

## Electronic Supplementary Information

### Mesoporous $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Thin Films Synthesized via the Sol-gel Process for Light-driven Water Oxidation

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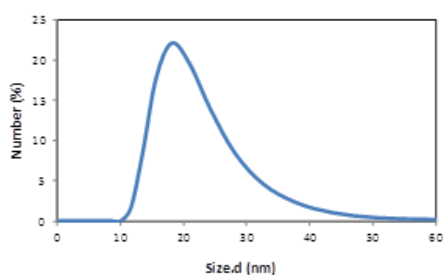
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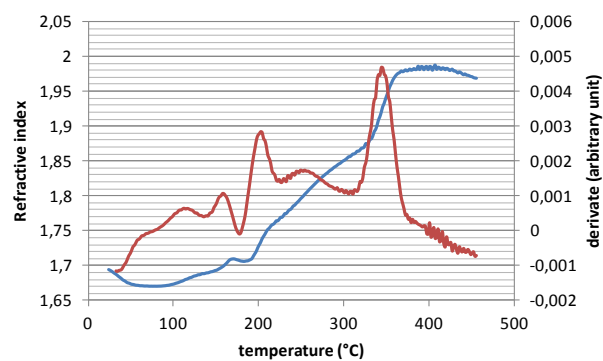
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Temperature (°C)	Crystallite size (nm)
400	14
425	15
450	18
500	30
600	47

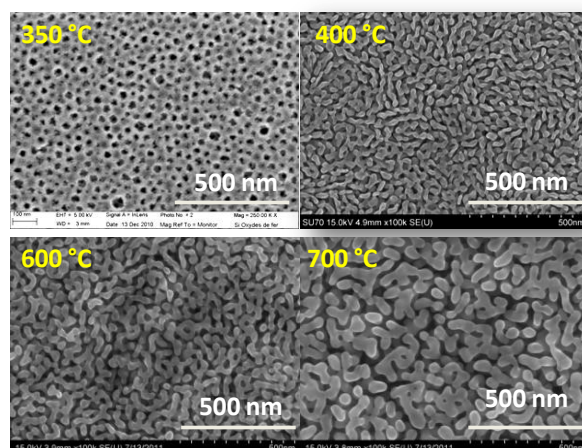
**Table S1.** Evolution of the size of the crystallites in the hematite films as a function of the sintering temperature



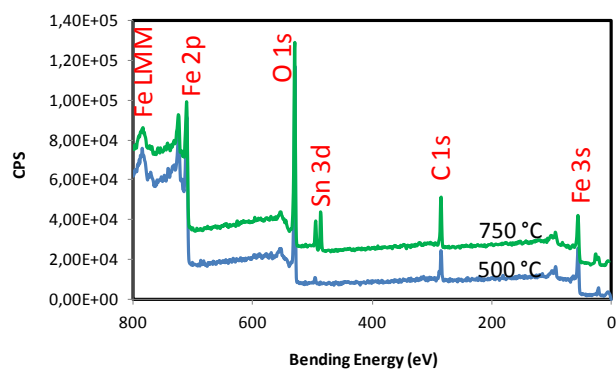
**Figure S1.** Size distribution of the micelles in the sol-gel solution from dynamic light-scattering measurements



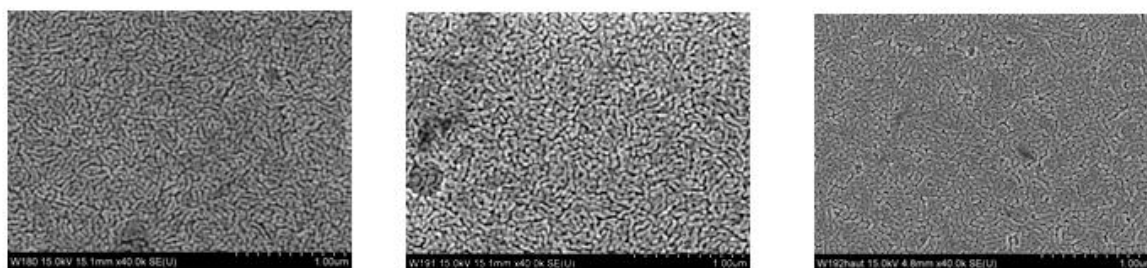
**Figure S2.** Refractive index (blue) and its derivate as functions of the temperature for hybrid organic-inorganic films: variation of the thickness (dark blue) and derivate of the thickness (red) as functions of the temperature.



