Supporting Information

Key factors boosting the performance of planar $ZnFe_2O_4$ photoanodes for solar water oxidation

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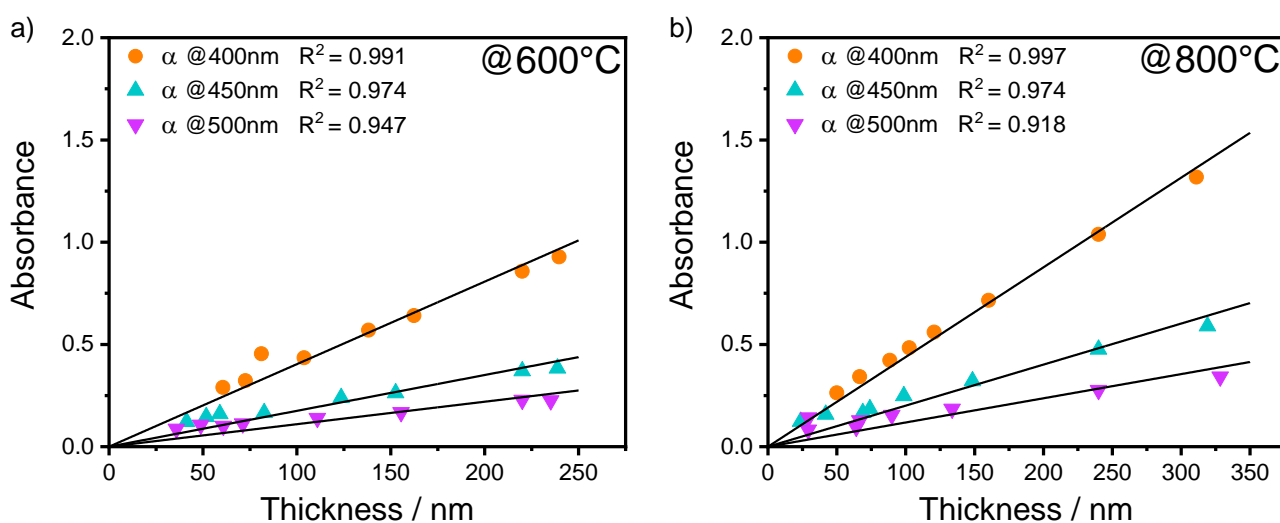
Figure S1. Absorbance at selected wavelengths vs. the film thickness for (a) the 600 °C and (b) the 800 °C films series. Absorbance (*A*) has been calculated as $A = 2 - \log(T\%)$ with *T%* referring to the percent transmittance. The best linearity