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Supporting Information

Direct Solar Charging of an Organic–Inorganic, Stable, and Aqueous Alkaline Redox Flow Battery with a Hematite Photoanode

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Supporting information

S1: Photoelectrode production

Hematite photoanodes preparation:

Thin and compact hematite photoanodes were prepared using spray pyrolysis technique. Fluorine-doped tin oxide (FTO) conductive glass substrates (Solaronix TCO22-7, Switzerland) were carefully cleaned and heated to 500 °C on a heating plate. An underlayer of TEOS was deposited using a glass atomizer with a precursor solution of 10 % tetraethyl orthosilicate (Sigma-Aldrich) in ethanol solution (10 mL per 18 cm^2). After naturally cooling to room temperature, the substrates were re-heated to 500 °C and sprayed with 70 mL per 24 cm^2 of a 10 mM iron acetylacetonate (Fluka) solution in ethanol. The spraying was done by a spraying nozzle system (Spraying Systems Co. model SU J4B-SS) using a stainless steel pressurized tank and a pressure inside the tank of approximately 1 bar (by atmospheric air) from a height of 20 cm above 8 samples of 1 x 3 cm^2 (1 mL of solution was sprayed every 45 seconds). After deposition, the samples were annealed at 500 °C for 30 min and allowed to cool to room temperature. One end of the FTO/glass was covered to allow applying a silver electrical contact.

Hematite post synthetic annealing

Hematite samples were modified based on a previous report.[1] Simply, the as-synthesized sampled were placed in a Teflon-lined autoclave inside a small open glass flask. 0.2 mL 10 mM iron acetylacetonate solution in ethanol were placed outside the flask and the autoclave was heated to 140 °C for 5.5 hours using a 350 °C/h heating ramp and left to cool in the oven. This treatment promotes surface defect patching.[1]

Polyaniline electrodeposition

Polyaniline was deposited onto already annealed samples due to a visibly more homogeneous layer on these samples instead of untreated hematite. The procedure is based on a previous report.[2] Briefly, a hematite sample was placed as the working electrode in a 3-electrode glass cell filled with 0.2 M aniline (Sigma-Aldrich) in 0.5 M H_2SO_4 solution and with a Pt-wire counter electrode and sat. Ag/AgCl reference electrode (Metrohm, Switzerland). The electrodeposition was done by applying a constant positive current of 5 $\mu A \cdot cm^{-2}$ for 5 min using an Autolab potentiostat (Metrohm, NOVA 1.10.3 software) – Figure S1.1a. A fresh solution of aniline was used for each deposition. The samples were washed with distilled water and subsequently immersed in 1 M NaOH and washed again. Just after deposition the color on TCO glass was green, but after NaOH treatment it turned blue, (typical in an emeraldine structure) – Figure S1.1b. The thickness of the film was estimated to 15 nm by assuming 100 % current efficiency and an aniline density of 1.0217 g/cm^3.

