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ARTICLE

Defect engineering nanostructured LaFeO₃ photoanodes improves the activity for solar water oxidationReceived 00th January 20xx,
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LaFeO₃ (LFO) is recognized as a candidate material for solar water oxidation but its photoelectrochemical response yet remains modest and stagnant. With the aim of advancing LFO photoanodes for oxygen evolution reaction (OER), here, a nanorod array-type electrode combined with defect and surface engineering protocols was demonstrated, delivering a benchmark performance of 0.4 mA cm⁻² at 1.23 V vs RHE with an onset below 0.55 V vs RHE. It was found that oxygen defects activate the surface towards OER, while coating with NiFeO_x suppressed the surface recombination. It was discovered, however, that the performance was limited by a rapid (nanosecond timescale) bulk recombination as well as the ultrashort hole diffusion length (< 5 nm). Overall, this work provides guidelines to accelerate the progress on LFO as well as novel insights that afford a better understanding of oxide perovskite photoanodes.

Introduction

Sourcing commodity chemicals, like hydrogen, from abundant feedstocks and solely using renewable energy is key to decarbonize our economic model and meet the increasingly stringent international policies on carbon emission.^{1–4} Photoelectrochemical (PEC) tandem cells for solar water splitting are recognized to be capable of carrying on this energetic transition provided that competitive margins in manufacturing cost, efficiency and durability are achieved.⁵ In fact, there have been encouraging advances in the development of low-cost, stable and high-performing photocathodes for solar water reduction, for instance, Sb₂Se₃,⁶ Cu₂O,⁷ Cu₂ZnSnS₄,⁸ Cu(In,Ga)S₂,⁹ etc. However, it is the water oxidation half-reaction the one that currently poses serious hurdles for the realization of solar water splitting using tandem cells. Metal oxides such as TiO₂,¹⁰ α-Fe₂O₃,¹¹ WO₃,¹² ZnFe₂O₄,¹³ and BiVO₄,¹⁴ have been capturing most of the attention in recent years, offering not only long-term stability and cheap manufacturing, but also complementary light harvesting when integrated in tandem cells.¹⁵ Unfortunately, the photocurrent values delivered by these materials are still below the

requirements to realize a competitive tandem cell.¹⁶ Although research actively continues in further engineering and tweaking these state-of-the-art photoanodes to tap into their theoretical maximum performance,¹⁷ growing efforts are turning into exploring new materials whose broader electronic and compositional tunability could disrupt the field of solar water oxidation getting the PEC tandem technology finally off the ground.

Oxide perovskites (ABO₃; A = alkali or rare-earth metals; B = transition metals) have lately come into the spotlight owing to their earth-abundant composition, demonstrated catalytic activity and immense (opto)electronic flexibility.^{18,19} These features altogether have consolidated them as an excellent platform to enable a new generation of photoanodes. Perovskite oxides have garnered prominence as light absorbers for PEC systems due to their optimum band gaps for sunlight harvesting (1.1 – 2.4 eV).^{20,21} Currently, oxynitrides set the benchmark performance amongst oxide-based perovskites delivering photocurrent values up to 5 mA cm⁻² at 1.23 V vs RHE.²² However, the only minutes-long lifespan of most of oxynitrides under operation,²³ due to rapid corrosion, and the tedious multistep fabrication of these photoelectrodes has urged to redirect efforts toward the design of highly-active perovskite oxide photoanodes, which are more resilient to harsh oxidative conditions and amenable to simple solution processing.

Among the various oxide perovskites investigated so far as photoanodes, we are particularly interested in prospecting LaFeO₃ (LFO) given its suitable band gap (E_g) for sunlight harvesting, reported to range between 1.8 – 2.7 eV,^{24–27} and demonstrated catalytic activity toward OER.²⁸ Note that the valence band originates from the hybridization of O 2p and Fe 3d orbitals, whereas the conduction band is mainly made of La orbitals,²⁹ which anticipates the participation of lattice iron in

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Electronic Supplementary Information (ESI) available: Experimental details, XRD, SEM, XPS, IPCE, GC calibration, determination of minority carrier diffusion length, EIS analysis, IMPS analysis, steady-state photoluminescence, stability, electrochemical surface area (ECSA), detailed XPS fitting. See DOI: 10.1039/x0xx00000x

the hole transport mechanism and grounds the similarities with other ferrites.³⁰ Admittedly, the dual role of LFO as light absorber and electrocatalyst affords the design of single-material photoanodes, circumventing the complexity of multijunction electrodes. Surprisingly, despite this competitive advantage the performance of LFO photoanodes remains far behind other ferrites.^{13,31} Several groups have explored the possibility of activating LFO photoanodes by compositional engineering, *i.e.*, replacing partially La^{3+} or Fe^{3+} with low-valent ions such as Mn^{2+} , Cu^{2+} , Sr^{2+} , *etc.* although in all cases the photocurrent values barely surpassed the few tens of $\mu\text{A cm}^{-2}$ while the late onset potential ($> 1.6 \text{ V vs RHE}$) hardly improved with respect the onset recorded in the dark.^{32,33} Alternatively, Peng *et al.* demonstrated that the incorporation of a co-catalyst such as Co-Pi enhanced the photocurrent, although to simply reach a very modest $7 \mu\text{A cm}^{-2}$ at 1.2 V vs RHE .³⁴ Overall, these early studies hint at the presence of massive carrier losses that prevent the extraction of the vast majority of photogenerated carriers (note that the photocurrent limit for LFO is 12.5 mA cm^{-2})³⁵, although no attempts to identify them have been undertaken. Understanding the key parameters that factor-in and limit the response is instrumental in developing a new generation of more efficient LFO photoanodes.

