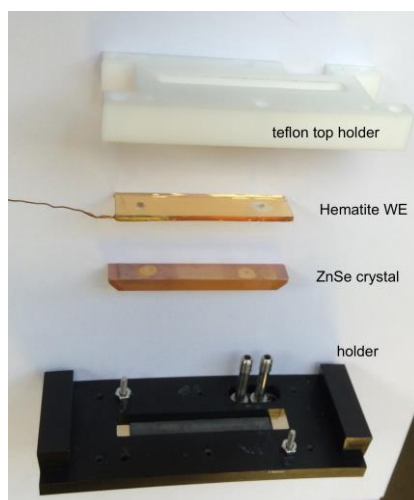


**Determination of Photoelectrochemical Water Oxidation Intermediates on  
Haematite Electrode Surfaces Using Operando Infrared Spectroscopy**

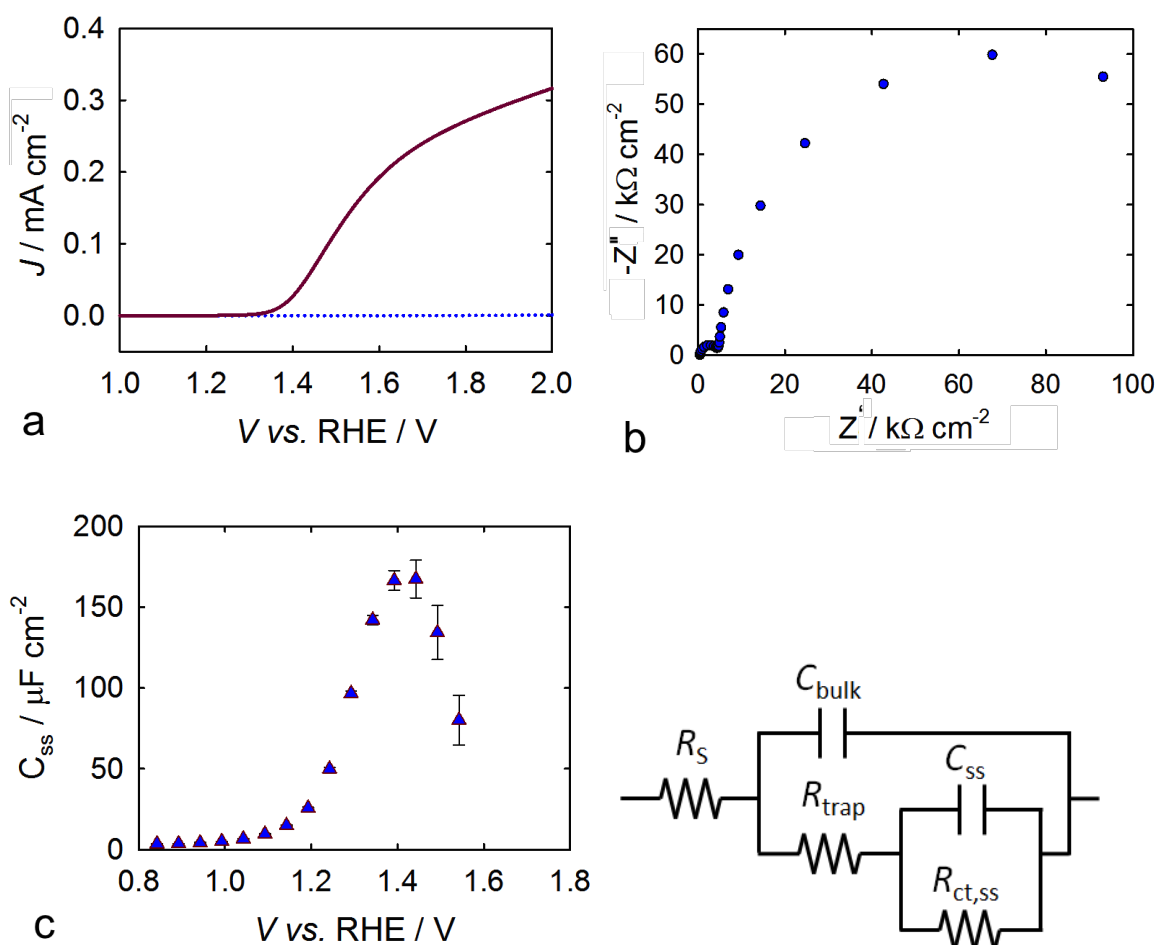
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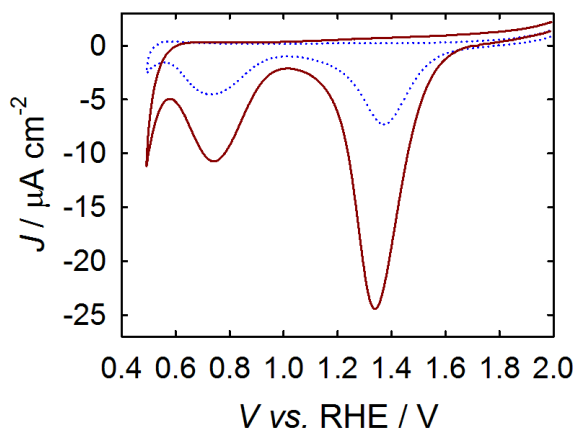


