Electronic Supplementary Information

Foreign In^{3+} Treatment Improving Photoelectrochemical Performanc of Hematite Nanosheets Array for Water Splitting

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Scheme S1. Schematic illustration of photoelectrochemical cell for water splitting. When light is incident on the semiconductor photoanode, the absorption of the photons creates energetic electrons (e^-) and holes (h^+) in the photoanode. The photo-generated electrons and holes will then participate in the hydrogen evolution reaction at the cathode and the water oxidation reaction at the photoanode, respectively.

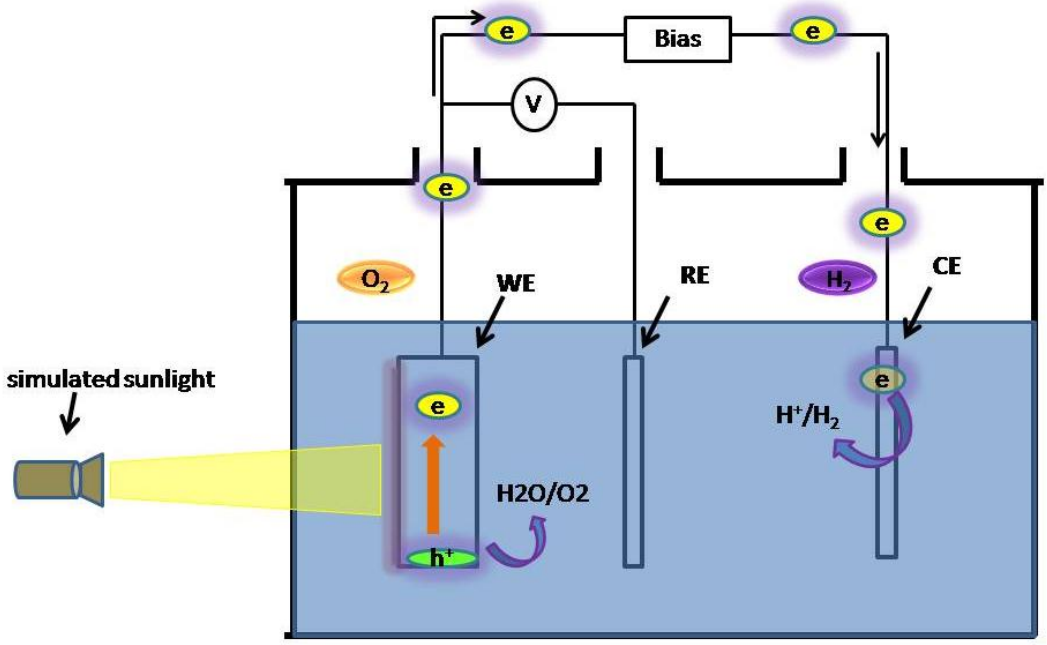
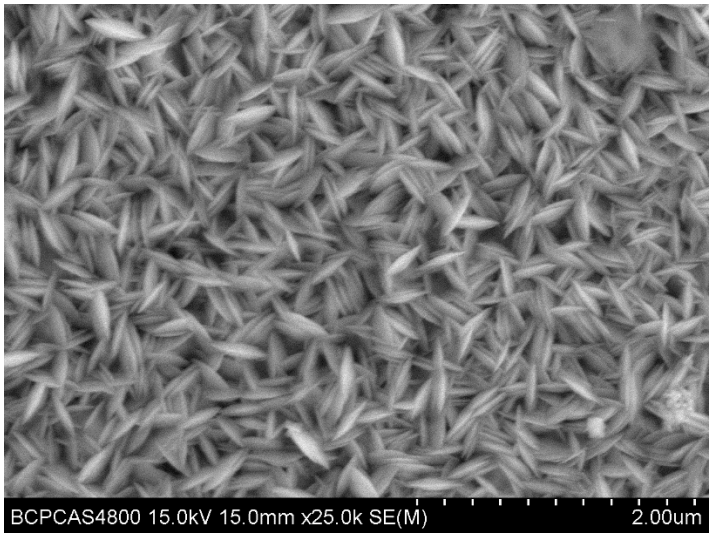


Figure S1. Low-amplification SEM images of the (a) untreated and (b) In-treated α-Fe_2O_3 nanosheets.

