

Electronic Supplementary Information (ESI)

Understanding charge transport in non-doped pristine and surface passivated hematite (Fe_2O_3) nanorods under front and back side illumination in context of light induced water splitting

Prince Saurabh Bassi^a, Li Xianglin^b, Yanan Fang^b, Joachim Say Chye Loo^a, James Barber^{a,c*}, Lydia Helena Wong^{a*}

^a*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798* ^b*Energy Research Institute @ NTU, Nanyang Technological University, 50 Nanyang Drive, Research Techno Plaza, X-Frontier Block, Level 5, Singapore, 637553*

^c*Department of Life Sciences, Imperial College London, London, SW7 2AZ, UK*

**Corresponding Authors, E-mail: j.barber@imperial.ac.uk, lydiawong@ntu.edu.sg*

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Section 1: Experiments

Pristine hematite nanorods were fabricated on FTO substrates using hydrothermal technique incorporated by Hemant et al¹. 1.95 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1.95 mmol Urea was dissolved in 13 mL DI water. Autoclaves of volume 25 mL were filled with 12.5 mL of solution and the cleaned FTO substrates were put in liner standing with FTO side facing towards the wall. FTO substrates were ultrasonically cleaned thoroughly with soap solution, DI water, ethanol, acetone and finally with DI water. They were subsequently dried using a stream of N_2 . To make a contact, small part of the FTO film was masked with a thermal tape which could withstand high temperature. Autoclaves were kept in oven and were heated at around $5^\circ\text{C}/\text{min}$ to 100°C and were left for 8 hrs before cooling them down naturally to room temperature. Substrates were taken out of liners and were rinsed with DI water to remove any precipitates

from the film surface. Afterwards the films were annealed with different annealing profiles: "550°C, 2hrs", "550°C, 5hrs", "650°C, 1 hr", "650°C, 5hrs" and "750°C, 20 mins". Annealing profile 550°C, 2 hrs represent sample annealed @ 2°C/min to 550°C and dwelled for 2 hours at the same temperature before cooling it down to room temperature naturally.

Atomic Layer Deposition (ALD) of TiO_x overlayer was performed on a Fiji 200 system using Tetrakis (Di Methyl Amido) Titanium (TDMATi) and H_2O as precursors at 120°C². The TDMATi source was maintained at 70 °C to achieve a suitable vapor pressure. The precursors were pulsed in the reactor with constant Ar flow at 40 Standard Cubic Centimeters per Minute (sccm), with the base pressure for deposition of 0.8 torr. The pulse time for Ti and H_2O were 0.6 and 0.1 sec, respectively. The purge time was 10 sec for both precursors. The growth rate per cycle of TiO_2 was 0.06 nm, which is consistent with a previous report³. After coating TiO_2 with 40 cycles, substrates were annealed in similar conditions of 650 °C, 5 hours.