was found for $\lambda = 400$ nm in both cases, with absorption coefficient values $\alpha_{600} = 0.0085$ nm^{-1} and $\alpha_{800} = 0.0093$ nm^{-1}.
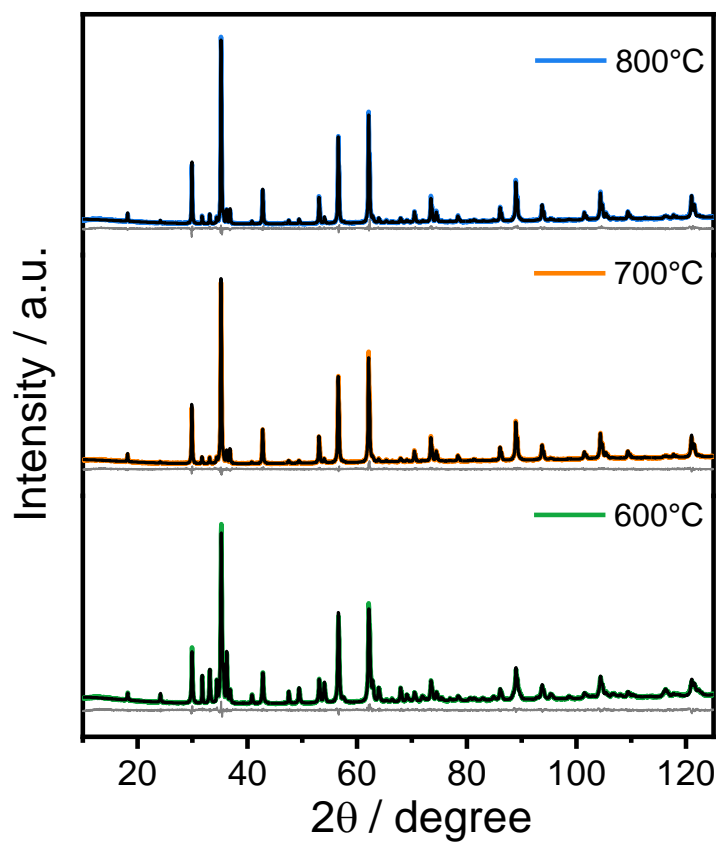
Figure S2. Rietveld refinement on PXRD of ZFO samples prepared at different temperatures. The coloured trace is the experimental pattern, the superimposed black trace is the fit Rietveld refinement and the grey trace below each pattern is the corresponding residual.
