

Supporting Information

Nano Gold Rush: On the Origin of the Photocurrent Enhancement in Hematite Photoanodes Decorated with Gold Nanoparticles

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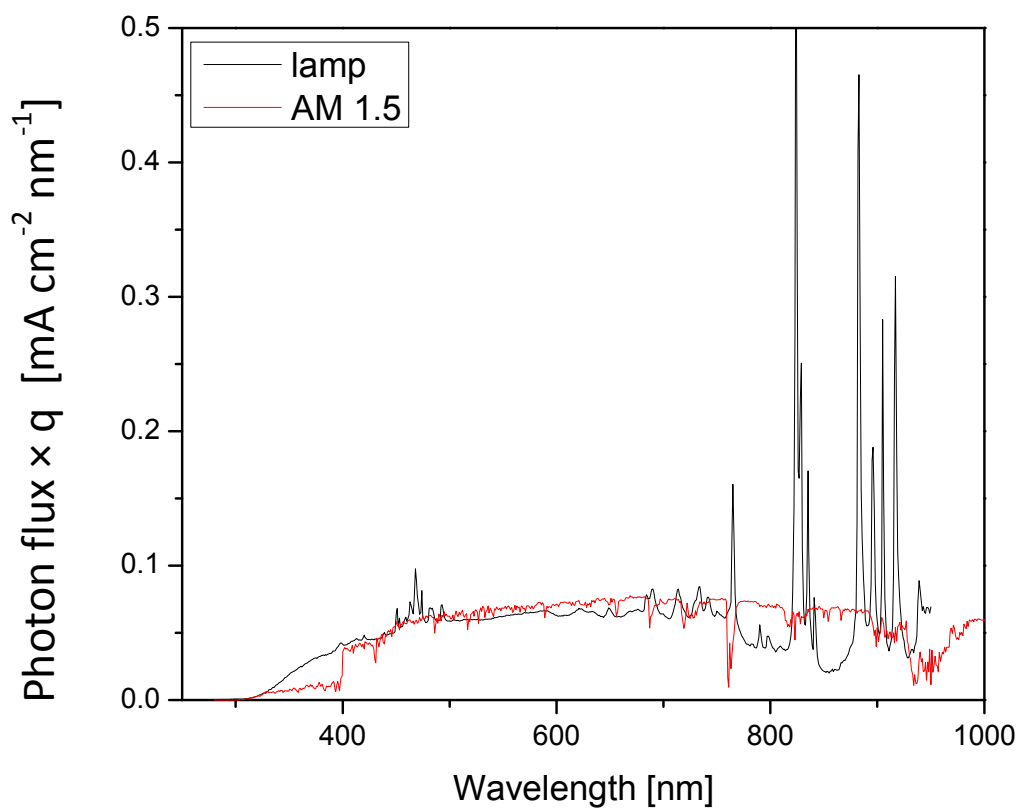


Figure S1: Comparison between the irradiance spectrum of the lamp (black line) and the AM1.5G spectrum (red curve). The irradiance is expressed in terms of the photon flux multiplied by the elementary charge (q), in units of mA cm⁻² nm⁻¹.

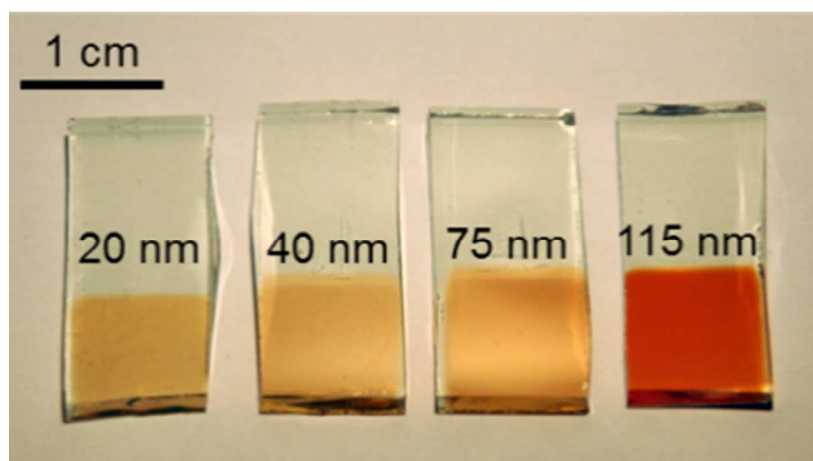


Figure S2: Photographs of hematite photoanodes with 20, 40, 75 and 115 nm thick Ti-doped hematite films on TEC15 substrates (without Au NPs).

