Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Efficient photocathode performance of Lithium ions doped $LaFeO_3$ nanorod array for hydrogen evolution

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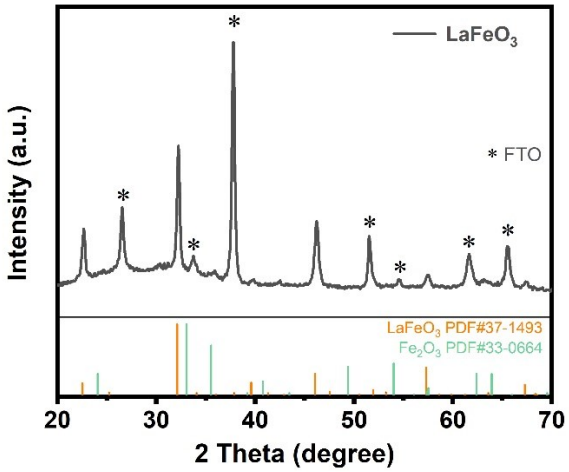

Figure S1. XRD pattern of $LaFeO_3$ film.

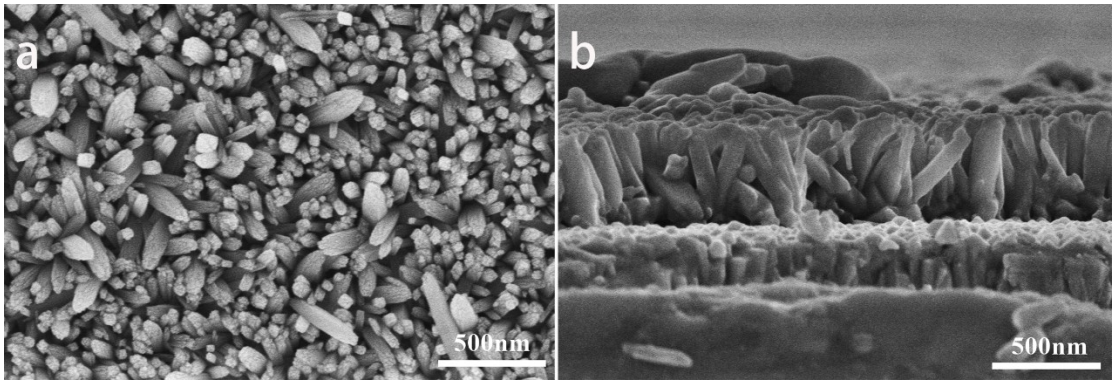

Figure S2. The top-view SEM images (a) and cross-view SEM (b) of β-FeOOH.

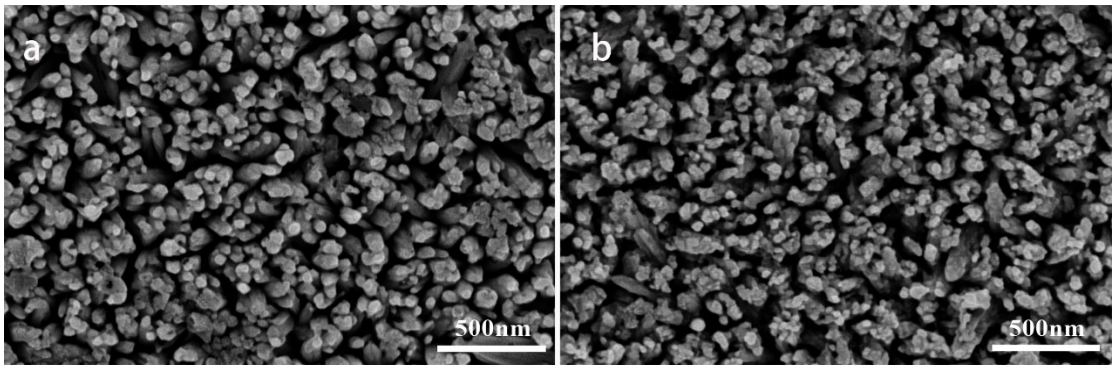

Figure S3. The top SEM images of (a) Li-LFO-1 and (b) Li-LFO-3.

