SUPPORTING INFORMATION

Photoelectrochemical Oxidation in Ambient Conditions Using Earth-abundant Hematite Anode: A Green Route for Synthesis of Biobased Polymer Building Blocks

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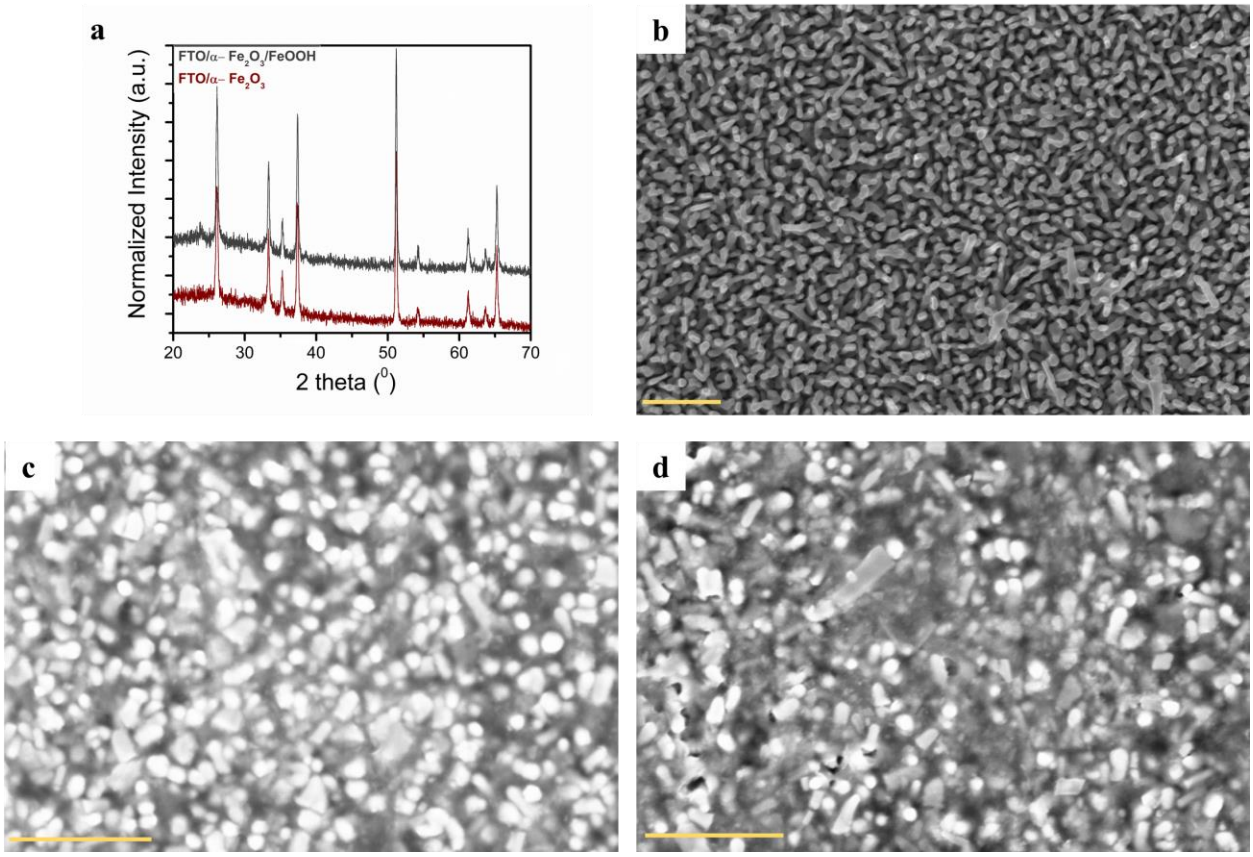

Figure S1. a) X-ray diffraction patterns for the bare (black trace) and modified hematite (red trace), **b)** and **c)** show the planar top view scanning electron micrographs of bare and modified hematite photoanode, respectively, before the PEC experiment, while **d)** shows a planar top view scanning electron micrograph after the 20 hour PEC run. The bar represents 1 μm.

