Supporting information

Boosting the Efficiency of Water Oxidation via Surface States on Hematite Photoanodes by Incorporating Bi^{3+} ions

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Table S1: Areas of deconvoluted peaks (%) obtained from the fitting of O 1s XPS spectra of bare hematite (BH) and Bi-incorporated hematite (Bi-H).

Film	Lattice Oxygen (%)	Oxygen Vacancies (%)	Surface Adsorbed Oxygen Species (%)
BH	65.5	24.0	11.5
Bi-H	60.5	29.0	10.5

Table S2: Donor densities (N_d) of bare hematite (BH) and Bi-incorporated hematite (Bi-H) electrodes measured at different frequencies (i.e. 0.1 kHz and 1.0 kHz).

Electrode	N_d at 0.1 kHz (10^{17} cm^{-3})	N_d at 1.0 kHz (10^{17} cm^{-3})
BH	6.65	4.64
Bi-H	9.90	6.61

Table S3: Computed lattice constants, Fe-O bond lengths, magnetic moment of iron atoms, and bandgap for bare hematite and Bi-incorporated hematite.

Parameter	Bare hematite	Bi-incorporated Hematite	Reported values for bare hematite	
Lattice constants				
a = b (Å)	5.120	5.146	5.04	[1]
c (Å)	13.89	13.91	13.75	[1]
Fe-O bond length (Å)	1.99, 2.13		1.94, 2.11	[1]
μ_{Fe} magnetic moment (μ_B)	4.28		4.6 9	[2]
Bandgap energy E_g (eV)	2.12		2.2 10	[3]

Table S4: PEIS fitting parameters and global errors (X^2) for bare hematite (BH) photoanode.

Potential Vs. RHE	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	CPE_{total} ($\times10^{-5}$F s^{a-1})	a	C_{ss} ($\times10^{-5}$ F)	R_1/R_2	X^2
0.8	756	610	44551	1.51	0.76	1.64	0.01	0.03
0.9	671	459	8321	2.10	0.65	5.37	0.06	0.02
1.0	566	550	1826	4.23	0.54	7.10	0.30	0.01
1.1	540	666	720	3.52	0.55	7.10	0.93	0.01

Table S5: PEIS fitting parameters and global errors (X^2) for Bi-incorporated hematite (Bi-H) photoanode.

Potential Vs. RHE	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	CPE_{total} ($\times10^{-7}$ F s^{a-1})	a	C_{ss} ($\times10^{-5}$ F)	R_1/R_2	X^2
0.8	283	1408	9268	7.63	0.78	3.97	0.15	0.04
0.9	289	1346	3549	6.15	0.80	5.89	0.38	0.02
1.0	287	1299	1828	8.02	0.78	6.87	0.71	0.02
1.1	275	1400	1176	11.9	0.76	5.34	1.19	0.03

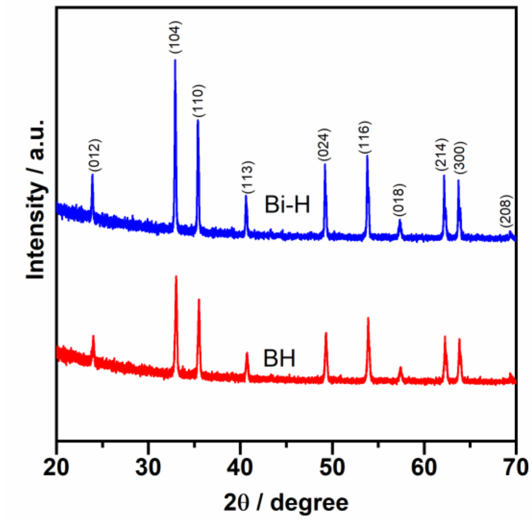

Figure S1. XRD patterns of bare hematite (BH) and Bi-incorporated hematite (Bi-H) powders.

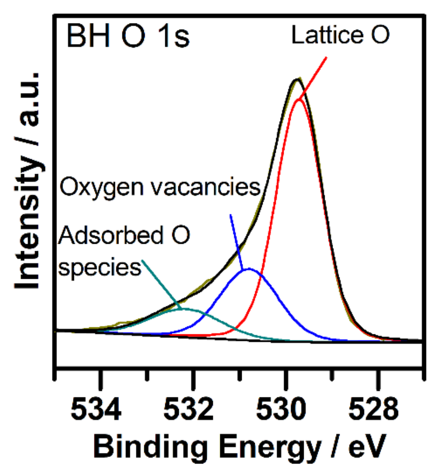

Figure S2. Deconvoluted O 1s XPS spectrum of bare hematite (BH) film.

