

## Supplementary materials

### Evaluation of the efficiency of photoelectrochemical activity enhancement for the nanostructured $\text{LaFeO}_3$ photocathode by surface passivation and co-catalyst deposition

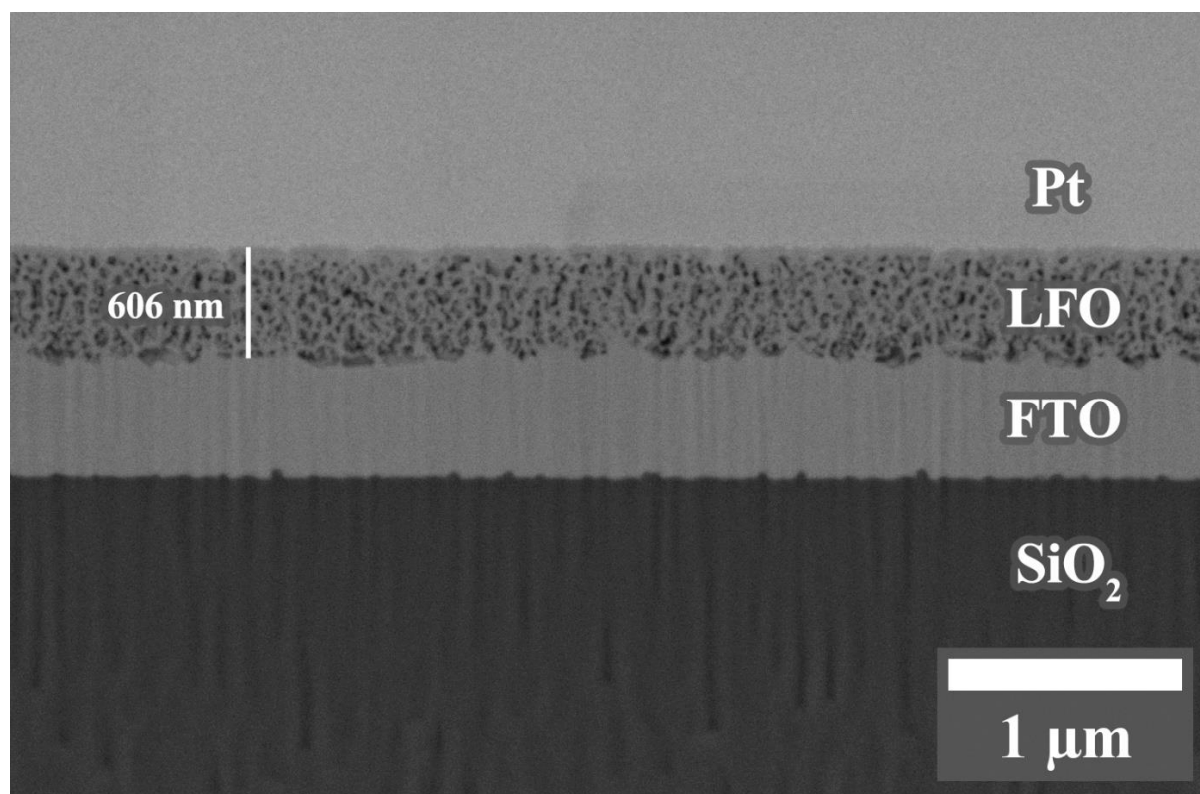
