

## Supplementary Materials

# Thickness-Dependent Photoelectrochemical Water Splitting Properties of Self-Assembled Nanostructured LaFeO<sub>3</sub> Perovskite Thin Films

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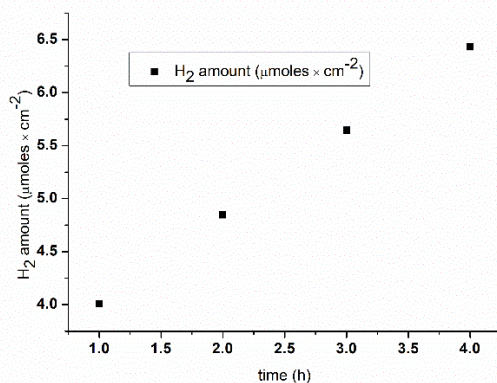
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## Unbiased Hydrogen Production Measurements

The photocatalytic hydrogen production measurements of LFO/STON thin films were performed in a glass cell (total volume of ca. 35 mL) with a quartz window for irradiation. The sample was immersed in 15 mL of NaOH aqueous solution under magnetic stirring. The irradiation of the sample was realized using a laser diode emitting at 405 nm. The generated hydrogen gas was quantitatively analyzed using a Shimadzu Nexis GC-2030 gas chromatograph (GC) equipped with a ShinCarbon ST micro-packed column and a barrier ionization discharge (BID) detector. High purity helium was used as carrier gas. The gas sample was injected into the GC using a HAMILTON syringe with a volume of 250  $\mu$ L. The GC parameters used to record chromatograms were: the injector pressure, temperature and split ratio 250 kPa, 150  $^{\circ}$ C, and 1:5, respectively, the column temperature, 35  $^{\circ}$ C and the detector temperature and discharge gas flow, 280  $^{\circ}$ C and 100 mL/min, respectively.



**Figure S1.** The photocatalytic hydrogen generation in time for the LFO/STON sample having 32 nm thickness.

## Optical Properties: Spectroellipsometry Data

**Table S1.** The fitting parameters used to obtain the dielectric function spectra for all analysed samples.

Thickness (nm)	Roughness (nm)	An	En (eV)	Br (eV)	MSE
14.1	0.3	1.7421	3.2072	0.9651	5.231
		2.6678	4.0374	0.4826	
		6.3246	4.6299	1.0706	
		8.0825	8.6943	2.9356	
21.2	7.4	1.3958	3.1603	0.7928	1.933
		2.5416	4.0138	0.4921	
		5.3508	4.5435	0.8439	
		11.757	9.1872	3.3178	
29.2	7.6	1.3066	3.0576	0.7310	1.561
		3.289	4.1173	0.5497	
		4.9815	4.6746	0.9063	
		11.642	9.3884	3.327	
31.3	1.2	0.2882	2.6422	2.269	1.335
		1.1577	3.1271	0.7818	
		4.0399	4.2221	0.8237	
		6.8136	7.2933	3.3636	
132.1	0.5	1.0662	2.9212	0.5608	2.044
		4.4495	4.3144	1.09	
		4.546	11.99	9.7818	
192.8	9.1	0.9059	3.0226	0.4734	2.183
		4.6067	4.2825	0.6108	
		6.3301	8.2568	5.8434	

## Compositional Analysis: Rutherford Backscattering Spectrometry (RBS) Analysis

**Table S2.** The cation composition and ratio for three different thicknesses LFO/STON thin films.

Sample	Composition		Fe/La
14 nm LFO/STON	Fe	La	1.217
	0.28 ( $\pm 3.5\%$ )	0.23 ( $\pm 1\%$ )	
29 nm LFO/STON	Fe	La	1.051
	0.206 ( $\pm 3\%$ )	0.196 ( $\pm 0.7\%$ )	
32 nm LFO/STON	Fe	La	0.727
	0.163 ( $\pm 3\%$ )	0.224 ( $\pm 1\%$ )	