Electronic Supplementary Information for

Bridging Surface States and Current-potential Response over Hematite-based Photoelectrochemical Water Oxidation

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Preparation of hematite photoanode

The hematite photoanode is prepared by chemical bath as previous reported.\(^1\) Clean FTO (2 cm×2 cm) substrates were vertically placed in a beaker containing 50 mL aqueous solution of FeCl\(_3\)-9H\(_2\)O (0.1 mol/L, Alfa) and urea (0.15 mol/L, Kermeol). Then it was sealed and maintained in an oven for 3 h at 100 °C. After washing with deionized water completely, we got light yellow FeOOH film.

For pure Fe\(_2\)O\(_3\) electrode, it can be produced by converting the FeOOH electrode at 600 °C for 3 hours in air with muffle furnace.

For Ti modified Fe\(_2\)O\(_3\) electrode, the FeOOH electrode should be immerged in 0.1 M TBT ethanol solution for 10 min. Then the electrode was totally washed with ethanol and annealed at 600 °C for 3 hours in air. This electrode is denoted as Ti-Fe\(_2\)O\(_3\). The procedure of preparing Pt-Fe\(_2\)O\(_3\) is all the same with the Ti-Fe\(_2\)O\(_3\), except that the 0.1 M TBT is replace with H\(_2\)PtCl\(_6\) aqueous solution (2 mg Pt/mL).

Activating hematite photoanode

After conversing FeOOH into hematite at 600 °C, the electrode was further subjected to a heat treatment in an over at temperature between 100 °C~200 °C. Typically, when temperature reaches the set point, the photoelectrode was put into the oven and kept for 30 min. Once finishing the treatment, it was drawn out directly and cooled down to room temperature naturally.

Deposition Al\(_2\)O\(_3\) layer by atom layered deposition
Al₂O₃ was deposited on Fe₂O₃ photoanode at 150°C by atom layered deposition (ALD) using trimethylaluminium(TMA) and water as precursors, N₂ as carrier gas. An ALD cycle of the Al₂O₃ deposition included four basic steps: TMA pulse (2 s) and delay (8 s), N₂ flow purge (20 s) and delay (1 s), water pulse (1 s) and delay (5 s), N₂ flow purge (20 s) and delay (1 s). And the total Al₂O₃ was deposited for two circles.

**H₂O₂ treatment to the Ti-Fe₂O₃**

After activating the Ti-Fe₂O₃ electrode at 200 °C, it was further treated in commercial H₂O₂ (35 %, Kermeol). Typically, a piece of Ti-Fe₂O₃ electrode was dimmed in 50 mL H₂O₂ contained in a beaker and then it was kept at 100 °C for 30 minutes. After this treatment, the electrode was totally washed with deionized water.

**(Photo)electrochemical measurement**

All tests were carried out in 1 M NaOH aqueous solution in a 3-electrode system with platinum as counter electrode, saturated calomel electrode (SCE) as the reference electrode, and hematite photoanode as working electrode. A quartz window is used to permit the penetration of simulated AM 1.5 G sunlight generated from the simulator (100 mW/cm², Newport Sol 3A, Class AAA Solar simulator).

For the cyclic voltammerty (CV) and linear sweep voltammerty (LSV), they were measured in the range of -0.8 V~0.6 V vs SCE at a scan rate of 50 mV/s (for LSV) or 100 mV/s (for CV) with a potentiostat (CHI 660D, Shanghai Chenhua Instrument Co., Ltd). For the electrochemical impedance spectroscopy, it was measured with a galvanostat/potentiostat (Iviumstat, Ivium
Technologies) in the frequency of $10^{-1}$~$10^5$ Hz by applying a 20 mV AC signal at different potential. The data were simulated using equivalent circuit with Zview program.

The potential referred to SCE was transferred to reversible hydrogen electrode (RHE) scale using Nernst equation:

$$E_{(RHE)} = E_{(SCE)} + 0.059pH + 0.2411$$
Figure S1. The top view (a) and cross-sectional view (b) of Fe$_2$O$_3$ electrode.

Figure S2. The CV of pure Fe$_2$O$_3$ electrode with (red) and without (black) illumination.
Figure S3. The CV of Pt-Fe$_2$O$_3$ electrode with (red) and without (black) illumination.

Figure S4. The equivalent circuit for simulation. $C_{ss}$ is the capacitance of surface states; $C_{bulk}$ is the capacitance of space charge layer; $R_s$ is the serial resistance; $R_{ct}$ is the resistance of charge transfer during reaction.

Figure S5. The distribution of surface states on Ti-Fe$_2$O$_3$ electrode: (a) comparison between the results from EIS ($C_{ss}$) and CV; (b) comparison between EIS ($C_{ss}$) and differential of current to potential (dj/dV). The $C_{ss}$ and dj/dV are fitted with Gauss plots.
Indeed, due to a thermal fluctuation, the probability \( W(E) \) we find a surface state at energy level of \( E \) is:

\[
W(E) = \frac{1}{\sqrt{4\pi kT \lambda}} \exp\left(-\frac{(E_t - E)^2}{4\lambda kT}\right) \quad (S1)
\]

Where \( \lambda \) is the rearrangement energy of these surface states; \( E_t \) is the centre energy level of surface states. This equation clearly shows a Gauss distribution of surface states in Figure S5.

**Figure S6.** The schematic shown of the dispersion density of state for a redox couple due to thermal fluctuation.

REFERENCES