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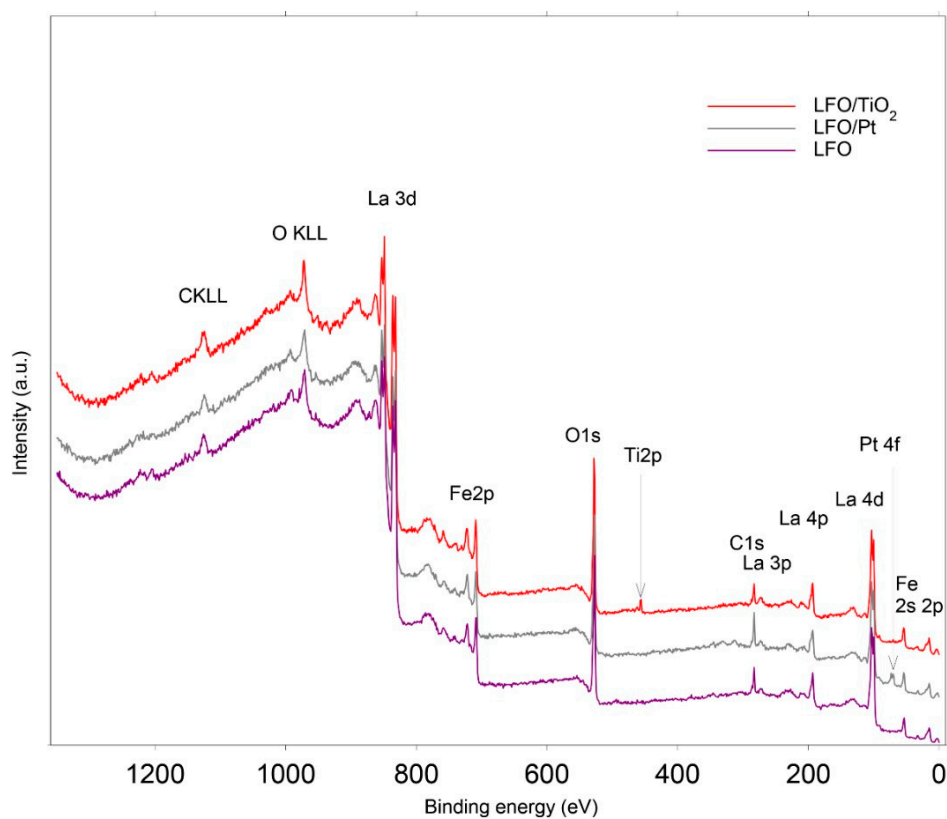
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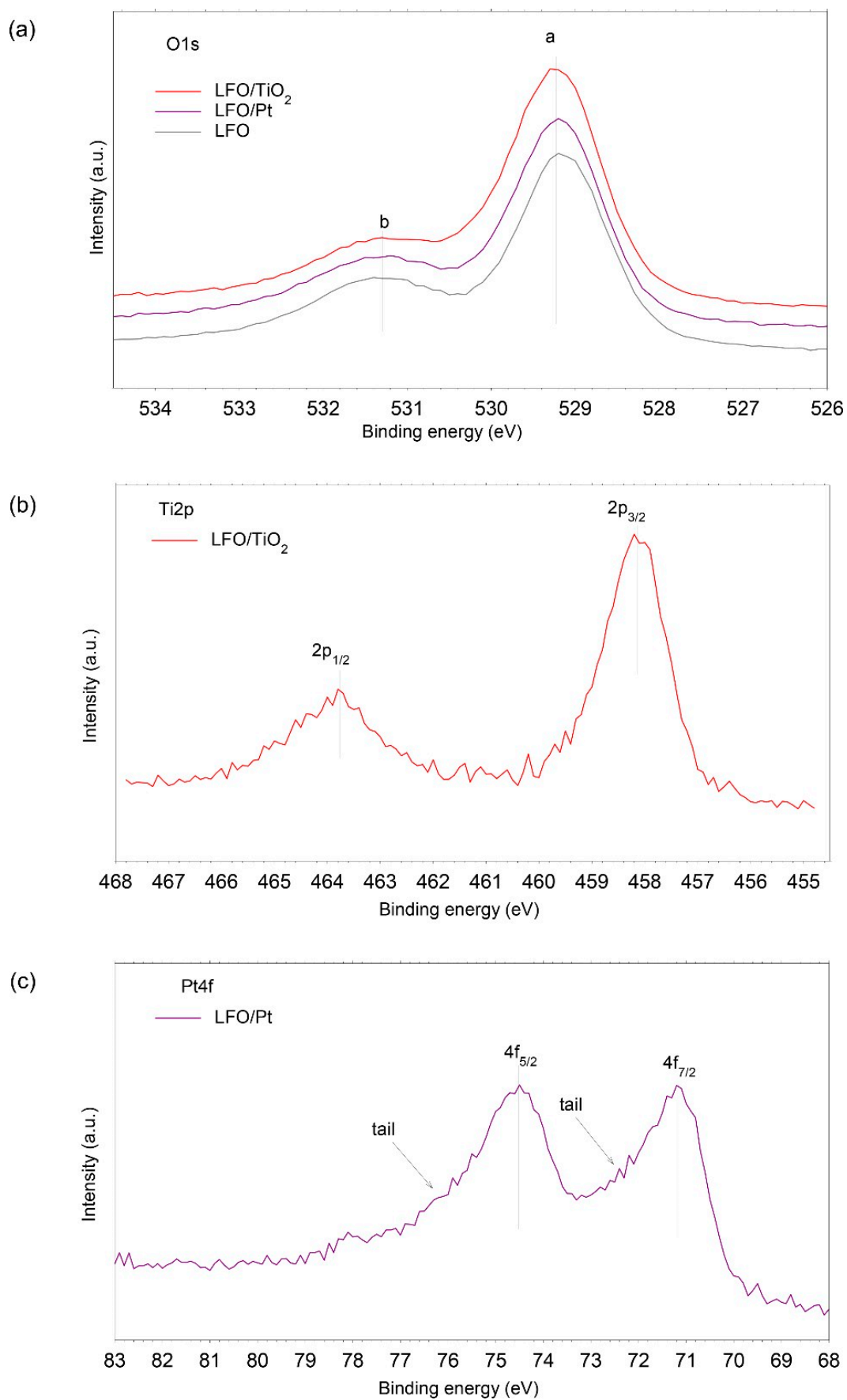
**Figure S1.** SEM image of FIB cross section of LFO film. Denoted thickness of the film is corrected for specimen tilt.