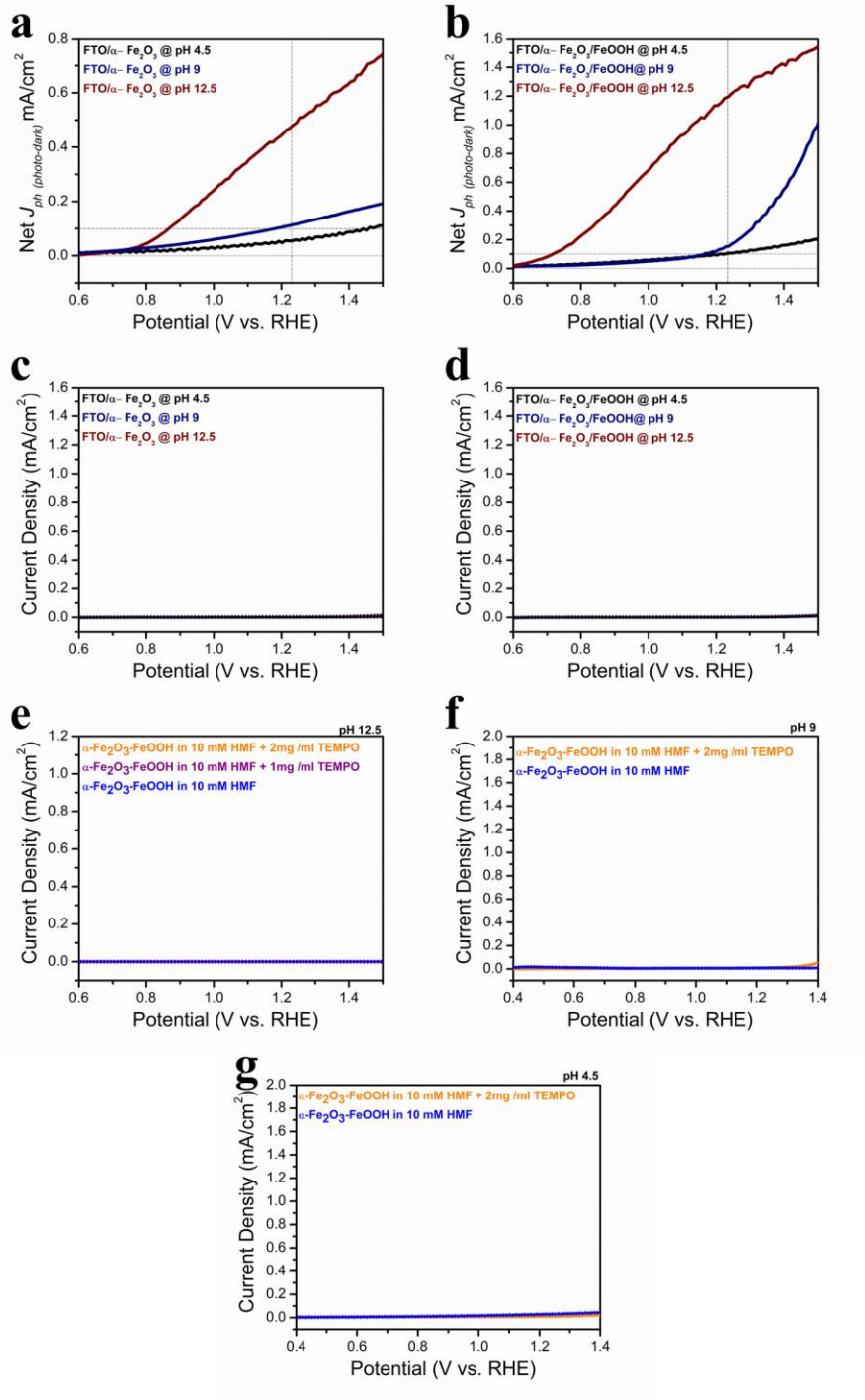

Figure S2. LSVs for the a) bare and b) modified hematite photoanodes at different pH values (4.5, 9.0, and 12.5) in 1 M Na_2SO_4 solution, and the corresponding dark current for c) bare and d) modified photoanodes, respectively. The dark current response for 5-HMF oxidation at e) pH 12.5, f) pH 9.0, and g) pH 4.5, are also shown.

Table S1. V_{onset} potentials obtained for modified hematite under different pH conditions and the net photocurrent density recorded at 1.4 V_{RHE} (in square bracket- orange color).