(a)



(b)

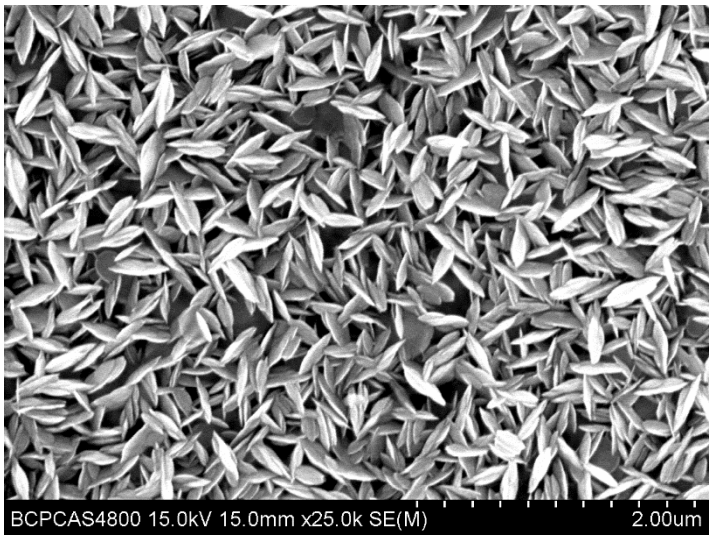


Figure S2. EDX spectra of (a) untreated and (b) In^{3+}-treated samples, which were prepared by hydrothermal reaction. The peaks of Sn, Si and Cl elements were most likely originated from the FTO layer and the glass substrate, respectively.

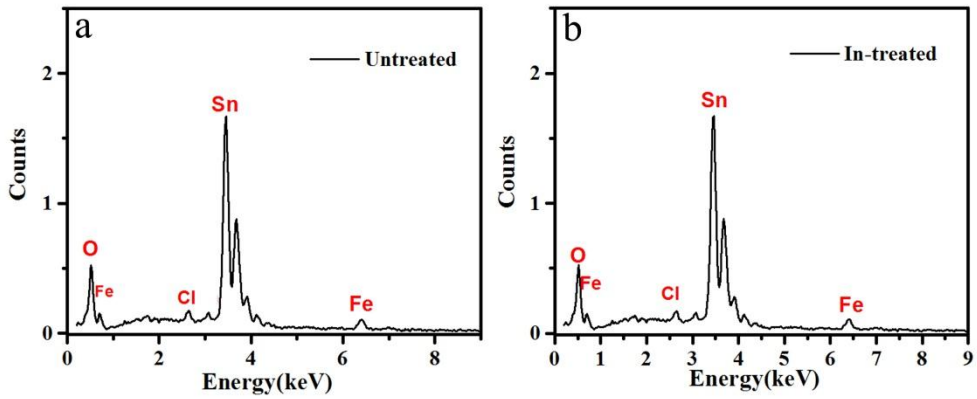


Figure S3. The SEM image (a) and (b) EDX spectrum of the Zn^{2+}-treated hematite sample, which was prepared by hydrothermal reaction for two times.

