Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplementary information

Decoupling light absorption and charge transport properties in near IR-sensitized Fe_2O_3 regenerative cells.

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Experimental section

Hematite nanorods were grown directly on fluorine doped tin oxide (FTO) substrates as previously reported.[18] In short, the growth was carried out for 20 hrs at 100 ^{0}C using urea (Sigma Aldrich, reagent grade) which hydrolyses iron (III) chloride (Sigma Aldrich, reagent grade) to give FeOOH. Upon annealing at 500 ^{0}C for 30 minutes, FeOOH converts to α-Fe_2O_3 (hematite phase). For sensitization, sample was dipped in ethanolic solution of 0.2 mM SQ02 dye with 10 mM chenodeoxycholic acid (CDCA) for 3 hrs. The samples were then sealed using 25 µm Surlyn with Pt as counter electrode. The composition of electrolyte used was 0.6 M 1-butyl 3-methyl imidazolium iodide, 0.05 M Iodine, 0.1 M lithium iodide, 0.05 M 4-tert-butylpyridine in acetonitrile: valeronitrile (85:15) v/v. Current density-Voltage (J-V) plots were measured using solar simulator (San-EI Electric, XEC-301S, AM 1.5, 100 mW/cm^2). The current-voltage data under these conditions was obtained using Keithley model 2612A source meter. IPCE measurements were performed using PV300 (Bentham), with dual Xenon/quartz halogen light source, measured in DC mode with no bias light. Incident light intensity was calibrated using a photodiode detector (silicon calibrated detector, Newport). All the measurements were performed in air. UV-Vis absorption spectra were collected with a Shimadzu UV3600 spectrophotometer coupled with an integrating sphere. FTO substrates were used as a reference to account for the light absorption and reflection from FTO itself. Impedance spectroscopy was carried out using Autolab potentiostat which was coupled to Nova electrochemical software. A sinusoidal perturbation of 10 mV was applied between 100 KHz to 0.1 Hz to collect the impedance data under illumination at different applied DC bias. Red and blue LEDs with wavelengths of 627 nm (700mA, 306 lm) and 505 nm (700mA, 360 lm) respectively were used as light source.

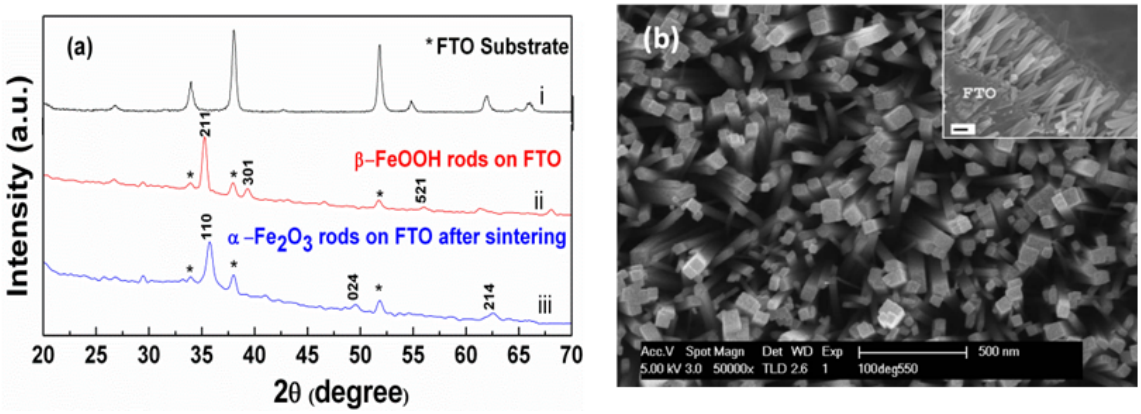

Fig. S1 (a) XRD of (i) FTO substrate for reference (ii) FeOOH and (iii) α-Fe_2O_3 nanorods grown on FTO. **(b)** FESEM image of nanorods grown on FTO, inset shows the cross sectional image, scale bar is 100 nm.

Fig. S1 (a) shows the XRD pattern of the nanorod sample before and after annealing. The α-Fe_2O_3 phase after annealing at 500 ^oC for 30 min (ICDD PDF No. 99-100-0141) is confirmed. No characteristic peaks for other impurities such as γ-Fe_2O_3 and Fe_3O_4 were observed. XRD patterns of FTO and β-FeOOH are also plotted in **Fig. S1 (a)** for comparison. The (110) diffraction peak is prominent compared to other peaks such as (012), (113) and (300), which could indicate that the α-Fe2O3 nanorods are highly oriented with respect to the substrate. **Fig. S1(b)** shows the top view FESEM images of the sample, annealed at 500 ^oC for 30 min, inset shows the cross-sectional image the nanorods on FTO. The diameter ranges from 100-150 nm and the length of nanorods is around 700-800 nm.

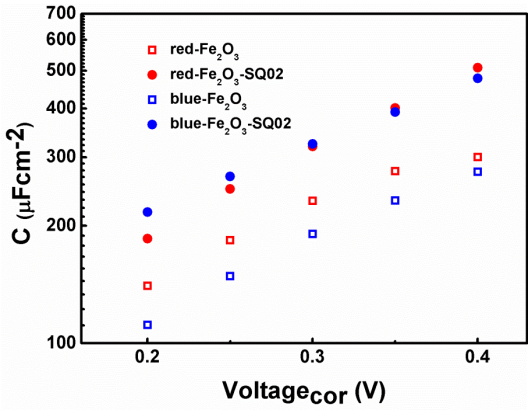

Fig S2. Capacitance of both Fe_2O_3 and Fe_2O_3-SQ02 samples under different illumination.

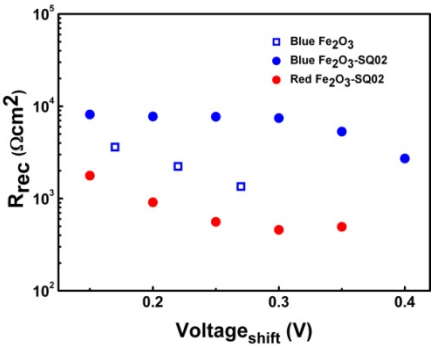

Fig S3. Charge transfer resistance of both Fe_2O_3 and Fe_2O_3-SQ02 samples under plotted vs. shifted voltage to account for shift in conduction band.