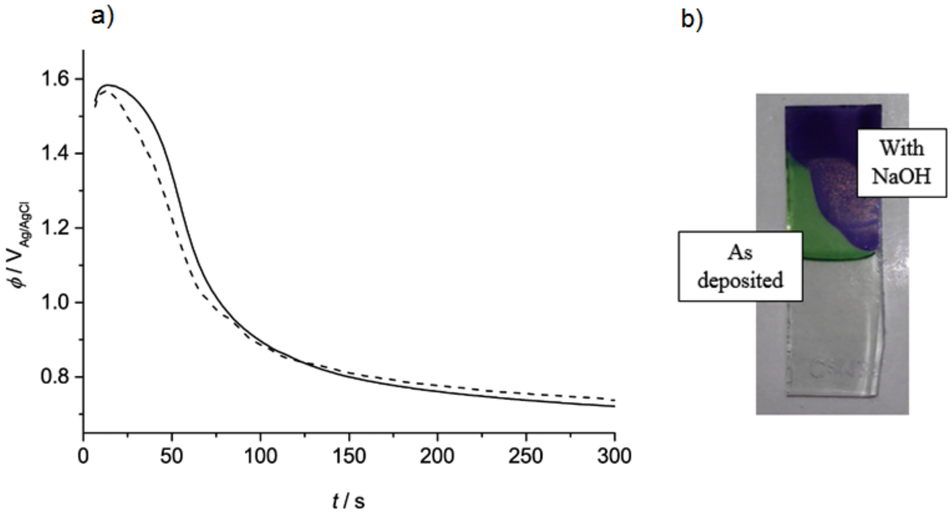


Figure S1.1: a) Potential as a function of time when performing the polyaniline electrodeposition for two representative hydrothermally treated samples. b) Polyaniline deposition (20 min, 5 µA·cm^{-2}) on TCO glass after dipping half the sample in 1 M NaOH.

A QUANTA-FEI field emission scanning electron microscope (FE-SEM) was used to evaluate the morphology of the samples.

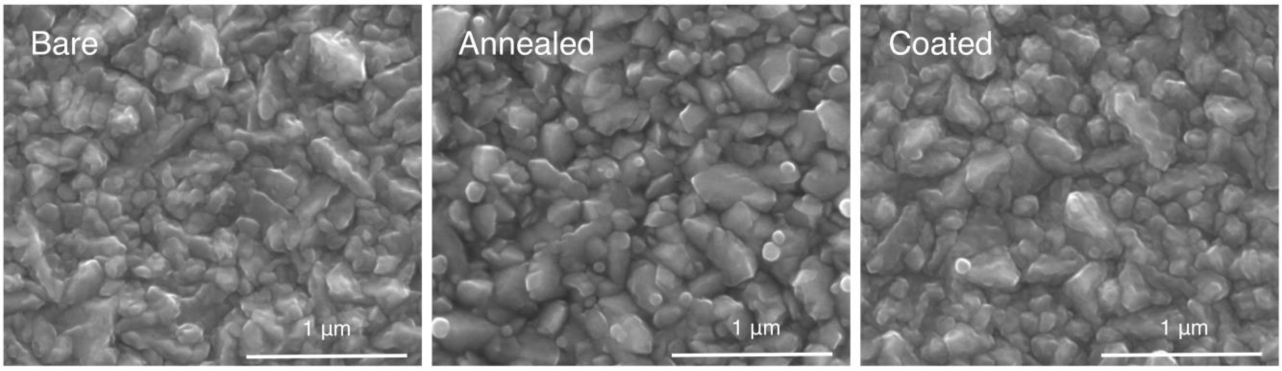


Figure S1.2: SEM top view of different prepared samples a) Untreated b) pressure annealed and c) pressure annealed with polyaniline on top.

S2: Cyclic voltammetry and charging/discharging in redox flow cell

The cyclic voltammograms of AQDS (Combi-Blocks, Inc. QA-7372) and potassium ferrocyanide (Sigma-Aldrich) were recorded in a 3 electrode glass cell with an Autolab potentiostat (Metrohm, NOVA 1.10.3 software) using a 3 mm freshly polished glassy carbon electrode (Chemical Instruments) as the working electrode, Pt-wire counter electrode and sat. Ag/AgCl (Metrohm, Switzerland) as reference electrode. The solutions of 1 mM AQDS or ferrocyanide in 1 M NaOH were purged with nitrogen before measurements.