**Supplementary Figure 1.** The ATR-IR cell assembly parts.

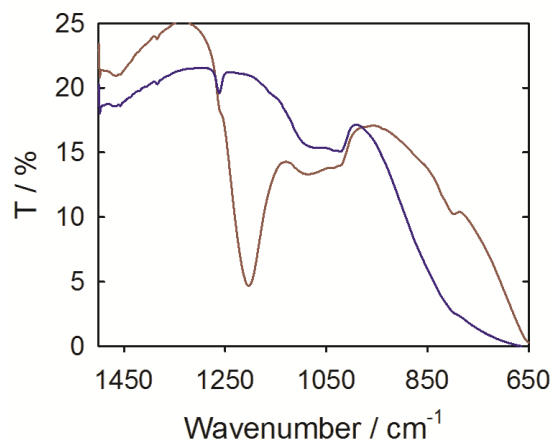
**Fitting EIS data:** EIS data were fitted using the equivalent circuit models shown below. The justification and physical meaning of using this model is described elsewhere.<sup>1</sup> This model, which was established for ALD thin films under white light illumination, was found that produces a comparable certainty under monochromatic illumination herein. A very small error associated with fitting was calculated which is included as error bars.



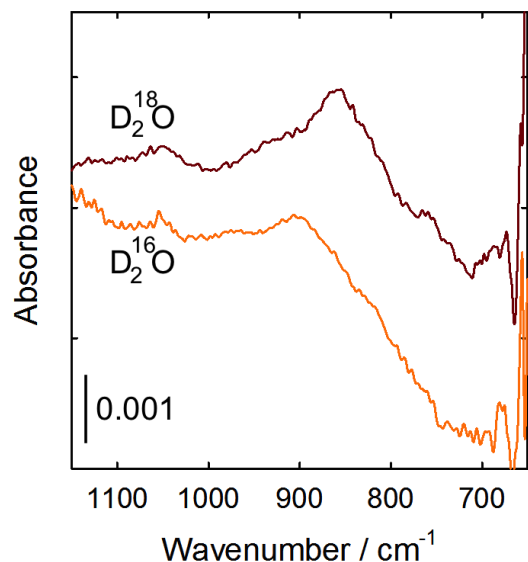
**Supplementary Figure 2.** a)  $J$ - $V$  curves of hematite electrodes measured in 0.1 M phosphate buffer (pH=7) in the dark (dotted blue) and under 395 nm monochromatic illumination (dark red). b) Nyquist plot measured at 1.33 V vs. RHE under illumination. c) Surface state capacitance measured at various applied potentials under illumination extracted from the fit of the experimental EIS data under illumination to the Equivalent circuit model shown on the right.



