

Supporting Information

Surface Interrogation Scanning Electrochemical Microscopy for a Photoelectrochemical Reaction – Water Oxidation on a Hematite Surface

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(Same diagram with Figure 3 in the main manuscript but with error bars)

SI-SECM Tip-Substrate Approach and Alignment

A gold ultramicroelectrode (UME, $a = 12.5 \mu\text{m}$, $\text{RG} = 3$) and the hematite ($\alpha\text{-Fe}_2\text{O}_3$) thin film coated on FTO glass were used as a tip electrode and a substrate electrode of SI-SECM, respectively. The substrate electrode is placed under the tip electrode as shown in Scheme 1 and 2 in the main manuscript. The position of a tip electrode is controlled by inchworm stepper motors and piezo controllers in three dimensions. For the substrate electrode, only tilt correction is available by a three point stage positioner. The two electrodes approached each other using negative feedback without light illumination and with no bias potential to the substrate electrode. Once the two electrodes roughly approached, the tilt of the stage was corrected by obtaining current profiles in x and y directions repeatedly until a symmetrical profile is obtained in both directions. During the tilt correction, light irradiated and bias potential was applied to the substrate electrode to distinguish the photo-active area. The two electrodes further approached each other to a distance of $3.8 \mu\text{m}$. The final negative feedback approach curve and the SECM image in x-y two dimensions are shown below in Figure S1 (left). According to the SECM image, the diameter of the photo-active area of the substrate electrode was $\sim 40 \mu\text{m}$. The right-hand side image of Figure S1 is the CVs recorded for the tip and substrate electrodes simultaneously to determine a collection efficiency of the current SI-SECM setup for a photochemical reaction. Compared to diffusion limited current of the tip electrode due to the titrant generation, diffusion limited current of the substrate electrode due to the titrant consumption is $\sim 87\%$. We modified a SI-SECM setup to control the photo-active area of the substrate electrode more precisely but there is still a room for improvement.

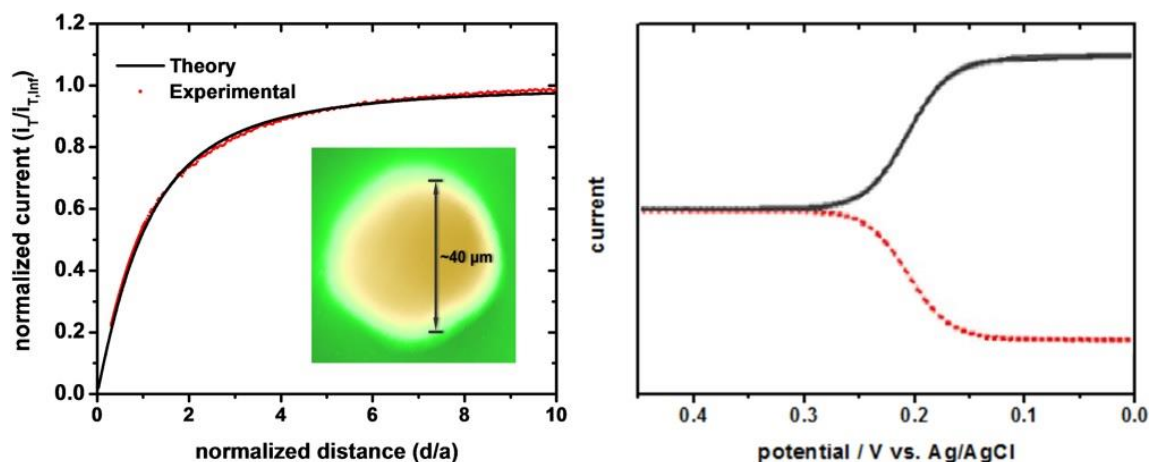
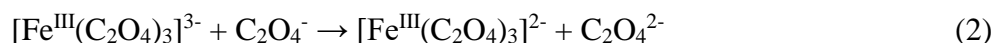
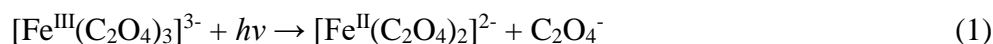


Figure S1. (Left) Approach curve recorded using negative feedback without illumination; (Left, Inset) SECM image to determine the light irradiated area (diameter $\sim 40 \mu\text{m}$); (Right) CVs recorded for the tip and substrate electrodes simultaneously to determine the collection efficiency. Solution composition: 1 mM aqueous ferrocene methanol.

Shutter Calibration for the SI-SECM Setup with Chemical Actinometry

The shutter was calibrated with chemical actinometry to control the irradiation time of the substrate electrode. Potassium ferrioxalate ($\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$), one of representative chemical actinometers, was used for this purpose. As light irradiates the solution containing the actinometer, the following set of reactions occur.



