

1 **Supporting Information**

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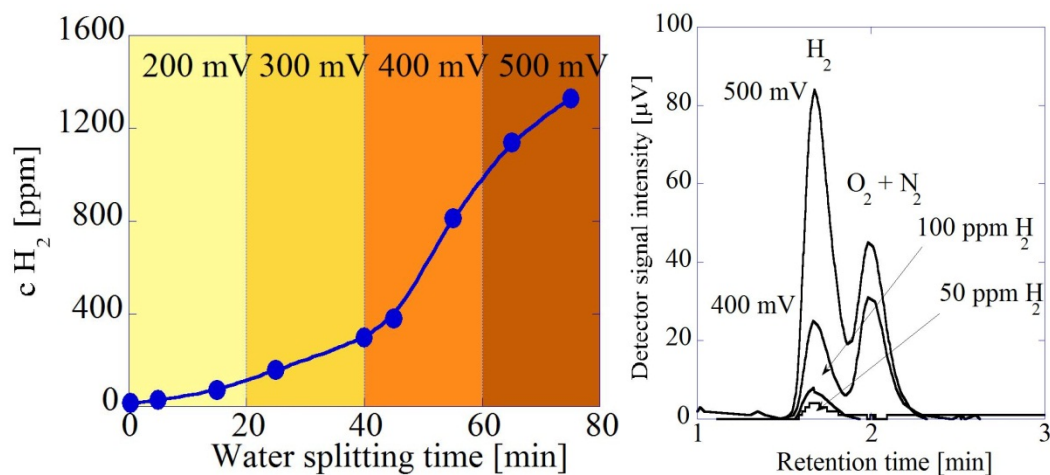
4 **Fig. S1.** Spectro-photoelectrochemical cell constructed from PEEK used for anodisation  
5 studies.

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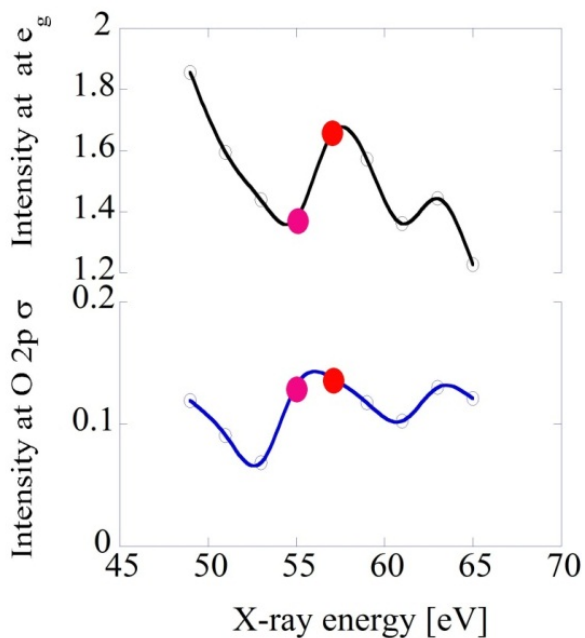
7 *Gas chromatography measurements of H<sub>2</sub>*

8 H<sub>2</sub> was generated with solar simulator light source under the aforementioned described  
9 experimental conditions in a specifically designed gas-tight Teflon PEC cell for online H<sub>2</sub> gas  
10 detection and quantification with a gas chromatograph (GC-2014, Shimadzu). The generated  
11 H<sub>2</sub> is recirculated with Ar carrier gas by a membrane pump at 0.1 bar overpressure enabling  
12 us to monitor H<sub>2</sub> evolution online. For calibration, two reference gases containing 50 and 100  
13 ppm H<sub>2</sub> in Ar are used. 10 μL samples of the PEC cell headspace are injected to the Hayasep  
14 D column (10 Ft x 1/8 in SS). The H<sub>2</sub> amount exceeded our estimates and did not fit in the  
15 entire calibration range. The calibration curve was thus extrapolated to give an estimation of  
16 the evolved H<sub>2</sub>. The shown values should not be considered as absolute values.

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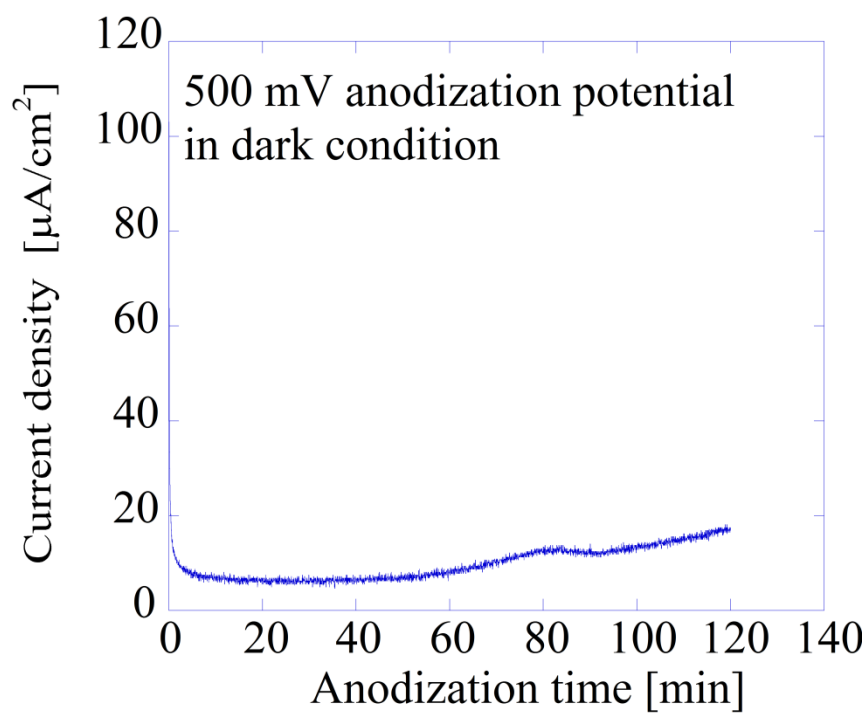


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2 **Fig. S2:** Left - Evolution of hydrogen concentration with bias potential varied from 200 mV  
3 to 500 mV during 80 minutes water splitting time, as obtained from gas chromatograms.  
4 Right - Representative chromatograms for 5 minutes collection at 400 mV and 500 mV bias  
5 potential of hematite anodised for 10 minutes at 700 mV, plus two chromatograms from 50  
6 ppm and 100 ppm  $H_2$  reference gases.



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11 **Fig. S3.** Variation of the relative intensities of the O 2p  $\sigma$  peak and the  $e_g$  peak for the selected  
12 x-ray energies. Compare references [25, 26].

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4 **Fig. S4.** Evolution of the current density at 500 mV in dark condition.

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