# **Electronic Supplementary Information**

# Surface Hydroxylated Hematite Promotes Photoinduced Hole Transfer for Water Oxidation

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#### **Experimental section**

#### Synthesis of hematite nanowires

Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanowires were grown on a fluorine-doped tin oxide (FTO) substrate according to a previously reported method.<sup>[1]</sup> A Teflon-lined stainless steel autoclave was filled with 20 ml aqueous solution containing 0.15 M of ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O, Acros 99+%) and 1 M sodium nitrate (NaNO<sub>3</sub>, Fisher 99.4%). The solution pH was adjusted to 1.5 by adding HCl solution. A FTO substrate pre-cleaned with acetone, ethanol and distilled water was put into the autoclave. The autoclave was heated at 95 °C for 4 hours and allowed to cool down at ambient conditions. A uniform layer of iron oxyhydroxide ( $\beta$ -FeOOH) film (yellow in color) was formed on the FTO substrate. The  $\beta$ -FeOOH film was washed with distilled water to remove any residual salts. To convert  $\beta$ -FeOOH into hematite, the film was further sintered in air at 550 °C for 30 min, followed by annealing at 800 °C for additional 20 min.

Hematite nanoparticle film was prepared according to a previous study.<sup>[2]</sup> 10 mM FeCl<sub>3</sub> ethanol solution was drop-deposited onto pre-cleaned FTO and blow-dried with compress air. The dried glass was heated on a hotplate in air at 350 °C for 5 min. This procedure was repeated for 20 times and the prepared films were then annealed in air at 550 °C for 4 h.

#### Ultrasonic treatment

A piece of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/FTO was immersed in a beaker containing 20 ml of distilled water, and sonicated in a commercial sonicator (90W, 50 Hz) at room temperature for 10 s. For samples ultrasonically treated in saturated H<sub>2</sub>O<sub>2</sub> and FeCl<sub>3</sub> (0.15 M) solution, the sonication times were 10 s and 10 min, respectively.

#### **Material characterizations**

To understand the effect of ultrasonication treatment, all the material characterizations were performed on the same sample(s) before and after sonication. The morphologies of hematite films were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800, 5kV). XRD patterns were characterized with a Rigaku Americas Miniflex Plus operating at 40 kV and 40 mA. XPS analysis was carried out on a Physical Electronics PHI 1600 ESCA system with an Al K $\alpha$  X-ray source (E = 1486.6 eV). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. Laser Raman spectra (LRS) was performed on a Jobin-Yvon (France-Japan) T64000 type Laser Raman spectroscopy using Ar<sup>+</sup> laser beam. Transmission electron microscopy (TEM) images were collected using a JEOL JEM-2100F TEM operated at 200 kV. UV-vis spectra of the samples were measured by a UV-vis-NIR Spectrophotometer (Shimadzu UV-2450). Attenuated total reflection Fourier transform infrared (ATR FTIR) spectra were collected on a Nicolet Nexus 5700. Contact angle measurements were carried out on a commercial instrument (OCA 20, DataPhysics Instruments GmbH, Filderstadt).

#### Photoelectrochemical and electrochemical measurements

Photoelectrochemical and electrochemical measurements of the electrodes were performed in a three-electrode configuration using hematite nanowire films as working electrode, saturated Ag/AgCl as reference electrode, and a platinum foil as counter electrode. 1.0 M KOH aqueous solution (pH 13.6) or 1.0 M KOH with 0.5 M H<sub>2</sub>O<sub>2</sub> was used as the electrolyte. An electrochemical workstation (CHI 660D) was used to measure the current-voltage curves, current-time curves, and Mott-Schottky plots. Current-voltage curves of samples were measured at a scan rate of 10 mV/s under the irradiation of a 150 W xenon

lamp (100 mW/cm<sup>2</sup>, Newport 6255) equipped with an AM 1.5G filter (Newport 81094). The illuminated area of the working electrode was  $0.5 \text{ cm}^2$ .

Electrochemical Impedance Spectroscopy (EIS) analysis was performed in a 1.0 M KOH aqueous solution over a frequency range from 10<sup>5</sup> to 0.1 Hz. Data were fitted using Zsimpwin software. Mott-Schottky plots were obtained from the capacitance values at various potentials fitted from the dark EIS measurements.

