

## Supporting Information

### **Optimization of charge transport in a Co-Pi modified hematite thin film produced by a scalable electron beam evaporation for photoelectrochemical oxidation of water**

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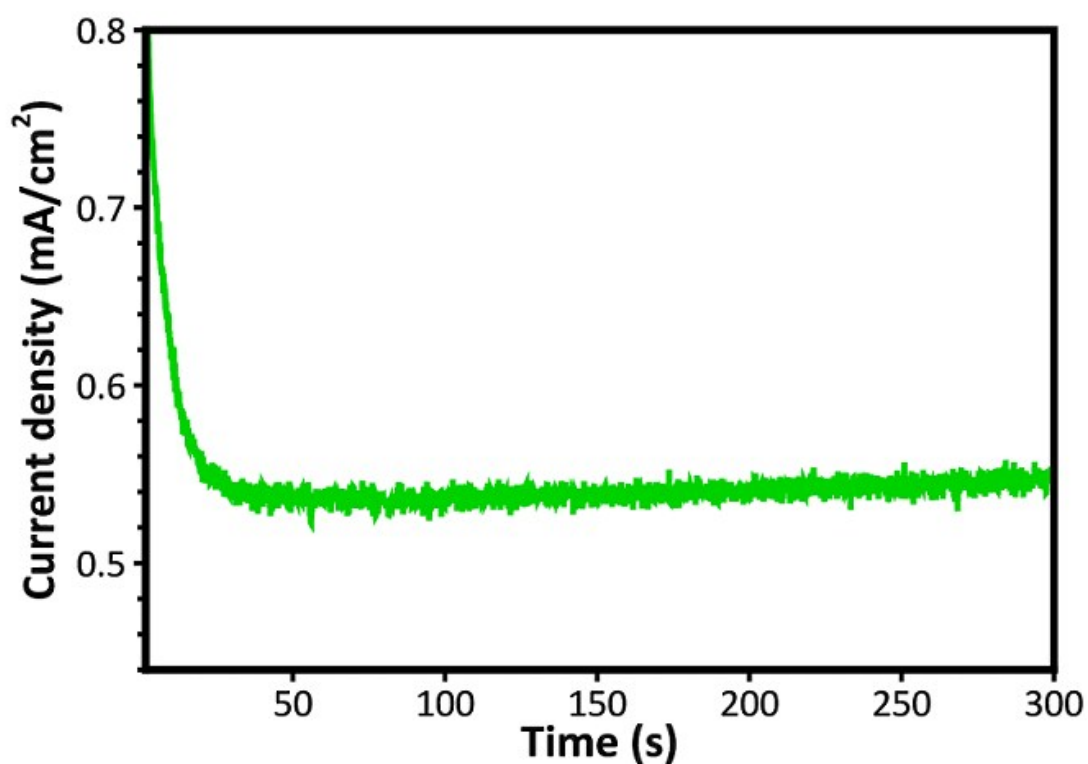
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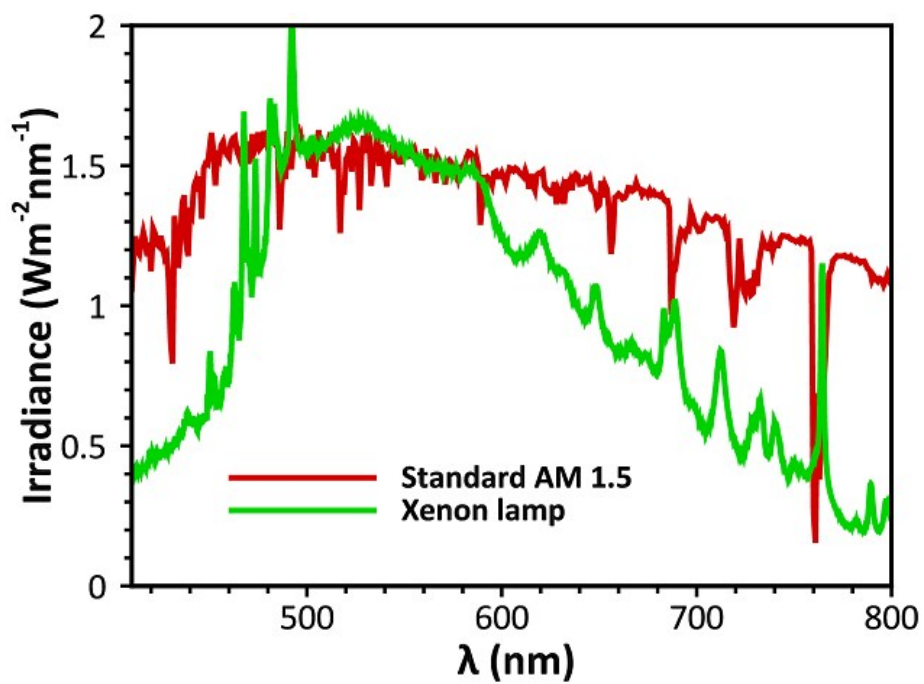
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## Co-Pi modification of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin films

