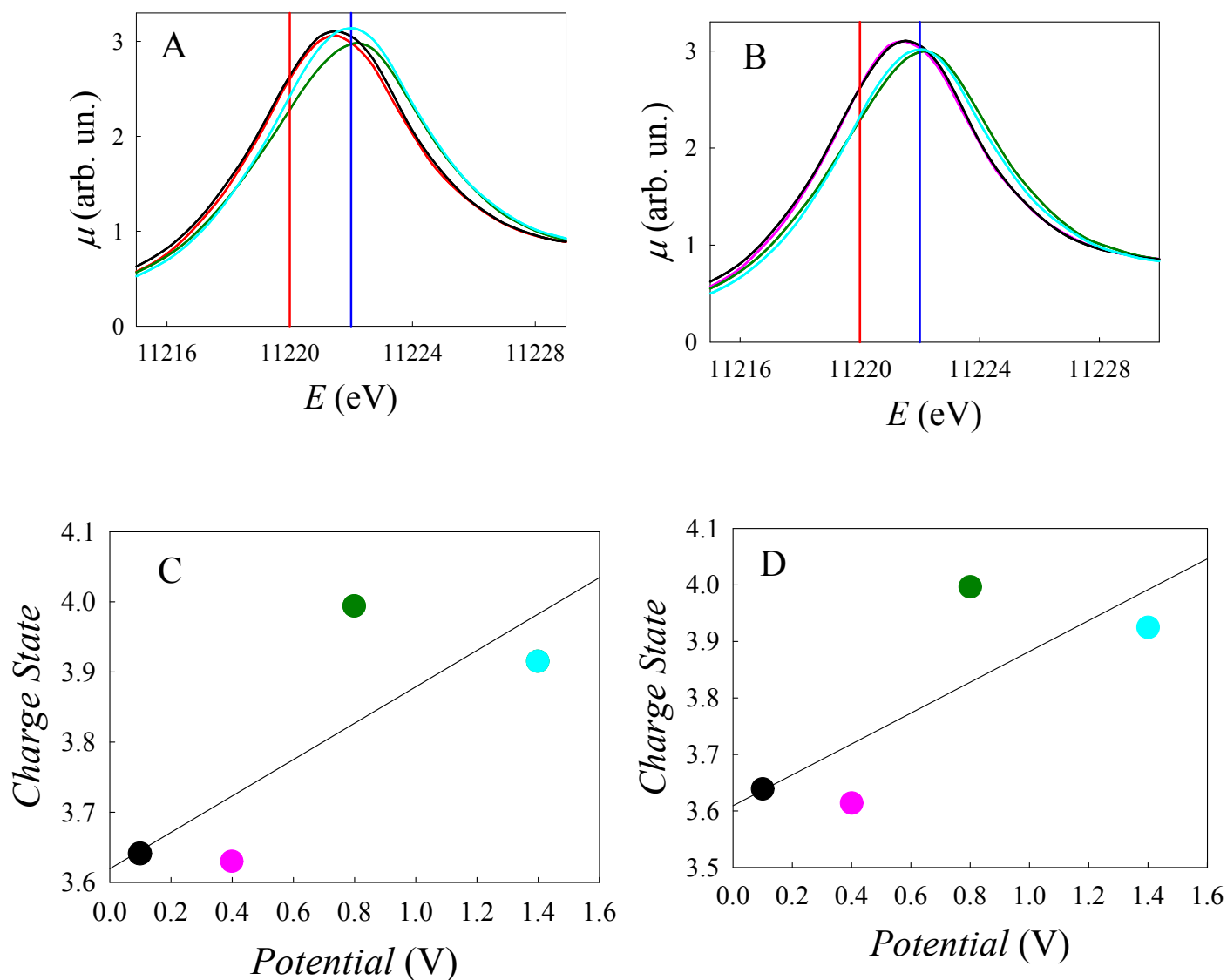


Figure S4: Ir L_{III} XANES spectra acquired in Uv-vis light (A) and dark (B) conditions under different potential values: 0.1 V (black line), 0.4 V (pink line), 0.8 V (green line) and 1.4 V (cyan line). For reference, the absorption edges of Ir(III) and Ir(IV) standards are indicated as vertical lines, red and blue respectively. The charge state Vs applied potential graphs are illustrated for the light (C) and dark (D) conditions. Charge states have been obtained from XANES fitting procedures.

In Fig. S2, the positions of the absorption edges of IrCl₃ and IrO₂ standards are indicated by vertical lines as references for Ir(III) and Ir(IV) respectively. Both in presence (A) and in absence (B) of the

UV-Vis light, an increase in the applied potential determines a shift of the White Line maximum towards higher energies. When the potential is lower than 0.5 V, the position of the absorption peak suggests that the mean oxidation state of the photo-absorber (i.e., Ir) is located between (III) and (IV). When the potential reaches larger values (0.8, 1.4 V) the absorption edge position is similar to that of IrO₂, thus the oxidation state of Ir is very close to (IV). This confirms what was previously observed by means of FEXRAV analysis (Figure S1): in both dark and light, the decrease in the absorption signal, occurring when the potential is lower than 0.8 V, can be explained by a shift of the absorption energy towards lower values.