## **Supplementary Figures**



**Fig. S1.** SEM and TEM images of hematite nanowire films collected (a, c) before and (b, d) after sonication.



Fig. S2. XRD patterns collected for hematite nanowire films before and after sonication. Dashed lines highlight the diffraction peaks of hematite. Other peaks belong to  $SnO_2$  from FTO substrate.



Fig. S3. High resolution TEM image collected from the edge of SH-hematite nanowire.



**Fig. S4.** Cyclic voltammetry curves of a hematite film collected in 1.0 M KOH solution at different scan rates a) before and b) after sonication, in a potential window between -0.25 to 0 V vs. Ag/AgCl. c) Plots of capacitive current density as a function of scan rate for hematite and SH-hematite films.



**Fig. S5.** The statistical plot of the photocurrent response obtained at 1.23 V vs. RHE under one sun illumination in 1M KOH from 10 different batches of hematite samples before and after sonication treatment.



**Fig. S6.** Linear sweep voltammograms of hematite films collected under one sun illumination in 1.0 M KOH aqueous electrolyte before and after sonication in a) 1M HCl and b) 1 M KOH solution.



**Fig. S7.** Linear sweep voltammograms of hematite nanoparticle films collected under one sun illumination in 1.0 M KOH aqueous electrolyte before and after sonication.



**Fig. S8.** Linear sweep voltammograms collected from SH-hematite samples prepared under different sonication durations.



**Fig. S9.** The current-time curves of untreated hematite and SH-hematite photoanodes collected under 1 sun illumination in 1M KOH solution. The values represent the percentage of current decay after 10 hours.



**Fig. S10.** UV-visible diffuse reflectance spectra collected from the hematite film before and after sonication.



Fig. S11. Mott-Schottky plots of the hematite film before and after sonication.



Fig. S12. Plot of charge transfer efficiency of hematite and SH-hematite as a function of applied potential.



**Fig. S13.** (a) XPS survey scan spectra and (b) core level C 1s spectra of hematite and SH-hematite samples.



Fig. S14. Core level Fe 2p XPS spectra of hematite and SH-hematite films.



**Fig. S15.** IR spectra of untreated hematite and SH-hematite samples. Dashed lines highlight the characteristic peaks of Fe-O and Fe-OH. The IR spectrum of FeOOH nanowires is added for comparison.



**Fig. S16**. Linear sweep voltammograms collected for hematite and UT-hematite electrodes in 1.0 M KOH solution in the dark.



**Fig. S17**. Current-time plots of the hematite photoanodes before and after sonication collected at potentials of a) 0.9 V and b) 1.2 V vs. RHE in 1.0 M KOH.



**Fig. S18.** Cyclic voltammograms obtained from hematite and SH-hematite electrodes in the dark at the scan rate of 1V/s. Before measurement, the photoanodes were held at 2.0 V vs. RHE under one sun illumination for 60 s to charge the surface states.



**Fig. S19.** Schematic illustrations of charge transfer pathways in hematite and SH-hematite. CB and VB are conduction band and valence band.  $E_f$  is Fermi energy level. Green lines represent the surface states created due to the presence of surface hydroxyl species. The dashed arrows represent electron-hole recombination. The grey and black arrows represent light absorption and hole transfer paths, respectively. Path (1): photoinduced hole transfer from valence band to water; path (2): surface hydroxyl species mediated photoinduced hole transfer from valence band to water.



Fig. S20. Illustration of the surface modification of hematite under sonication in water with and without the addition of  $H_2O_2$ .



Fig. S21. The LSV curves of hematite photoanodes collected under one sun illumination in 1.0 M KOH solution. Black line: pristine hematite photoanode, Red line: hematite photoanode ultrasonicated in saturated  $H_2O_2$  solution for 10 s.



**Fig. S22.** TEM image collected from a hematite nanowire ultrasonicated in FeCl<sub>3</sub> solution for 10 min.

### References

- [1] L. Vayssieres, N. Beermann, S. E. Lindquist, A. Hagfeldt, *Chem. Mater.* 2001, 13, 233-235.
- [2] G. M. Wang, Y. C. Ling, D. M. Wheeler, K. E. N. George, K. Horsley, C. Heske, J. Z. Zhang, Y. Li, *Nano Lett.* 2011, 11, 3503-3509.