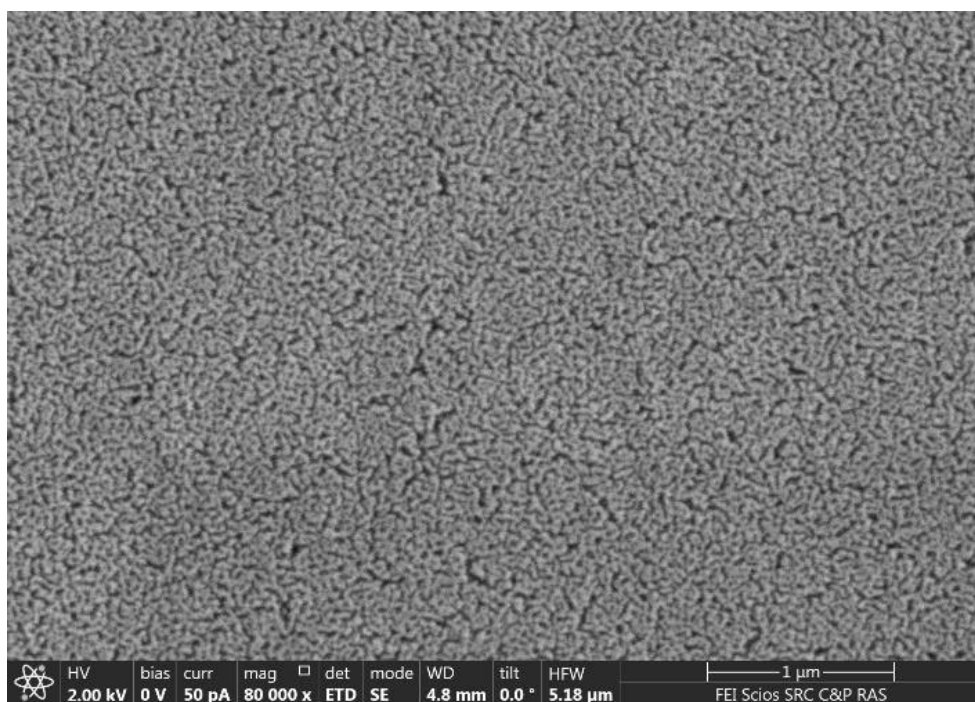
**Figure S2.** XPS survey spectra taken from LFO, LFO/Pt and LFO/TiO<sub>2</sub> electrodes. Spectra were shifted along the Y-axis for presentation.