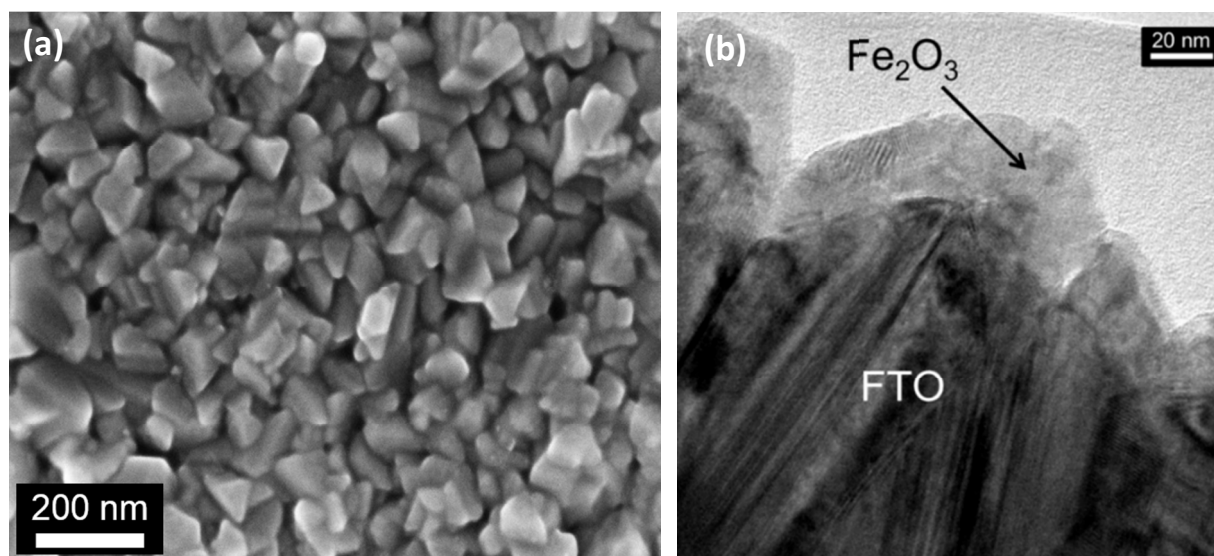


Figure S3: Typical top-view HRSEM (a) and cross-section TEM micrographs (b) of the hematite photoanodes (without Au NPs).

