Supporting Information



Figure I: Red curve: Crystalline mWO₃ reference spectra scanned from Kuntz *et al.* [2010]^{*}; Blue curve: X-Ray diffraction spectra of the powder obtained after pyrolysis of 0.5M ammonium tungstate / 0.5M poly(4-styrenesulfonic acid) aqueous solution.



Figure II: AFM scan of the film surface obtained by spin coating of an ammonium tungstate/PSS aqueous solution, on FTO glass. Some halos with diameter comparable to the spheroid diameter obtained after pyrolysis are visible. The height of these features is lower than 50 nm and the roughness from the FTO substrate is not visible, suggesting a flat and continuous film.

Figure III: AFM scan of the film surface obtained after pyrolysis of the film presented in Figure II. The film is no more continuous and the mWO₃ spheroids are now clearly visible. It is possible to observe the FTO substrate roughness between the spheroids.

^{*}Joshua D. Kuntz, Octavio G. Cervantes, Alexander E. Gash, and Zuhair A. Munir. *Combustion and Flame*, **157** (8):1566-1571, August 2010. doi:10.1016/j.combustfflame.2010.01.005.





Figure IV: UV-visible absorption spectroscopy of hematite films of different thickness obtained by spin coating of solutions composed of $Fe(NO_3)_3$ at different concentrations, dissolved in pure ethanol.

Figure V: Variation of the thickness calculated from Beer-Lambert law at 400 nm depending on the Fe(NO₃)₃ concentration used to prepare the hematite film (blue circles). The full line represent the linear fitting leading to the relationship: $L = 54 \times [Fe(NO_3)_3]$



Figure VI: Comparison of the photocurrent transient amplitude at 0.9V vs Ag/AgCl when different concentrations of $Fe(NO_3)_3$ are spin coated on bare FTO glass substrates and on the microstructured mWO₃ films



Figure VII: Comparison of the photocurrents obtained with hematite coated on bare FTO glass (green line), hematite coated on a flat mWO_3 film (red line) and hematite coated on microstructured mWO_3 (blue line)



Figure VIII: Photocurrent densities obtained for the mWO₃ films composed of spheroids with different size distributions, with a 5 nm hematite overlay. These photoelectrochemical experiments were carried in a 0.05M phosphate buffered saline solution (PBS) (pH \approx 7) using an Ag/AgCl reference electrode.