According to the mechanism, one photon is involved in the oxidation reaction that two iron(III) species lose two electrons and become two iron(II) species. By varying the irradiation time, we recorded amperograms (< 1 s) and observed the height of current spike which appears when the shutter opened. A gold ultramicroelectrode ($a = 12.5 \mu\text{m}$, $\text{RG} = 3$), platinum wire, Ag/AgCl electrode were used as a working electrode, counter electrode, and a reference electrode, respectively. 5 mM aqueous $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ solution was prepared and used as an electrolyte. The below image (left of Figure S2) is a typical amperogram showing several spikes with the different shutter open time. There was a linear relation between the height of current spike and shutter open time (right of Figure S2).

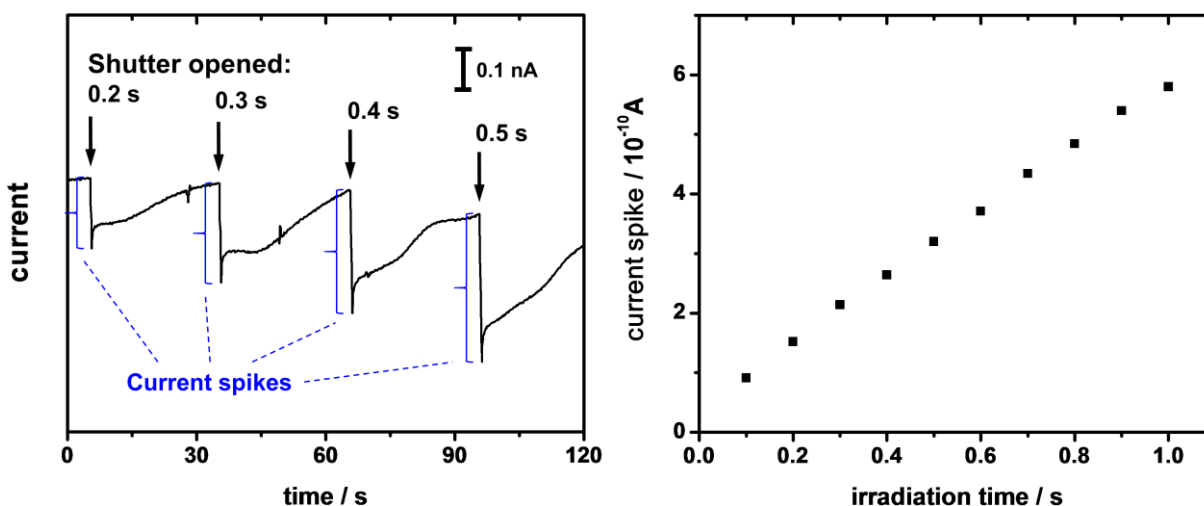


Figure S2. (Left) Amperogram recorded while the shutter open times varied to control the amount of irradiation; (Right) Linear relation between the height of current spike when the shutter opens (from the left diagram) and the irradiation time. A gold ultramicroelectrode ($a = 12.5 \mu\text{m}$, $\text{RG} = 3$), platinum wire, Ag/AgCl electrode were used as working, counter, and reference electrodes, respectively. 5 mM aqueous $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ solution was used as a photoactive molecule.

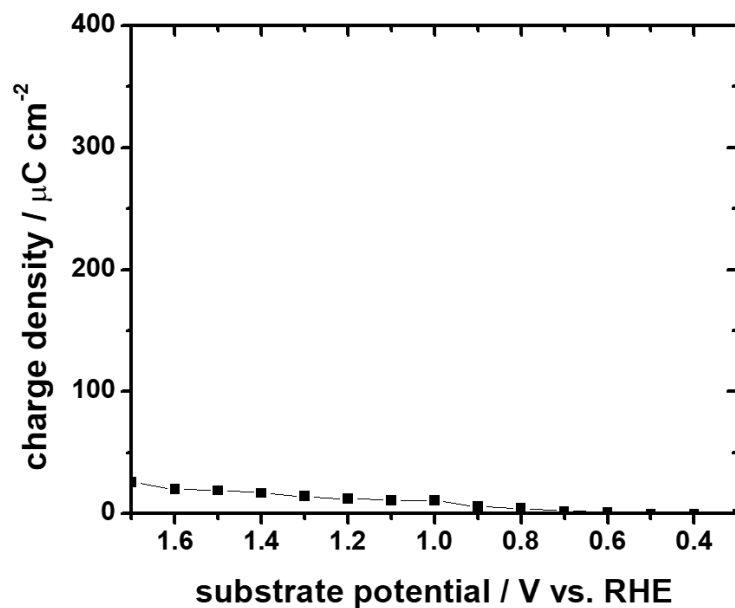


Figure S3. Oxygen collection experiment results for background correction for data presented in Figure 2B. the experiments were separately performed without the titrant. Other experimental details are same with the Fe^{4+} titration experiments.