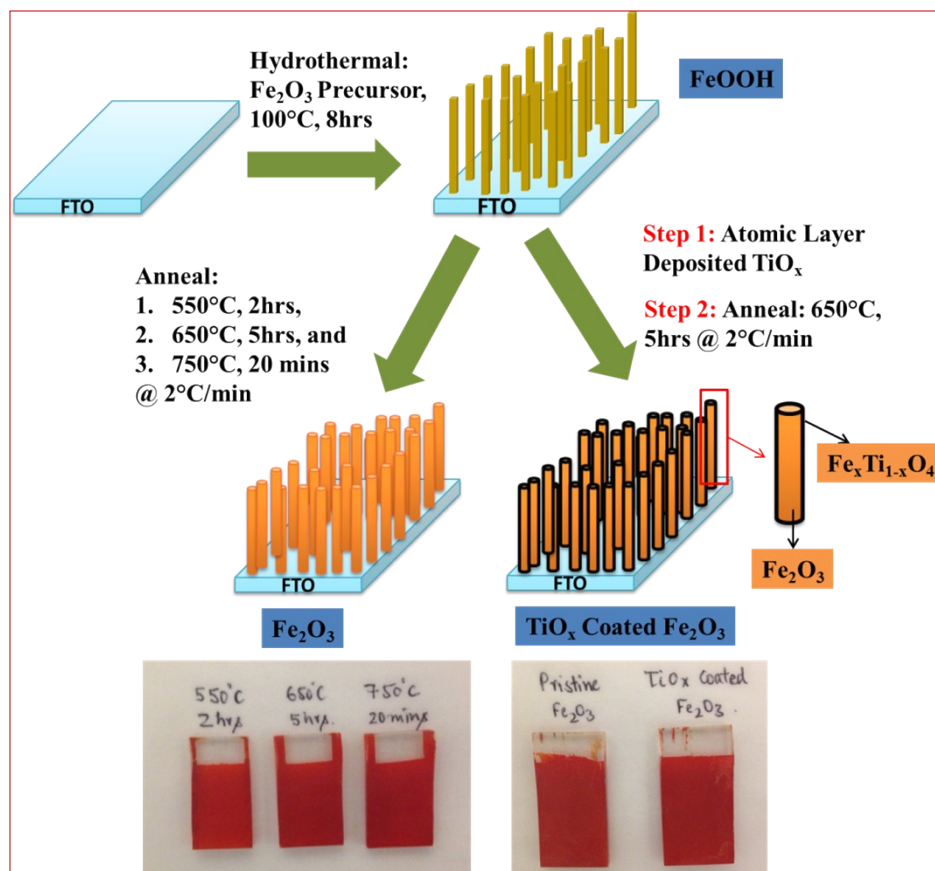


Fig. S1: Process methodology of fabrication of pristine Fe₂O₃ nanorods and TiO_x coated nanorods using hydrothermal technique

Section 2: Morphological and Structural Characterization of Thin Films

The morphology of thin film samples was observed with Field Emission Scanning Electron Microscopy (FESEM, JEOL, JSM-7600F, 6kV). Films were coated with Au/Pt to avoid charging problems. The phase for pristine films was determined from thin film X-ray diffraction (XRD) using a Shimadzu LabX-XRD-6000 equipment. Measurements were done using Cu K α radiation ($\lambda=1.5418\text{\AA}$) on grazing incidence geometry with incident angle fixed at 1° and 2θ scanned from 20° to 60° at a scanning rate of $1^\circ/\text{min}$. HRTEM Analysis (JEOL 2010) was performed using thin film samples scratched from FTO substrates, dispersed in methanol and eventually loaded onto the copper grip. Ultraviolet-visible (UV-Vis) measurements were performed using Perkin Elmer UV-Vis spectrophotometer. Samples were kept in the integrating sphere to evaluate diffuse reflectance using a BaSO₄ pellet as the reference. This yielded normalized absorption spectra which were directly used in the plots.

Section 3: Photoelectrochemical Characterization of Thin Film Photoanodes

PEC measurements were performed with a CHI 660D working station (CH Instruments, Inc.) using a three-electrode electrochemical system comprising of Platinum coil and Ag/AgCl as counter and reference electrode respectively with 1M NaOH (pH=13.6) electrolyte. Photoactive surface area (using mask on the setup) was fixed at 0.125 cm^2 . Simulated sunlight from a 150 W xenon solar simulator (96000, Newport Corp.) through a solar filter (KG3) with intensity equivalent to standard AM1.5 sunlight ($100\text{ mW}/\text{cm}^2$) was irradiated on the sample (front or backside). The electrolyte was aqueous solution of 1 M NaOH (pH 13.6) degassed by purging N₂ gas for 10 min. The hematite electrode was scanned at $50\text{ mV}/\text{s}$ between -0.4 V and 1.0 V vs. Ag/AgCl. For measurements in the presence of the hole scavenger H₂O₂, the electrolyte was 1M NaOH +0.5M H₂O₂ with other conditions kept same as mentioned above.

To calculate applied bias with respect to Reversible Hydrogen Electrode, V_{RHE} potential, Nernst equation was used as follows:

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 * \text{pH} + V_{\text{Ag/AgCl}}^0 ,$$

where $V_{Ag/AgCl}$ is the voltage bias with respect to Ag/AgCl reference electrode, and $V_{Ag/AgCl}^0$ is the standard potential of Ag/AgCl at 25°C equal to 0.197 V.