**Table S1.** Surface element concentrations on the electrode surface calculated based on the XPS data.

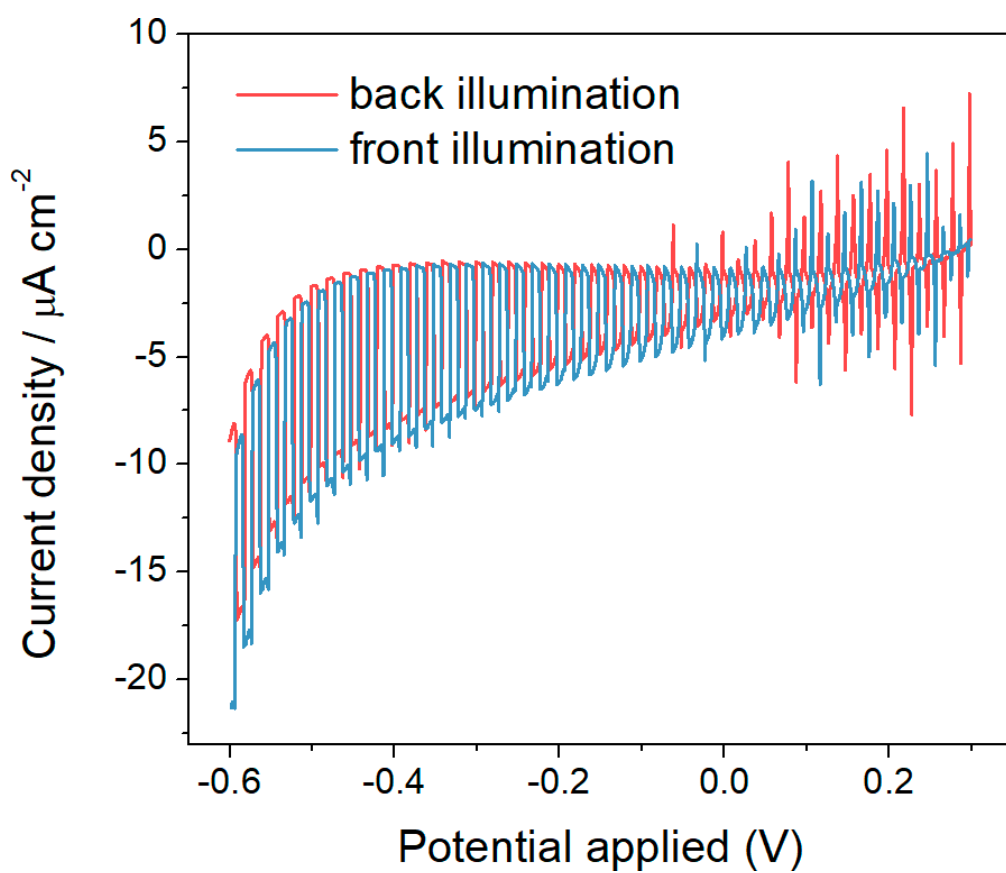
Sample	C, at%	O, at%	La, at%	Fe, at%	Ti, at%	Pt, at%
LFO	22.3	54.9	11.4	11.4	ND	ND
LFO/Pt	28.3	49.8	10.3	10.7	ND	0.9
LFO/TiO <sub>2</sub>	18.0	55.9	12.2	12.1	1.8	ND



