## Nanostructured Fe<sub>2</sub>O<sub>3</sub>/Cu<sub>x</sub>O Heterojunction for Enhanced Solar Redox Flow Battery Performance

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Photoanode	Redox couples	j (mA/cm²)	STC	SOEE
P/Cu <sub>x</sub> O (This work)	Na <sub>4</sub> Fe(CN) <sub>6</sub> in NaOH/ AQDS in NaOH	0.46	0.35%	0.18%
α-Fe <sub>2</sub> O <sub>3</sub> porous NPs <sup>1</sup>	Na <sub>4</sub> Fe(CN) <sub>6</sub> in NaOH/ AQDS in NaOH	0.22	0.17%- 0.23%	0.11%
Polyaniline coated $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> thin-film <sup>2</sup>	ated $Na_4Fe(CN)_6$ in NaOH/ AQDS in NaOH $0.0$		0.03%	
α-Fe <sub>2</sub> O <sub>3</sub> thin-film/ DSSC <sup>3</sup>	I <sub>2</sub> in NH <sub>4</sub> I/ AQDS in NH <sub>4</sub> I	0.03	0.03%	
		0.18	0.15%	
α-Fe <sub>2</sub> O <sub>3</sub> thin-film/ DSSC <sup>4</sup>	Na <sub>4</sub> Fe(CN) <sub>6</sub> in NaOH/	0.04	0.03%	
	AQDS in NaOH	0.39	0.29%	0.15%
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanocubes/ DSSC <sup>4</sup>	Na₄Fe(CN) <sub>6</sub> in NaOH/ AQDS in NaOH	0.04	0.03%	
		1.36	1%	0.44%

### Supporting Information 1 – Comparison of hematite SRFBs performance

Table S1. Solar Redox Flow Cell based on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode reported in literature and their performance, including photocurrent density, solar-to-chemical efficiency (STC) and solar-to-output energy efficiency (SOEE). Cells filled in grey refer to performance of dye-sensitized-solar-cell (DSSC) assisted devices while white cells refer to unassisted devices.



### Supporting Information 2 – Schematic of samples preparation

**Figure S1.** (a) Schematic of the synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Cu<sub>x</sub>O film photoanodes; (b) Schematic of the synthesis process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopillar array; (c) Schematic of the synthesis of nanostructured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Cu<sub>x</sub>O photoanode. All the materials were sputtered on the ITO substrate.

Sample type	Sputtered Fe (nm)	Sputtered Cu (nm)	NaOH	Annealing	Sample
Planar Fe <sub>2</sub> O <sub>3</sub>	15	0	NO	YES	15F
	30	0	NO	YES	30F
	50	0	NO	YES	50F
Planar Fe <sub>2</sub> O <sub>3</sub> -CuO	15	30	NO	YES	15/30 F-CuO
Planar Fe <sub>2</sub> O <sub>3</sub> -Cu <sub>x</sub> O	15	30	YES	YES	15/30 F-Cu <sub>x</sub> O
	30	30	YES	YES	30/30 F-Cu <sub>x</sub> O
	50	30	YES	YES	50/30 F-Cu <sub>x</sub> O
Nanopatterned Fe <sub>2</sub> O <sub>3</sub>	30	0	NO	YES	P100 P150 P200
Nanostructured Fe <sub>2</sub> O <sub>3</sub>	30	0	NO	YES	Р
Nanostructured Fe <sub>2</sub> O <sub>3</sub> -Cu <sub>x</sub> O	30	30	YES	YES	P/Cu <sub>x</sub> O

Table S2. Summary of sample preparation process.



#### Supporting Information 3 – Schematic of SRFB structure

Figure S2. Schematic of the SRFB used in this work, CE1 and CE2 are carbon felt 1 and carbon felt 2.

This integrated SRFB system consists of one photoelectrode and two carbon felt electrodes. For the twoelectrode test, the photoanode in the anolyte was used as the working electrode, with a 39 AA carbon felt in the catholyte serving as the counter electrode (CE2). In the photocharge-discharge tests, the photocharging process involved the photoanode as the working electrode and CE2 as the counter electrode. During discharge, the CE2 in the catholyte acted as the working electrode, while another 39 AA carbon felt in the anolyte was used as the counter electrode (CE1). Thus, the complete photochargedischarge test is effectively a three-electrode system. **Supporting Information 4 – Cross section TEM-EDX measurements** 



Figure \$3. Cross section TEM-EDX of 15/30 F-Cu<sub>x</sub>O, Tin in purple, iron in red and Cu in orange.