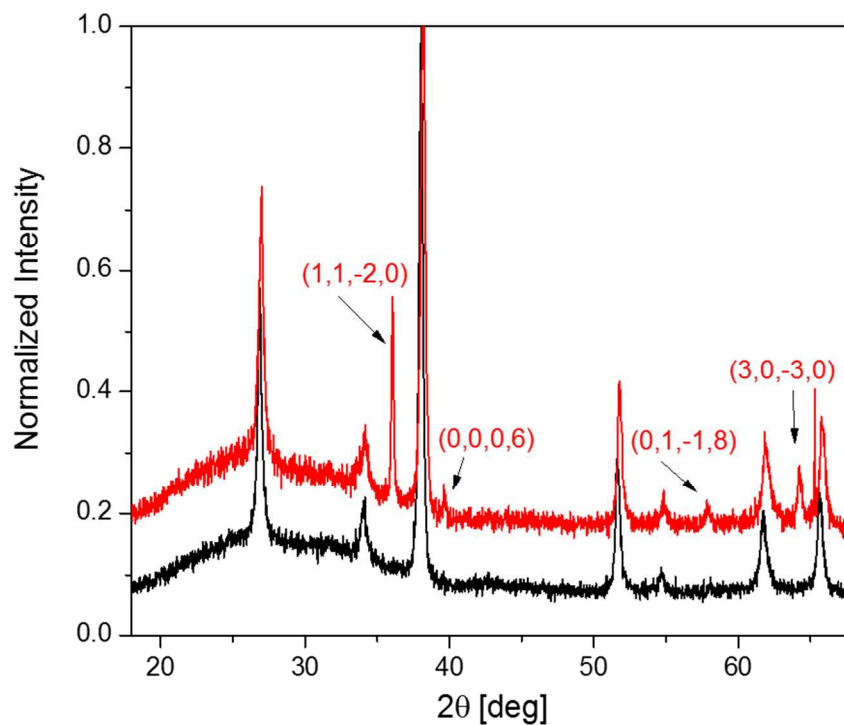


Figure S4: Typical XRD diffractograms of TEC15 substrates with and without hematite film (red and black line curves, respectively). The additional peaks in the red diffractogram correspond to different Bragg reflections of hematite, as marked in the figure.

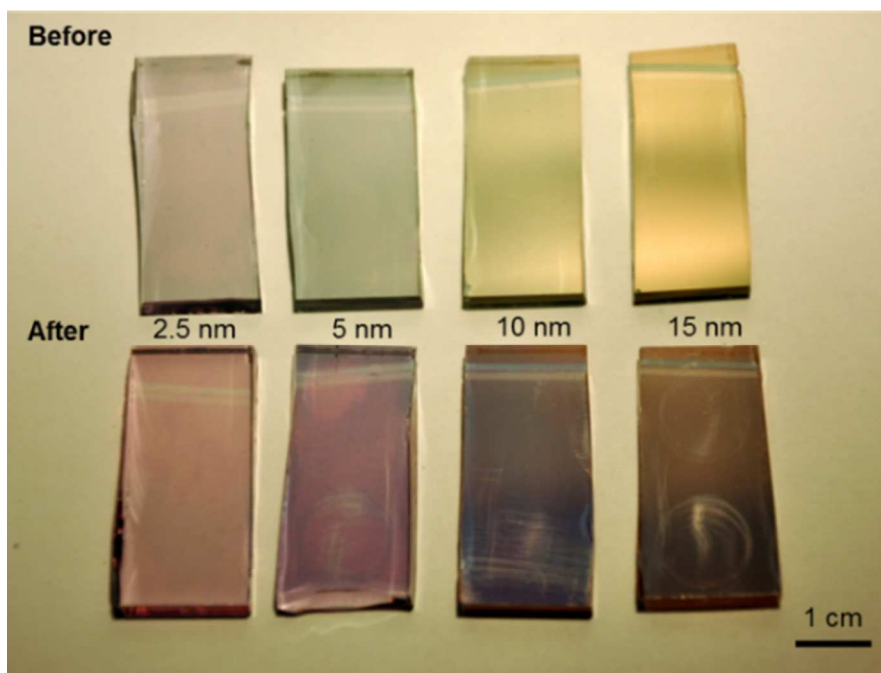


Figure S5: Photographs of TEC15 substrates coated with 2.5, 5, 10 and 15 nm thick Au films before (top) and after (bottom) the dewetting process.