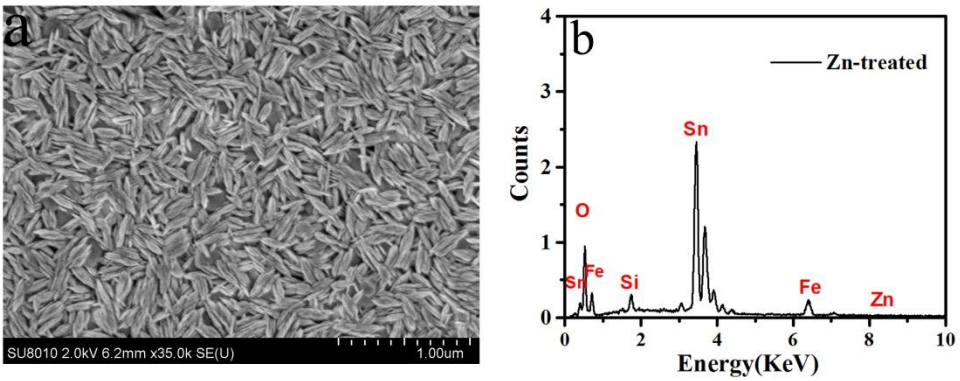


Figure S4. The SEM image (a) and (b) EDX spectrum of the Zr^{4+}-treated hematite sample, which was prepared by hydrothermal reaction for two times.

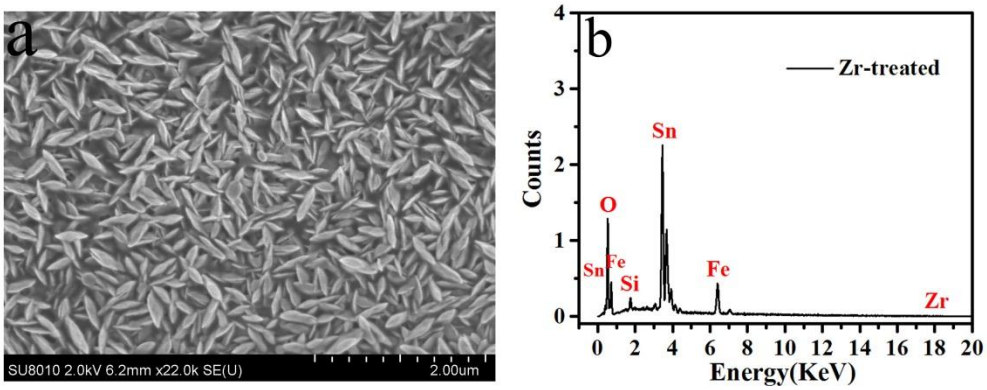


Figure S5. EDX spectra of (a) the untreated and (b) the In-treated Fe_2O_3 samples, which were obtained in the same conditions, except for choosing iron(III) chloride as the Fe source. The peaks of Si and Sn elements were most likely originated from the FTO glass.

It turns out when we replaced the potassium hexacyanoferrate () by iron(III) chloride as the Fe source, the In element was clearly detected in Fe_2O with In^{3+}-treatment.

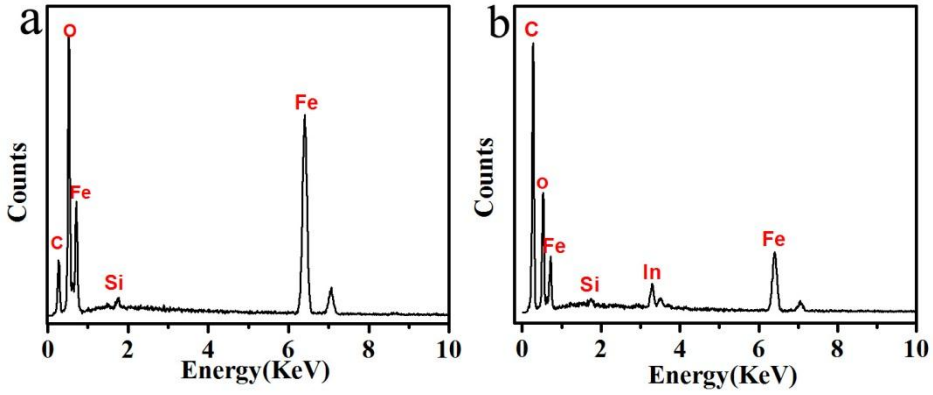


Figure S6. The SEM images of (a) the untreated and (b) the In^{3+}-treated samples, which were prepared by the hydrothermal reaction for one time.