The RF cell charging/discharging experiments were conducted in a single flow cell shown in the figure below. The RF cell is based on a Fraunhofer cell (RF25-015-T & RF25-014-N, 25 cm^2) and consists of carbon felt electrodes, bipolar plates, current collectors and a cation exchange membrane. In order to facilitate current collection, solid copper plates were employed. Graphite plates were used as bipolar plates. Carbon felt was used as electrodes on both sides of the cell. Nafion-117 was adopted as a cation exchange membrane and PTFE gaskets were used for sealing the cell assembly. To assemble the cell, current collectors were screwed together by 4-11 bolts with bipolar plates, electrodes and gaskets in between. For circulating the electrolytes (100 ml on both sides) through the cell, 2 DDA pumps at a flow rate of 25 mL/min with Teflon tubing were utilized. Anolyte and catholyte were composed of 0.1 M AQDS in 1 M NaOH and 0.2 M $K_4Fe(CN)_6$ in 1 M NaOH, respectively and purged with nitrogen before use. Charge/discharge studies were carried out under constant current of 0.5 A, upper limit of 1.2 V during charge and lower limit of 0.2 V during discharge. An Aim-TTi QPX1200SP 1200 watt DC Power Supply was used for charging and an Aim-TTi LD400P 400 Watt Programmable DC Electronic Load for discharging the cell. A multimeter was used to measure the voltage.

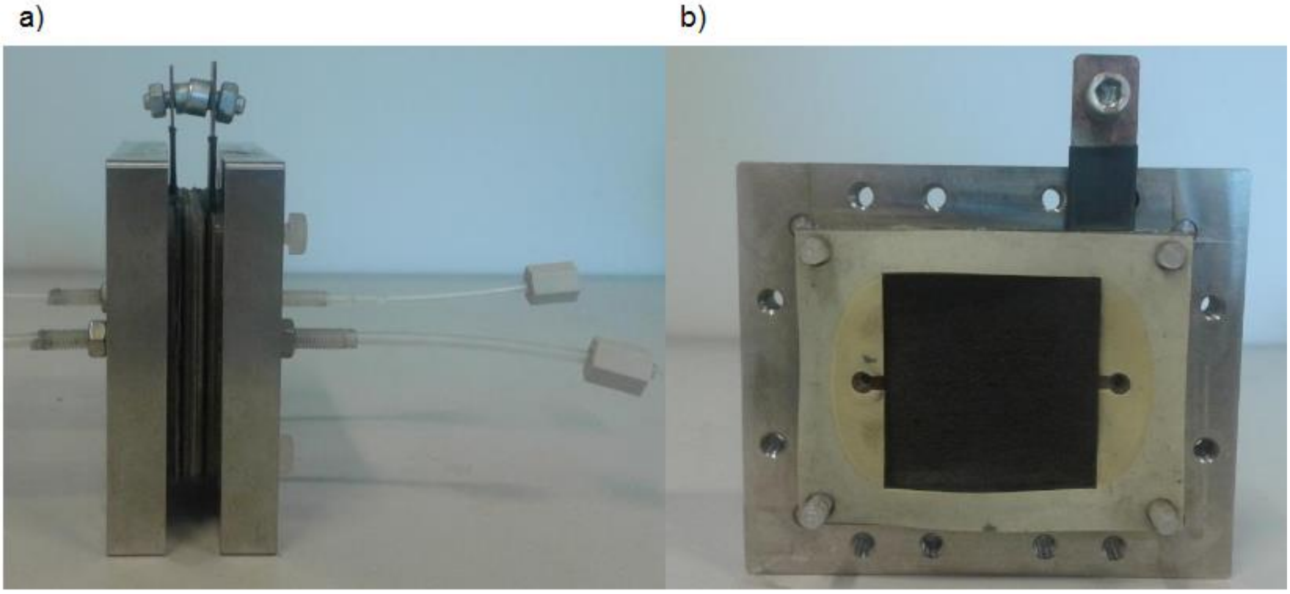


Figure S2.1: a) Assembled cell, side-view and b) carbon felt and gaskets inside the cell.