The cross section comes from a focused ion beam (FIB) lamellar sample with carbon protected on top. It can be seen that the 15 nm film Fe results in 30 nm  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> after annealing, while the average thickness of the Cu<sub>x</sub>O is ~15 nm.

#### Supporting Information 5 – Band alignment measurements



**Figure S4.** (a) Tauc plots, (b) Mott-schottky test and (c) UPS test of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Cu<sub>x</sub>O to get bandgap, work function and valence band maxima (VBM); respectively.

The band gap value is estimated by identifying the intersection point between the linear portion of Tauc's plots and the X-axis. These plots of the absorption coefficient ( $\alpha$ ) were obtained using a UV-visible spectrophotometer (Shimadzu, UV-2600i) within the wavelength range of 300–800 nm. Mott–Schottky (MS) measurements were conducted under dark conditions using a three-electrode homemade cell via CHI 760E potentiostat. The photoanode served as the working electrode, while a Pt foil (99.99% purity, Alfa Aesar) acted as the counter electrode. Additionally, a leakage-free Ag/AgCl electrode (Innovative Instruments, Inc) was utilized as the reference electrode. The experiment was performed within a potential range of -0.8 to 1.2 V vs Ag/AgCl under anolyte, employing an applied frequency of 1 kHz to investigate the intrinsic electrical properties. The flat band potential ( $F_{fb}$ ) value can be determined using the following equation<sup>5</sup>:

$$C^{-2} = \frac{2}{q\epsilon_0 \epsilon_s N_D} \left[ V - F_{fb} - \frac{KT}{q} \right]$$

# Supporting Information 6 – Investigation of NaOH treatment time and Cu film thickness



**Figure S5**. (a) Photoresponse behavior of 15/30 F-Cu<sub>x</sub>O with different NaOH treatment time; (b) Photocurrent performance of 15F-based heterojunctions with varying thicknesses of deposited Cu films subsequently treated for 20 h in NaOH.

Supporting Information 7 – Scanning electron microscope of planar sample



**Figure S6.** SEM of (a) 15F and (b) 15/30 F-Cu<sub>x</sub>O.

## Supporting Information 8 – Stability of planar sample



Figure S7. Stability test (1h) of 15/30 F-Cu<sub>x</sub>O with photoresponse before and after.

# Supporting Information 9 – Optical performance of hematite films with different thicknesses



Figure S8. UV-Vis absorption spectrum of 15F, 30F and 50F.

### Supporting Information 10 – Optical simulation



**Figure S9.** Simulated 2D absorption spectra of the (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film with different thickness and (b) 30F-based  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopillar arrays with varying diameters under a periodicity of 300 nm.

# Supporting Information 11 – Photoresponse testing of various planar p-n junctions



**Figure S10.** (a) The influence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thickness on the photoelectrochemical performance; Photoresponse of (b) 30F-based and (c) 50F-based heterojunctions with varying thicknesses of deposited Cu films treated for 20 h in NaOH.

As a comparison, we measured the absorption spectra and photochemical activity of pure hematite films with different thicknesses (Figure S8 and Figure S10) under back illumination in ambient air conditions as described in Experimental Section. The measured absorption curves align well with numerical calculations (Figure S9a). The light absorption demonstrates a notable increase from 15F to 30F, followed by saturation upon reaching 50F. Yet, due to the limited charge mobility within hematite<sup>6</sup>, electron-hole recombination significantly constrains the performance of the photoanodes. The photocurrent density decreases from 15F (0.12 mA/cm<sup>2</sup>) to 30F (0.07 mA/cm<sup>2</sup>) and experiences a significant decrease at 50F (0.01 mA/cm<sup>2</sup>) thereafter (Figure S10a). Despite efforts to construct p-n junctions to improve charge transfer, the best samples obtained with thicker hematite films only exhibit a photocurrent density of 0.14 mA/cm<sup>2</sup> and 0.06 mA/cm<sup>2</sup> for 30/30 F-Cu<sub>x</sub>O and 50/30 F-Cu<sub>x</sub>O, respectively (Figure S10b, c)

### Supporting Information 12 – Electrochemical impedance spectroscopy analysis



Figure S11. The (a) measured and (b) fitting EIS results of 15F and 15/30 F-Cu<sub>x</sub>O. The inset is the equivalent electrical circuit.