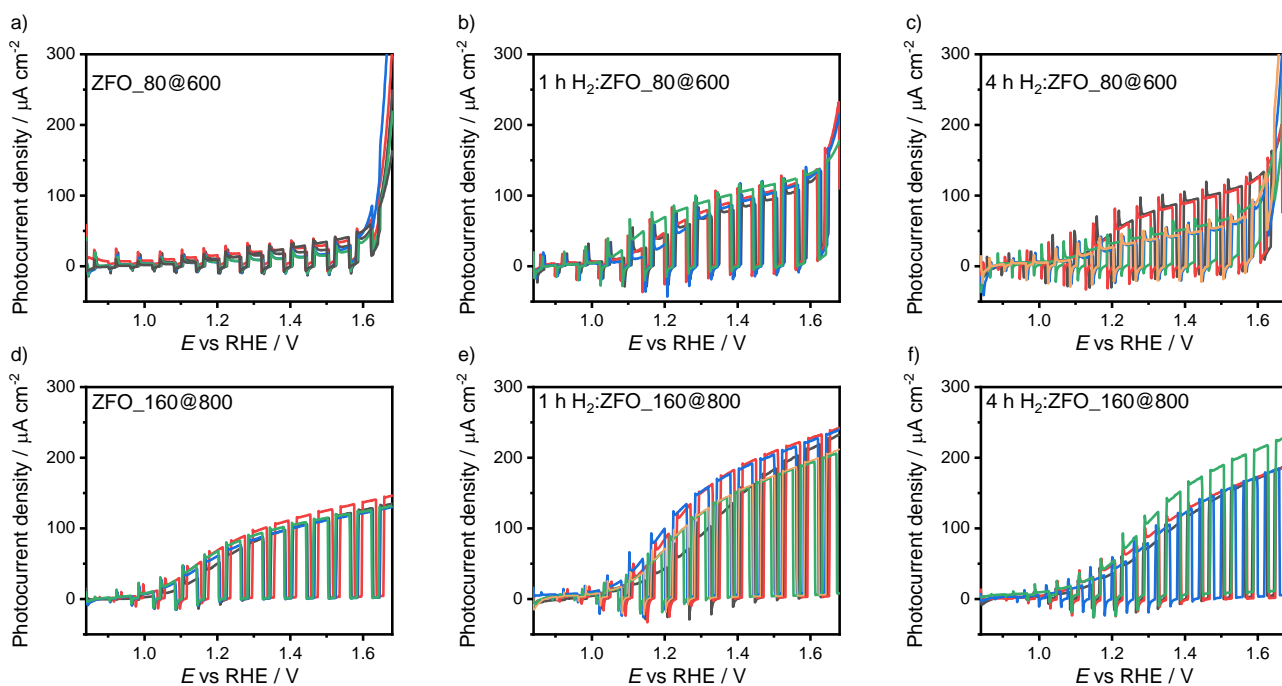
Figure S3. *J-V* curves reproducibility for representative samples of the two series, the 80 nm- and 160 nm-thick films calcined at 600 °C or 800 °C, respectively. The LSV plots were recorded with the two films (a,d) in their pristine form, (b,e) after 1 h-long hydrogenation and (c,f) after 4 h-long hydrogenation, in 1.0 M NaOH electrolyte solution under back-side irradiation.
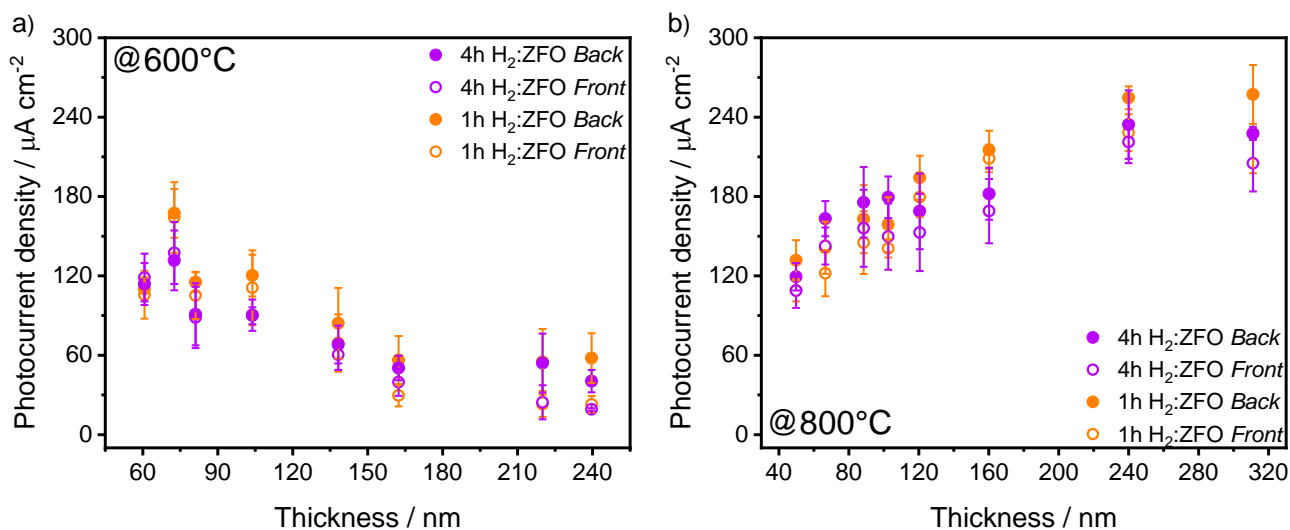