Incident Photon to Current Efficiency (IPCE) was measured using a xenon light source (MAX5303, Asahi Spectra Co. Ltd.) and a monochromator (CMS5100, Asahi Spectra Co. Ltd.). Electrochemical impedance spectroscopy (EIS) measurements were carried out using an automated potentiostat (Metrohm Autolab) in a three-electrode electrochemical system. Counter electrode, reference electrode and electrolyte were same as that used for PEC measurements. Measurements for Nyquist plots were performed both in dark and light conditions at 1.23V vs. RHE from 75000 to 0.1 Hz. Mott Schottky plots were extracted for a potential scan of 0 V to +2 V vs. RHE in dark at 1 KHz. The intercept of the linear region in curve yields the flat band potential and the slope gives the donor concentration based on relation (1) shown below:

$$\left(\frac{A_S}{C_{SC}}\right)^2 = \frac{2}{q\epsilon_0 \kappa N_D} \left(V - E_{FB} - \frac{K_B T}{q}\right) \quad (1)$$

Where C_{sc} is the space charge capacitance, A_s is the active area of device, E_{FB} is the flat band potential, N_D is the donor density, V is applied bias, K_B is Boltzmann constant, T is the absolute temperature, q is charge, κ is dielectric constant of active material and ϵ_0 is the vacuum permittivity.

Bulk/Surface Charge transport Efficiency was extracted from the photoelectrochemical measurements performed in the presence of 0.5M H_2O_2 in 1M NaOH with all the pre-conditions kept similar to the photocurrent measurements.

Photocurrent density obtained from water oxidation is termed as J_{H_2O} and from H_2O_2 oxidation as $J_{H_2O_2}$.

Photocurrent density measured for water oxidation, J_{H_2O} is represented as follows:

$$J_{H_2O} = J_{abs} \times \eta(\text{catalysis}) \times \eta(\text{separation})$$

Due to absence of any hole injection barrier, $\eta(\text{catalysis}) = 1$ (i.e. in the presence of H_2O_2)

Hence, $\eta(\text{separation}) = J_{H_2O}/J_{abs}$ and,

$$\eta(\text{catalysis}) = J_{H_2O} / J_{H_2O_2}$$

where $J_{H_2O_2}$ is the photocurrent density measured with H_2O_2 photo-oxidation.

J_{abs} is the photocurrent density obtained when all the absorbed photons are completely converted into current density. It is calculated by integrating the absorbance spectra with standard AM 1.5G spectrum.

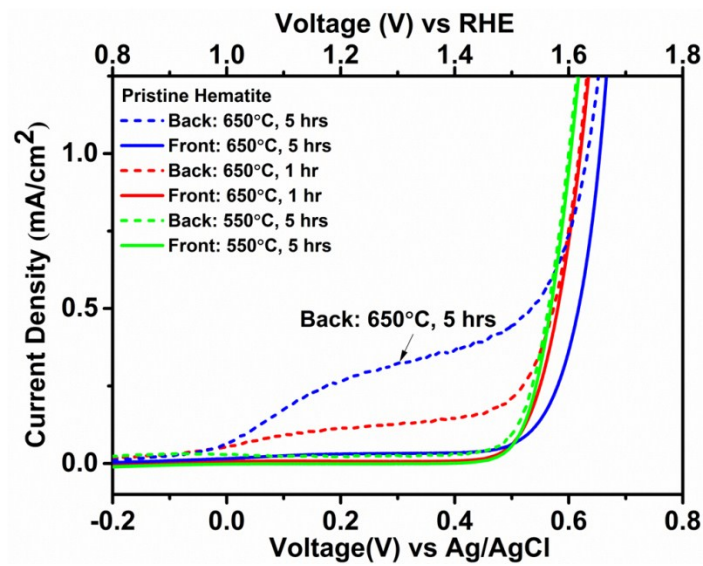


Fig. S2: J-V Plots for different annealing profiles i.e. blue curves represent samples annealed at 650°C and dwelled for 5 hrs, red at 650°C dwelled for 1 hr and green at 550°C dwelled for 5hrs.