(a)

(b)

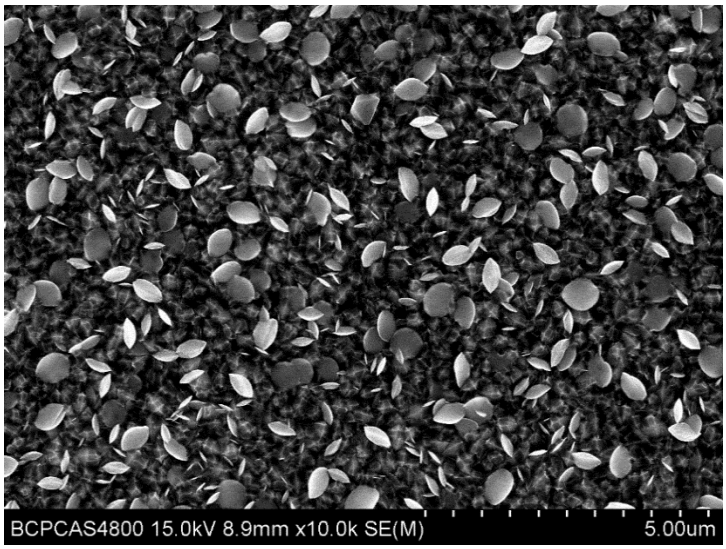


Figure S7. Scheme of hexagonal phase hematite crystal and the planes of (1 -1 0 0) and (1 1 -1/2 0)