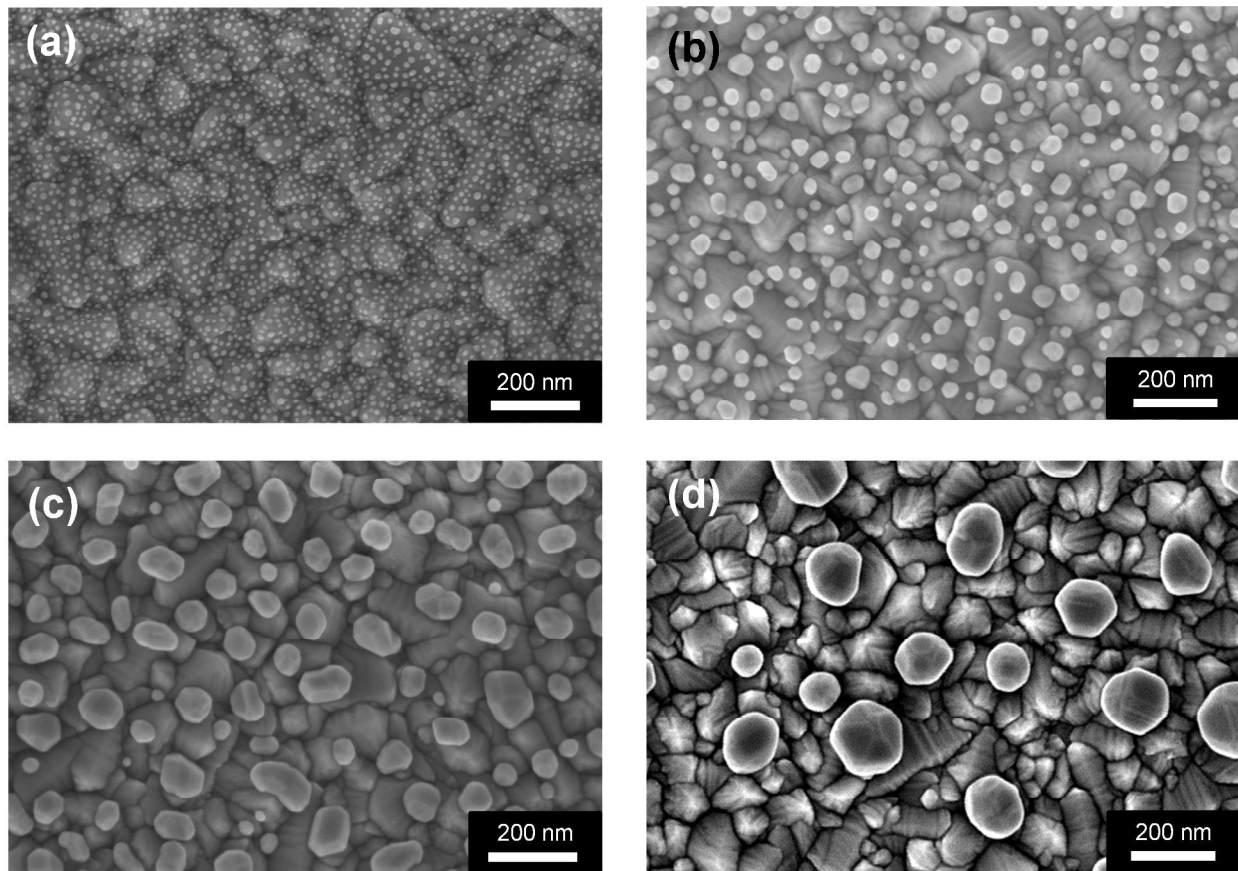


Figure S6: Plan view HRSEM images of Au NPs on TEC15 substrates after the dewetting process. The thickness of the Au films before the dewetting process was 2.5, 5, 10 or 15 nm for figures (a), (b), (c) or (d), respectively.