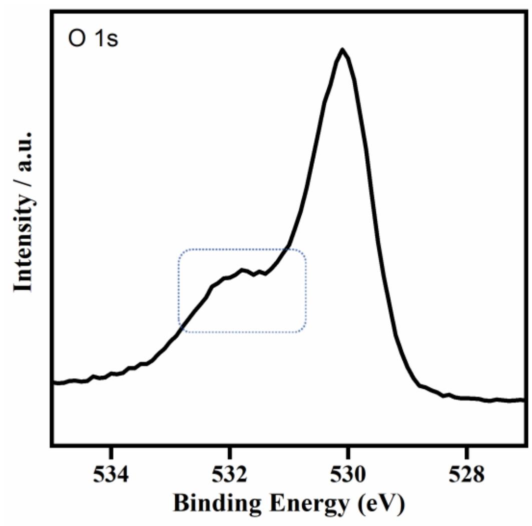

Figure S3. XPS spectrum of O 1s core-level of hydrogen-treated hematite film at 350 ºC for 1 h (10 % H_2, 90 % Ar, flow rate 50 ml min^{-1}).

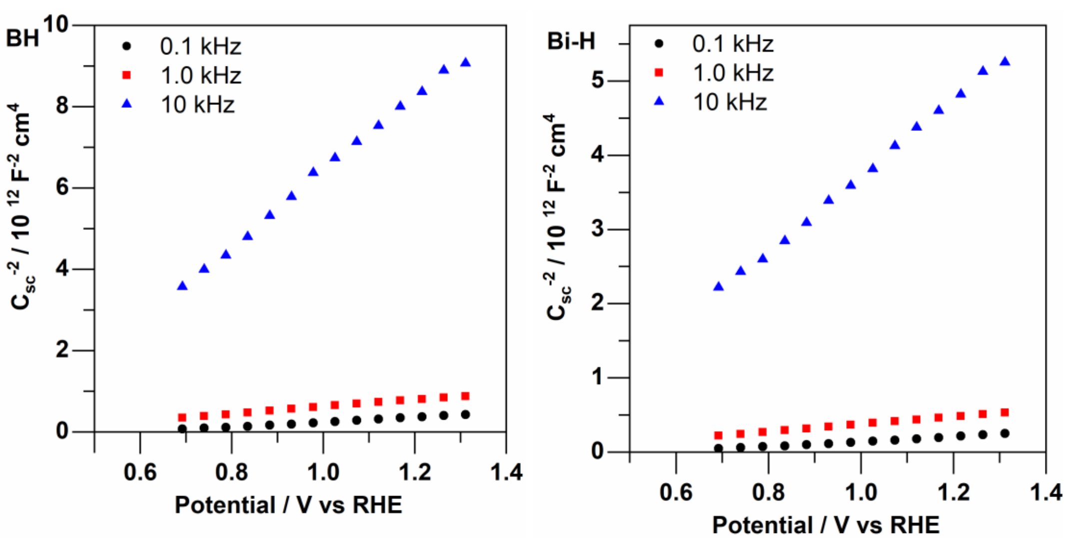

Figure S4. Mott-Schottky plots of bare hematite (BH) and Bi-incorporated hematite (Bi-H) electrodes measured at different frequencies in the dark in an aqueous solution of 1.0 M NaOH.

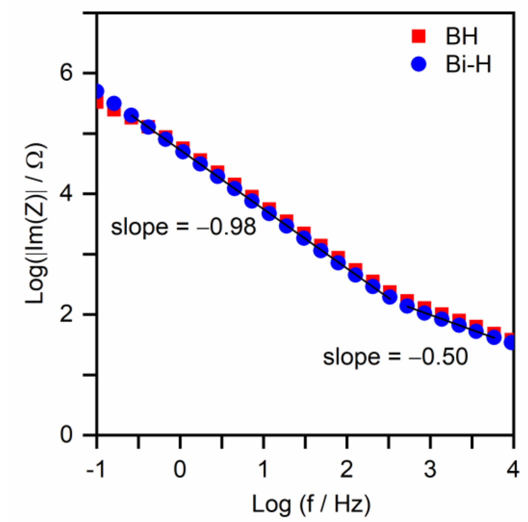

Figure S5. Bode plot for BH and Bi-H electrodes measured at 1.0 V_{RHE}.