Experimental Condition	**1M Na_2SO_4** [J_{ph} (@1.4 V_{RHE}) mA/cm^2]	**1M Na_2SO_4 + 10 mM 5-HMF** [J_{ph} (@1.4 V_{RHE}) mA/cm^2]	**1M Na_2SO_4 + 10 mM 5-HMF + 1mg/mL TEMPO** [J_{ph} (@1.4 V_{RHE}) mA/cm^2]	**1M Na_2SO_4 + 10 mM 5-HMF + 2mg/mL TEMPO** [J_{ph} (@1.4 V_{RHE}) mA/cm^2]
V_{onset} (pH 12.5)	0.81 [1.4]	0.78 [1.8]	0.72 [3.2]	0.59 [7.8]
V_{onset} (pH 9.0)	1.16 [0.54]	0.75 [1.3]		0.54 [3.7]
V_{onset} (pH 4.5)	1.12 [0.2]	0.73 [1.02]		0.40 [2.2]

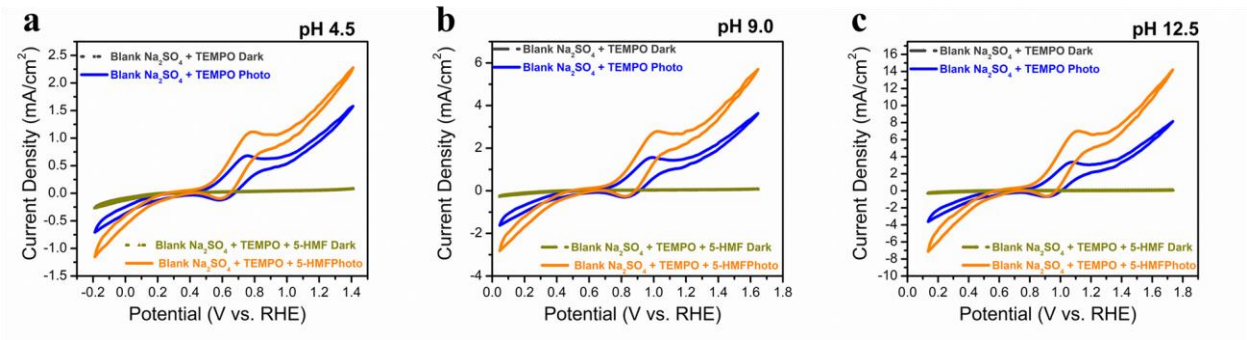

Figure S3. Cyclic voltammograms recorded in Na_2SO_4 + TEMPO with and without 5-HMF in dark and under illumination at **a)** pH 12.5, **b)** pH 9.0 and **c)** pH 4.5.

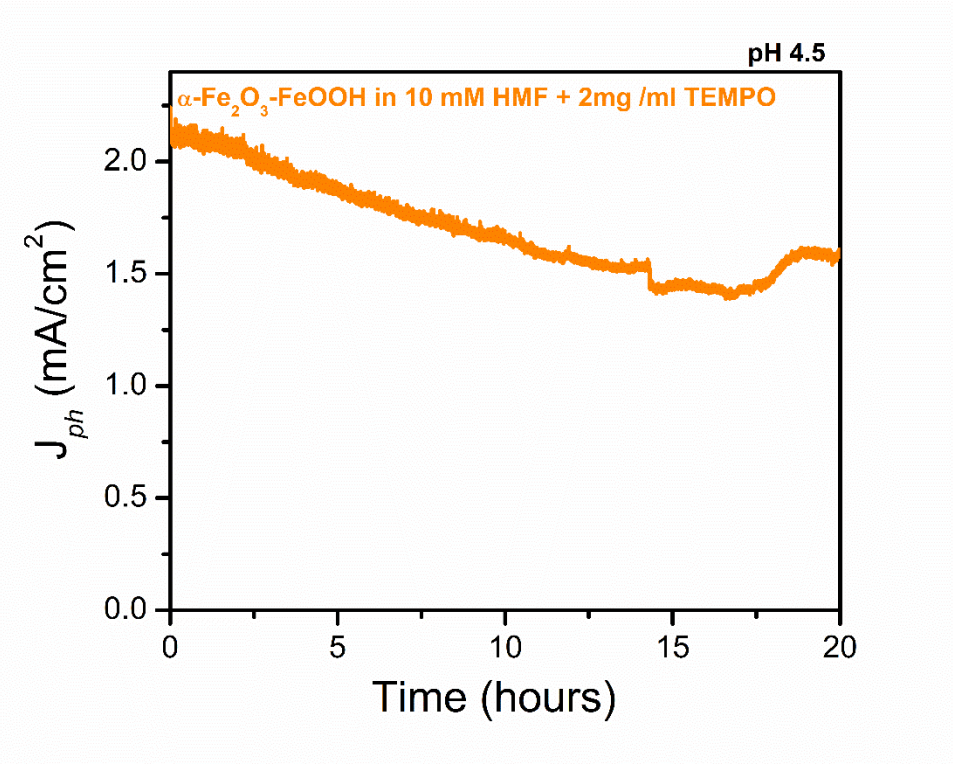

Figure S4. Chronoamperometry response for 5-HMF oxidation recorded under visible illumination and 1.1 V_{RHE} at 100 mW/cm^2 for α-Fe_2O_3-FeOOH in 1 M Na_2SO_4 solution at pH 4.5

