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Supplementary Information

Thermally-Enhanced Minority Carrier Collection in Hematite During Photoelectrochemical Water and Sulfite Oxidation

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Origin of the dark current in α-Fe_2O_3 photoanode

Figure S1 shows the current-voltage curves for α-Fe_2O_3 photoanode in the dark in 1M NaOH with and without the fast redox couple (100mM/10mM $Fe(CN)_6^{4-/3-}$). The equilibrium potential of the reversible redox couple is 1.23 V vs RHE, which is the same as the OER level and should give a similar band bending at the hematite/electrolyte interface. With the reversible redox couple, the dark current arises immediately past the redox potential, comparing to a 0.4 V overpotential in pure NaOH solution. This indicates that the ineffective diode characteristic of the hematite/electrolyte interface leads to significant current leakage, and that the dark current in the pure NaOH solution is limited by the rate of electrocatalysis.

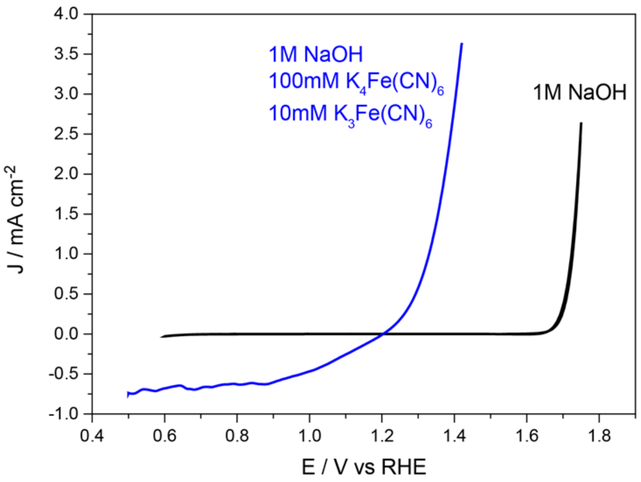

Figure S1. Current-voltage curves for α-Fe_2O_3 photoanode in the dark, with and without fast redox couple.

Tafel plot of the dark current density

Figure S2 shows the tafel plot of the dark current density for the Ti-doped Fe_2O_3 thin film photoanodes at various temperatures. The overpotential (η) is calculated from the applied bias subtracted by the OER redox potential at a given temperature. It is obvious that less overpotential is needed at higher temperatures for all the samples, which verifies the thermally enhanced nature of the reaction on the α-Fe_2O_3 surface. The shift in overpotential from 7 °C to 72 °C is approximately 60 to 90 mV for different dopant concentrations. Moreover, the Tafel slopes of the dark current densities for these hematite photoanodes are *ca.* 100 mV/dec and are weakly dependent on temperature and dopant concentration. This indicates that the reaction mechanism and the rate-determining step are the same within the investigated conditions.

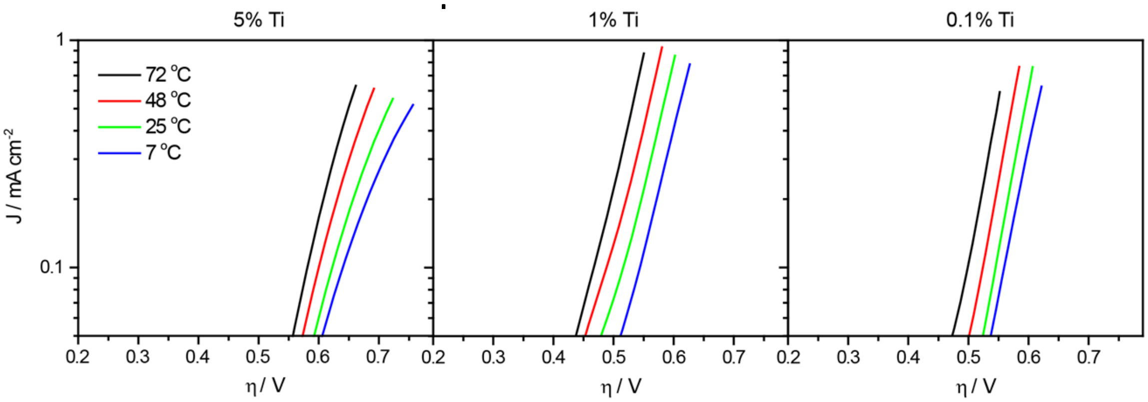

Figure S2. Tafel plots of the dark current densities for (a) 5%, (b) 1%, and (c) 0.1% Ti-doped α-Fe_2O_3 photoanodes under various temperatures.

Derivation of the photocurrent-bias relationship

We model the hematite photoanode as a Schottky junction solar cell, with its current collection interface shared with an electrolyzer. The current density of a solar cell is described as[1]

$$j = -j_0\left(e^{\frac{qV_{ph}}{n_{id}k_BT}} - 1\right) + j_{SC} \tag{S1}$$

Where V_{ph} is the photovoltage, j_0 is the reverse saturation current, j_{SC} is the short circuit current, and n_{id} is the ideality factor. For hematite photoanode under illumination, $V_{bias}(j) = V_{OER} + \eta(j) - V_{ph}(j)$, in which V_{bias} is the applied bias, V_{OER} is the OER redox potential at a given temperature and η is the overpotential. Therefore,

$$\frac{\partial V_{bias}(j)}{\partial j} = \frac{\partial \eta(j)}{\partial j} - \frac{\partial V_{ph}(j)}{\partial j} \tag{S2}$$

From Equation (S1), we get

$$\frac{\partial V_{ph}(j)}{\partial j} \approx -\frac{k_BT}{q}\frac{n_{id}}{j_{SC}} \tag{S3}$$

The approximation in Equation (S3) is made at $j_0, j << j_{SC}$. Equation (1) is then obtained by combining Equation (S2) and (S3).

Reverse saturation current at the α-Fe_2O_3/liquid junction

In comparison to a Schottky junction, the reverse saturation current at the α-Fe_2O_3/liquid junction is composed of the minority carrier diffusion current from the bulk (*i.e.*, holes from α-Fe_2O_3 to liquid), and the majority carrier emission current from the α-Fe_2O_3/liquid interface (*i.e.*, electrons from liquid or interfacial trap states to α-Fe_2O_3).

The hole diffusion current is

$$j_0^{minority} = \frac{D_p}{L_p N_D} q n_i^2 \tag{S4}$$

where D_p and L_p are the hole diffusivity and diffusion length in α-Fe_2O_3 thin film, respectively, N_D is the dopant concentration, n_i is the intrinsic carrier concentration, and q is the elemental charge. Since $n_i^2 \propto \exp\left(\frac{-E_g}{k_B T}\right)$, the hole diffusion current exhibits an activation energy of the α-Fe_2O_3 band-gap E_g, and it is also inversely proportional to the dopant concentration.[2]

The electron emission current can be described by thermionic emission which has an activation energy of the interfacial barrier between the conduction band minimum of the α-Fe_2O_3 and the OER redox level or the surface defect states.[3, 4]

The total reverse saturation current is then the sum of the majority and the minority current,

$$j_0 = j_0^{minority} + j_0^{majority} \tag{S5}$$

Unlike the semiconductor Schottky junction, in which $j_0^{majority}$ usually dominates, $j_0^{majority}$ at the α-Fe_2O_3/liquid junction can be comparable to $j_0^{minority}$ due to the lack of electron density of states at the redox level and the slow charge transfer at the electrochemical interface.

References

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