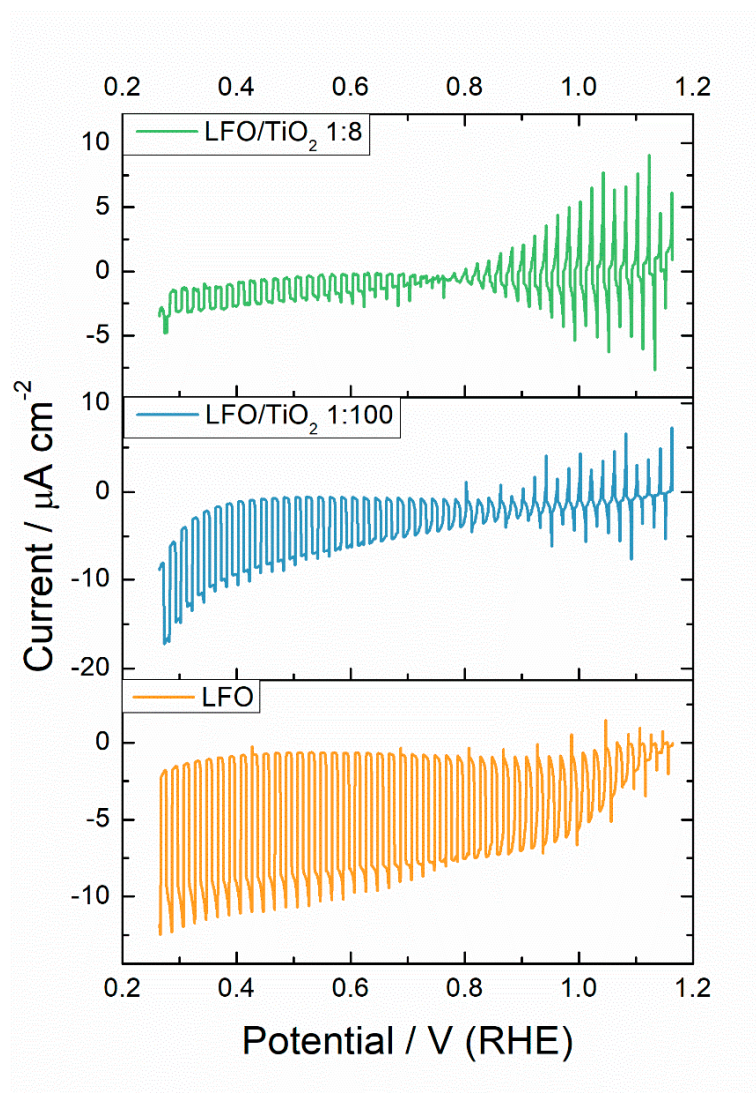
**Figure S3.** High resolution XPS spectra: O1s spectra for LFO, LFO/Pt and LFO/TiO<sub>2</sub> films (a), Ti2p spectrum for LFO/TiO<sub>2</sub> film (b), and Pt4f spectrum for LFO/Pt film (c).