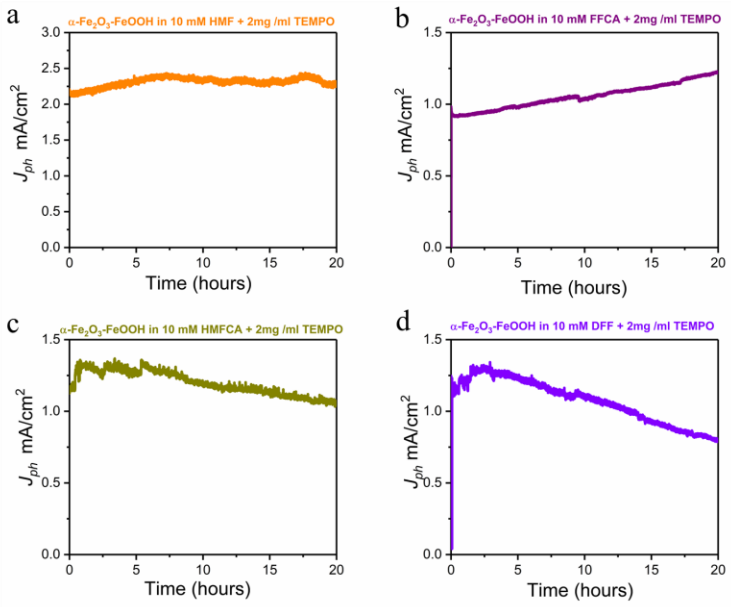

Figure S5. Chronoamperometry response for **a)** 5-HMF, **b)** FFCA, **c)** HMFCA, and **d)** DFF oxidation recorded under visible illumination and 1.1 V_{RHE} at 100 mW/cm^2 for α-Fe_2O_3-FeOOH in 1 M Na_2SO_4 solution (pH 9.0).

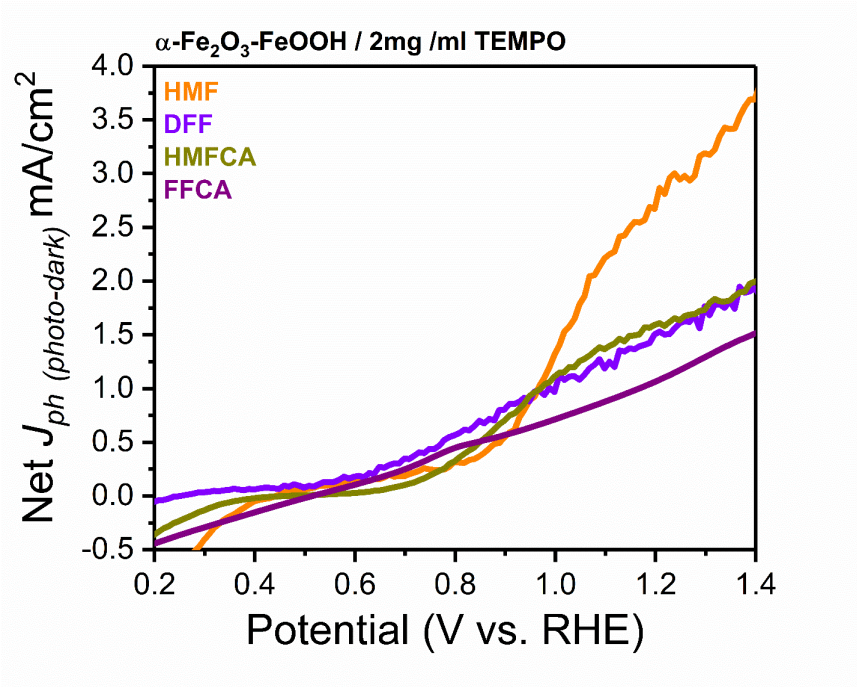

Figure S6. LSVs for the modified hematite photoanode recorded for different furan compounds as substrates at pH 9.0 in 1 M Na_2SO_4 solution.