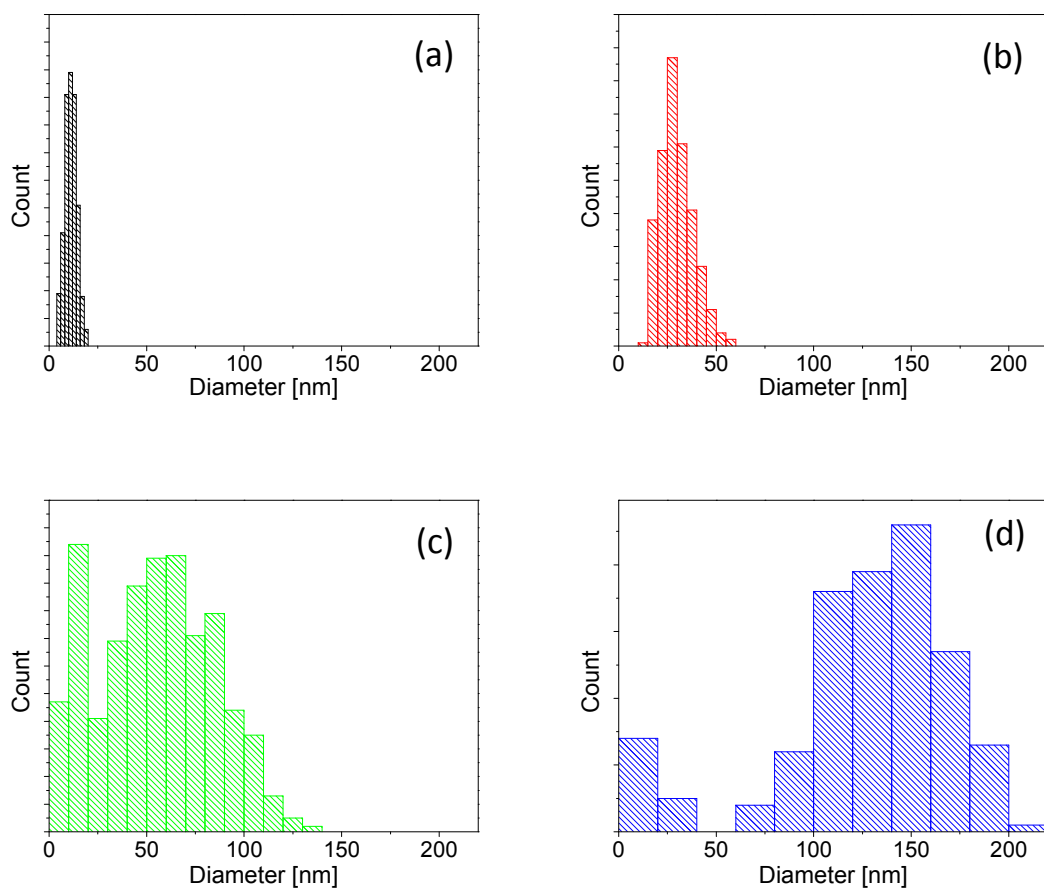
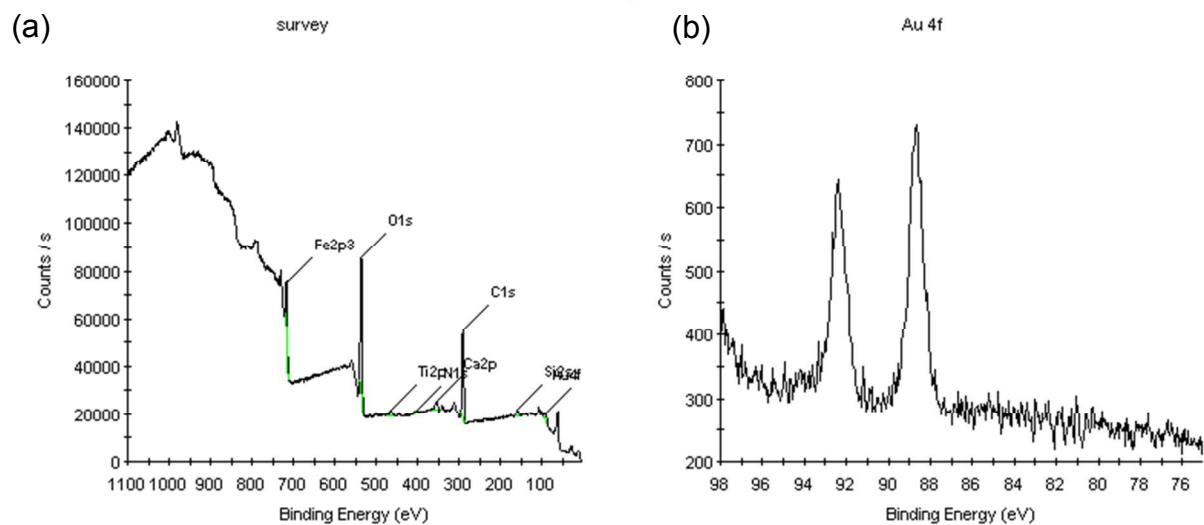


Figure S7: Size distribution histograms of Au NPs after dewetting of 2.5 (a), 5 (b), 10 (c) and 15 nm thick Au films (d) on TEC15 substrates obtained by image processing of Figures S6(a), (b), (c) and (d), respectively.