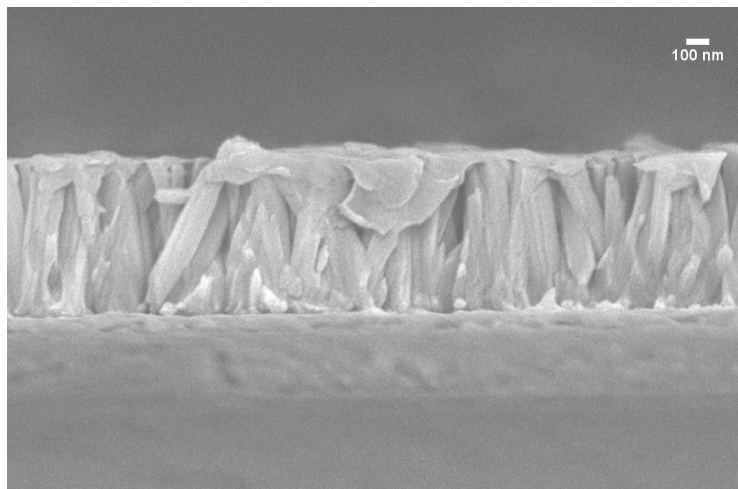


Fig. S3: FESEM Cross-section Image of pristine as-grown FeOOH Nanorods fabricated through hydrothermal synthesis at 100°C for 8 hours

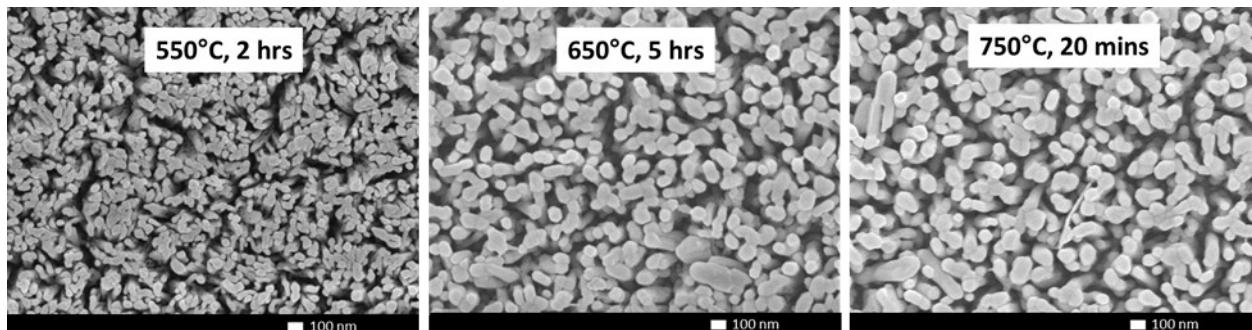


Fig. S4: FESEM top-view Images of pristine hematite nanorods fabricated with different annealing profiles

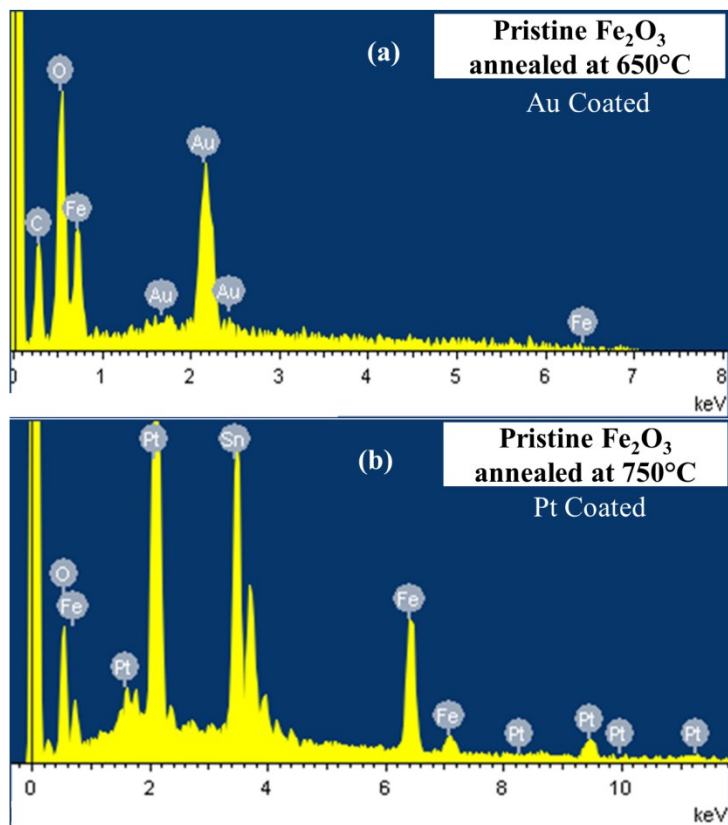


Fig. S5: EDS spectra of pristine Fe₂O₃ nanorods prepared with annealing profile: (a) 650°C, 5 hours and (b) 750°C, 20 mins.