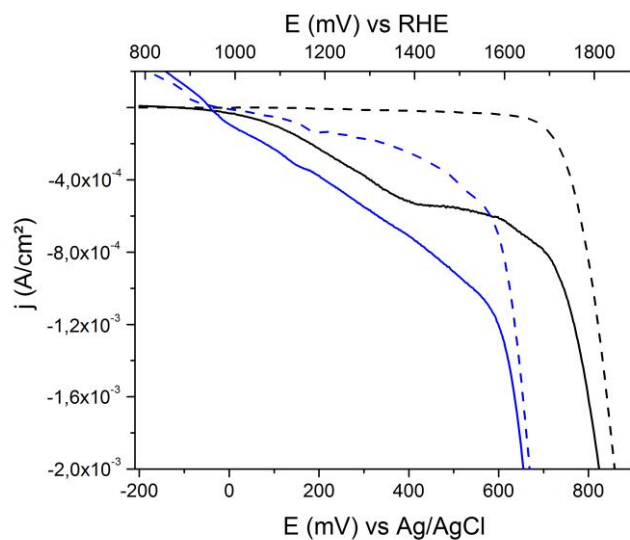
**Figure S3.** SEM images collected for  $\alpha$ - $\text{Fe}_2\text{O}_3$  thin films heat treated at various temperatures in air.



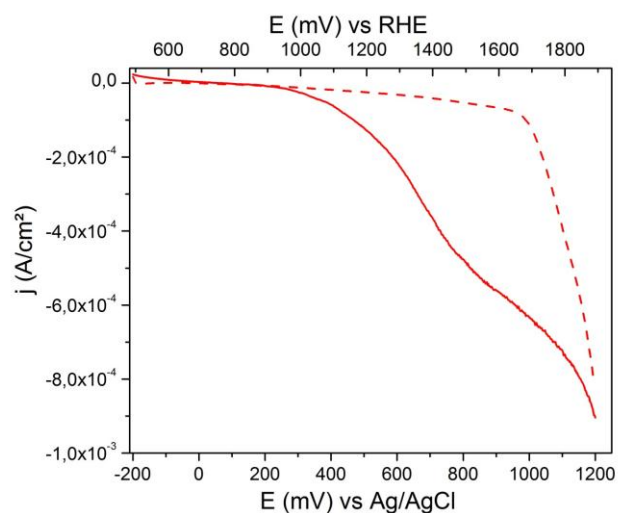
**Figure S4.** X-ray photoelectron spectroscopy survey data for the  $\alpha$ - $\text{Fe}_2\text{O}_3$  thin films sintered at 500 °C (blue) and 750 °C (green). The presence of Sn dopant is only observed in the sample sintered at 750 °C.



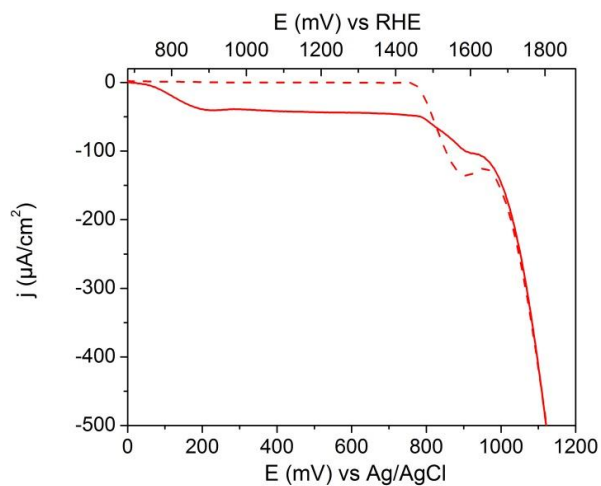
**Figure S5.** FE-SEM images of Co-modified 500 °C heat-treated 5-layer mesoporous films. Left. Impregnated; Middle electro-assisted deposition; Right. photo-assisted deposition.