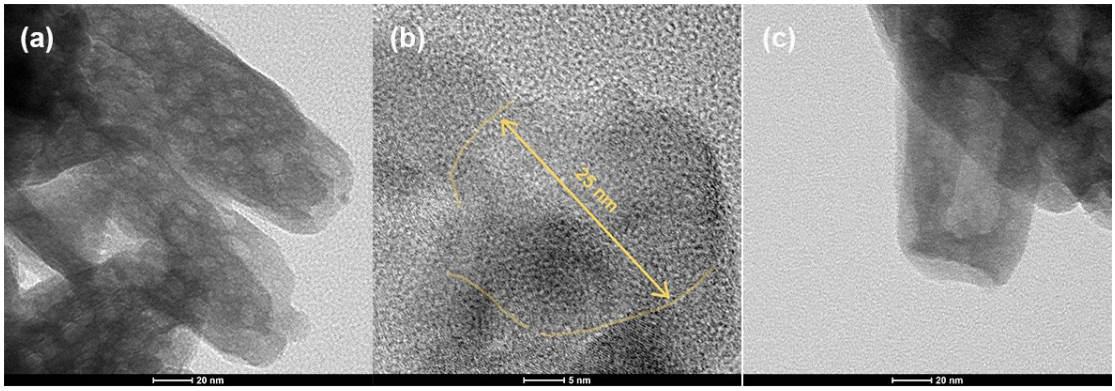

Figure S4. The HR-TEM images of (a)(b) pristine $LaFeO_3$ and (c) Li-doped $LaFeO_3$.

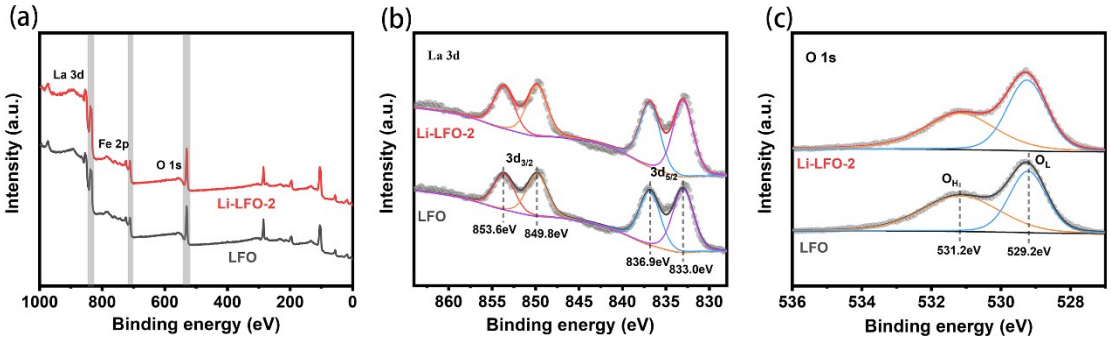

Figure S5. XPS survey spectra (a) and high-resolution of La 3d (b), O 1s (c).

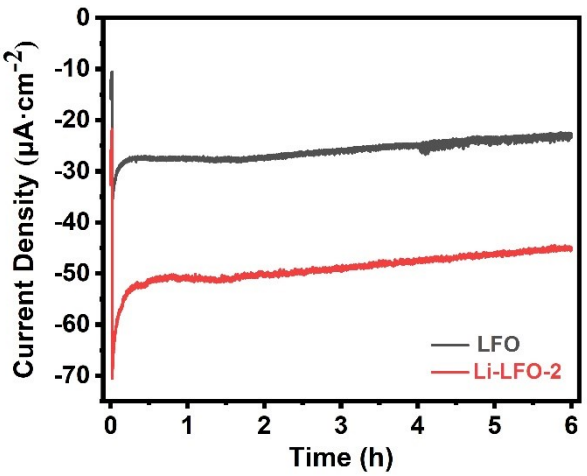

Figure S6. The chopped I-t curves at 0.4V vs. RHE for pristine and Li-doped $LaFeO_3$ for water reduction with N_2 bubbling.

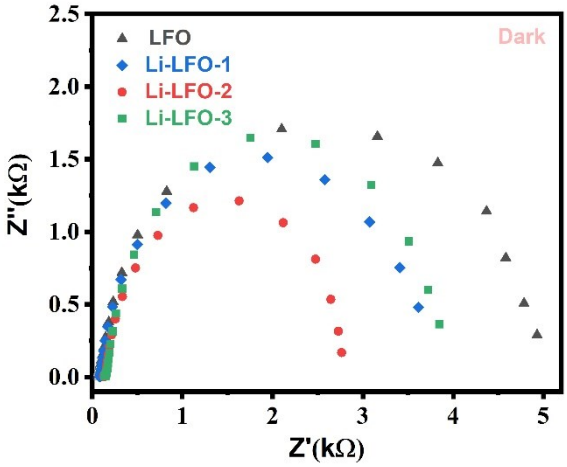

Figure S7. The EIS curves in light of pristine and Li-doped $LaFeO_3$ photocathodes measured in a solution saturated with O_2.