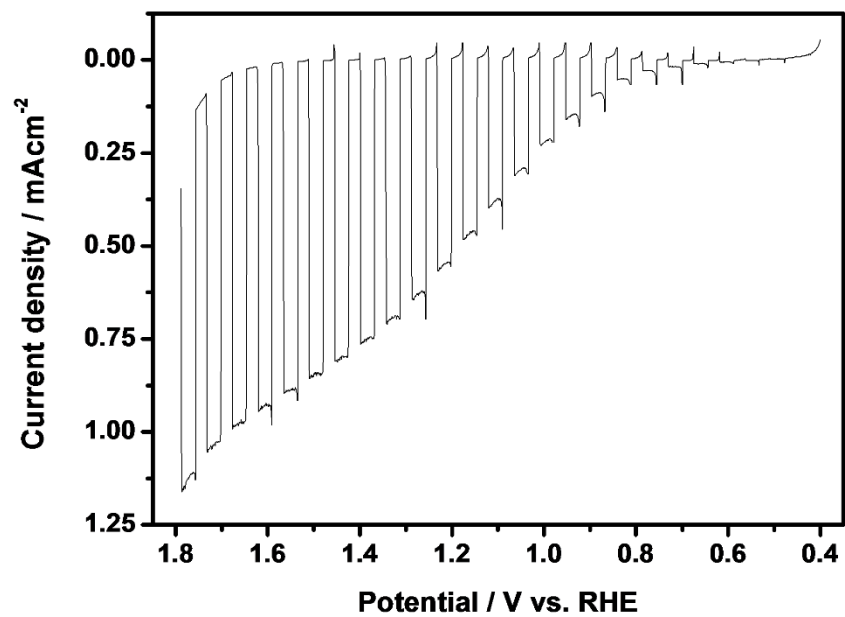


Figure S4: Bulk photocurrent density-potential curve of the hematite thin film. A platinum wire was employed as a counter electrode against a Ag/AgCl reference in 1 M NaOH electrolyte.

Calculation of the Surface Photo-active Sites Density by Titration of Fe^{4+/3+}

The density of the surface photo-active sites (Fe⁴⁺) can be measured by titration with SI-SECM. At 1.3–1.6 V vs. RHE, a plateau in Figure 1B, a charge density obtained by the titration is $285 \pm 20 \mu\text{C cm}^{-2}$. Since the current is governed by one-electron transfer event, the number of electrons corresponds to the number of the surface photo-active sites. The calculation is as follows:

$$\begin{aligned} & (2.85 \times 10^{-4} \text{ C cm}^{-2}) \times (6.24 \times 10^{18} \text{ e}^{-} \text{ C}^{-1}) \times (1 \times 10^{-14} \text{ cm}^2 \text{ nm}^{-2}) \\ & = 17.8 \text{ e}^{-} \text{ nm}^{-2} \\ & \sim 18 \text{ Fe atoms nm}^{-2} \end{aligned}$$

Measurement of the Pseudo-first-order Reaction Rate Constant

During t_{delay} , only water is capable of consuming the surface-bound photo-excited species on the substrate electrode. Because water is always in excess (55 M), pseudo-first order approximation can be used as shown below. The titration charge was converted to $\ln[\text{Fe}]$ and plotted as a function of t_{delay} (Figure 2 in the main manuscript) then the rate constant can be obtained from the slope of the plot according to the below equations:



$$d(\text{Fe}^{4+})/dt = -k'[\text{Fe}^{4+}] \text{ (pseudo-first-order rate equation)} \quad (5)$$

$$\ln[\text{Fe}^{4+}] = -k't + \ln[\text{Fe}^{4+}]_0 \quad (6)$$

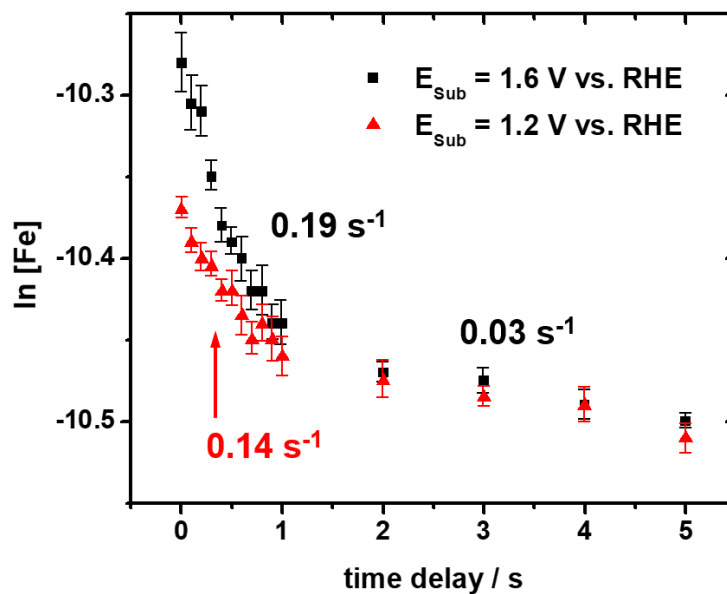


Figure S5. Results of a time-dependent titration of the photo-excited states (Fe^{4+}) on the hematite ($\alpha\text{-Fe}_2\text{O}_3$) surface. The titration charge was converted to $\ln[\text{Fe}]$ and plotted as a function of time delay (t_{delay}). Titration experiments were conducted in a 1 mM aqueous FcMeOH^+ solution (0.1 N borate/HCl buffer at pH 9).