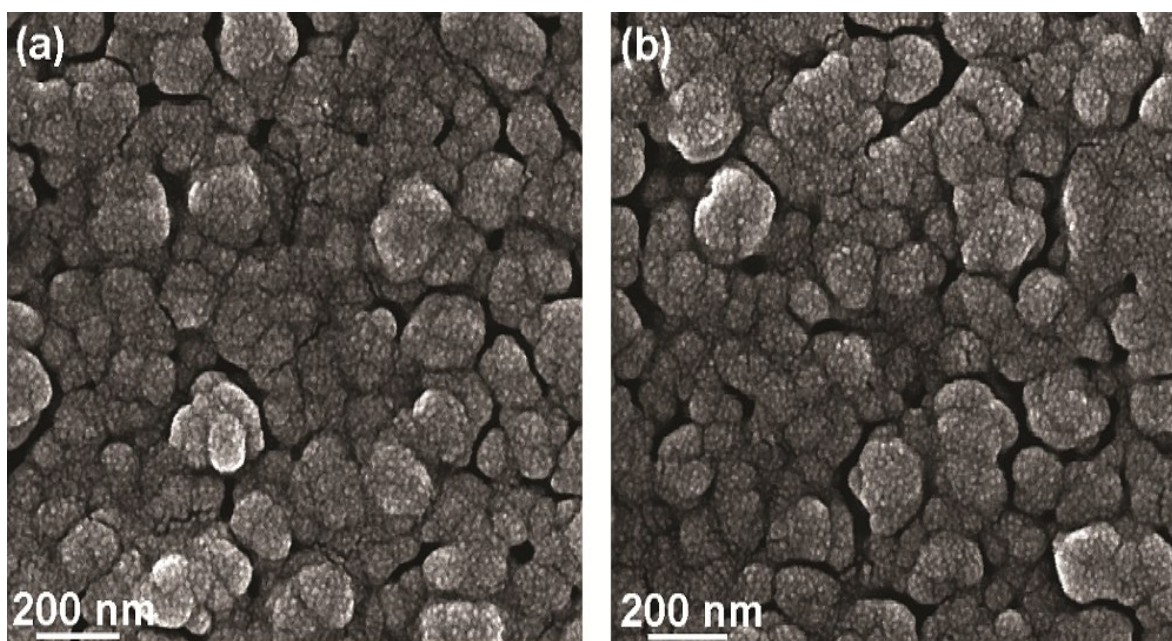
For surface modification of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin films, Co-Pi catalyst is deposited onto  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes by photo-assisted electrodeposition under light illumination by a Xenon lamp through the FTO side. All Co-Pi depositions are carried out in a three-electrode cell at a constant voltage of  $V=0.9$  vs Ag/AgCl inside a solution of 0.5 mM cobalt nitrate and 0.1 M potassium phosphate buffer at pH 7. A Pt wire is used as the counter electrode, and saturated Ag/AgCl is used as the reference electrode. Co-Pi is electrodeposited on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film set as the working electrode and the thickness of the deposited film is controlled by varying the duration of deposition. As shown in Fig. S1, typical current density during the deposition is about 540 ( $\mu$ A/cm<sup>2</sup>).