Considering that IrCl₃ and IrO₂ contain Ir(III) and Ir(IV), respectively, and taking into account the position of their absorption edges, a relationship between the absorption position and the charge state of the photo-absorber can be obtained. Fig. 2C and D show the trend of the charge states estimated as the potential increases for both the UV-Vis and dark conditions, respectively. The trend is very similar in the two cases and it shows that the charge state of Ir ranges from 3.6 to 4.0. We can conclude that the shift in the absorption peak and therefore in the oxidation state range of Ir is smaller if compared to data previously obtained by us¹ in absence of the semiconductor: this can be attributed to the ohmic drop due to the presence of hematite. We cannot exclude the presence of Ir in the close proximity of the support (FTO) that is therefore in a preferential connection with the potentiostat. However, given the good coverage of hematite achieved by PE-CVD, we can safely assume that this represents a negligible contribution to the overall electrochemical behaviour of the bilayer architecture.

Considerations on the increasing of X-ray absorption coefficient (μ) under illumination

As pointed out in the main text, in the EXAFS region (i.e. for $E > 11235$ eV) μ increases under illumination: this implies that an increased amount of absorber atoms (Ir) hit by the X-ray beam is present under illumination. Thanks to the control experiments (light-dark differential spectra of pure EIROF electrodes or dark-dark tests on the composite photoelectrode showed no appreciable differences) we can safely rule out any instrumental origin of this phenomena. Interestingly, an estimation of the increment of μ (as a percentage with respect to the value measured in the dark) at the considered applied potentials points to a trend as follows: approximately 3% at 1.4 V, 2% at 0.8 V, 1% at 0.4 V, while is not evident at 0.1 V. Considering the alkaline pH (at which the instability of IrO_x is known) and the fact that the photoelectrode undergoes light/dark cycles during the spectra acquisition, we can conclude that the difference in μ originates from dissolution/deposition cycles: under dark

conditions Ir is partially dissolved, while is deposited back on the hematite surface during the illumination cycle.

Cyclic voltammetric behaviour of the $\text{IrO}_x/\alpha\text{-Fe}_2\text{O}_3$ and of the $\alpha\text{-Fe}_2\text{O}_3$ photoelectrodes