S3: PEC cells

PEC half cell

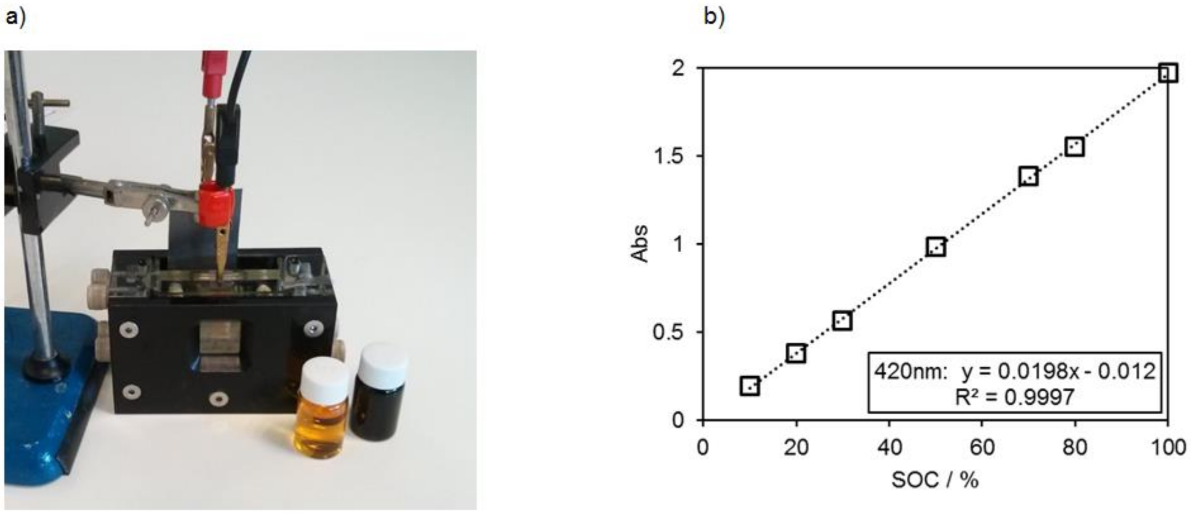
The photooxidation of ferrocyanide was studied using a small PEC cell – cappuccino cell - as described elsewhere.[3] The cell was filled with 0.2 M $K_4Fe(CN)_6$ (Sigma-Aldrich) in 1 M NaOH with varying concentration of $K_3Fe(CN)_6$ (Sigma-Aldrich) in a three-electrode configuration. A Pt wire was used as counter electrode and 3 M Ag/AgCl as reference electrode (Chemical Instruments, UK). The cell has a 7 mm front quartz window and the sample was placed 5 mm from the window in a sample holder. These tests eliminate the influence of the AQDS in the PEC/RF with two half-cells.

PEC/RF cell

The photoelectrochemical performance of the hematite photoanodes with redox pairs ferrocyanide| ferricyanide || AQDS|$AQDS^{2-}$ was measured in an open PEC cell (Figure S3.1a) with a transparent window in a 2-electrode setup making it possible to measure the absolute battery potential. The photoelectrochemical cell is based on a recently submitted report (*J. Azevedo, T. Seipp, J. Burfeind, C. Sousa, A. Bentien, J. Araújo, A. Mendes (submitted to Nano Energy)*) and is shown in the figure below. It is an open 2-chamber cell made from acrylic plastic for use with two electrolytes separated by a Nafion-117 membrane with a 3.2 cm^2 transparent acrylic window and a membrane area of 3.2 cm^2. Hematite or graphite felt plates (Sigracell) were used as the working electrode in one cell chamber and counter/reference electrode was short-circuited in the other chamber and connected to a graphite felt plate in the solution. The hematite area was reduced to 1 cm^2 by masking the samples with tape. The operating conditions in all experiments were as follows: starting anolyte was 0.1 M AQDS (Combi-Blocks, Inc. QA-7372) in 1 M NaOH and starting catholyte was 0.2 M $K_4Fe(CN)_6$ in 1 M NaOH.