Name	C1s	O1s	Fe2p3	Ti2p	Ca2p	Au4f	Si2s	N1s
At. %	52.47	35.38	4.16	0.78	1.98	0.37	3.69	1.16

Figure S8: XPS surface scan from a type 2 photoanode in which the Au NPs (obtained by dewetting a 10 nm thick Au film) are embedded under a 115 nm thick hematite film. (a) General scan; and (b) High resolution scan of the Au 4f peak.

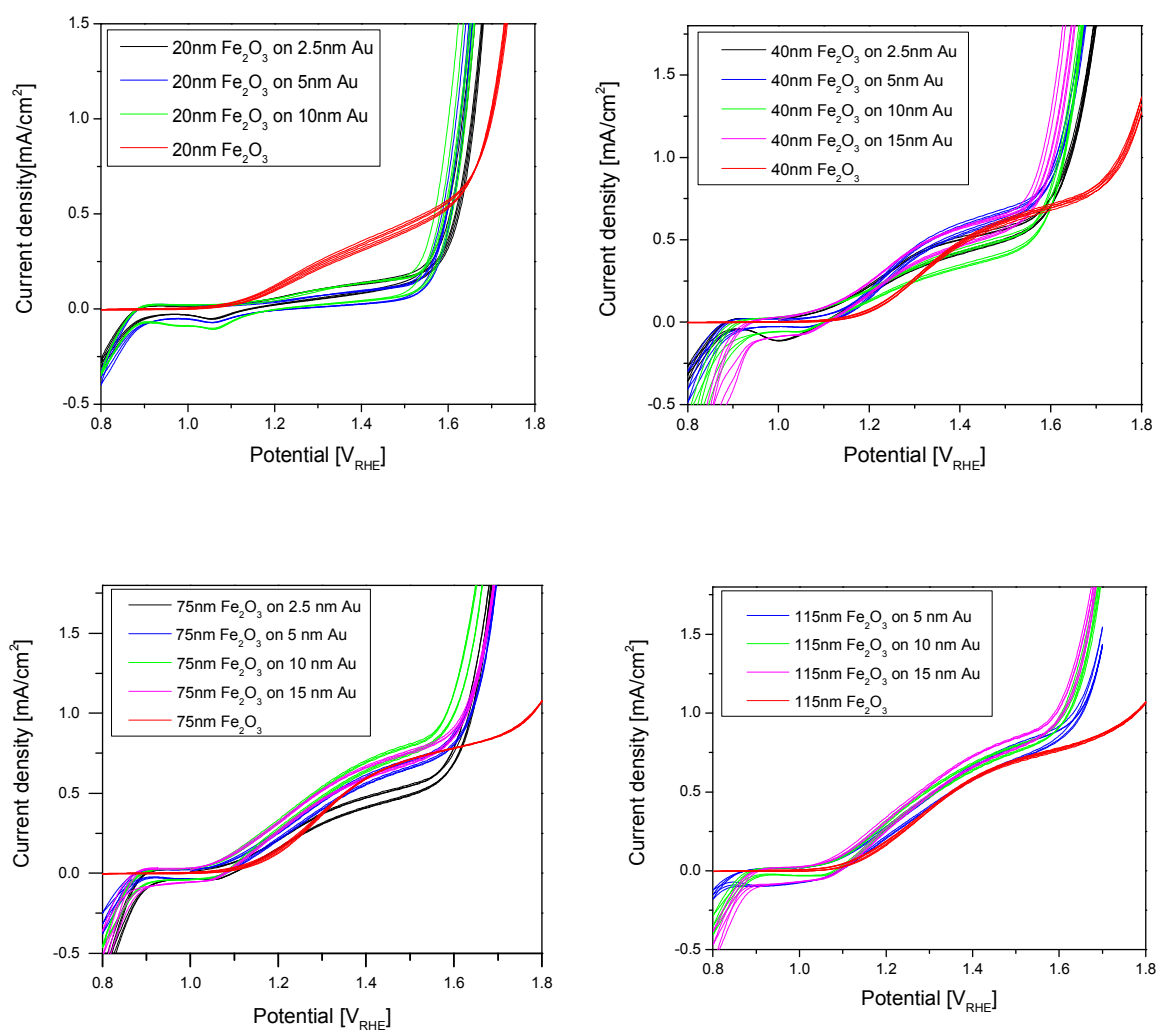


Figure S9: Cyclic voltammograms, measured under illumination, of 4 photoanodes of the type 2 configuration (with Au NPs embedded under hematite films).

