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Goethite and Hematite Hybrid Nanosheet Decorated YZnO NRs for Efficient Solar Water Splitting

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Supplemental Information



Figure S1: Schematic diagram of the deposition process, A, showing the setup including ultrasonic bath, and electrode positions. B Shows typical deposition current over time,

integrated to calculate charge density. C Shows the cyclic voltammetry with three electrode setup, used to determine the goethite potential, inset shows a slower scan speed linear sweep for greater accuracy.¹ Electrode deposition potential was determined by the difference between V_{oc} (-0.70) and goethite deposition potential (-0.14) as 0.56 V.



Figure S2: A Shows the integrated total charge density deposited and the nanosheet width against the duration of deposition. B Shows the charge density plotted against nanosheet width.



Figure S3: A Shows EDX mapping of the sample area of the 30 min deposition, with composite image of Zn and Fe (left) and component elements (right). B Shows an EDX line scan of Fe_2O_3 / FeOOH aggregates on the surface.



Figure S4: Shows the XPS high resolution scans for Fe2p and O1s in the Fe_2O_3 / FeOOH sample.



Figure S5: A Shows the equivalent circuit used to fit the Nyquist plots, and B shows the different R_{ct} values plotted against deposition duration, along with pure samples.



Figure S6: Shows the light/dark stepped linear sweep voltammetry of a comparative selection of anodes, with pristine ZnO A, and 5 minutes electrodeposition on pure ZnO B. C Shows the top performing sample, 5 minutes deposition on Y doped nanowires. Finally D shows the normalised logarithm of current decay from the chronoamperometry measurements.



Figure S7: Shows the comparison of all the dark currents for the optimisation.

No.	Sample Description	Photocurrent Density at 1.23 V _{RHE}	Reference
1	NiO-ZnO on Fe ₂ O ₃ films	Negligible	Zhang <i>et al.</i> ²
2	ZnO quantum dots on Fe ₂ O ₃ films	Negligible	Ikram <i>at al.</i> ³
3	ZnO NRs covered in Fe ₂ O ₃ nanoparticles	Negligible	Chakraborty <i>et al.</i> ⁴
4	ZnO NRs coated with Fe ₂ O ₃ , prior to Fe ₂ PO ₄ encapsulation	0.85 mA cm^{-2}	Qin <i>et al.</i> ⁵
5	ZnO NRs coated with Fe ₂ O ₃	1.27 mA cm^{-2}	Hsu <i>et al</i> . ⁶
6	This Work	0.91 mA cm^{-2}	n/a
7	Silicon doped nanostructured Fe ₂ O ₃ films	2.2 mA cm^{-2}	Kay <i>et al.</i> ⁷

Table S1: Displays a literature comparison of relevant structures and devices.

8	Co-doped ZnO nanorods with a transparent functionalizing MOF	0.15 mA cm^{-2}	Galan-Gonzalez <i>et</i> <i>al</i> . ⁸
9	Sn doped Fe ₂ O ₃ from FTO	1.0 mA cm^{-2}	Annamalai <i>et al.</i> 9
10	Zinc Ferrite modified Al-doped ZnO NR Arrays	1.72 mA cm^{-2}	Xu et al. ¹⁰



Figure S8: A shows the Mott-Schottky plot of the anodic deposition of Fe₂O₃, yielding V_{FB}

value of 0.69 V_{RHE} and dopant density of $1.19 \times 10^{26} \text{ m}^{-3}$. B shows the XPS survey scan of the hybrid junction and valence band determination, finally C shows the chopped illumination chronoamperometry test over a five minute period.

References

- Martinez, L.; Leinen, D.; Martín, F.; Gabas, M.; Ramos-Barrado, J. R.; Quagliata, E.; Dalchiele, E. A. Electrochemical Growth of Diverse Iron Oxide (Fe₃O₄, α-FeOOH, and γ-FeOOH) Thin Films by Electrodeposition Potential Tuning. *J. Electrochem. Soc.* 2007, *154* (3), D126.
- (2) Zhang, C.; Fan, W.; Bai, H.; Yu, X.; Chen, C.; Zhang, R.; Shi, W. Sandwich-Nanostructured NiO-ZnO Nanowires@α-Fe₂O₃ Film Photoanode with a Synergistic Effect and p-n Junction for Efficient Photoelectrochemical Water Splitting. *ChemElectroChem* **2014**, *1* (12), 2089–2097.
- (3) Ikram, A.; Sahai, S.; Rai, S.; Dass, S.; Shrivastav, R.; Satsangi, V. R. Enhanced Photoelectrochemical Conversion Performance of ZnO Quantum Dots Sensitized α-Fe 2 O 3 Thin Films. *Int. J. Hydrogen Energy* **2015**, *40* (16), 5583–5592.
- (4) Chakraborty, M.; Roy, D.; Biswas, A.; Thangavel, R.; Udayabhanu, G. Structural, Optical and Photo-Electrochemical Properties of Hydrothermally Grown ZnO Nanorods Arrays Covered with α-Fe₂ O₃ Nanoparticles. *RSC Adv.* **2016**, *6* (79), 75063–75072.
- (5) Qin, D. D.; Tao, C. L. A Nanostructured ZnO–ZnFe₂O₄ Heterojunction for the Visible Light Photoelectrochemical Oxidation of Water. *RSC Adv.* **2014**, *4* (33), 16968.
- (6) Hsu, Y. K.; Chen, Y. C.; Lin, Y. G. Novel ZnO/Fe₂O₃ Core–Shell Nanowires for Photoelectrochemical Water Splitting. ACS Appl. Mater. Interfaces 2015, 7 (25), 14157– 14162.
- (7) Kay, A.; Cesar, I.; Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α-Fe₂O₃ Films. J. Am. Chem. Soc. 2006, 128 (49), 15714–15721.
- (8) Galán-González, A.; Sivan, A. K.; Hernández-Ferrer, J.; Bowen, L.; Di Mario, L.; Martelli, F.; Benito, A. M.; Maser, W. K.; Chaudhry, M. U.; Gallant, A.; et al. Cobalt-Doped ZnO Nanorods Coated with Nanoscale Metal-Organic Framework Shells for Water-Splitting Photoanodes. ACS Appl. Nano Mater. 2020, 3 (8), 7781–7788.
- (9) Annamalai, A.; Subramanian, A.; Kang, U.; Park, H.; Choi, S. H.; Jang, J. S. Activation of Hematite Photoanodes for Solar Water Splitting: Effect of FTO Deformation. J. Phys. Chem. C 2015, 119 (7), 3810–3817.
- (10) Xu, Y. F.; Rao, H. S.; Wang, X. D.; Chen, H. Y.; Kuang, D. Bin; Su, C. In Situ Formation of Zinc Ferrite Modified Al-Doped ZnO Nanowire Arrays for Solar Water Splitting. J. *Mater. Chem. A* 2016, 4 (14), 5124–5129.