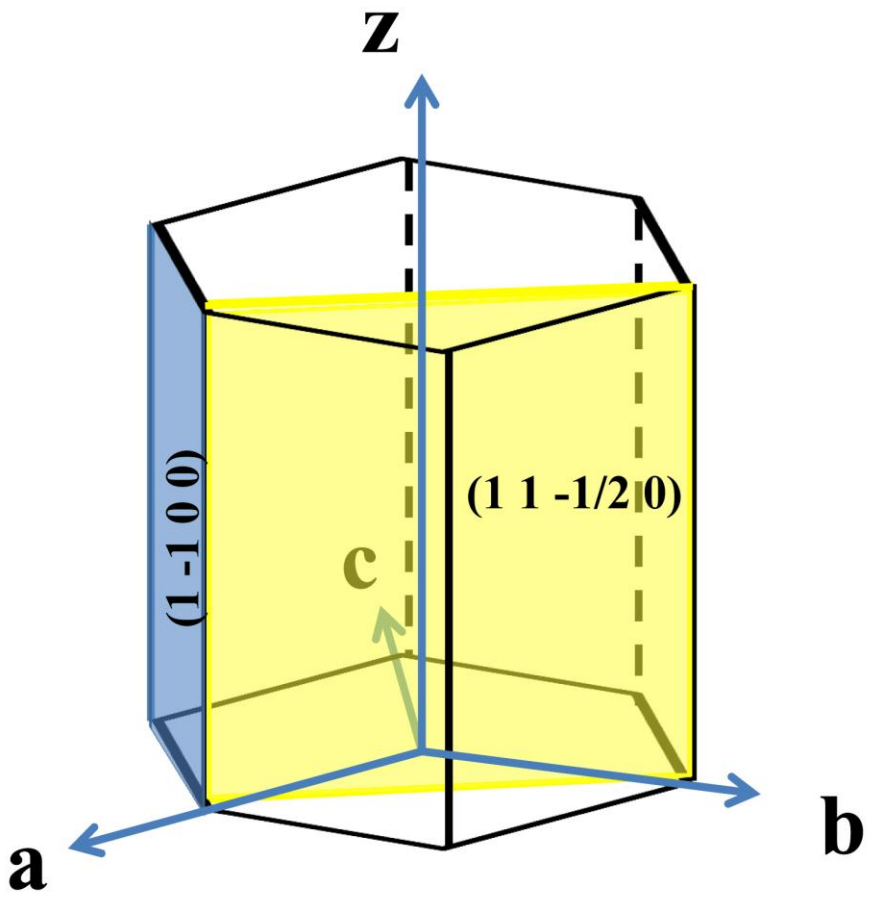


Figure S8. LSV curves for the samples that were prepared by more In source content: the molar ratios of In:Fe were 30% and 60% (under the irradiation of 100 mW cm^{-2})

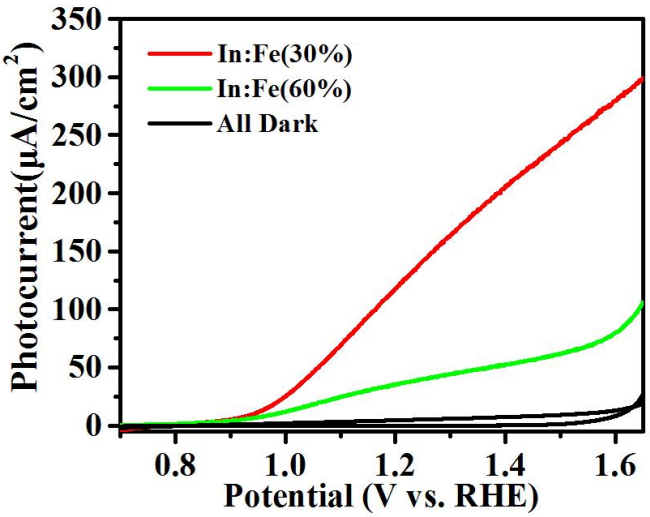


Figure S9. UV-vis spectrum of the In-treated photoanode loaded with Co-Pi

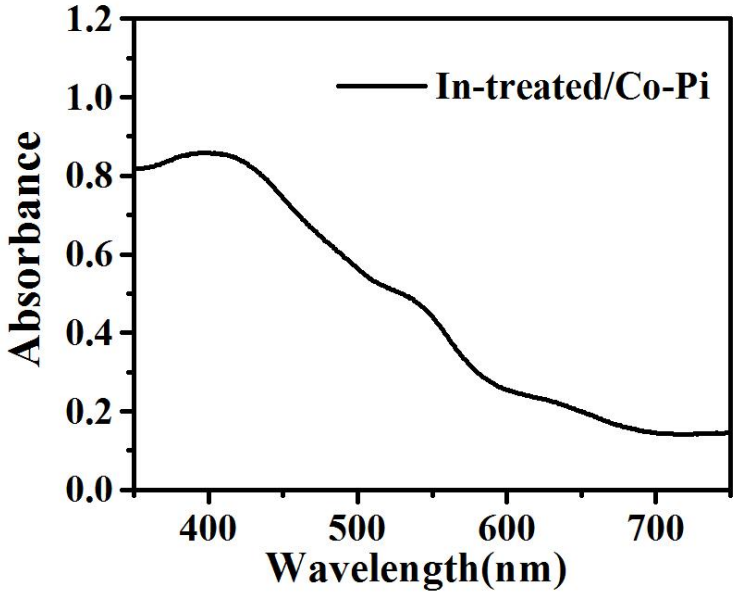


Figure S10. XRD patterns for the samples that were prepared by more In source content: the molar ratios of In:Fe were 30% and 60%. The unmarked peaks are all attributed to SnO_2 in FTO substrate.

The patterns shows that when more In source exceeding 30 % was added in the precusor solution, the mixure of In_2O_3 and Fe_2O_3 grew on the FTO substrate rather than pure Fe_2O_3 or In^{3+}-doped Fe_2O_3.