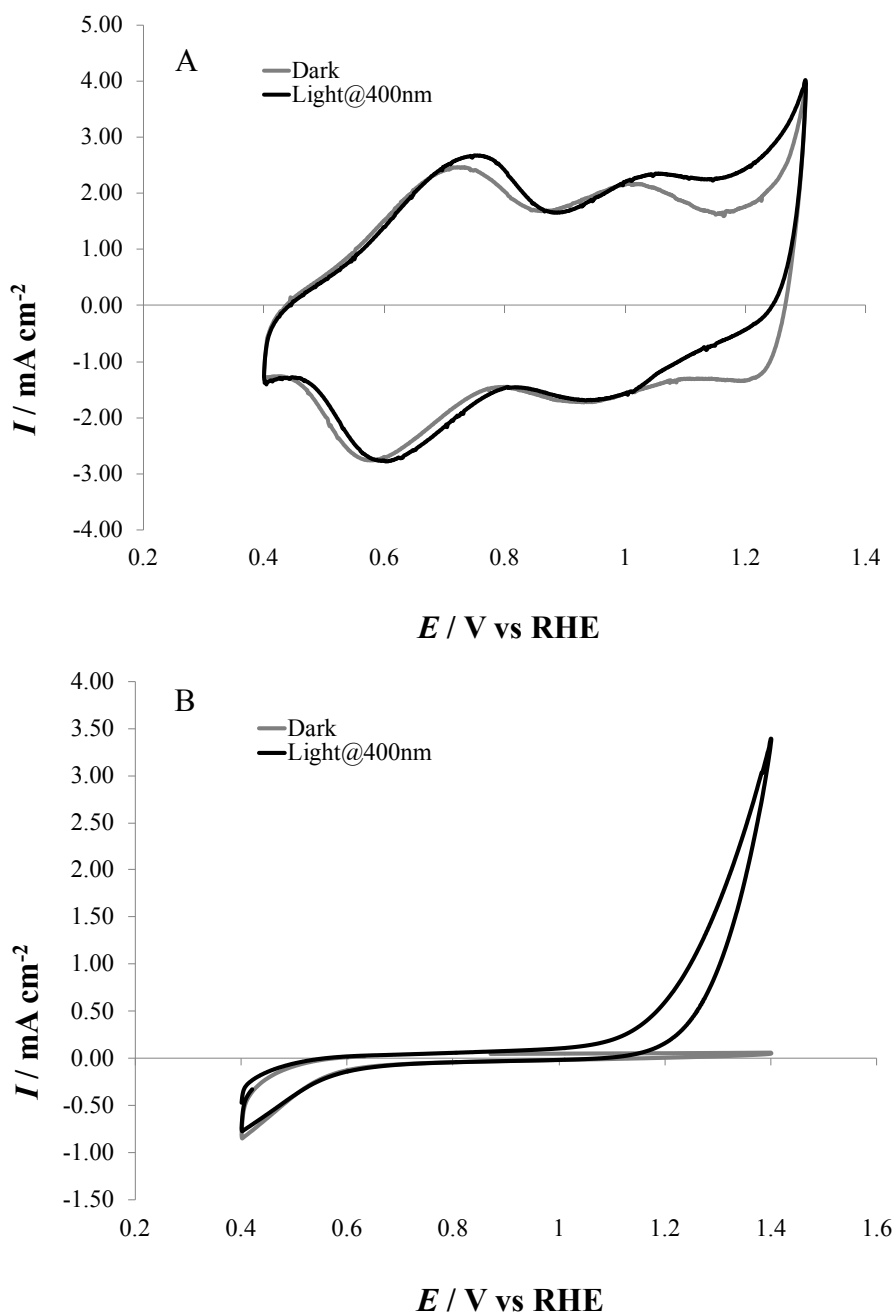


Figure S5. CV at 20mV s^{-1} in $1\text{M HK}_2\text{PO}_4$ of (A) the $\text{IrO}_x/\alpha\text{-Fe}_2\text{O}_3$ and of (B) the bare $\alpha\text{-Fe}_2\text{O}_3$ photoanodes under illumination by the focused light of the 400 nm LED (red line) and in the dark (blue line). All CVs are recorded in the XAS hutch in the same conditions adopted for operando XAS experiments.

CVs reported in Figure S4A denotes the poor photoactivity of the hematite/IrO_x composite, whose origin is discussed in the main text. Photocurrent is mainly observed for $E > 1$ V (RHE), whereas at lower potentials the typical “bumps” related to IrO_x pseudocapacitive phenomena are clearly observed. In particular, the couple at about 0.6-0.8 V is relevant to the Ir(III) to Ir(IV) couple, while the Ir(IV) to Ir(V) one is evidenced at 0.9-1.1 V. As evident, the current associated to these transitions are not appreciably modified after illumination.

Figure S4B reports CV recorded on a pure hematite photoanode in the dark and under illumination. The anodic photocurrents at $E > 1$ V are associated to water oxidation, whereas currents at $E < 0.6$ V are likely due to dissolved O₂ reduction and/or to a partial reduction of Fe(III) to Fe(II).

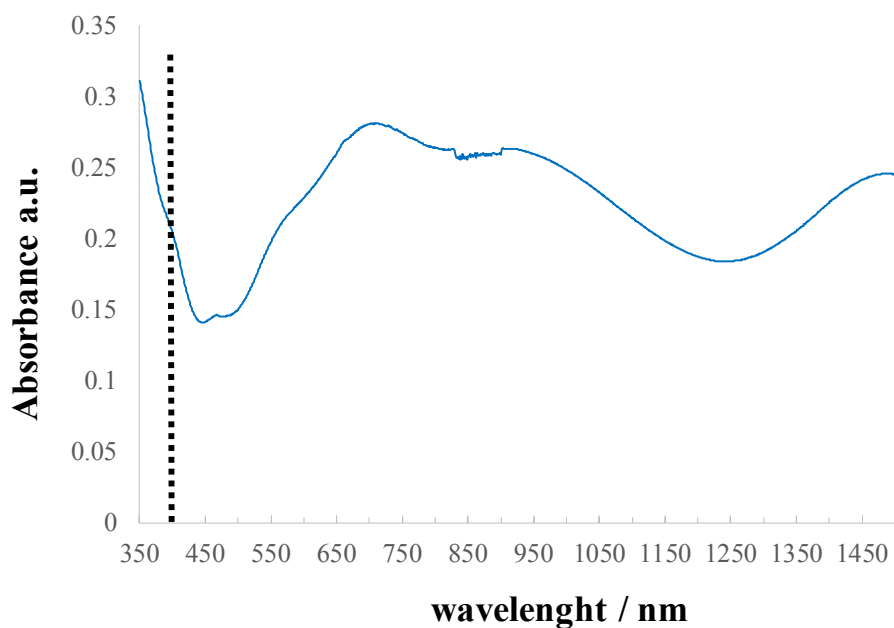


Figure S6. UV-Vis spectra of an FTO/IrO_x electrode. The IrO_x layer was deposited onto a clean FTO substrate applying 0.1 mA cm⁻² for 800 s in the deposition bath described in the main manuscript.

References

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