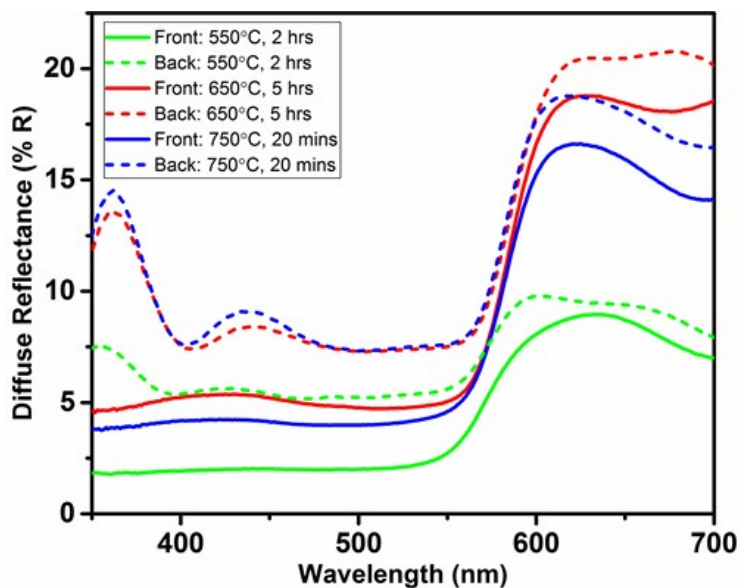


Fig S6: UV-Vis diffuse reflectance spectra for pristine Fe_2O_3 films annealed under different profiles

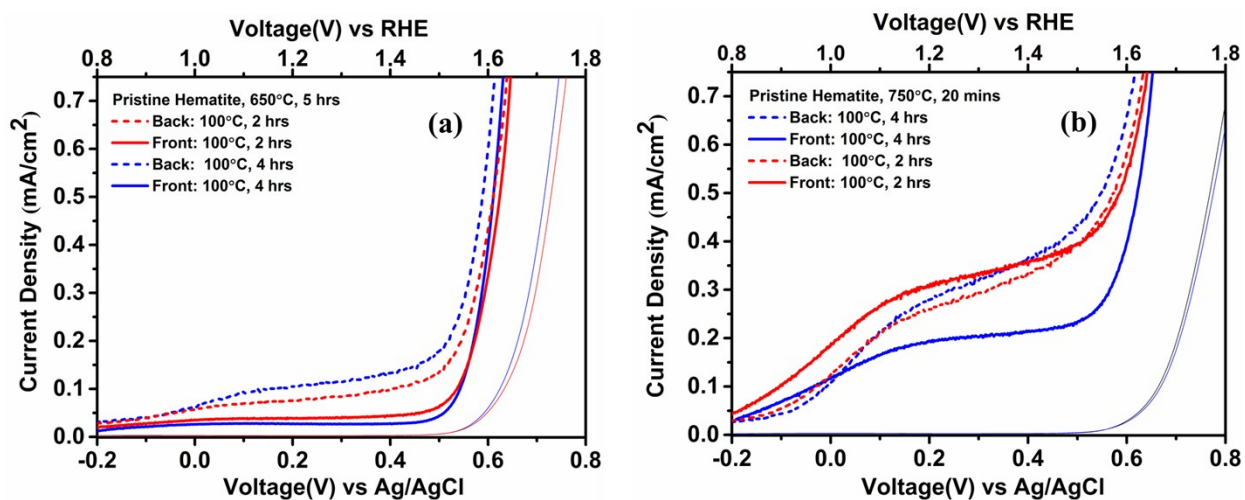


Fig. S7: JV plots for pristine Fe_2O_3 nanorods deposited at 100°C , 4 hrs and 100°C , 2 hrs hydrothermal conditions and annealed at (a) 650°C , 5 hrs and (b) 750°C , 20 mins