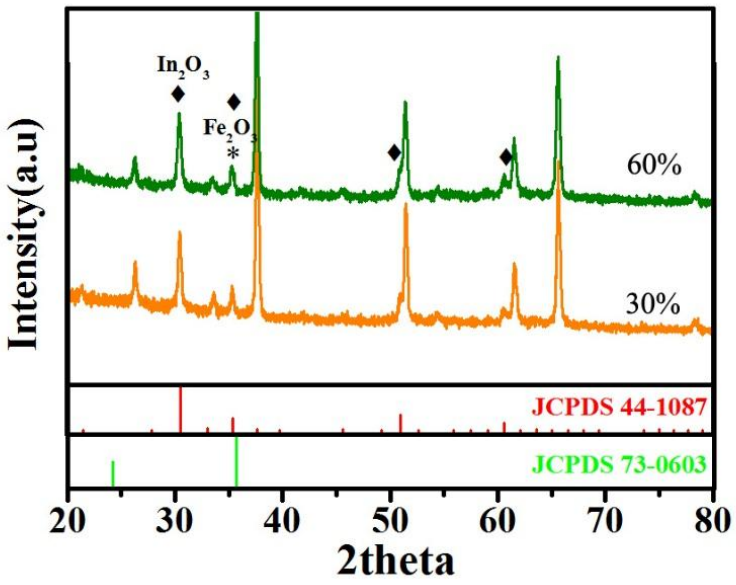


Figure S11. Cyclic voltammetry curves at various scan rates (10, 20, 40, 60, 80, 100, 120 mV/s) of (a) the untreated sample in the range of 0.926-1.026V vs. RHE. (b) Charging current density differences ($\Delta J=J_a-J_c$) plotted against scan rates of the untreated sample. The linear slope, equivalent to twice the electrochemical double-layer capacitance (C_{dl}) was used to represent the electrochemical active surface area(ECSA). ΔJ was measured at 0.976 V vs. RHE. The C_{dl} can be calculated to be ~ 100.9 $\mu F/cm^2$.

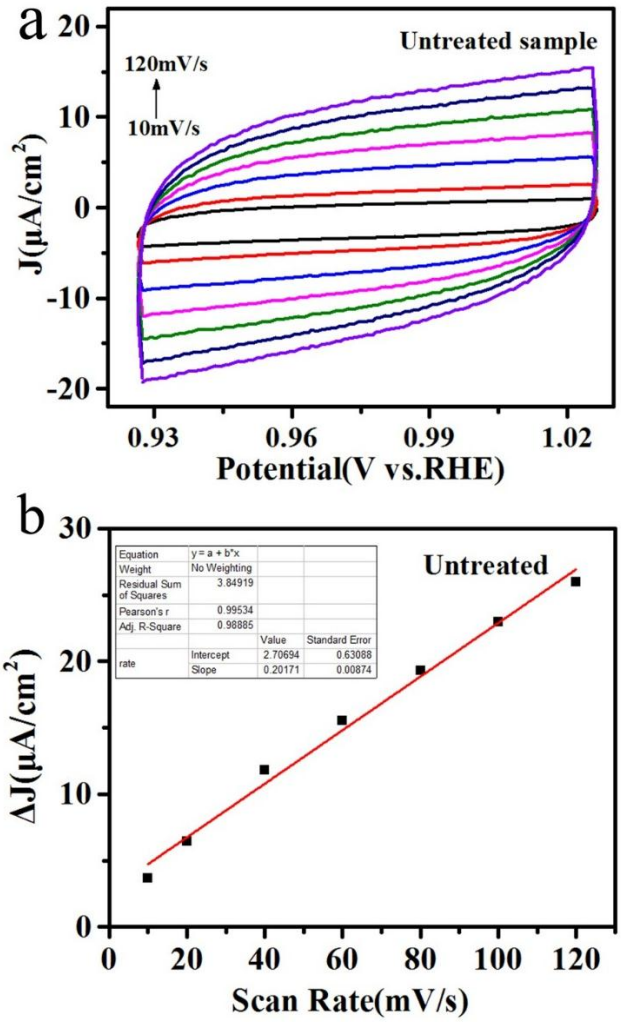


Figure S12. Cyclic voltammetry curves at various scan rates of (a) In-treated sample in the range of 0.926-1.026V vs. RHE. (b) Charging current density differences ($\Delta J=J_a-J_c$) plotted against scan rates of the untreated sample. The calculated C_{dl} of the untreated sample was ~ 128.9 μF/cm^2.

