**Supplementary Information**

# Effects of heating rate and deposition cycle on the structural, optical, and photoelectrocatalytic properties of electrodeposited hematite films

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**Table S1.** The FWHM, crystal size, microstrain, and dislocation density of electrodeposited hematite thin films.

| Sample | Bragg angle (2θ) | FWHM (degrees) | Crystal size (nm) | Strain ε x $10^{-3}$ | Dislocation density ɖ x $10^{15}$ Lin/$m^2$ |
|---|---|---|---|---|---|
| **2ºC/min** | 35.766 | 0.424 | 19.7 | 5.78 | 2.58 |
| **10ºC/min** | 35.787 | 0.288 | 29.0 | 3.92 | 1.19 |
| **35ºC/min** | 35.792 | 0.284 | 29.4 | 3.86 | 1.16 |
| **Rapid annealing** | 35.776 | 0.324 | 25.8 | 4.41 | 1.50 |
| **ED-15C** | 36.153 | 0.368 | 22.7 | 4.98 | 1.94 |
| **ED-30C** | 35.843 | 0.319 | 26.2 | 4.32 | 1.46 |
| **ED-60C** | 35.787 | 0.288 | 29.0 | 3.90 | 1.19 |
| **ED-80C** | 35.741 | 0.278 | 30.0 | 3.76 | 1.11 |

**Table S2.** A comparison of the experimental 2-theta values for the XRD peaks obtained for the samples and the standard reference values given in the JCPDS file number 00-033-0664.

| XRD planes (hkl) | Experimental 2 theta value (degrees) | Reference standard 2 theta value: JCPDS no. 00-033-0664 (degrees) |
|---|---|---|
| 12 | 24.28 | 24.14 |
| 104 | 33.31 | 33.15 |
| 110 | 35.81 | 35.61 |
| 113 | 40.98 | 40.86 |
| 24 | 49.62 | 49.48 |
| 116 | 54.18 | 54.09 |
| 214 | 62.54 | 62.45 |
| 300 | 64.14 | 63.99 |

