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 $FeCl_3 \cdot 9H_2O$ (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 ^oC. After washing with deionized water completely, we got light yellow FeOOH film.

For pure Fe_2O_3 electrode, it can be produced by converting the FeOOH electrode at 600 ^oC for 3 hours in air with muffle furnace.

For Ti modified Fe_2O_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 ^oC for 3 hours in air. This electrode is denoted as Ti-Fe_2O_3. The procedure of preparing Pt-Fe_2O_3 is all the same with the Ti-Fe_2O_3, except that the 0.1 M TBT is replace with H_2PtCl_6 aqueous solution (2 mg Pt/mL).

Activating hematite photoanode

After conversing FeOOH into hematite at 600 ^oC, the electrode was further subjected to a heat treatment in an over at temperature between 100 ^oC~200 ^oC. 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_2O_3 layer by atom layered deposition

Al_2O_3 was deposited on Fe_2O_3 photoanode at 150°Cby atom layered deposition (ALD) using trimethylaluminium(TMA) and water as precursors, N_2 as carrier gas. An ALD cycle of the Al_2O_3 deposition included four basic steps: TMA pulse (2 s) and delay (8 s), N_2 flow purge (20 s) and delay (1 s), water pulse (1 s) and delay (5 s), N_2 flow purge (20 s) and delay (1 s). And the total Al_2O_3 was deposited for two circles.

H_2O_2 treatment to the Ti-Fe_2O_3

After activating the Ti-Fe_2O_3 electrode at 200 °C, it was further treated in commercial H_2O_2 (35 %, Kermeol). Typically, a piece of Ti-Fe_2O_3 electrode was dimmed in 50 mL H_2O_2 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/cm^2, 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 impedence spectroscopy, it was measured with a galvanostat/potentiostat (Iviumstat, Ivium

Technologies) in the frequence 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:

$$E(RHE)=E(SCE)+0.059pH+0.2411$$

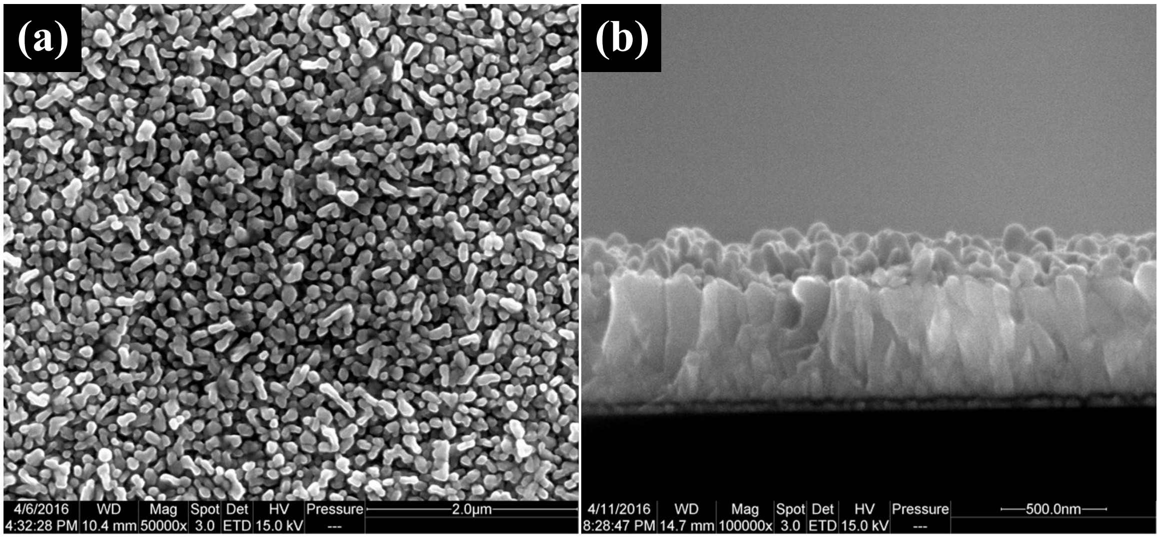

Figure S1. The top view (a) and cross-sectional view (b) of Fe_2O_3 electrode.

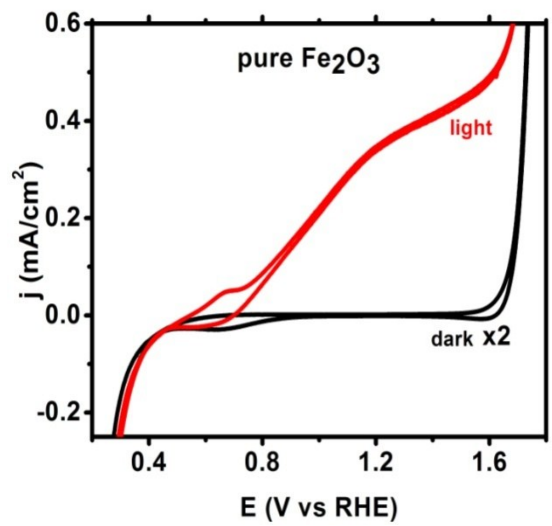

Figure S2. The CV of pure Fe_2O_3 electrode with (red) and without (black) illumination.