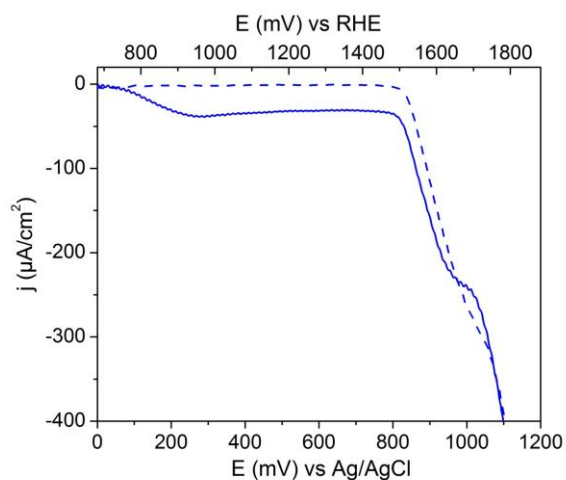
**Figure S6.** Current density vs applied potential ( $j$ -V) plots recorded at  $5 \text{ mV}\cdot\text{s}^{-1}$  in  $0.1 \text{ M KOH}$  ( $\text{pH } 13$ ) in the dark (dashed) and under illumination (plain) for pristine  $750 \text{ }^\circ\text{C}$  heat-treated 5-layers mesoporous films. The response for the same Co-impregnated sample is shown in blue.



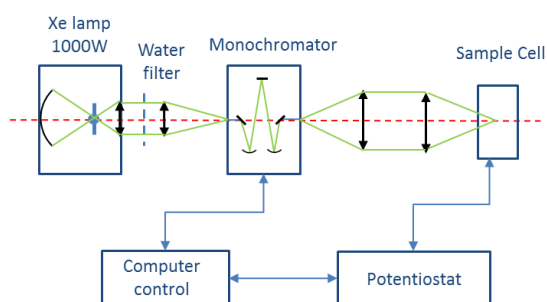
**Figure S7.** Current density vs applied potential ( $j$ -V) plots recorded at  $5 \text{ mV}\cdot\text{s}^{-1}$  in  $0.1 \text{ KPi}$  buffer ( $\text{pH} = 8$ ) in the dark (dashed) and under illumination (plain) for pristine  $750 \text{ }^\circ\text{C}$  heat-treated 5-layers mesoporous films



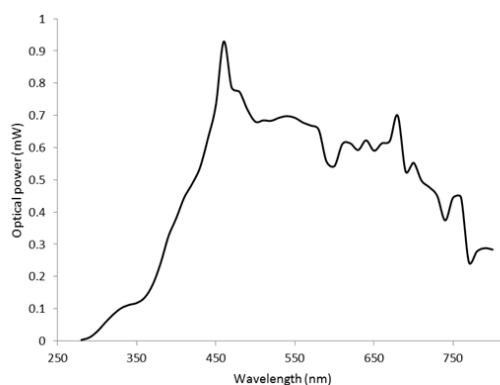
**Figure S8.** Current density vs applied potential ( $j$ -V) plots recorded at  $5 \text{ mV}\cdot\text{s}^{-1}$  in 0,1 KPi buffer (pH = 8) in the dark (dashed) and under illumination (plain) measured for  $500^\circ\text{C}$  heat-treated 5-layers mesoporous nanostructured hematite films decorated with electrodeposited  $\text{O}_2$ -CoCat.



**Figure S9.** Current density vs applied potential ( $j$ -V) plots recorded at  $5 \text{ mV}\cdot\text{s}^{-1}$  in 0,1 KPi buffer (pH = 8) in the dark (dashed) and under illumination (plain) measured for  $500^\circ\text{C}$  heat-treated 5-layers mesoporous nanostructured hematite films decorated with photo-electro deposition  $\text{O}_2$ -CoCat.



**Figure S10.** Schematic setup for incident-photon-to-current efficiency measurement.



**Figure S11.** Wavelength-dependent optical power reaching the sample during the ICPE measurement.