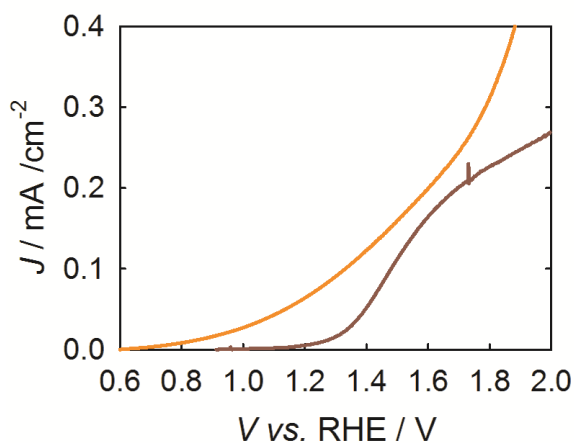
**Supplementary Figure 3.** Cyclic voltammetry curves scanned in dark at 500 mV/s immediately after holding the electrode potential at 2 V for 60 s under illumination (solid dark red) and in the dark (dotted blue).



**Supplementary Figure 4.** The transmittance of the ZnSe IR element in contact with 0.2 M KCl in  $\text{H}_2\text{O}$  (blue) and  $\text{D}_2\text{O}$  (dark red).



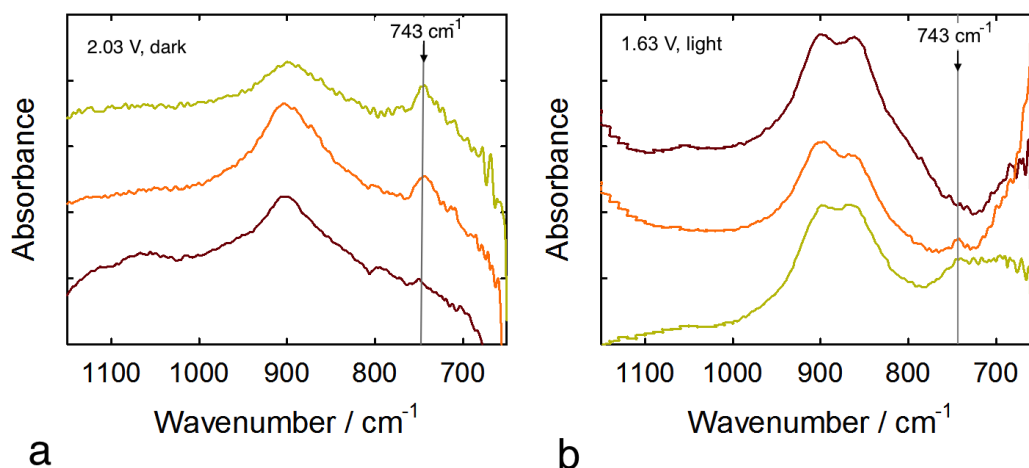
**Supplementary Figure 5.** *Operando* IR absorption spectra of a hematite electrode annealed at 800 °C collected at 1.63 V under illumination. No resolvable peak was observed at 743 cm<sup>-1</sup> for multiple experiments in contact with either D<sub>2</sub><sup>16</sup>O or D<sub>2</sub><sup>18</sup>O.