Electrochemical Impedance Spectroscopy (EIS) analysis was performed with frequency ranging from 10 kHz to 10 mHz under 1 sun illumination to further investigate the mechanisms that occur at the photoanodes. The electrical circuit (the inset of Figure S11a) was used as a model to fit the PEC redox couple oxidation reaction process in the photoanodes. Where  $R_{series}$  represents the series resistance, which includes the resistance at the ITO/photoanode interface, the ionic conductivity in the electrolyte and the external contact resistance;  $R_{sc}$  and  $C_{sc}$  are models of charge transfer behavior in the internal semiconductor, while  $R_{ct}$  and  $C_{ct}$  are the analogous reactions that take place at the semiconductor/electrolyte interface. The fitting Nyquist plots are shown in Figure S11b, which is similar to the measured EIS results.

# Supporting Information 13 – SEM and optical microscopy image of different patterns



Figure S12. SEM of (a, d) P100, (b, e) P150 and (c, f) P200 before and after annealing; (g) Optical microscopy image of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopillar arrays.

The corresponding optical, white-light transmission images (Figure S12g) exhibit the different optical appearances of the three patterns, providing a direct way to observe the tunability of the optical properties with varying diameters.

#### Supporting Information 14 – Microscale absorption measurements



Figure S13. Microscale absorption measurements of the fabricated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopillar arrays as well as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films.

The absorption depth for incident photons of hematite<sup>7</sup> is 40-100 nm for wavelengths ranging from 450 to 550 nm. A significant enhancement in broadband light absorption can be observed from Figure S13 as the thickness of the thin film sample increases from 15F (~30 nm hematite) to 30F (~60 nm hematite). However, the hole diffusion length limitation for hematite<sup>8</sup> necessitated a sacrifice in the thickness of the photoanode. Nanoengineering could potentially serve as a solution strategy to balance optical performance and charge carrier transport. It is worth noting that all the 30F-based nanopillar arrays (even those with only a 10 nm thickness of continuous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film underneath) exhibit comparable optical absorption to the 30F sample, significantly stronger than the 15F sample. This enhancement could be attributed to the light-trapping effect of the nanopillar arrays<sup>9</sup>. Additionally, P200 enables sunlight to induce optical resonances at 550 nm and 600 nm, consistent with our simulation findings (Figure S9b). This phenomenon can enhance the light intensity within the photoanode<sup>10</sup>.

### Supporting Information 15 – Tip approaching curve



**Figure S14.** Tip approach curve. Experimental current–distance curves (points) obtained with the tip approaching the hematite film part of the substrate. The solution contained 4 mM  $Fe(CN)_6^{4-}$  and 0.4 M NaOH. Tip potential  $E_T=0.4$  V vs. Ag/AgCl and an unbiased grounded substrate in dark.

## Supporting Information 16 – SEM for nanostructures



**Figure S15.** SEM of (a) P and (b) P/Cu<sub>x</sub>O.

## Supporting Information 17 – Photoresponse and stability for nanostructures



**Figure S16.** Stability of j-t for P/Cu<sub>x</sub>O.

### **Supporting Information 18 – EIS analysis for nanostructures**



Figure S17. The (a) measured and (b) fitting EIS results of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> P and P/Cu<sub>x</sub>O. The inset is the equivalent electrical circuit. By using the same equivalent electrical circuit as Figure S11, we can get the R<sub>series</sub>, R<sub>sc</sub>, R<sub>ct</sub> and C<sub>sc</sub> for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> P is 160  $\Omega$ , 4075  $\Omega$ , 2028  $\Omega$  and 0.03×10<sup>-3</sup> F, respectively. The R<sub>series</sub>, R<sub>sc</sub>, R<sub>ct</sub> and C<sub>sc</sub> for P/Cu<sub>x</sub>O is 90  $\Omega$ , 500  $\Omega$ , 757  $\Omega$  and 1.4×10<sup>-3</sup> F, respectively.

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