Supporting Information

Promoting Active Electronic States in LaFeO$_3$ Thin-Films Photocathodes via Alkaline-Earth Metal Substitution

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Figure S1. Topography and composition of alkaline-earth metal cation (AMC) substituted LaFeO$_3$ (LFO).

Figure S2. XRD analysis of AMC substituted LaFeO$_3$ (LFO).

Figure S3. Deconvolution of La 3d, Fe 2p, O 1s XPS bands of 7% Sr substituted LFO thin-film

Figure S4. Photoelectrochemical responses of AMC substituted LFO in the presence of O$_2$.

Figure S5. Photoelectrochemical responses of AMC substituted LFO under O$_2$ free conditions.

Figure S6. Dynamic photocurrent transient responses of pristine and 7% Ba substituted LFO.

Figure S7. Oxygen reduction reaction in the dark as a function of Ba$^{2+}$ content.
Figure S1. Topography and composition of alkaline-earth metal cation (AMC) substituted LaFeO$_3$ (LFO): Top view scanning electron micrographs (a) and energy dispersive analysis of X-rays spectra (b) of pristine and 7% AMC substituted LFO thin-films.
Figure S2. XRD analysis of AMC substituted LaFeO$_3$ (LFO): (a) XRD patterns of the pristine and 7% AMC substituted LFO refined to the $pm-3m$ cubic phase JCPDS-ICDD database file 01-075-0541; evolution of the (110) peak as a function of extent of LFO substitution by (b) Sr$^{2+}$, (c) Ca$^{2+}$ and (d) Mg$^{2+}$. (e) Lattice constant extracted from full-profile structural Pawley refinement shown in (a). Despite the flat difference curve, the refinement could not converge below Rp and Rwp of 18% and 23%, respectively. The uncertainty in the refinement arises from the scatter in the experimental XRD and nanoscale crystalline domain of the thin-films. Although the trend is clear and unambiguous, the absolute values of the estimated lattice parameters must be considered cautiously.
Figure S3. Deconvolution of La 3d, Fe 2p, O 1s XPS bands of 7% Sr substituted LFO thin-film. The La 3d shows two photoemission peaks at 833.9 (La 3d$^{5/2}$) and 850.9 eV (La 3d$^{3/2}$) with a 17eV spin-orbit component between the doublet, confirming the La$^{3+}$ oxidation state. The Fe 2p spectrum shows the Fe 2p$^{3/2}$ around 710 eV and Fe 2p$^{1/2}$ at 724.0 eV, with a satellite peak at 724.2 eV. The Fe 2p peak is deconvoluted into three components, with the most prominent associated with Fe$^{3+}$ species and the other two peaks at higher binding energies (BE) correspond to higher iron oxidation states. The O 1s peak shows a sharp band around 529 eV linked to the oxygen in the perovskite lattice, while the other two contributions are assigned to a hydroxyl group and carbonated species. The discussion in the main text focused on the evolution of the Fe 2p$^{3/2}$ and O 1s bands as a function of AMC substitution. However, we also noticed that the higher BE components of the O 1s appear to be affected by AMC substitution (see Figure 2b and 2d of the main text). We rationalise this observation as variations in the relative intensity of the hydroxyl and carbonated photo-emission responses, as opposed to shifts in the binding energy.
Figure S4. Photoelectrochemical responses of AMC substituted LFO in the presence of O$_2$: Linear sweep voltammograms (LSV) of (a) Mg$^{2+}$, (b) Sr$^{2+}$ and (c) Ca$^{2+}$ substituted LaFeO$_3$ thin-films recorded at 5 mV/s under a square wave 405 nm illumination and photon flux of 3.25×10$^{15}$ cm$^{-2}$ s$^{-1}$. LSV curves of the pristine and 7% AMC substituted films recorded under identical conditions: (d) after preparation, (e) after 1 hr of continuous illumination and (f) after 45 days exposed to air. All experiments are recorded under O$_2$-saturated aqueous solution containing 0.1 M Na$_2$SO$_4$ at pH 12.
Figure S5. Photoelectrochemical responses of AMC substituted LFO under O₂ free conditions. LSVs (5 mV/s) of LFO films with different substitution levels of Mg²⁺, Ca²⁺ and Sr²⁺ performed under 405 nm square wave light perturbation (photon flux of 3.25×10¹⁵ cm⁻² s⁻¹) in Ar-saturated 0.1M Na₂SO₄ aqueous solution pH 12.
Figure S6. Dynamic photocurrent transient responses of pristine and 7% Ba substituted LFO. Transient photocurrent responses of pristine and 7% Ba\textsuperscript{2+} substituted LFO thin-films at 0.45 V vs RHE in Ar-saturated (a) and O\textsubscript{2}-saturated (c) 0.1M Na\textsubscript{2}SO\textsubscript{4} aqueous solution (pH 12). The films are illuminated with a 405 nm LED (3.25×10\textsuperscript{15} cm\textsuperscript{2} s\textsuperscript{-1} photon flux). (b) displays photocurrent transients normalised by the maximum photocurrent under Ar-saturated solution, showing a comparatively smaller photostationary current at 7% Ba\textsuperscript{2+} substituted films. (d) shows normalised photocurrent responses in O\textsubscript{2} saturated solutions. The figure shows that AMC substitution not only increases the overall photocurrent (c) but also decreases the response time during the on and off-transients. This is linked to the dampening of the A-states responsible for majority carrier trapping upon AMC substitution.
Figure S7. Oxygen reduction reaction in the dark as a function of Ba$^{2+}$ content. Electrochemical responses Linear-sweep voltammograms recorded at 5 mV/s for pristine and Ba substituted LaFeO$_3$ in O$_2$-saturated Na$_2$SO$_4$ aqueous solutions (pH 12) in the dark.