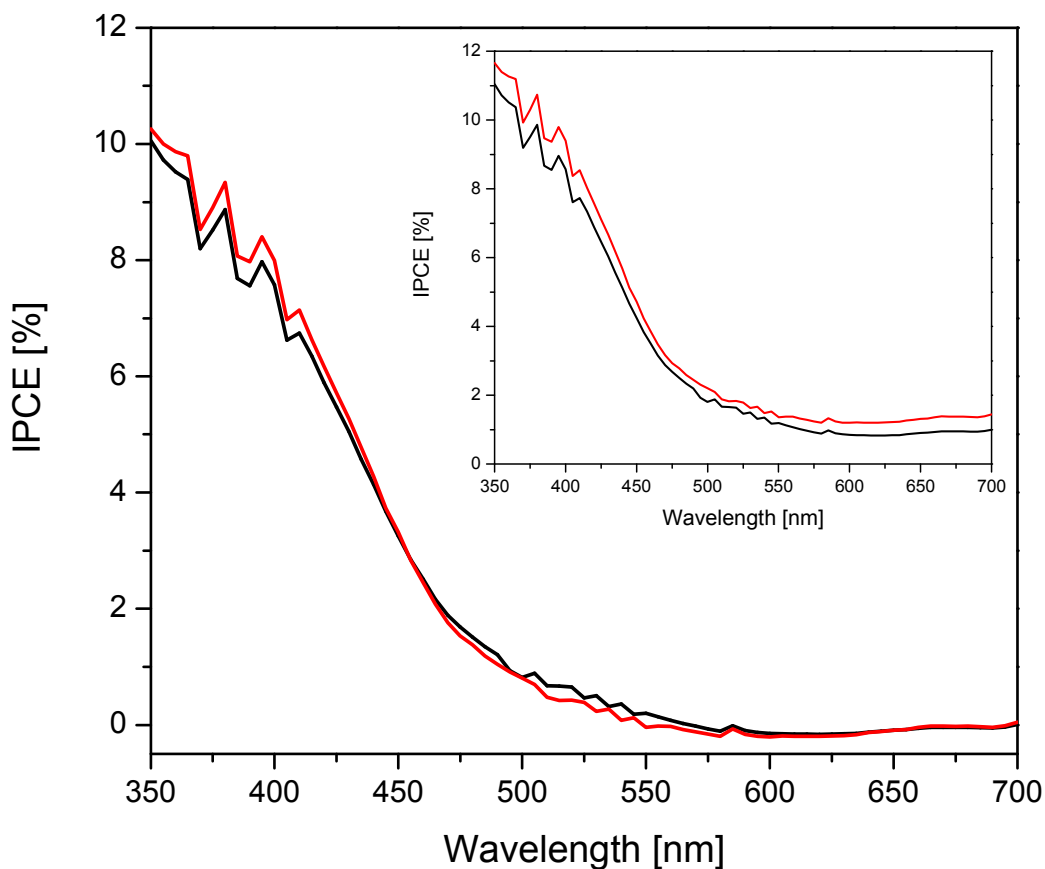


Figure S10: IPCE spectra of the champion hematite photoanodes with the thickest (115 nm) hematite films with and without Au NPs embedded under the hematite film (red or black curves, respectively). The current was measured at a potential of 1.53 V_{RHE}, and the IPCE was calculated according to equation (1) in the experimental section by subtracting the dark current from the measured current under illumination, $J_{photo}(\lambda, U) = J_{meas.}(\lambda, U) - J_{dark}(U)$. The inset shows the false spectra obtained without subtracting the dark current.