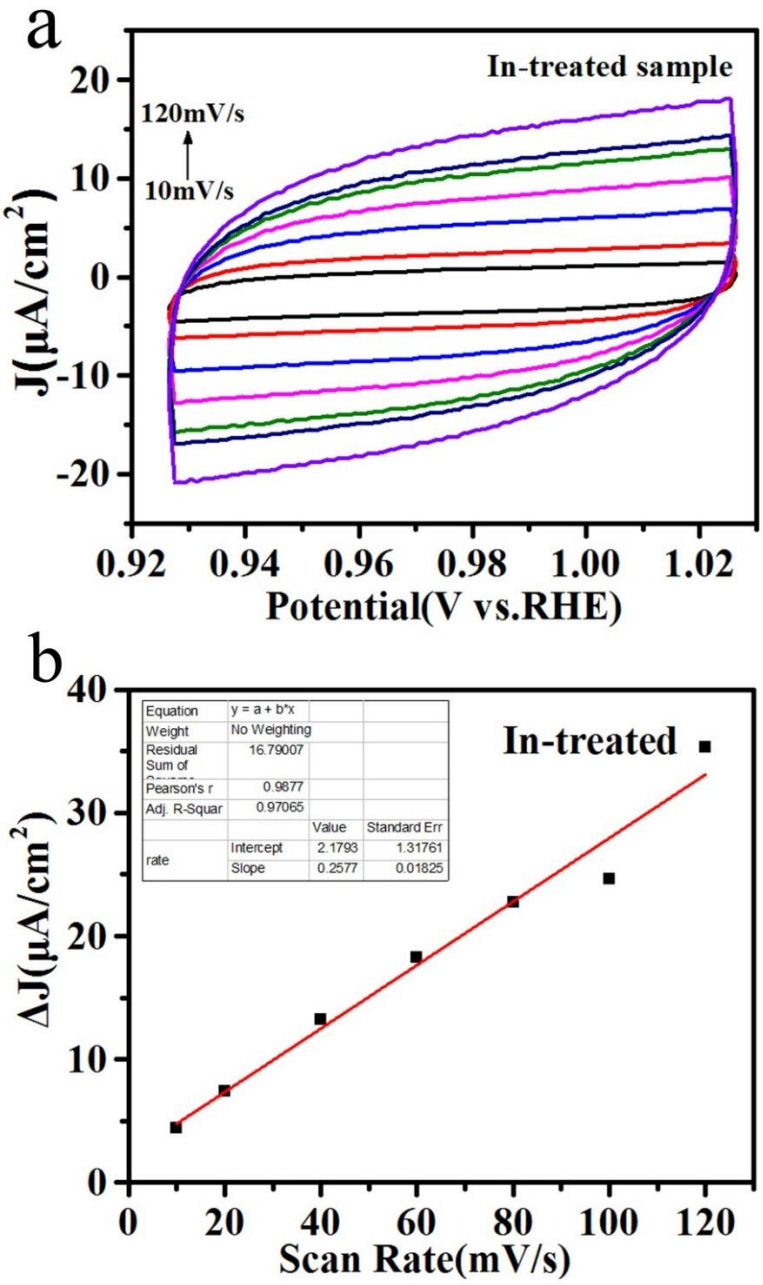
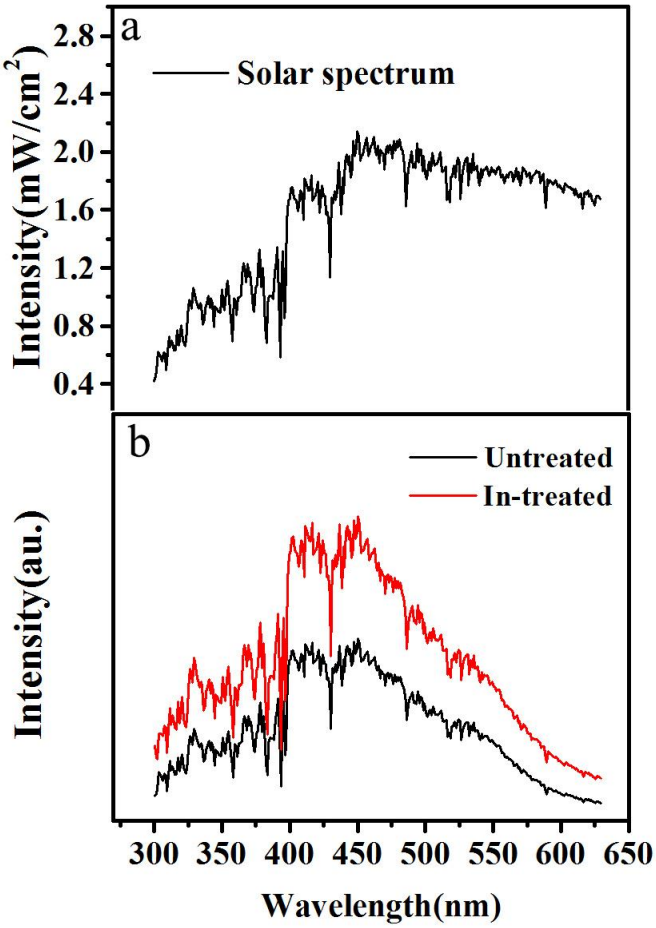