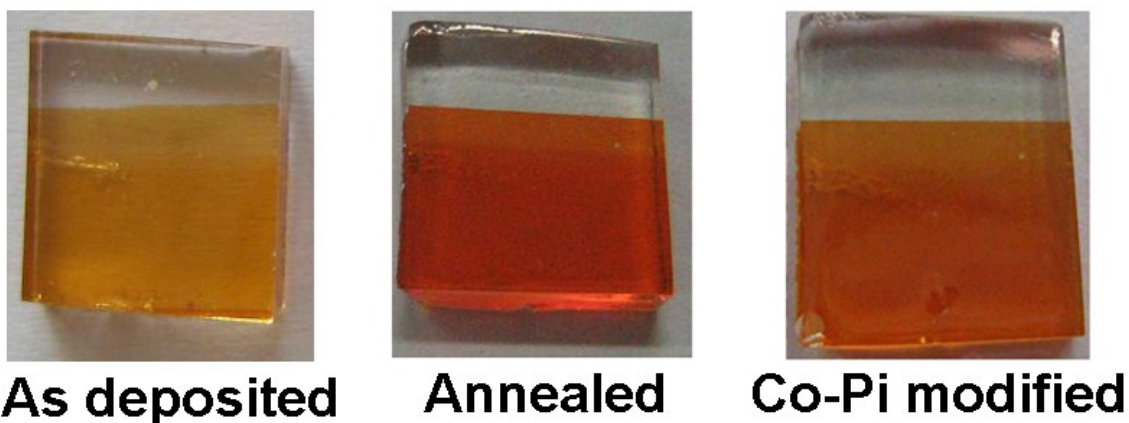
**Fig. S1.** Typical current density during Co-Pi electrodeposition on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode at the bias voltage of 0.9 V vs Ag/AgCl in 0.1 M KPi buffer with pH= 7, for 5 min.



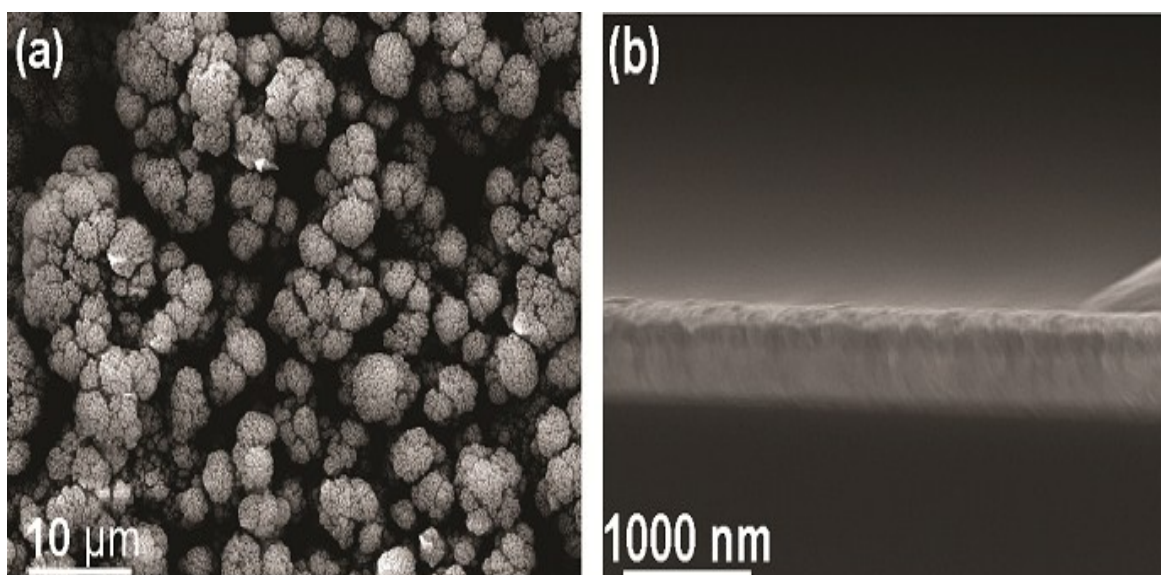
**Fig. S2.** Spectral irradiance of the standard AM1.5 (red) and the used xenon lamp solar simulator (green) irradiance as a function of wavelength.



**Fig. S3.** Scanning electron micrographs of  $\alpha\text{-Fe}_2\text{O}_3$  thin film before (a) and after (b) annealing at 600 °C for 4 h.



**Fig. S4.** Photographs of different samples including the bare hematite thin film with the thickness 175 nm before and after annealing process and the Co-Pi modified hematite photoelectrode. Immediately after synthesis, the hematite film appears dark yellow, but upon annealing at 600 °C, the color of the films changes to reddish orange. Co-Pi surface modification makes the reddish orange film to become gloomy.