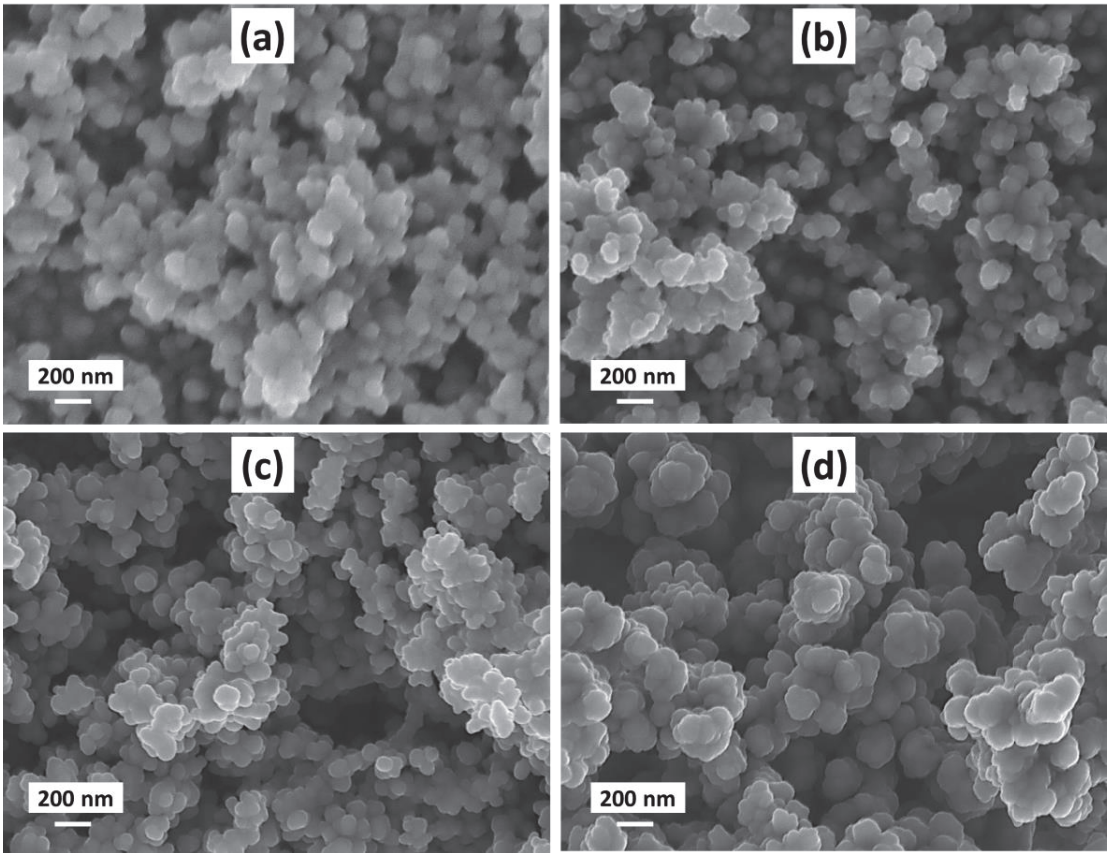


**Fig. S1.** SEM images of (a) ED-15C, (b) ED-30C, (c) ED-60C, and (d) ED-80C hematite samples

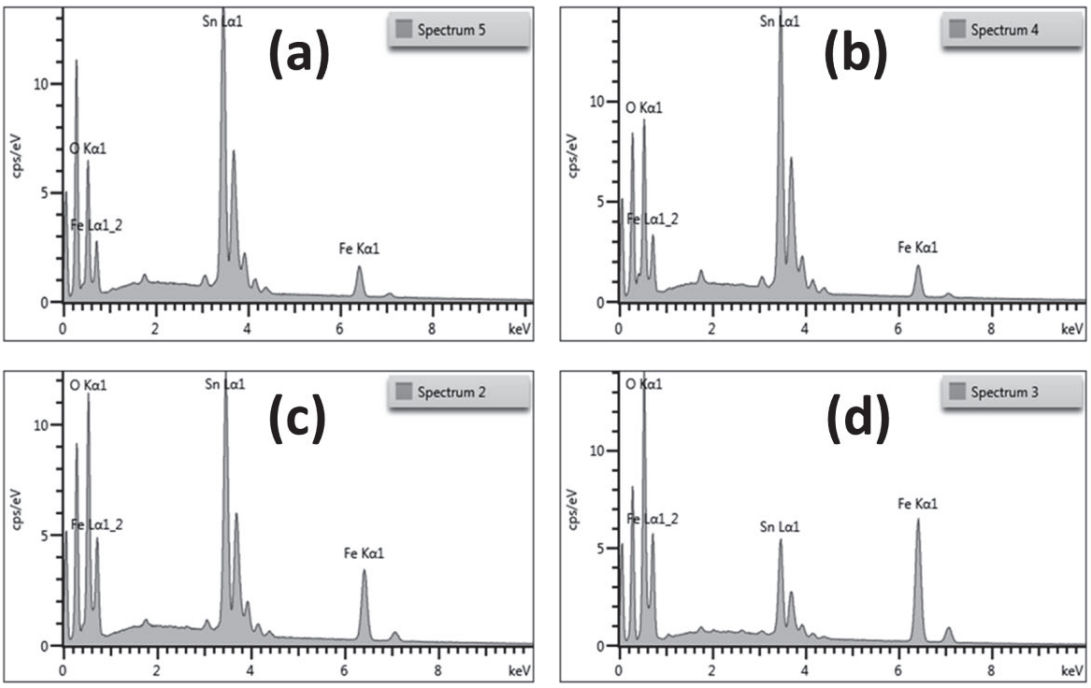


**Fig. S2.** EDS results for hematite films deposited at (A) 15, (B) 30, (C) 60, and (D) 80 deposition cycle numbers respectively.

**Mott-Schottky relation**

The Mott-Schottky (M-S) engaged in evaluating the donor densities and flat band potentials of the electrodeposited hematite films from the M-S plots given in Fig. 6 is given in Equation S1.

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon e A^2 N_D} \left(V - V_{fb} - \frac{KT}{e}\right) \quad \text{(S1)}$$

where $C$ denotes the interfacial capacitance, $A$ represents the surface area of the photoelectrode, $\varepsilon = 80$ and represents the dielectric constant of hematite, $\varepsilon_0$ denotes the permittivity of free space, $e$ is the electronic charge, $V$ is the applied potential, K is the Boltzmann constant and T represents the temperature [1]. The value of A, used for each of the electrodes was about 1.8 $cm^2$: the surface area of the photoanodes dipped into the electrolyte.