**Figure S4.** SEM image of LFO/TiO<sub>2</sub>(1:100) electrode.

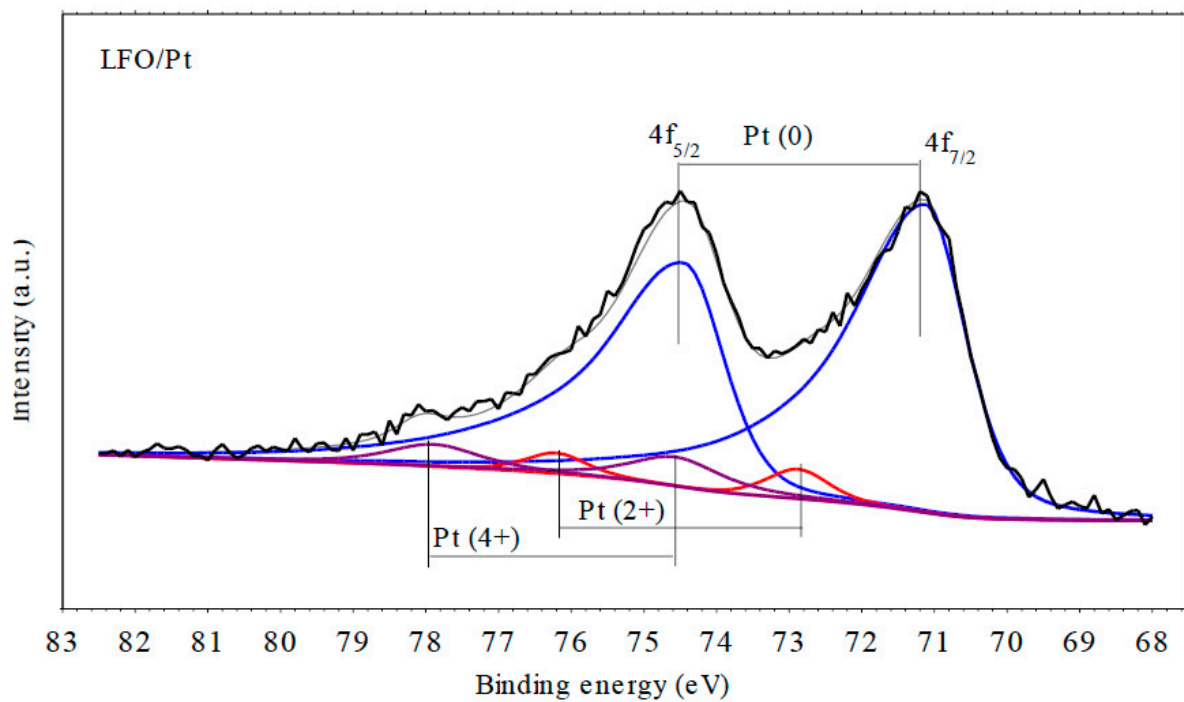


**Figure S5.** Linear sweep voltammograms at  $5 \text{ mV s}^{-1}$  under a square-wave 460 nm light perturbation for pristine LFO/TiO<sub>2</sub>(1:100) in deaerated 0.1 M NaOH under front-side and back-side illumination.

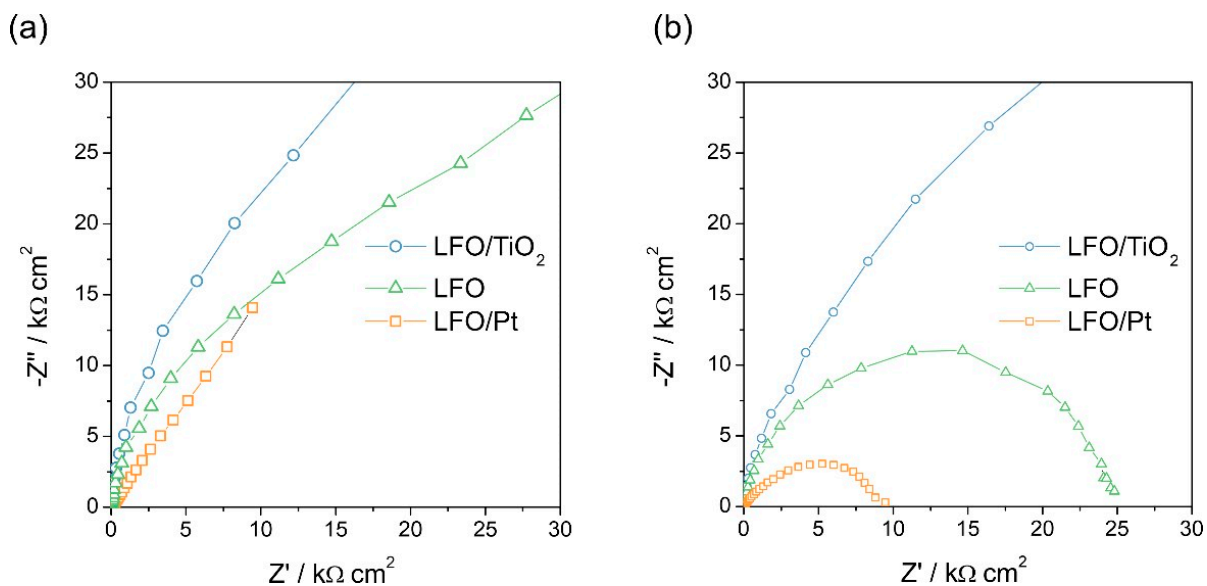


**Figure S6.** Linear sweep voltammograms at  $5 \text{ mV s}^{-1}$  under a square-wave 460 nm light perturbation for pristine LFO, LFO/TiO<sub>2</sub>(1:8) and LFO/TiO<sub>2</sub>(1:100) samples in deaerated 0.1 M NaOH.