**Fig. S5.** Scanning electron micrographs of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film modified by 5 min Co-Pi electrodeposition showing (a) top view, (b) cross view.

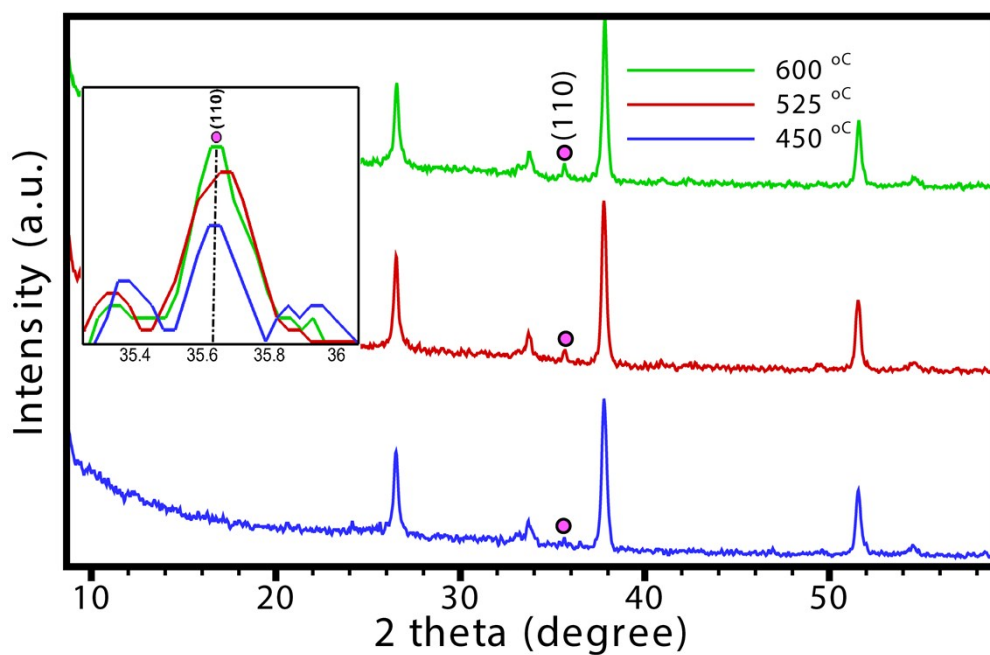


Fig. S6. XRD patterns of the hematite thin film with thickness of 175 nm annealed at different temperatures.

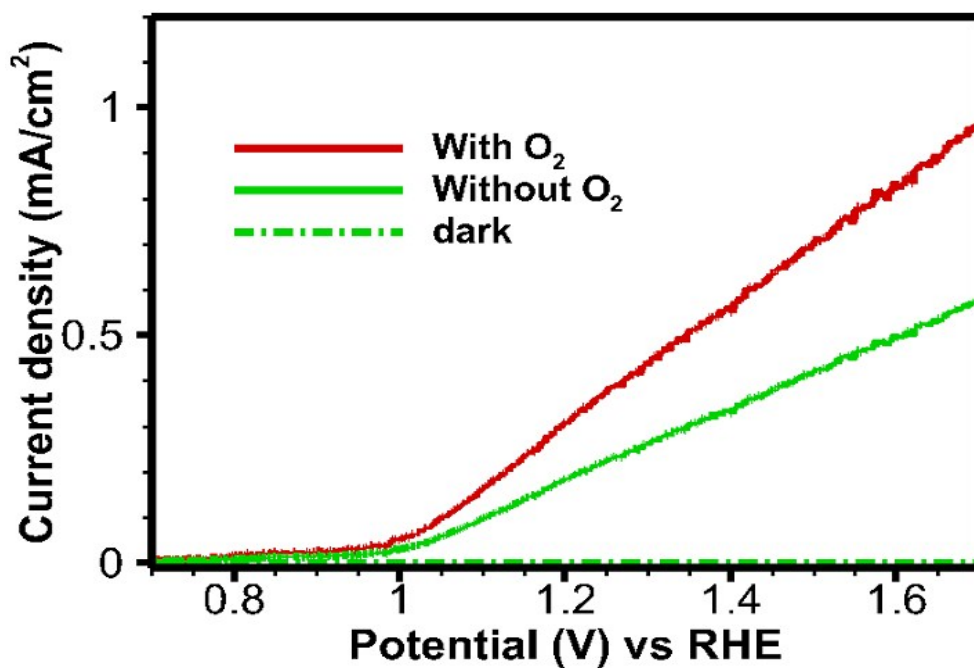


Fig. S7. photocurrent vs voltage of hematite films of thickness 150 nm and deposited with or without O<sub>2</sub> flow during the deposition.