Figure S4. Photocurrent density *(J)* values at 1.5 V *vs.* RHE recorded with the films prepared at (a) 600 °C and (b) 800 °C after 1 h- (orange) and 4 h-long hydrogen treatment (violet), *vs.* the film thickness. *J* values were collected in 1.0 M NaOH solution under either back- (full circles) or front-side (void circles) irradiation.
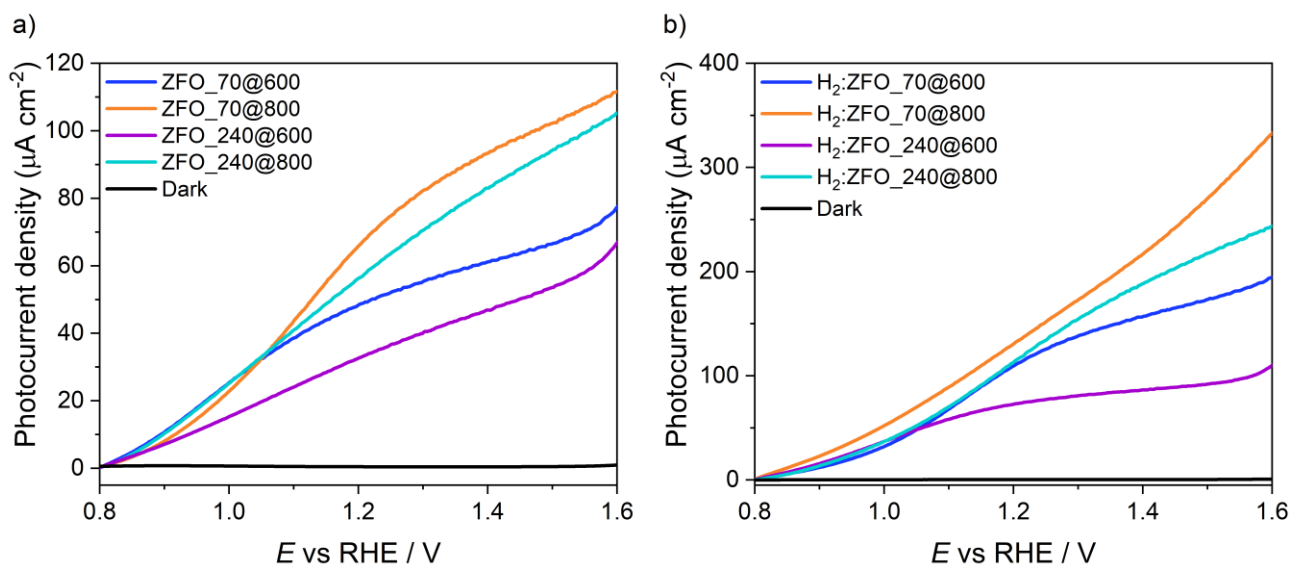
Figure S5. *J-V* curves recorded in 1.0 M NaOH electrolyte solution containing 0.5 M Na_2SO_3 under back-side irradiation for the 70 nm and 240 nm-thick films annealed at either 600 °C or 800 °C, either before (a) or (b) after 1 h-long H_2-treatment.