The state-of-charge (SOC) is the degree of electrochemical transformation of the redox couples on both sides of the battery resulting in a certain battery voltage according to the Nernst equation. The PEC cell was charged to different SOC by applying a fixed potential, according to Nernst equation, until only residual current was measured. The charge was conducted using graphite felt electrodes at the anode and at the cathode sides. When each SOC was achieved, the electrode at the anode side was exchanged by the hematite photoelectrode to measure the photoresponse in the PEC/RF cell arrangement. The AQDS solution was bubbled 10 min with nitrogen in the beginning and after each new SOC was reached. The yellow color of the ferro/ferricyanide solution (10 % SOC) and the red color of the AQDS solution is seen in the two flasks (Figure S3.1a). The SOC was determined in three ways: measuring the open-circuit potential (OCP) before recording the j-ϕ curves of each sample, measuring the OCP after recording the j-ϕ curves and by measuring the UV absorbance of the ferrocyanide solution at 420 nm.

For photoresponse experiments, a solar simulator Newport 67005 or Newport 94011A with AM 1.5 air mass filter was calibrated to 1 sun (100 $mW \cdot cm^{-2}$) with a c-Si photodiode (Newport). Current-potential linear sweeps (positive direction) were recorded at a scan rate of 10 $mV \cdot s^{-1}$ and with a resolution of 5 mV. The potential was controlled with a ZENNIUM workstation (Zahner Elektrik, Germany) or a CHI660E (Chemical Instruments).



S3.1: a) PEC battery cell and b) UV Standard curve for 0.2 M ferrocyanide/ferricyanide solution in 1 M NaOH diluted 100 times for peaks at 420 nm referenced to 1 M NaOH

S 4: Prolonged illumination UV test

To ascertain that the photoelectrochemical process indeed does produce ferricyanide in the PEC/RF cell, a coated hematite sample was left in the battery under illumination starting from 0 % SOC for 7 h. The absorption from a sample of the ferri/ferrocyanide solution was measured at different times, as the ferricyanide absorbs at 420 nm as opposed to ferrocyanide. As a control, a 0 % SOC ferrocyanide solution was also left in the light in a separate transparent container with similar area/volume ration as in the battery and the absorbance measured. The absorbance of the control sample increases at just below 400 nm due to a photo-induced side reaction, but was stable during the whole test and with absorbance significantly lower than for the test in the PEC/RF cell using hematite.

The UV spectra were measured with reference to a 0 % SOC solution of ferrocyanide in 1 cm path length quartz cuvettes.