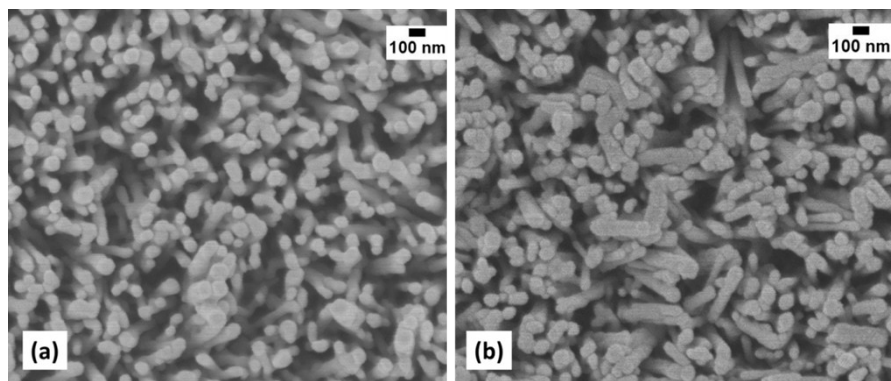


Fig. S8: Top-view FESEM Images of (a) pristine, and (b) TiO_x coated Fe_2O_3 nanorods

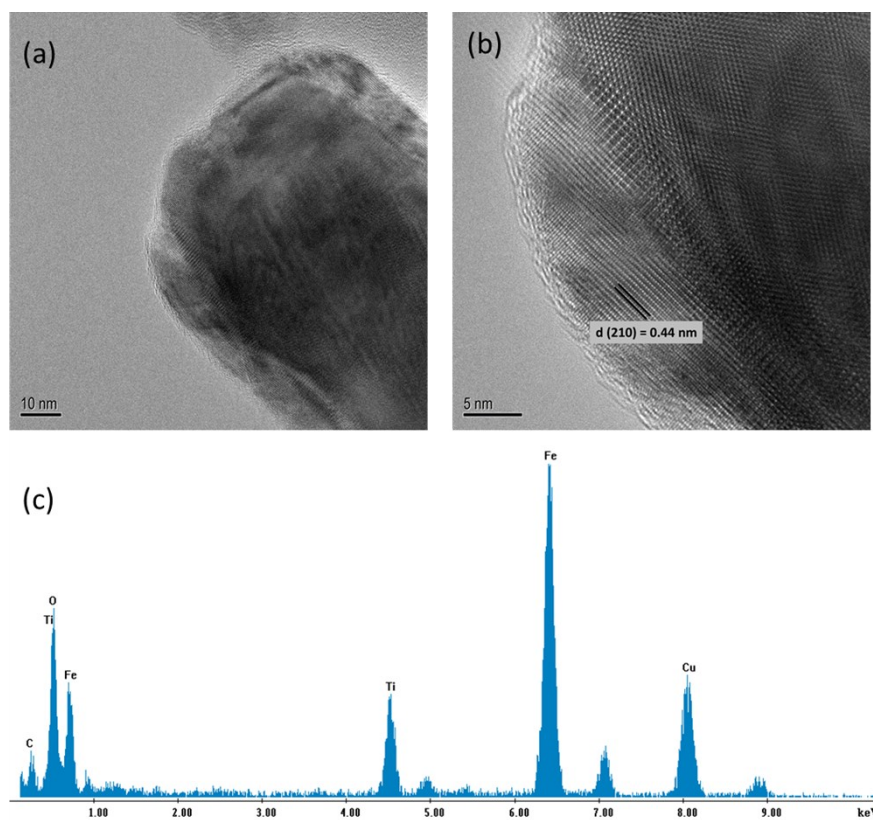


Fig. S9: (a) HRTEM image showing a conformal layer on top of Fe_2O_3 nanorods, (b) interplanar spacing for the overlayer and (c) EDX spectra demonstrating signature of Ti with approximate atomic ratio of Fe/Ti: as 2:1

References

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