The first linear regions of the M-S plots in Fig. 6 of the main manuscript were fitted and the slope (S) of the plots was used to calculate the $N_D$ values for the samples in line with the relation in equation S2 deduced from Equation S1.

$$S = \frac{2}{\varepsilon_0 \varepsilon e A^2 N_D} \quad \text{(S2)}$$

The S values obtained for the plots were positive slope obtained as expected, which confirms the n-type semiconducting property of hematite [2]. The linear region of the M-S plots of the samples was extrapolated to intercept the potential $V_0$ along the $V$-axis where $\frac{1}{C^2} = 0$. This simplifies equation S1 to $V_0 = V_{fb} + (KT/e)$ where the $V_{fb}$ values can be extracted. Table 1 of the main manuscript presents approximate values of $N_D$ and $V_{fb}$ calculated for electrodeposited hematite photoanodes.

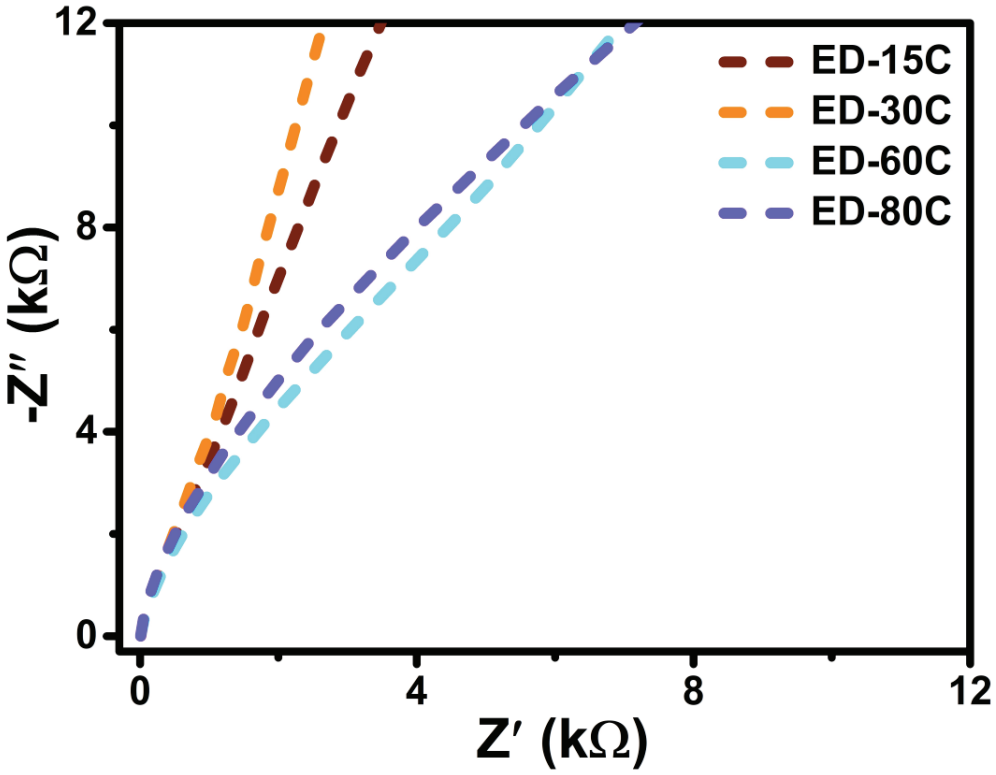


**Fig. S3.** Expanded view of the PEIS Nyquist plots for electrodeposited hematite photoanodes prepared at different deposition cycles.

**Reference**


1. Liang, Y., C.S. Enache, and R. van de Krol, *Photoelectrochemical Characterization of Sprayed [alpha]-Fe2 O3 Thin Films: Influence of Si Doping and SnO2 Interfacial Layer.* International Journal of Photoenergy, 2008. **2008**.

2. Iandolo, B., et al., *Correlating flat band and onset potentials for solar water splitting on model hematite photoanodes.* RSC advances, 2015. **5**(75): p. 61021-61030.