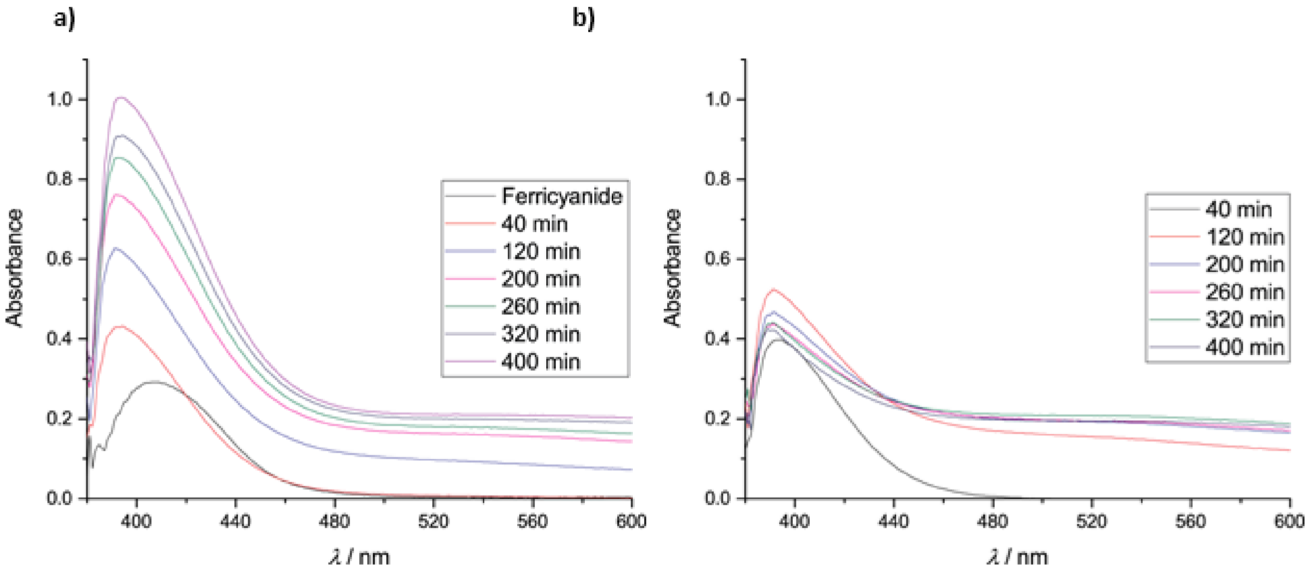


Figure S4.2 a) The absorbance of the ferrocyanide side of the PEC/RF cell as a function of unbiased solar charging time of 40-400 min under 1 sun illumination.
b) The absorbance of a 0 % SOC solution ferrocyanide left under 1 sun illumination in a separate transparent container (cuvette) with same light area-to-volume ratio for the same time as a).

S5: Efficiency determination

The incident-solar-to-chemical conversion efficiency of a coated hematite sample was determined by recording the photoelectrochemical response in the PEC/RF cell as reported elsewhere[4] and the result is seen in the figure below. The maximum efficiency is around 0.08 % at a current density of 0.27 mA·cm^{-2}.

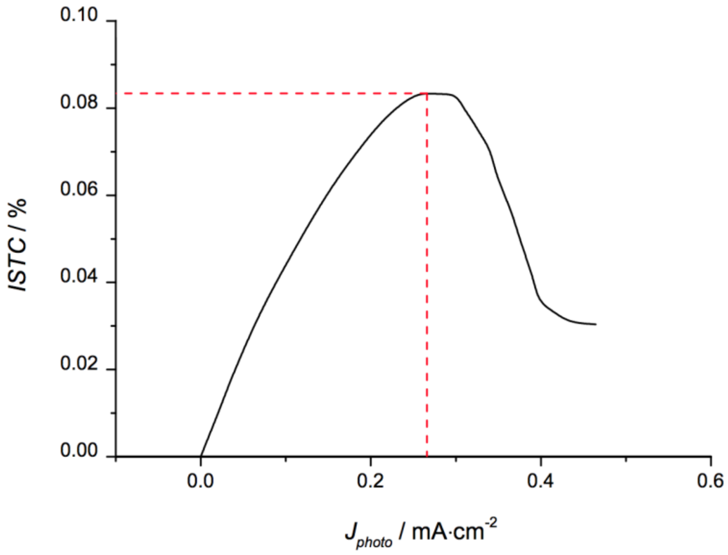


Figure S5.1: Incident solar-to-chemical conversion efficiency of a coated hematite sample as a function of current density.

S6: Absorption measurements

Absorption spectra of the samples were measured and the average absorption from 300-600nm is 58%. UV-VIS spectra of hematite samples were measured using a Shimatzu UV-3600 UV-VIS-NIR spectrophotometer, equipped with a 150 mm integrating sphere and using $BaSO_4$ as 100 % reflectance standard.