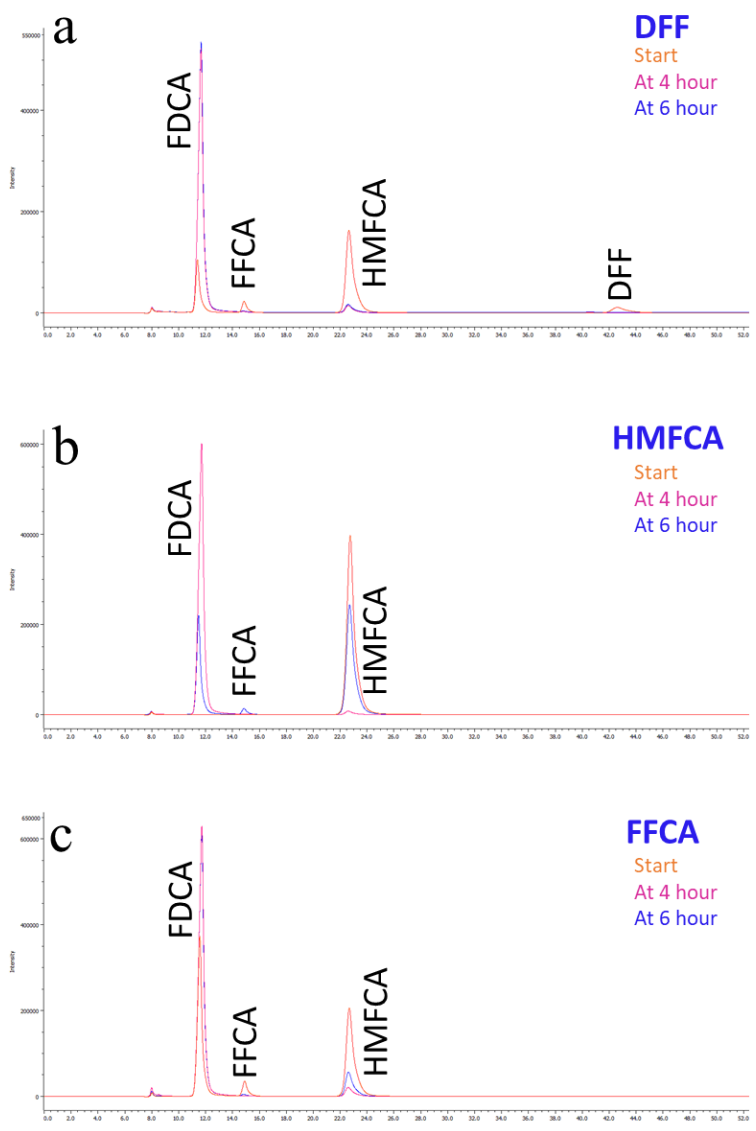

Figure S7. HPLC chromatograms of the photooxidation of (a) DFF, (b) HMFCA, and (c) FFCA in 1M Na_2SO_4 solution at pH 12.5 with 2 mg/mL TEMPO.

Table S2. Comparison of the system presented in this study with other photoelectrochemical or photocatalytic systems reported in the literature on 5-HMF oxidation to FDCA.

Photoelectrode/ Photocatalyst	**Initial HMF Concentration (mM)**	**Illumination Condition**	**Reaction Condition**	**Conversion/ Yield %**		**Ref.**
				HMF	**FDCA**	
Hematite photoanode	10	Blue LED cold white-Thor Labs (100 mW/cm^2)	12.8 mM TEMPO, 1 M Na_2SO_4, (pH 12.5), 1.1 V_{RHE}, room temperature, 5.5 h	99.2	90.7	This study
$BiVO_4$ photoanode	5	AM 1.5 G (100 mW/cm^2)	7.5 mM TEMPO, 0.5 M borate buffer (pH 9.2), 1.04 V_{RHE}, 40 ^{0}C	99.24	98.85	[1]
CoPz/g-C3N_4	0.8	Xe Light /UV-Visible (500 mW/cm^2)	$Na_2B_4O_7$ buffer (pH 9.18) room temperature, 14 h	99.1	96.1	[2]
Ni/CdS nanosheet	10	440-460 nm blue LED (8 W)	10 mg of Ni/CDS, 10 M NaOH, 2 h	~ 100	~ 100	[3]
ZnO/PPy	8	450 nm blue LED (102 W/cm^2)	50 mg of catalysts, aq. media, 40 ^{0}C, 6 h	30	5.4	[4]

References

1. Cha, H.G.; Choi, K.-S. Combined biomass valorization and hydrogen production in a photoelectrochemical cell. *Nat. Chem.* **2015**, *7*, 328.
2. Xu, S.; Zhou, P.; Zhang, Z.; Yang, C.; Zhang, B.; Deng, K.; Bottle, S.; Zhu, H. Selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid using O2 and a photocatalyst of Co-thioporphyrazine bonded to g-C3N4. *Journal of the American Chemical Society* **2017**, *139*, 14775-14782.
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