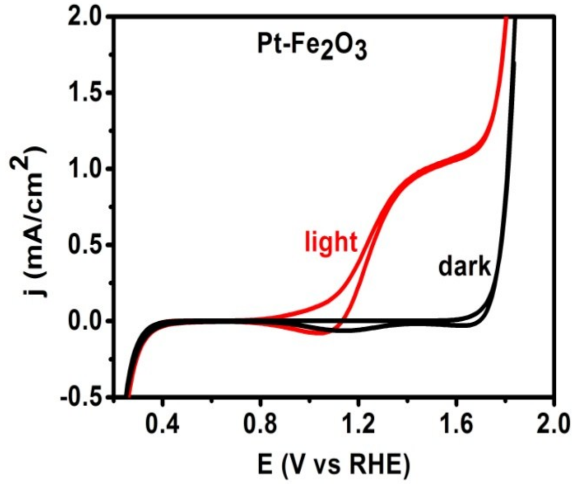

Figure S3. The CV of Pt-Fe_2O_3 electrode with (red) and without (black) illumination.

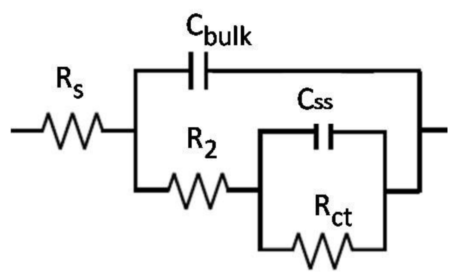

Figure S4. The equivalent circuit for simulation. C_{ss} is the capacitance of surface states; C_{bulk} is the capacitance of space charge layer; R_s is the serial resistance; R_{ct} is the resistance of charge transfer during reaction.

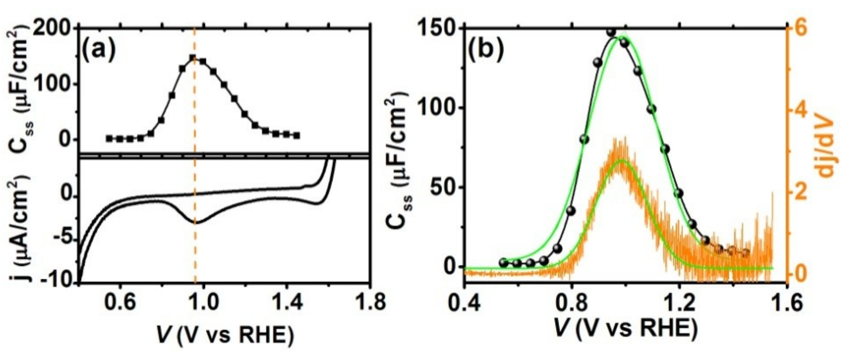

Figure S5. The distribution of surface states on Ti-Fe_2O_3 electrode: (a) comparison between the results from EIS (C_{ss}) and CV; (b) comparison between EIS (C_{ss}) and differential of current to potential (dj/dV). The C_{ss} and dj/dV are fitted with Gauss plots.

Indeed, due to a thermal fluctuation, the probability (W(E)) we find a surface state at energy level of E is:[2]

$$W(E) = \frac{1}{\sqrt{4\pi kT\lambda}}\exp[-(E_t - E)^2 / 4\lambda kT] \qquad \text{(S1)}$$

Where λ 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 FigureS5.

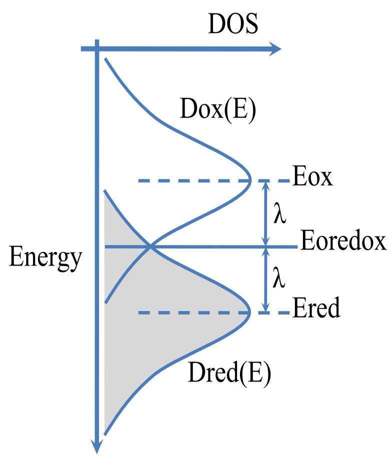

Figure S6. The schematic shown of the dispersion density of state for a redox couple due to thermal fluctuation.

REFERENCES

1. Z. Wang, G. Liu, C. Ding, Z. Chen, F. Zhang, J. Shi and C. Li, *The Journal of Physical Chemistry C*, 2015, **119**, 19607-19612.
2. S. R. Morrison, 1980.