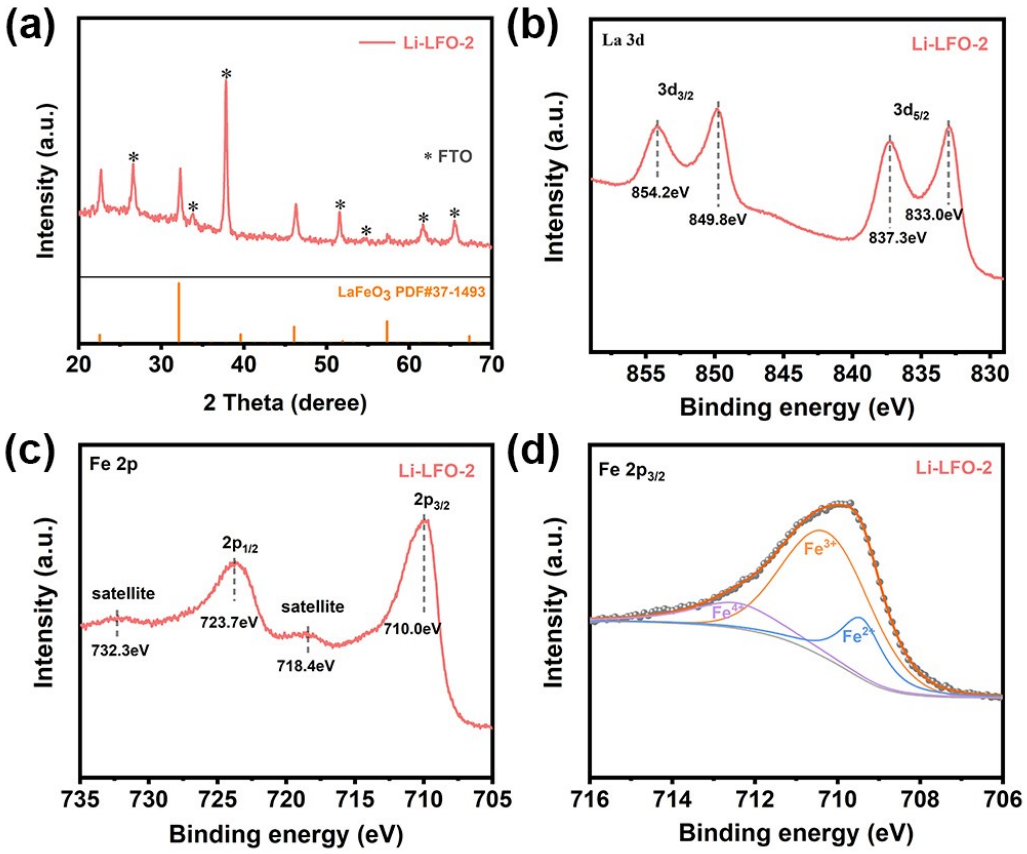

Figure S8. (a) XRD spectra, (b) XPS high-resolution spectra of La 3d, (c) XPS high-resolution spectra of Fe 2p and (d) peak fitting of Fe $2p_{3/2}$ of Li-LFO-2 photocathode.

Table S1. The crystallite size calculated based on XRD information

hkl	2θ(°)	β(rad)	D（nm）	Average crystallite size
（101）	22.660	0.380	22.34	22.10 nm
（121）	32.240	0.326	26.58	
（202）	46.200	0.448	20.20	
（240）	57.539	0.493	19.26	

Debye-Scherrer : $$D_{hkl} = \frac{K\lambda}{\beta\frac{\pi}{180} \cdot \cos\theta}$$

D_{hkl} is the grain diameter perpendicular to the crystal plane (hkl) direction. K is the Scherrer constant, and $K = 0.943$（$cube\ grain$）. λ is the incident X-ray wavelength, and $\lambda = 0.15406\ nm$（$Cu\ K\alpha$）. θ is the Bragg diffraction angle. β is the half-width of the diffraction peak.

Table S2. $LiNO_3$ drop-cast solution concentrations and percentages of Lithium in the $LaFeO_3$ film

concentration of Li in drop-cast solution	atomic % of Li in $LaFeO_3$
0.5 mM	0.75%
1.0 mM	3.8%
1.5 mM	5.7%

Table S3. The photocurrents of the $LaFeO_3$ photocathodes for PEC water reduction in the literature.

Photocathode and modification	Preparation	Potential	Current density	Reference
$LaFeO_3$	Electrodeposition	0.4 V (vs. RHE)	-10μA·cm^{-2}	1
$LaFeO_3$	magnetron sputtering	0 V (vs. RHE)	-25μA·cm^{-2}	2
(NiP+P1*)@ $LaFeO_3$	spray pyrolysis	0.6 V (vs. RHE)	-20μA·cm^{-2}	3
Au/ $LaFeO_3$	sol–gel	0.6 V (vs. RHE)	-20μA·cm^{-2}	4
Ni-$LaFeO_3$	spray pyrolysis	0.6 V (vs. RHE)	-66μA·cm^{-2}	5
Li- $LaFeO_3$	Hydrothermal template method	0.4 V (vs. RHE)	-50μA·cm^{-2}	This work

Reference

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[2] M. K. Son, H. Seo, M. Watanabe, M. Shiratani, T. Ishihara, *Nanoscale,* 2020,**12**,9653-9660.

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