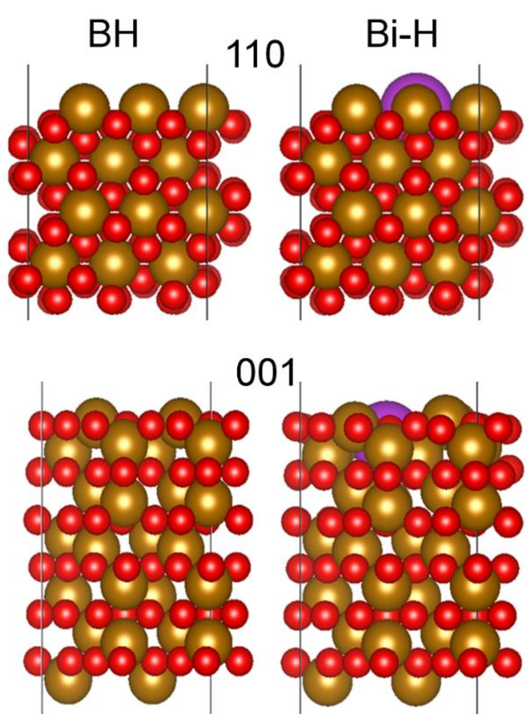

Figure S6. Slabs of bare hematite (BH) and Bi-incorporated hematite (Bi-H) used for the calculation of the formation surface energies of (001) and (110) surfaces.

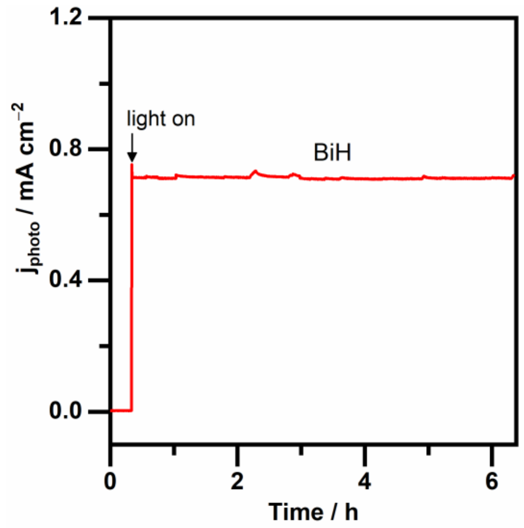

Figure S7. Chronoamperometry curve measured for Bi-incorporated hematite (Bi-H) photoanode under standard illumination in 1.0 NaOH at 0.53 V vs. Pt.

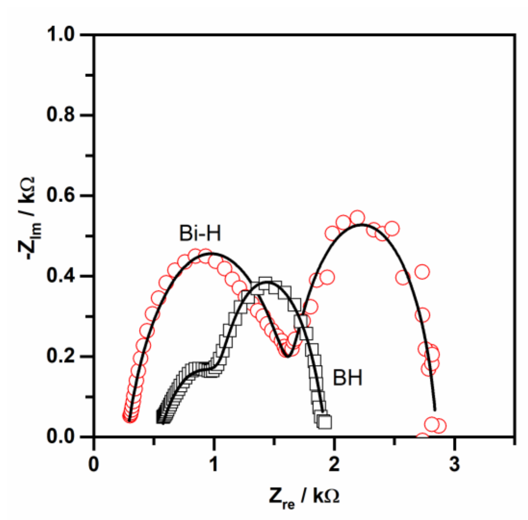

Figure S8. Nyquist plots of bare hematite (BH) and Bi-incorporated hematite (Bi-H) photoanodes measured at 1.1 V vs RHE under illumination (1.0 sun, AM 1.5 G) in 1.0 M NaOH.

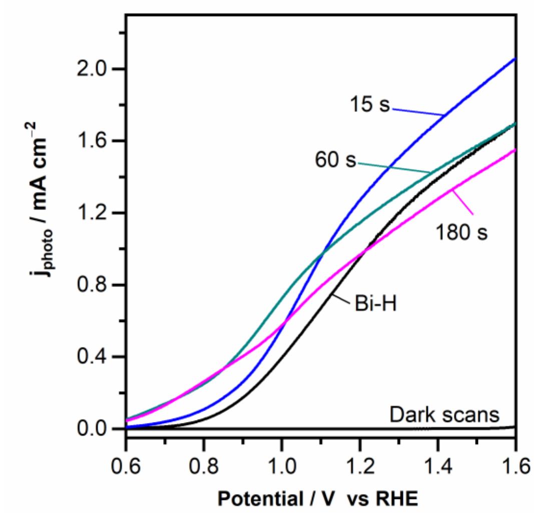

Figure S9. Effect of Co-Pi photo-assisted deposition time on the photoelectrochemical activity of Bi-incorporated hematite photoanodes. Potential (0.4 V vs Ag/AgCl); Illumination conditions (AM 1.5 G, 1.0 sun); Electrolyte (1.0 M aqueous solution of NaOH).