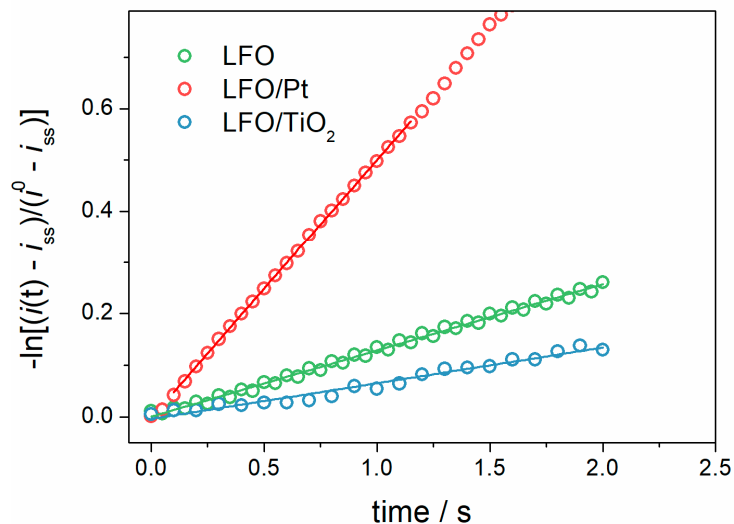




**Figure S7.** Pt4f spectrum fitting.



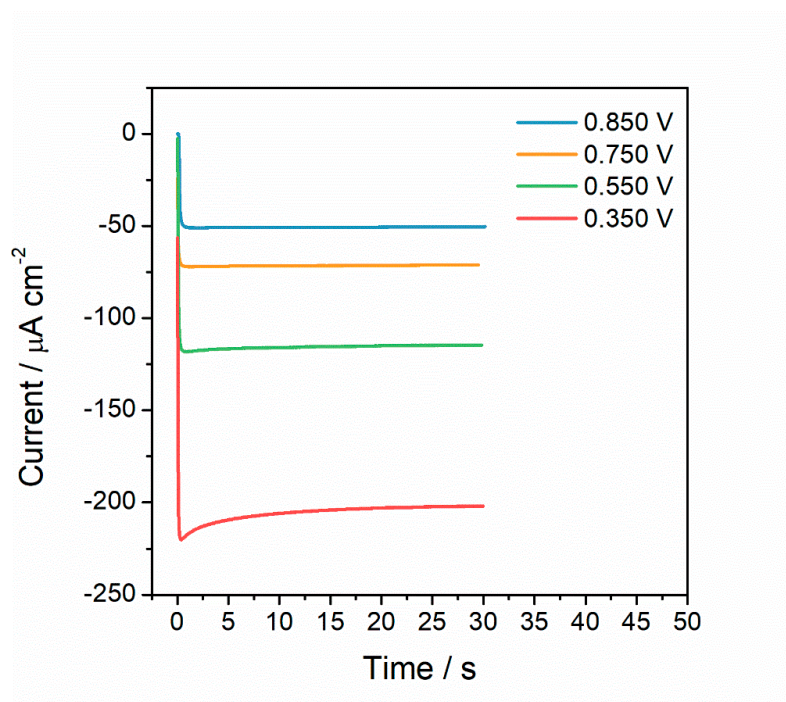
**Figure S8.** Impedance spectra of LFO/TiO<sub>2</sub>(1:100), LFO and LFO/Pt electrodes registered under illumination in deaerated 0.1 M NaOH (a) and in O<sub>2</sub>-saturated 0.1 M NaOH (b).



**Figure S9.** Linearized  $\ln\left(\frac{i(t)-i_{ss}}{i^0-i_{ss}}\right)$  vs. time plots for LFO, LFO/Pt and LFO/TiO<sub>2</sub> at 0.55 V vs. RHE. Symbols are experimental data points, lines are linear approximations.

**Table S2.** Charge transfer rate constants and recombination rate constants determined from transient photocurrent measurements for LFO, LFO/Pt and LFO/TiO<sub>2</sub> electrodes.

