Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Hematite Photoelectrodes for Water Splitting - Evaluation of the Film Thickness Role by Impedance Spectroscopy

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The Nyquist spectra for three different applied potentials for each sample are shown in Figure S1. For all samples, the overall impedance response decreases with the applied potential. For 1.7 V_{RHE} the resistances are very low since at this potential the photoelectrochemical system behaves like a simple electrolyzer and thus the current is generated by the potential difference supplied by the electrochemical workstation. The good agreement between experimental and fitted data indicates that the proposed electrical analogue is adequate – Figure S1.

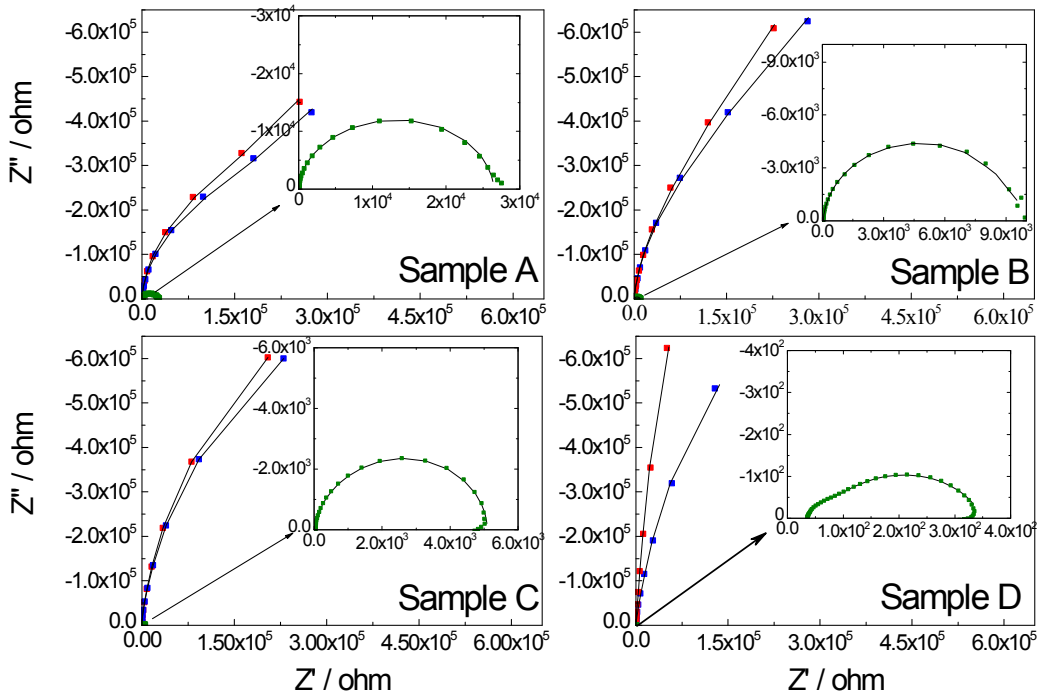

Figure S1. Nyquist spectra for samples A – D at 1.2 V_{RHE}, 1.4 V_{RHE} and 1.7 V_{RHE}. Dots represent the experimental data (■ - 1.2 V_{RHE}, ■ - 1.4 V_{RHE}, ■ - 1.7 V_{RHE}); lines represent the fitted model given in Figure 4.

Two more photoelectrodes with thicknesses 7 nm and 30 nm were prepared and characterized to validate the proposed electrical analogue. The *J-V* characteristic curve of the 7 nm-thick sample showed, however, a very low photocurrent density, mainly due to the small amount of α-hematite deposited over the conductive glass by the spray pyrolysis method. In fact, the light and dark currents obtained were quite similar, indicating a defect coat were the electrolyte contacts directly with the TCO - Figure S2. In what concerns the thicker sample, it produced a lower photocurrent than samples A, B and C – Figure S2. Nonetheless, it was possible to ascertain that also this 30 nm sample responds quite well to the proposed electrical model and the two RC components under studied were distinguished – Figure S3.

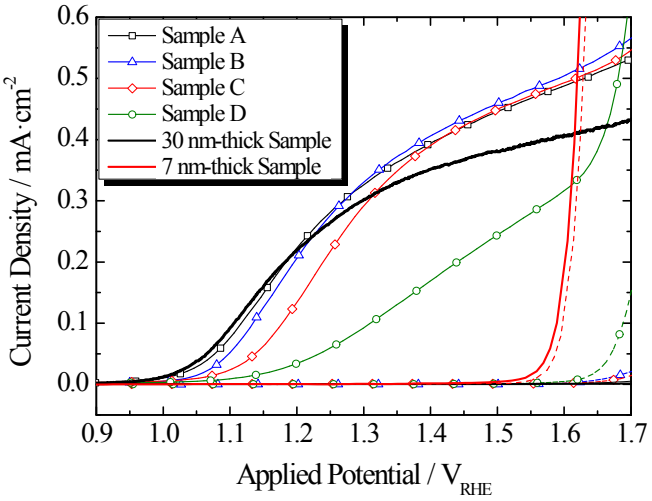

Figure S2. Comparison between the photocurrent density-voltage characteristics of the prepared photoanode samples A to D in the dark (dashed lines) and under simulated 1 sun illumination with the 7 nm- and 30 nm-thick samples, red and black lines, respectively.

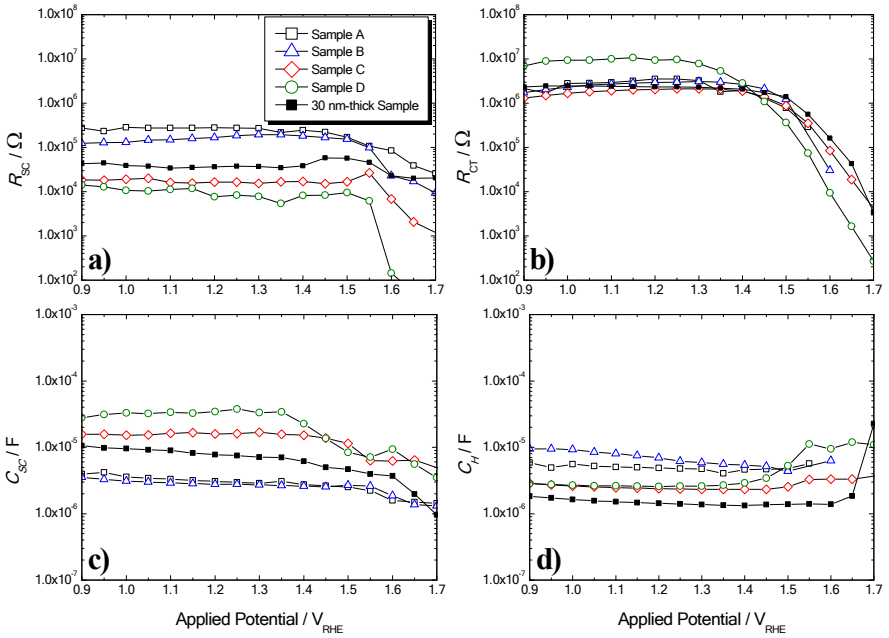

Figure S3. Comparison between the impedance results obtained by fitting the experimental data to the equivalent electrical circuit shown in Figure 5 of samples A, B, C and D with the 30 nm-thick sample: a) Bulk semiconductor resistances; b) Charge transfer resistance; c) Space charge capacity; d) Helmholtz capacity.