Figure S13. (a) solar spectrum in the wavelength range of 300-625 nm (AM 1.5G); (b) adsorption spectra integrated over solar spectrum for the untreated and In-treated hematite photoanodes between 300 and 625 nm wavelength.



The calculation of overall faradaic efficiency for oxygen evolution:[1]

(1). The oxygen generated over 4.5h from the PEC cell for In-treated hematite photoanode was ~25.91μmol/cm^2. The average photocurrent density was ~0.60 mA/cm^{-2}.

Total generated electrons (N/cm^2): $(0.60 \times 10^{-3} A \times 1.62 \times 10^4 s) / (1.6 \times 10^{-19})$ (1)

Total electrons for oxygen generation (N/cm^2): $25.91 \times 10^{-6} \times 6.02 \times 10^{23} \times 4$ (2)

Faradaic efficiency= (2)/(1) ×100% ≈ 100%. (3)

(2). The oxygen generated over 4.5h from the PEC cell for untreated hematite photoanode was ~7.18μmol/cm^2. The average photocurrent density was ~0.18 mA/cm^{-2}.

Total generated electrons (N/cm^2): $(0.18 \times 10^{-3} A \times 1.62 \times 10^4 s) / (1.6 \times 10^{-19})$ (4)

Total electrons for oxygen generation (N/cm^2): $7.18 \times 10^{-6} \times 6.02 \times 10^{23} \times 4$ (5)

Faradaic efficiency= (5)/(4) ×100% ≈ 94.97%. (6)

References:

1. Shi, X.; Choi, I. Y.; Zhang, K.; Kwon, J.; Kim, D. Y.; Lee, J. K.; Oh, S. H.; Kim, J. K.; Park, J. H., Efficient photoelectrochemical hydrogen production from bismuth vanadate-decorated tungsten trioxide helix nanostructures. *Nat. Commun.* **2014,** 5, 4775.