## Cyclic voltammetry measurements of the bare and the Co-Pi deposited hematite photoanode

Cyclic voltammetry measurements of the bare and the Co-Pi deposited samples during 5 cycles have been shown in Fig. S8. The results indicate that the photocurrent in both Co-Pi and bare samples represent stable and steady state behaviors for both anodic and cathodic sweeps.

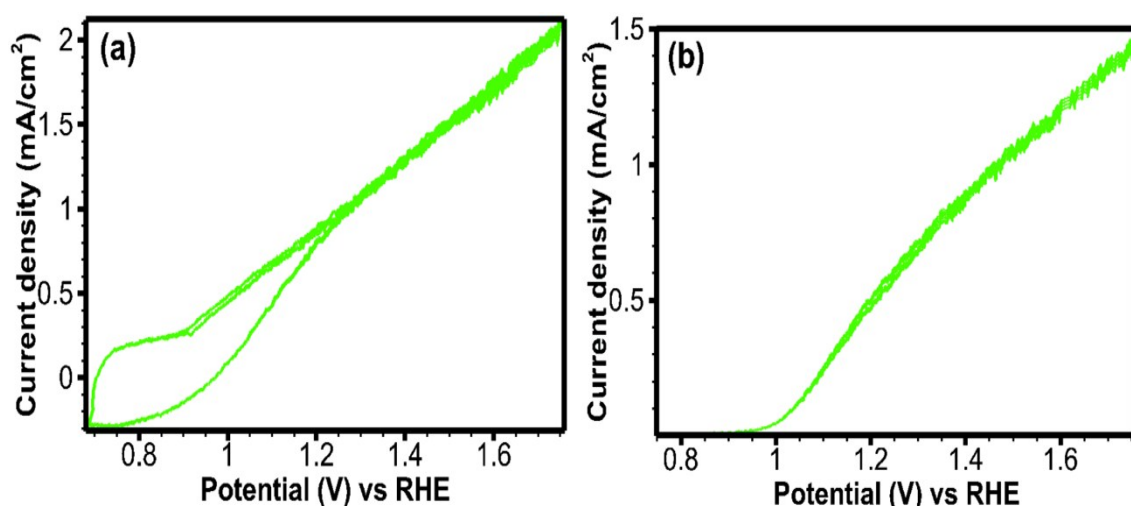
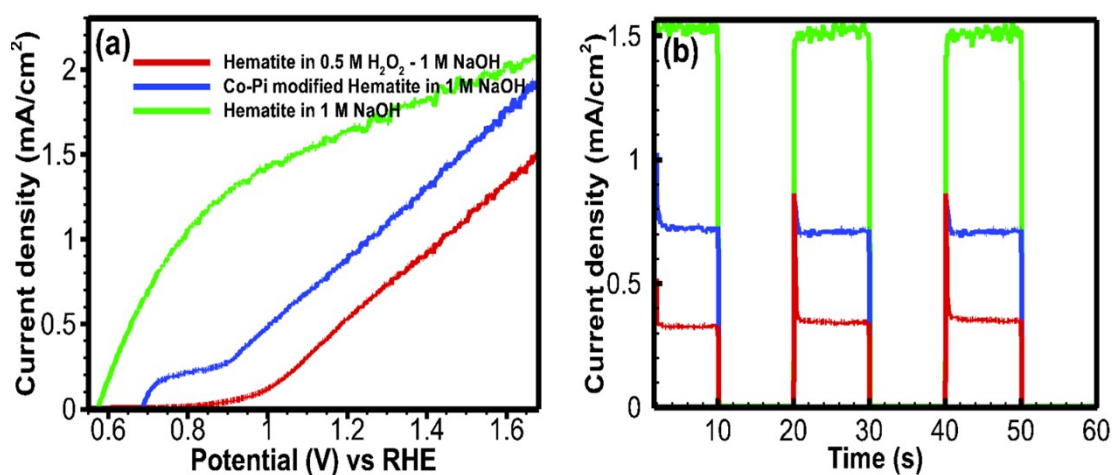


Fig. S8. Cyclic voltammetry of (a) Co-Pi modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (b) bare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes for 5 cycle of bias sweeping.