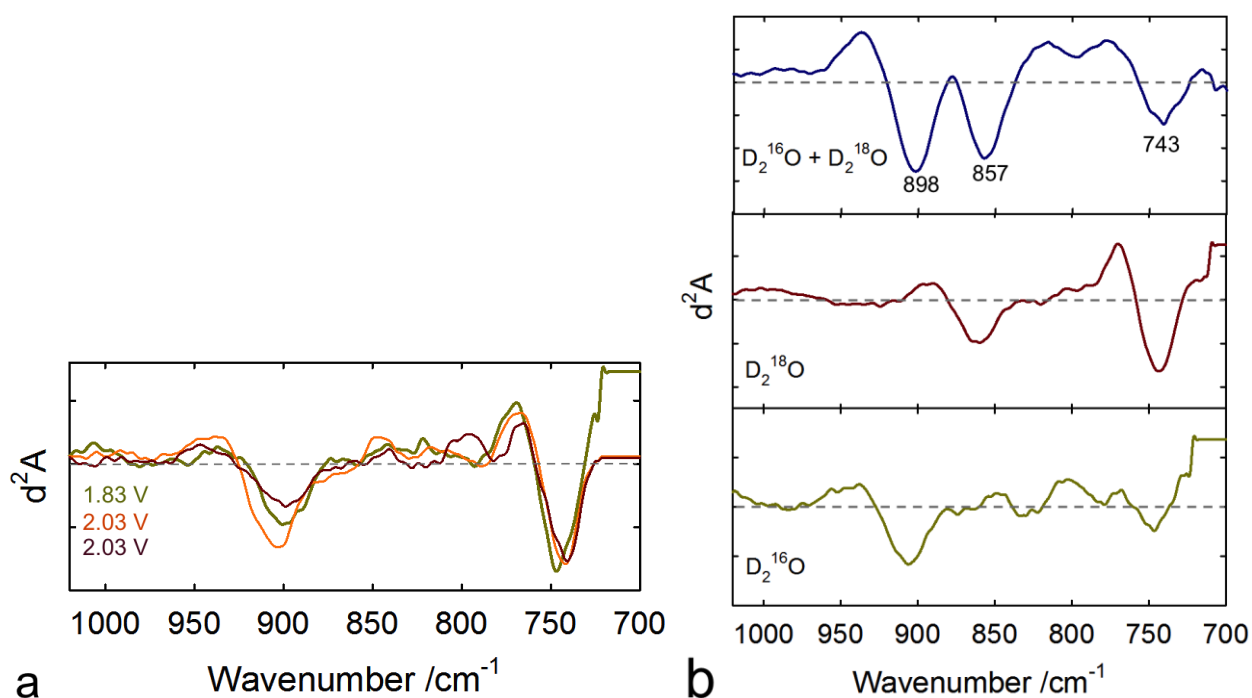
**Supplementary Figure 6.** *J-V* curves of a hematite electrode in contact with 0.2 M KCl (dark red) and 0.2 M KI (orange) in D<sub>2</sub>O under 395 nm monochromatic illumination. In the presence of iodide, the holes are consumed by the fast iodide oxidation reaction. Fast hole collection by iodide minimizes surface recombination which is evident from the early photocurrent onset potential.<sup>2</sup>

### Signal Reproducibility

For a single measurement setup several spectra were collected to insure the signal reproducibility. For example, spectra shown below in Supplementary Figure 7a are collected in the same day with those shown in Figure 1c. In all cases and for potentials positive of the water oxidation onset, two absorption peaks are observed at 743 and 898  $\text{cm}^{-1}$ . It can be seen that 743  $\text{cm}^{-1}$  peak shows variable intensities. The intensity variation is attributed to intrinsically low signal to noise in this region which is right at the edge of the experimental cut-off and is strongly affected by traces of  $\text{H}_2\text{O}$  incorporated in the cell. Shown in Supplementary Figure 7b is another example of spectra collected in a different day, using  $\text{D}_2^{18}\text{O}/\text{D}_2^{18}\text{O}$  as electrolyte. 743  $\text{cm}^{-1}$  peak is again resolvable although with significantly lower intensity.



**Supplementary Figure 7.** *Operando* IR absorption spectra in  $\text{D}_2^{16}\text{O}$  in dark (a), and 1:1 ratio of  $\text{D}_2^{18}\text{O}/\text{D}_2^{18}\text{O}$  under illumination (b).



**Supplementary Figure 8.** a) Representative second derivative plots of *operando* IR absorption spectra taken in  $D_2^{16}O$  in the dark. Corresponding absorption spectra are shown in Figure 1c and Supplementary Figure 7. b) Also shown are second derivative plots from absorption spectra displayed in Figure 3 in the text.

1. Klahr, B., Gimenez, S., Fabregat-Santiago, F., Hamann, T. & Bisquert, J. Water oxidation at hematite photoelectrodes: the role of surface states. *J. Am. Chem. Soc.* **134**, 4294–302 (2012).
2. Bjorksten, U., Moser, J. & Gratzel, M. Photoelectrochemical Studies on Nanocrystalline Hematite Films. *Chem. Mater.* **6**, 858–863 (1994).