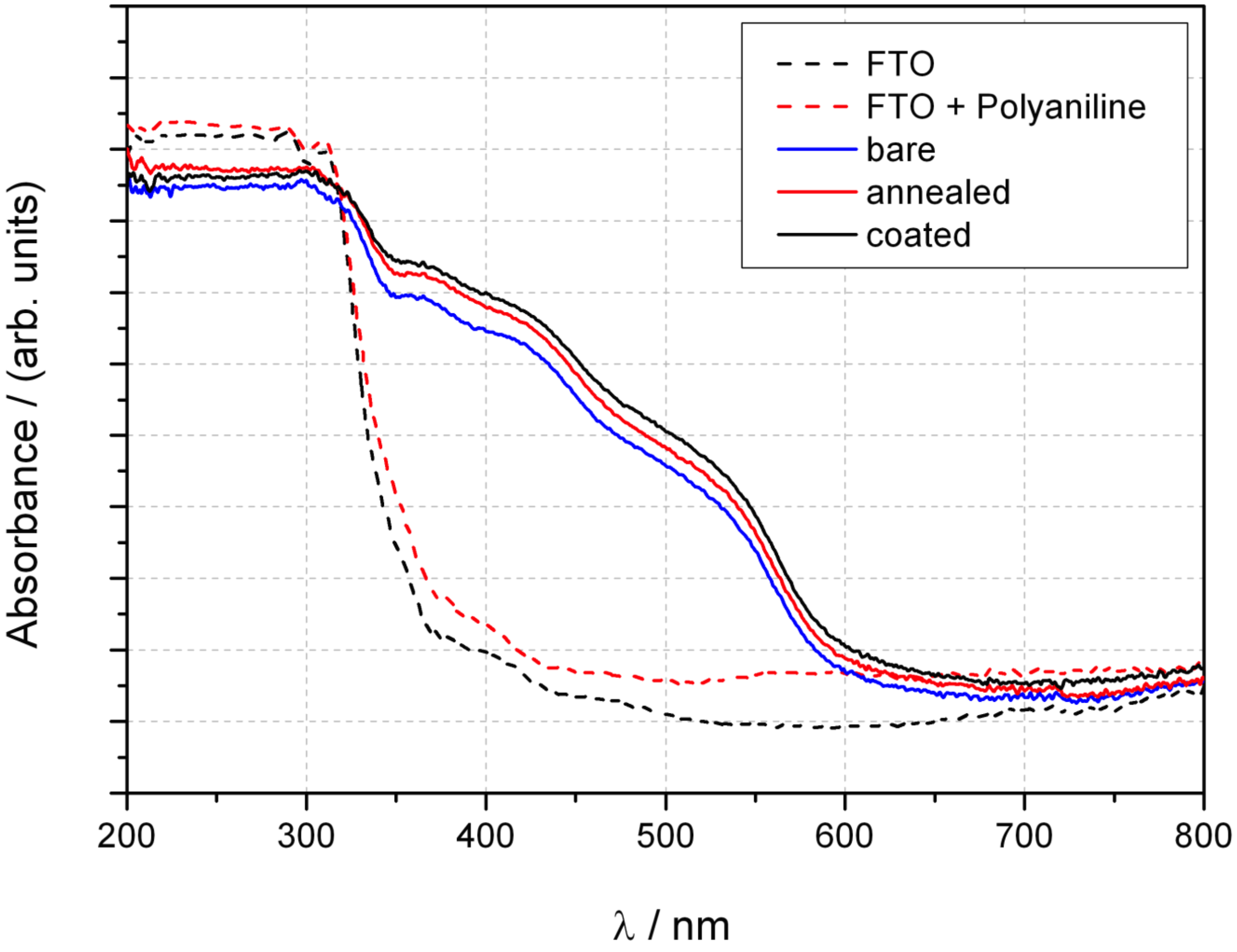


Figure S6.1: Absorption measurements for bare TCO glass polyaniline directly on TCO glass, bare hematite, annealed and coated.

References

[1] J. Azevedo, L. Steier, P. Dias, M. Stefik, C. Sousa, J. Araujo, A. Mendes, M. Graetzel, S. Tilley, *Energy & Environmental Science* **2014**, *7*, 4044-4052.
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[4] H. Dotan, N. Mathews, T. Hisatomi, M. Gratzel, A. Rothschild, *Journal of Physical Chemistry Letters* **2014**, *5*, 3330-3334.