## Photocurrent measurements of bare hematite films under addition of 0.5M H<sub>2</sub>O<sub>2</sub> into the NaOH electrolyte

H<sub>2</sub>O<sub>2</sub> acts as a hole scavenger in this case by more taking holes from hematite and suppressing the electron-hole recombination at the interface. Because of the more negative reduction potential of H<sub>2</sub>O<sub>2</sub> (+0.68V) relative to H<sub>2</sub>O (1.23V), H<sub>2</sub>O<sub>2</sub> has a much higher oxidation rate than H<sub>2</sub>O and can be used as a suitable replacement for H<sub>2</sub>O to overcome the weakness of hematite in slow oxidation kinetics.<sup>1</sup>



**Fig. S9.** Steady state photocurrent density (a) and photocurrent-time (b) of bare hematite photoanode in either 1 M NaOH–0.5 M H<sub>2</sub>O<sub>2</sub> (green curve) or 1 M NaOH (red curve) and Co-Pi modified hematite in 1 M NaOH (blue curve). These tests are based on this assumption that oxidation kinetic activity of H<sub>2</sub>O<sub>2</sub> is faster than NaOH. For this reason, the charge transfer across the semiconductor/electrolyte is more efficient for 0.5 M H<sub>2</sub>O<sub>2</sub>-1 M NaOH electrolyte than 1 M NaOH one. This leads to elimination of surface charge recombination and ideal behavior in chronoamperometry measurements as seen in the figure.

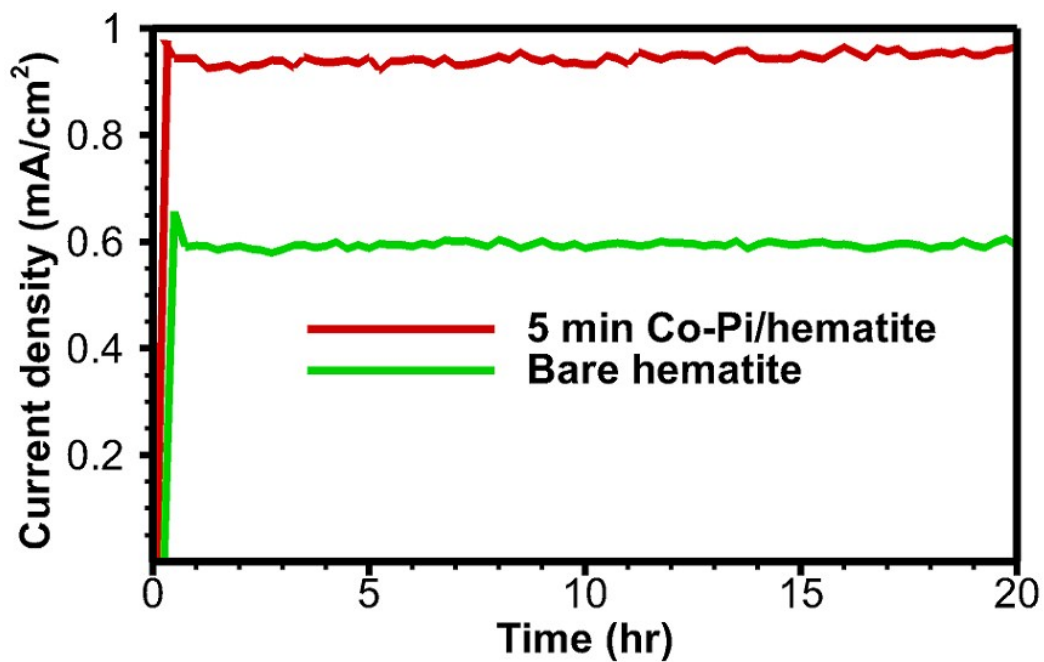


Fig. S10. Stability of water oxidation current in pH 13 for both bare and 5-min Co-Pi deposited hematite photoanodes during 20 hours of light illumination at  $V=1.23$  V (vs RHE).

## References

[S1]. Dotan, H.; Sivula, K.; Grätzel, M.; Rothschild, A.; Warren, S. C., Probing the photoelectrochemical properties of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) electrodes using hydrogen peroxide as a hole scavenger. *Energy & Environmental Science* **2011**, 4 (3), 958-964.