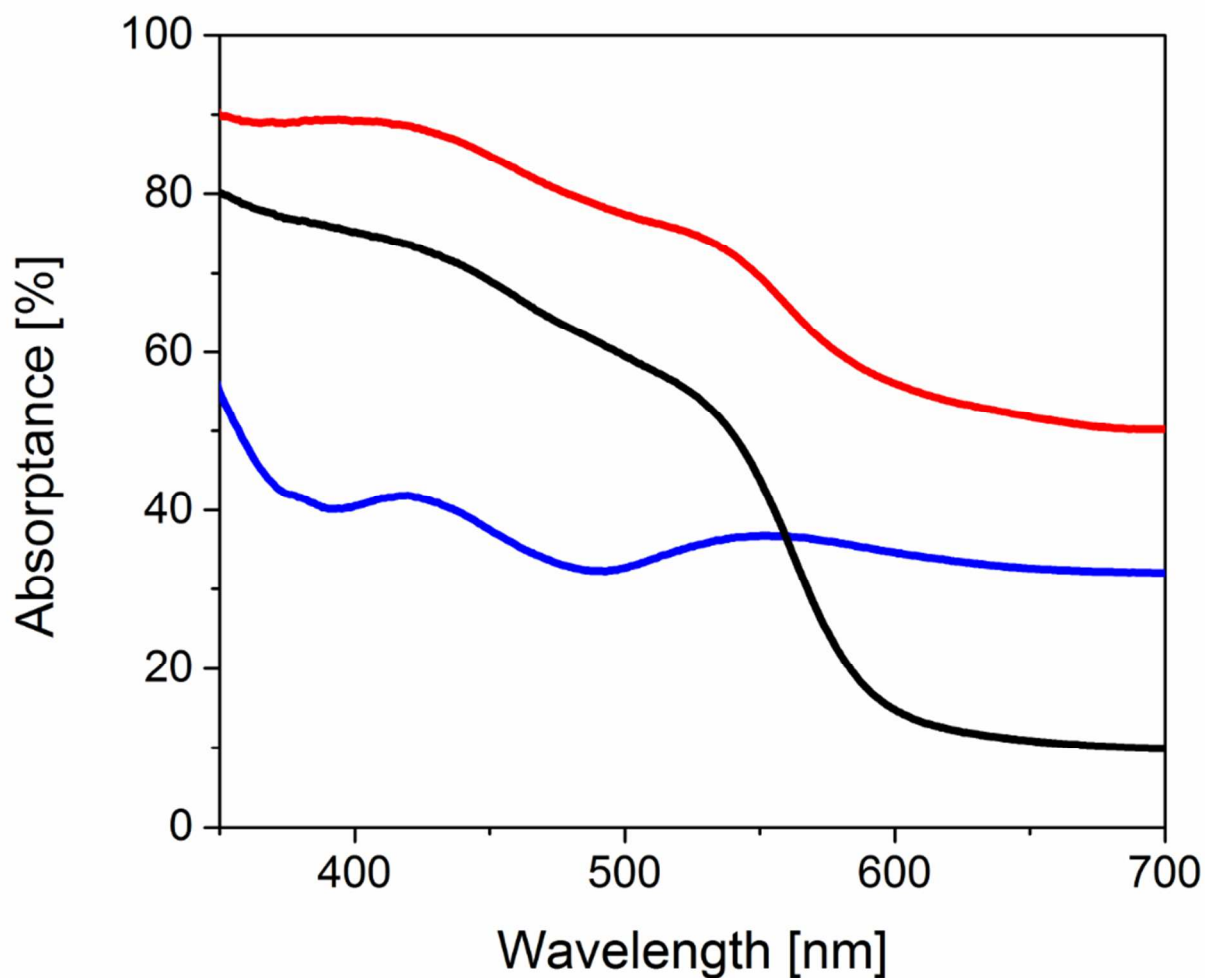


Figure S11: Absorption spectra of the champion photoanodes comprising 115 nm thick hematite films with (red curve) or without (black curve) Au NPs embedded under the hematite layer. The Au NPs were obtained by dewetting of 15 nm thick Au films prior to the deposition of the hematite film. The blue curve shows the absorption spectrum of an Au NP decorated TEC15 substrate without hematite in which the Au NPs were obtained by dewetting of a 15 nm thick Au film.