<i>E</i> , V	LFO		LFO / Pt		LFO / TiO <sub>2</sub>	
	<i>k</i> <sub>tr</sub> , s <sup>-1</sup>	<i>k</i> <sub>rec</sub> , s <sup>-1</sup>	<i>k</i> <sub>tr</sub> , s <sup>-1</sup>	<i>k</i> <sub>rec</sub> , s <sup>-1</sup>	<i>k</i> <sub>tr</sub> , s <sup>-1</sup>	<i>k</i> <sub>rec</sub> , s <sup>-1</sup>
0.95	0.102	0.012	0.783	0.218	-	-
0.85	0.100	0.020	0.565	0.160	-	-
0.75	0.082	0.024	0.480	0.194	-	-
0.65	0.089	0.038	0.494	0.271	-	-
0.55	0.081	0.044	0.489	0.354	0.036	0.003
0.45	0.074	0.069	0.498	0.440	0.039	0.006
0.35	0.096	0.089	0.476	0.473	0.045	0.009
0.25	0.122	0.149	0.529	0.558	0.038	0.020



**Figure S10.** Potentiostatic photocurrent transients registered during the illumination periods for the LFO/Pt electrodes at potential 0.850, 0.750, 0.550, 0.350 V vs. RHE in  $\text{O}_2$ -saturated 0.1M NaOH solution.

**Table S3.** Comparison of the photocurrent densities with the literature data.

Sample composition	Solution	Photocurrent density at 0.5 V vs. RHE in deaerated solution	Photocurrent density at 0.5 V vs. RHE in $\text{O}_2$ saturated solution	Ref.
LFO	0.1 M NaOH	$10 \mu\text{A cm}^{-2}$	$35 \mu\text{A cm}^{-2}$	This work
LFO/Pt		$30 \mu\text{A cm}^{-2}$	$115 \mu\text{A cm}^{-2}$	
LFO	0.1 M $\text{Na}_2\text{SO}_4$ (pH 12)	$0.1 \mu\text{A cm}^{-2}$	-	[1]
LFO/ $\text{TiO}_2$ /Pt		$1.5 \mu\text{A cm}^{-2}$	-	
Mg-doped LFO	0.1 M $\text{Na}_2\text{SO}_4$ (pH 12)	ca. $1 \mu\text{A cm}^{-2}$	$30 \mu\text{A cm}^{-2}$	[2]
Zn-doped LFO	0.1 M NaOH	-	$60 \mu\text{A cm}^{-2}$	[3]
LFO		ca. $1 \mu\text{A cm}^{-2}$	$10 \mu\text{A cm}^{-2}$	
LFO	0.1 M KOH	$10 \mu\text{A cm}^{-2}$	$25 \mu\text{A cm}^{-2}$	[4]
Li-doped LFO		$30 \mu\text{A cm}^{-2}$	$70 \mu\text{A cm}^{-2}$	
LFO (electrodeposited)	0.1 M NaOH	$10 \mu\text{A cm}^{-2}$	$200 \mu\text{A cm}^{-2}$	[5]



## References

1. Sun, X., Tiwari, D., Fermin, D.J., Nanostructured LaFeO<sub>3</sub> Photocathodes with Onset Potentials for the Hydrogen Evolution Reaction Over 1.4 V vs. RHE, *J. Electrochem. Soc.*, **2019**, *166*, H764-H768.
2. Sun, X., Tiwari, D., Fermin, D.J., Promoting Active Electronic States in LaFeO<sub>3</sub> Thin-Films Photocathodes via Alkaline-Earth Metal Substitution, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 31486-31495.
3. Diez-Garcia, M.I., Gomez, R., Metal Doping to Enhance the Photoelectrochemical Behavior of LaFeO<sub>3</sub> Photocathodes, *ChemSusChem*, **2017**, *10*, 2457-2463.
4. Li, Y., Wang, T., Gao, B., Fan, X., Gong, H., Xue, H., Zhang, S., Huang, X., He, J., Efficient photocathode performance of lithium ion doped LaFeO<sub>3</sub> nanorod arrays in hydrogen evolution, *New J. Chem.*, **2021**, *45*, 3463-3468.
5. Wheeler, G.P., Choi, K.-S., Photoelectrochemical Properties and Stability of Nanoporous p-Type LaFeO<sub>3</sub> Photoelectrodes Prepared by Electrodeposition, *ACS Energy Lett.*, **2017**, *2*, 2378-2382.