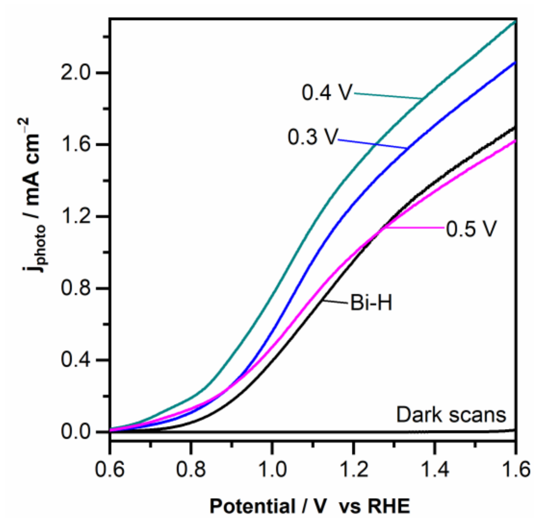

Figure S10. Effect of Co-Pi photo-assisted deposition potential on the photoelectrochemical activity of Bi-incorporated hematite photoanodes. Deposition time (15 s); Illumination conditions (AM 1.5 G, 1.0 sun); Electrolyte (1.0 M aqueous solution of NaOH).

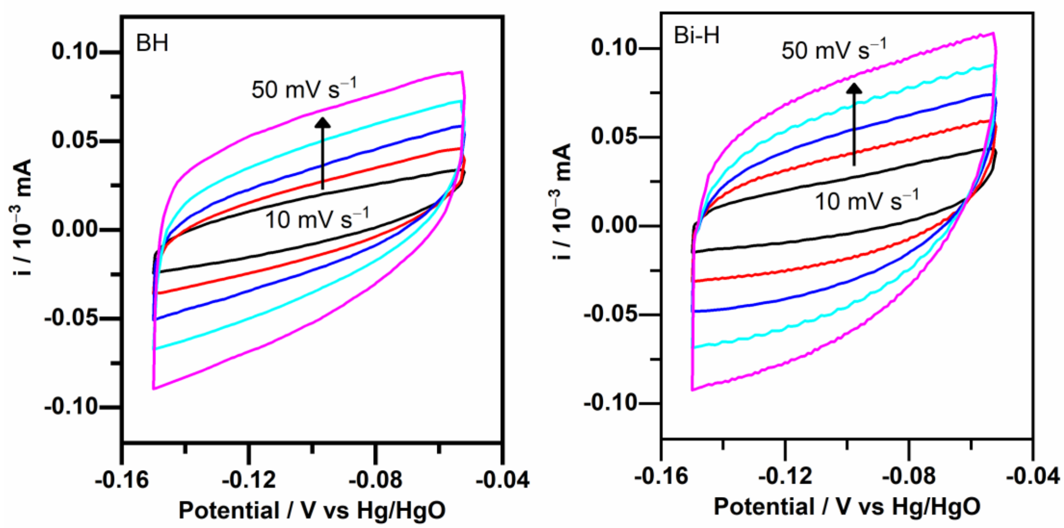

Figure S11. CV curves recorded at different scan rates (i.e. 10, 20, 30, 40, and 50 mV s^{-1}) for bare hematite (BH) and Bi-incorporated hematite (Bi-H) electrodes.

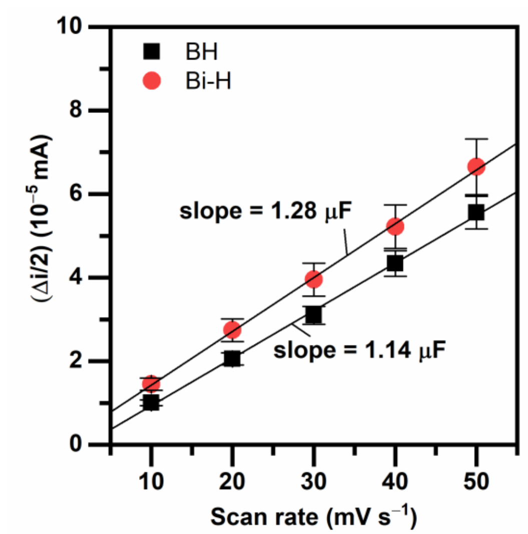

Figure S12. Average capacitive current against scan rate for BH and Bi-H electrodes.

References

[1] L.W. Finger, R.M. Hazen, J. Appl. Phys., 51 (1980) 5362-5367.
[2] J.M.D. Coey, G.A. Sawatzky, Journal of Physics C: Solid State Physics, 4 (1971) 2386-2407.
[3] B. Gilbert, C. Frandsen, E.R. Maxey, D.M. Sherman, Physical Review B, 79 (2009) 035108.

End of supporting information