Intensity modulated photocurrent spectroscopy measurements

The IMPS response was fit to a phenomenological model,[1,2] according of the following equation:[3]

$$J(\omega) = \frac{J_h}{1 + (i\omega\tau_h)^{\alpha_1}} - \frac{J_r}{1 + (i\omega\tau_r)^{\alpha_2}} \tag{S1}$$

From the aforementioned fit model, the following parameters can be extrapolated: the bulk hole available for water oxidation (J_h) and the photocurrent losses due to surface recombination (J_r), and two time constants for bulk hole current (τ_h) and for surface recombination (τ_r). The non-ideality factor indicated as α_1 and α_2, used to describe the deformation of the semicircles due to frequency dependence dielectric constant, were selected to be close to 1.

The so derived parameters at 1.5 V *vs*. RHE, for each of the 8 compared films, are shown in **Figure S6**.
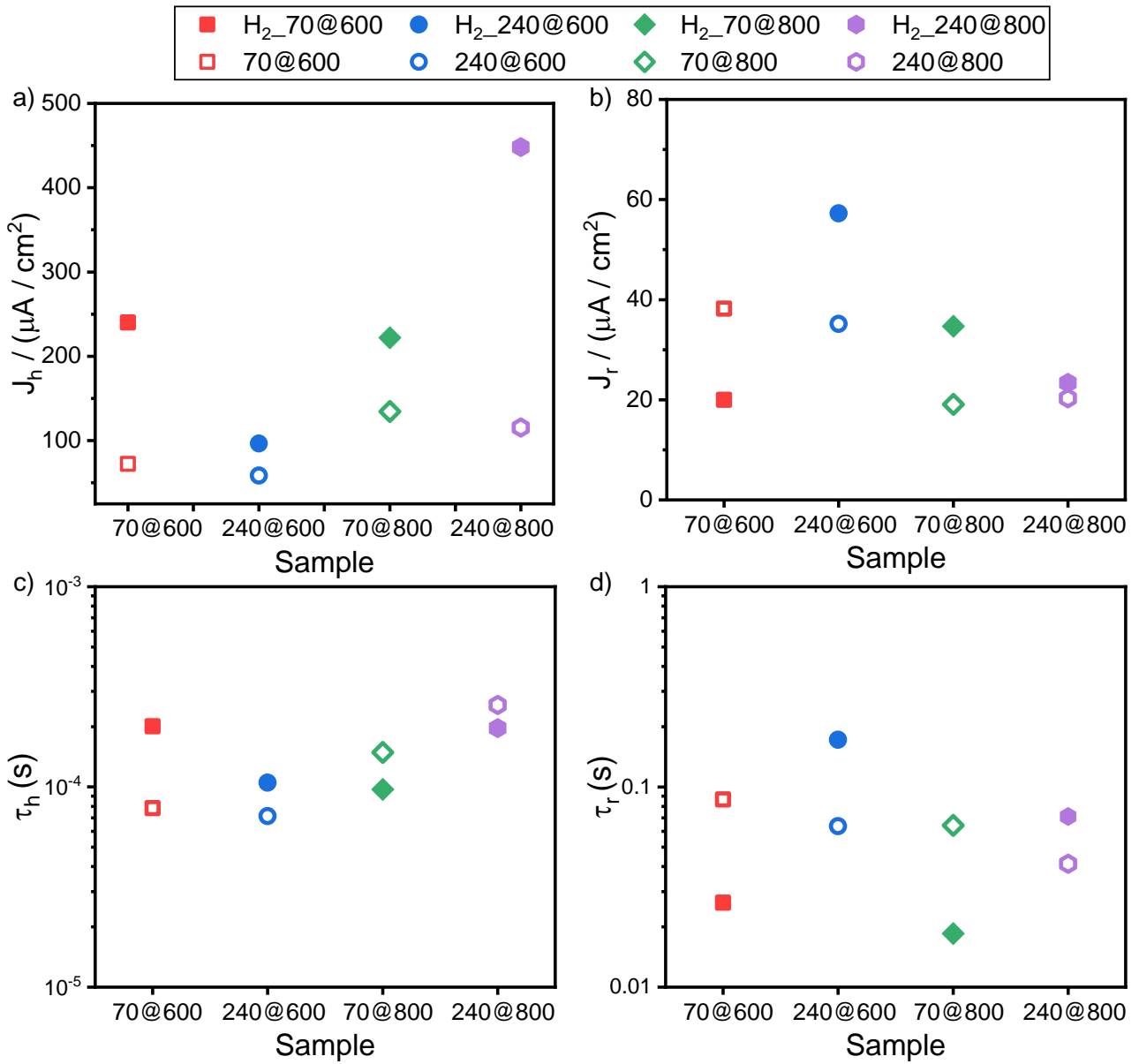
