**Photoelectrochemistry (PEC) measurements.**

Photocurrent density (in mA cm-2), PEC impedance spectroscopy (PEIS), incident photon-to-current efficiency (IPCE) and Faradaic efficiency were investigated in a three-electrode PEC quartz cell. Simulated sunlight on an circular 0.283cm2 area was supplied by a 300 W Xe Lamp (LOT Quantum Design) using an AM 1.5G filter (which simulates the terrestrial solar spectrum at ground level). Illumination intensity was set to 1 sun (100 mW cm-2) by calibration with a silicon photodiode linked to an ILT1400 Radiometer Photometer. An Ivium Compacstat.h mobile potentiostat was used with IviumSoft version.2.6 software. In the three electrode system, the working electrode was the as-prepared hematite photoanode, the counter electrode a Pt wire, and an Ag/AgCl (in 3.5 M KCl) electrode the reference electrode. 1 M KOH solution (pH 13.9) was used as an electrolyte. The working electrode was illuminated from the back side (glass side). Photocurrent density - potential (*J-V*) curves were recorded at a scan rate of 20 mV s-1. The measured potentials vs. Ag/AgCl (*EAg/AgCl*) were converted to RHE potential ($E\_{RHE}^{°}$) following the Nernst equation (eq 2):

$E\_{RHE}^{°}=E\_{Ag/AgCl}^{°}+E\_{Ag/AgCl}+0.059 pH$ (2)

where $E\_{Ag/AgCl}^{°}$ = + 0.205 V

**Photo-electrochemical impedance spectroscopy**

In PEIS measurements, a potential perturbation of 10 mV was applied at a frequency range from 105 to 0.1 Hz. The data were collected at direct current potentiostatic conditions from 0.7 to 1.3 VRHE at a step of 0.05 V and fitted using Zview software (version 3.5, Scribner®). Simulated solar illumination (AM1.5G, 100mW cm-2) was used to illuminate the back (glass) faces of the FTO slide supports.

**Cyclic voltammetry for surface area**

Electrochemically active surface area (ECSA) of photoanodes was investigated using cyclic voltammetry (CV), scanning from 0 to 0.17 VAg/AgCl at scan rates between 10 and 200 mV s-1, in 1 M KOH solution (pH =13.9).31 ECSA is proportional to the double layer capacitance (*Cdl*), which is estimated from the slope of the plot *ΔJ* vs. scan rate and dividing by two.32 *ΔJ* is equal to (*Ja–Jc*), where *Ja* and *Jc* are the anodic and cathodic current densities, respectively, in this case taken at 0.1 VAg/AgCl in the CV scans.33, 34 Sample slides were measured in triplicate and consistent *Cdl* values were obtained.

**Hole scavenger measurements.**

Underlying differences in charge transport properties and surface catalytic properties between samples prepared with different LA levels were studied by adding 0.5 M H2O2 as a hole scavenger into the 1 M KOH electrolyte to eliminate surface recombination.35

**X-ray diffraction (XRD)**

Samples analyzed by powder X-ray diffraction (XRD) were recorded on a Bruker D8 powder diffractometer. FeOOH samples were dried in air and lightly ground by hand before measurement. Hematite photoanodes did not need any preparation for XRD.

**Crystal modelling**

Crystal modelling and powder XRD diffraction pattern calculation were obtained with Crystalmaker 10.1.1 and CrystalDiffract 6.7.2 software, respectively, and using published crystal structure cif files.

**Scanning Electron Microscopy (SEM)**

Field-emission scanning electron microscopy (FESEM, JEOL JSM-6301F) was employed to observe photo-electrode surfaces and cross-sectional morphology and determine film particle sizes. Samples were not coated before SEM observation. Energy dispersive X-ray spectroscopy (EDXS) was conducted on a JEOL JSM-6480LV SEM at low magnification (~250μm diameter sample area) for elemental composition (for elements heavier than N).

**Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) was carried on a JEOL 2100 Plus to characterize the morphology of the samples, the presence of amorphous material, and the lattice fringes of hematite crystals (using ImageJ). FeOOH samples onto carbon-coated copper TEM grids were prepared from suspensions diluted in 2-propanol followed by brief sonication, drop casting and drying. Samples of hematite photoanodes for TEM imaging were prepared by carefully scraping hematite material from the ABS-FTO slide into 2-propanol, followed by brief sonication. Then, one drop of suspension was placed onto the TEM grid and air dried before TEM analysis.

**UV-Visible spectroscopy**

UV-Visible spectroscopy of photoanode slides was conducted by diffuse reflectance light absorption measurements on an Agilent UV/Vis Cary 100 spectrometer fitted with a diffuse reflection integrating sphere. Tauc plots were carried out to calculate direct and indirect band gap, using exponents *n*=2 and *n*=1/2, respectively.

**Raman spectroscopy**

Raman spectroscopy of dried powders was conducted on a Renishaw inVia Raman microscope using: Laser wavelength: 532nm, Power: 1% (0.7mW), Exposure time: 100s, Accumulations: 3. Comparison to known samples in the RRUFF mineral database analysed by Raman with a 532nm laser was made.

**X-ray photoelectron spectroscopy (XPS)**

Hematite photoanode slides were also analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher Scientific K-alpha+ spectrometer using a micro-focused monochromatic Al x-ray source (72 W) over an area of approximately 400 microns. Data was recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scan with 1 eV and 0.1 eV step sizes respectively. Data analysis was performed in CasaXPS using a Shirley-type background and Scofield cross sections, with an energy dependence of -0.6. Charge neutralization of the sample was achieved using a combination of both low energy electrons and argon ions.

**Measurement of oxygen evolution from photoanode**

A custom-made 110ml square quartz cell with PFTE lid and air-tight ports for sample, Pt counter, reference electrode and N2 bubble line was used. An O2 sensor probe was used to measure O2 evolution from the hematite photoanode. The sensor probe was a Pyroscience Firesting O2 sensor housed in a robust tip, coupled with a temperature probe for continuous temperature compensation. The probe tip houses a fluorescent dye that fluoresces relative to O2 presence on brief flash illumination. The sample photoanode, Pt counter and Ag/ AgCl reference electrode were placed in 1 M KOH electrolyte and air-tight sealed in the chamber lid. The chamber electrolyte and headspace were flushed with N2 for 30 min before the photoanode (0.55cm-2 exposed area) at an applied potential of 1.23V vs RHE was illuminated at 100 mW cm-2 for 1 hour. Evolution of O2 was continuously monitored with the Pyroscience probe and the O2 generation rate used to calculate Faradaic efficiency.

**Faradaic efficiency calculation**

To calculate the Faradaic efficiency, first the amount of O2 evolved in the headspace of the PEC cell was calculated using the ideal gas law and measurements of the %O2 and O2 in the electrolyte solution was estimated using Henry’s law and added to the measured values in the headspace. Next, the theoretical amount of O2 expected for a water oxidation reaction with 100% Faradaic efficiency was calculated. The following equation (eq S1) was used:

𝑄=(𝑒‒)∗𝐹 (S1)

where *Q* is the charge in C, obtained from the photocurrent-time curve;  *n (e-)* is the number of electrons in mol; and F is the Faraday constant (96485.3329 C mol-1). The theoretical amount of O2 generated was calculated by dividing *n (e-)* by four, which is the number of electrons involved in the oxidation of water. Finally, the Faradaic efficiency was calculated by dividing the amount of O2 evolved in the headspace by the theoretical amount of O2 expected for 100% Faradaic efficiency (µmol / µmol x 100).