Supporting Information

Suppressed charge recombination in hematite photoanode via protonation and annealing

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Figure S1. Photocurrent densities of hematite in Ar-saturated 0.5 M NaOH electrolyte (pH=13.0) under simulated solar light AM 1.5G illumination with a power density of 100 mW cm⁻²: (a) As-prepared hematite, protonated (negative polarized) hematite at 0.2 V_RHE for 200 s, protonated hematite annealed at 120 °C for 1 h in air; (b) Hematite annealed at 80 °C for different time after protonation. (c) Hematite annealed at 150 °C and 250 °C for different time after protonation. The photocurrent densities of as-prepared and 120 °C-1 h annealed hematite are shown for comparison in (b-c). (d) Hematite after the 1st, 2nd and 7th protonation. Before the 2nd and 7th protonation, hematite was treated by one and six rounds of protonation and annealing, respectively.
Figure S2. (a) Photograph of a hematite photoelectrode. (b) Photocurrent densities for as-prepared hematite, hematite treated only by annealing at 120 °C-1h without pre-protonation, protonated hematite and 120 °C-1h annealed hematite with pre-protonation.

Figure S3. (a) Nyquist plots measured at 0.98 V_RHE under AM 1.5 G illumination. (b) The fitted parameters for bulk transport resistance $R_{\text{bulk}}$ and time constant $(RC)_{\text{bulk}}$, hematite-electrolyte charge transfer resistance $R_{\text{ct}}$ and time constant $(RC)_{\text{ct}}$, obtained at 0.98 V_RHE.

| Sample          | $R_{\text{bulk}}$ / Ω | $R_{\text{ct}}$ / Ω | $(RC)_{\text{bulk}}$ / ms | $(RC)_{\text{ct}}$ / ms |
|-----------------|------------------------|----------------------|---------------------------|-------------------------|
| As-prepared     | 44.9                   | 116.2                | 0.79                      | 48                      |
| 3rd protonated  | 44.3                   | 287.9                | 1                         | 70                      |
| 3rd annealed    | 33.0                   | 105.2                | 0.66                      | 38                      |
Figure S4. Open circuit potentials (OCP) measured in dark and under AM 1.5G illumination in 0.5 M NaOH electrolyte saturated with O$_2$. OCP in dark stands for the quasi-Fermi level of holes $E_{F,p}$, while OCP under light stands for the quasi-Fermi level of electrons $E_{F,n}$. The difference between $E_{F,n}$ and $E_{F,p}$ gives the photovoltage $V_{ph}$.
Figure S5 a) Zoom-out SEM image of as-prepared hematite, b-d) AFM images of as-prepared, protonated and annealed hematite.
Figure S6. XRD patterns for as-prepared, protonated and annealed hematite.
Supporting Information Discussion

Electrochemical surface area

The total Helmholtz capacitance is calculated according to the following equation:

\[ C = \frac{\int i dV}{2sU} \]  

(1)

where \( C \) is the Helmholtz capacitance, \( i \) is the current, \( V \) is the potential, \( s \) is the potential scan rate, \( U \) is the potential window. Using a specific Helmholtz capacitance\(^{1-3}\) of 20 µF cm\(^{-2}\) for hematite, the surface area of hematite is calculated to be 4.45 cm\(^2\).

Donor density and Flat band potential. The complex impedance plane plots measured in dark were fitted with an equivalent circuit (inset of Figure 4a) which has been proved to best represent the dark phenomena.\(^3\) The fitted space charge layer capacitances were used to plot Mott-Schottky curves as shown in Figure 4a. \( R_s \) is the resistance of electrolyte; \( C_{sc} \) is the capacitance of the space charge layer; \( C_H \) is the Helmholtz layer capacitance (8.9×10\(^{-5}\) F) which is obtained from the cyclic voltammetry measurement; and \( R_{ct} \) is the charge transfer resistance. \( R_s \) is almost constant in the range of 13.0–14.5 Ω.

The flat band potential and donor density can be obtained from the intercept and slope of Mott-Schottky curves through the following equation:\(^4-5\)

\[ \left( \frac{A}{C_{sc}} \right)^2 = \frac{2}{\varepsilon_r \varepsilon_0 N_0} (V - E_{fb} - \frac{k_B T}{e}) \]

(2)

where \( V \) is the applied potential, \( E_{fb} \) is the flat band potential, \( C_{sc} \) is the space charge layer capacitance, \( A \) is the electrochemical active surface area (4.45 cm\(^2\), determined by cyclic voltammetry measurement in dark assuming a specific capacitance of 20 µF cm\(^{-2}\) for Helmholtz layer\(^{1-3}\)), \( \varepsilon_0 \) is the vacuum dielectric constant (8.854×10\(^{-14}\) F cm\(^{-1}\), a value of 80 is taken for the hematite dielectric constant \( \varepsilon_r \)), \( e \) is the elementary charge, \( k_B \) is the Boltzman constant and \( T \) is the absolute temperature. A linear fit was performed in the potential range between 0.75 and 0.95 V_{RHE} to obtain the slope and intercepts for determining the donor density and flat band potential of the hematite. According to literature,\(^3\) in the potential range close to the flat band potential, the space charge
layer is thin, and the Mott-Schottky assumption is best approximated. The obtained flat band potentials and donor densities are shown in Figure 4b.

The flat band potential of the as-prepared sample is 0.66 V_RHE, similar to the value reported in literature for hematite prepared by hydrothermal method.\(^6\) It is noteworthy that the flat band potential progressively shifts to more positive potentials (downward shift) upon repeated protonation and annealing, and the same trend is found also for the open circuit potentials under light, \(i.e.,\) the quasi-Fermi level of electrons \(E_{F,n}\). This is mainly due to the accumulation of protons near the surface.\(^7\) However, a more positive flat band potential requires more external potential to initiate photocurrent, \(i.e.,\) a late onset potential.\(^8\) Thus the flat band shift is not the reason for enhanced PEC performance.

**Photovoltage**

The quasi-Fermi level of holes \(E_{F,p}\) \(i.e.,\) the open circuit potential in dark,\(^6,9-10\) is negatively shifted after the 1\(^{st}\) protonation, but positively shifted after the 1\(^{st}\) annealing (~22 mV, see Figure S4). The 3\(^{rd}\) annealing further shifts \(E_{F,p}\) of ~38 mV towards more positive values, which is of the same order for the negative shift of onset potential (Figure 1a, ~80 mV shift after two rounds of protonation and anneal). A more positive value of \(E_{F,p}\) means higher oxidative power of holes and needs less external bias to compensate the kinetic overpotential, similar to the thermodynamic contribution by the NiFeO\(_x\) decoration on hematite.\(^6\) Apparently, the positive shift of the quasi-Fermi level of holes is responsible for the cathodic shift of the onset potential and the higher photocurrents upon repeated protonation and annealing treatments.

The difference between \(E_{F,n}\) and \(E_{F,p}\) gives the photovoltage \(V_{ph}\), which is 0.21 V for the as-prepared hematite. The 1\(^{st}\) annealing treatment did not change \(V_{ph}\), and the 3\(^{rd}\) annealing results in a slightly higher value of 0.23 V. The slight increase of the photovoltage value may also contribute to the improvements of PEC performances.

**Supporting References**

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