Figure S6. Extracted IMPS fit model parameters at 1.5 V *vs.* RHE for the 70 nm- and 240 nm-thick films calcined at either 600 °C or 800 °C: (a) bulk photocurrent available for water oxidation (J_h), (b) photocurrent losses due to surface recombination (J_r) and time constants for (c) bulk hole current (τ_h) and (d) for surface recombination (τ_r).
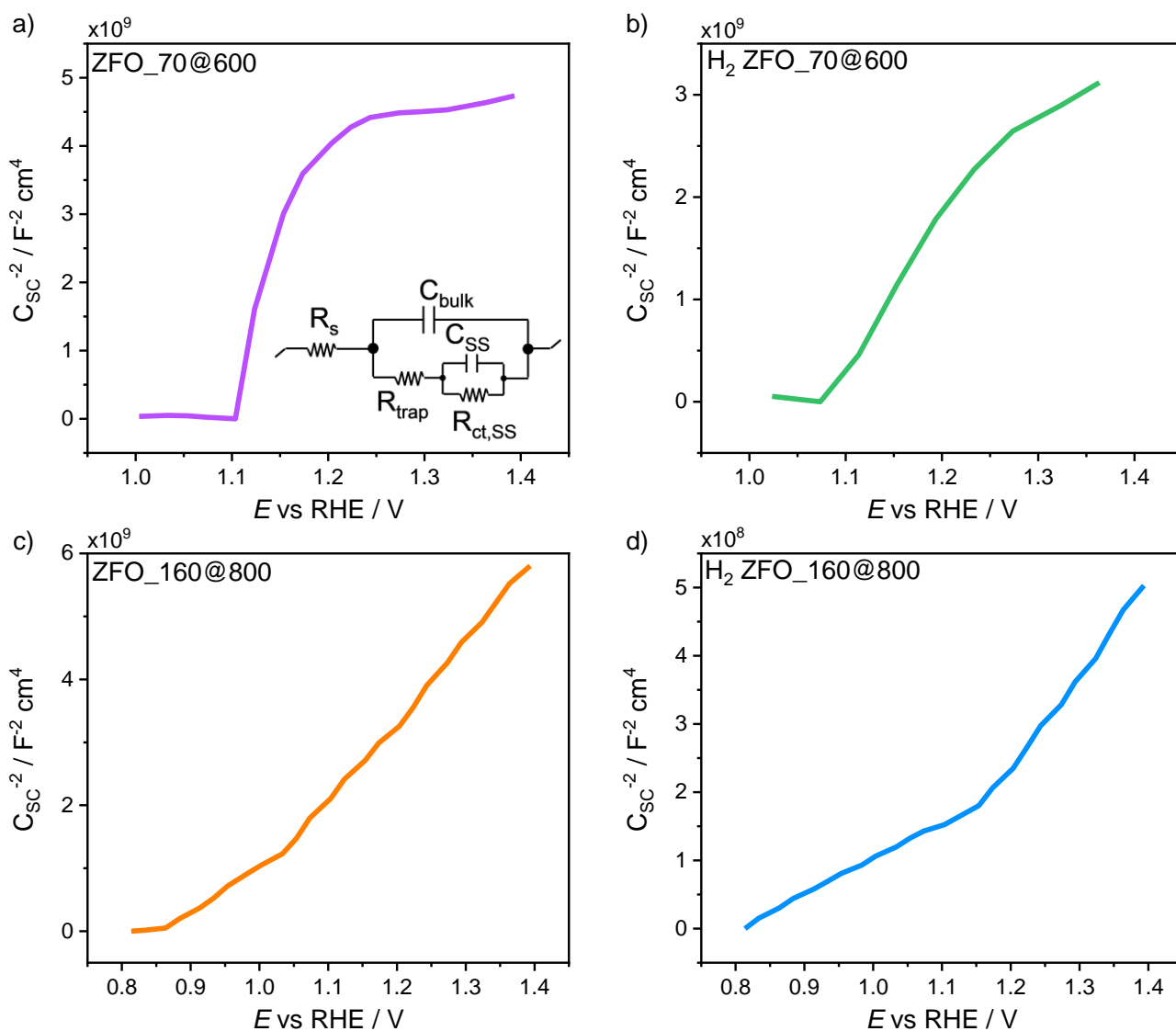
Figure S7. Mott-Schottky plots obtained with (a,b) ZFO_70@600 and (c,d) ZFO_160@800 films in their (a,c) pure and (b,d) hydrogenated forms, from PEIS measurements carried out in 1.0 M NaOH under AM 1.5 G solar simulated irradiation.

References

1   D. Klotz, D. S. Ellis, H. Dotan and A. Rothschild, *Phys. Chem. Chem. Phys.*, 2016, **18**, 23438–23457.

2   D. Klotz, D. A. Grave and A. Rothschild, *Phys. Chem. Chem. Phys.*, 2017, **19**, 20383–20392.

3   F. Boudoire, Y. Liu, F. Le Formal, N. Guijarro, C. R. Lhermitte and K. Sivula, *J. Phys. Chem. C*, 2021, **125**, 10883–10890.