In this work, we introduced for the first time a nanorod array-type LFO electrode, combining oxygen defect engineering and surface passivation with NiFeO_x to set a new benchmark performance among LFO photoanodes for solar water oxidation at photocurrent values of 0.4 mA cm^{-2} (at 1.23 V vs RHE) and onset potentials of 0.55 V vs RHE . We found that oxygen defects and NiFeO_x act synergistically to activate the reactive interface by reducing the overpotential for OER and the surface recombination. Our investigations evidenced however, the existence of significant photogenerated carrier losses at ultrashort timescales as well as a weak space-charge field and small diffusion length, which altogether limit the PEC response.

Results and discussion

As illustrated in Fig. 1, LFO photoanodes were prepared by using a modified version of the method previously reported by our group to fabricate spinel ferrite thin film electrodes.³⁶ In brief, a nanorod array of $\beta\text{-FeOOH}$ (iron precursor) was directly grown on the transparent conductive substrate (F-doped SnO_2) by using a chemical bath deposition. Subsequently, this film was

coated by drop-casting an excess of $0.5 \text{ M La}(\text{NO}_3)_3$ (lanthanum precursor) aqueous solution (approx. 5 mL) and drying. Subsequent annealing at 650°C in air triggered the formation of LFO coated with a crust of La_2O_3 , which originated from the excess of lanthanum precursor. Pristine LFO was obtained by selectively etching away this surface oxide. Detailed experimental procedure on sample preparation can be found on Electronic Supplementary Information (ESI). Note that although three different temperatures, namely 550 , 650 and 750°C , were tested, we will next focus our attention on LFO films prepared at 650°C since they deliver the best performance while not showing any sign of deleterious phase segregation (Fig. S2).

Cross-sectional and top-view scanning electron microscopy (SEM) images (Fig. 2a,b) evidence that the LFO thin-film consists of randomly oriented nanorods with an average diameter of *ca.* 90 nm that give rise to a 550 nm -thick film. Raman spectroscopy together with X-ray diffractograms (XRD) were utilized to confirm the phase purity and identify the crystal structure of the film. First, Fig. 2c shows a representative Raman spectrum of an as-prepared LFO thin film, which displays four distinct bands at 270 , 410 , 660 and 1295 cm^{-1} characteristic for the orthorhombic structure. The weak bands at 270 and 410 cm^{-1} have been assigned to A_g and B_{3g} modes, respectively, whereas the stronger bands at 660 and 1295 cm^{-1} have been reported to be related to two-phonon scattering phenomena.^{37,38} Second, the XRD pattern of the as-prepared LFO thin film presented in Fig. 2d confirms its single phase orthorhombic perovskite structure (JCPDS #37-1493).^{26,39} It is worth noting that this synthetic route promoted crystal texturing, that is, preferential orientations during the ferrite formation. Indeed, when comparing the relative intensities of the diffractogram peaks with the standard powder diffraction pattern (Table S1) it is obvious that the (101) and (202) orientations are favoured in these films. Finally, the UV-Vis absorption spectrum displays a weak absorption onset at $\sim 750 \text{ nm}$ followed by a steeper increase from 590 nm downwards (Fig. 2e). Tauc plot analysis^{40,41} suggests the presence of both a direct- and an indirect-allowed transition with a band gap energy associated of approximately 2.13 eV (E_g^D) and 1.64 eV (E_g^I), respectively, near the absorption edge⁸ (Fig. 2e, inset). It is worth mentioning that albeit there is no yet consensus on which electronic transition energies dictate the light absorption of LFO, most of experimental studies agree on the presence of a direct-allowed

Fig. 1. Schematics of the fabrication steps to produce nanorod array thin films of LFO. From left to right: the hydrothermal synthesis of a nanorod array of FeOOH (Fe precursor) on the conductive substrate is followed by coating with a solution of $\text{La}(\text{NO}_3)_3$ (La precursor). Subsequent annealing of the film at 650°C yields the LFO thin film after etching the resulting surface La_2O_3 . The corresponding circle or square included in each step highlights the nanostructure and composition of the thin film.

Fig. 2. (a) Cross-sectional and (b) top-view SEM image of as-prepared LFO thin films, as well as the (c) Raman spectrum and (d) XRD, including a reference diffraction pattern. (e) Thin film UV-vis absorption spectrum of LFO and (inset) the corresponding Tauc plot analyses at the near absorption edge.

transition with (E_g^D) a value ranging from 2.1 – 2.7 eV.^{24,26,27} Surprisingly, the indirect-allowed transition has been overlooked in previous Tauc plot analyses despite the noticeable, but weak, light absorption at long wavelengths (> 590 nm).^{24,26} All in all, these results confirmed the formation of single-phase LFO and ruled out the presence of other phases such as α -Fe₂O₃, FeO, FeOOH or La₂O₃.

Understanding the catalysis phenomena requires to precisely identify the nature of the semiconductor surface, and LFO particularly well-known to be prone to non-stoichiometry exhibiting oxygen vacancies and La:Fe ratio departing from unity.^{25,30} Therefore, high-resolution X-ray photoelectron spectroscopy (XPS) spectra of La 3d, Fe 2p and O 1s were recorded to define the chemical composition and oxidation state of the LFO surface (see ESI for details). The surface composition extracted from XPS revealed a slightly La-rich surface (La/Fe 1.2 ± 0.1). We, however, confirmed a bulk La/Fe ratio of 1.0 ± 0.1 by ICP-MS that matched well with the fed stoichiometry. Note that finding La-excess on the surface of LFO is not rare, and indeed previous reports have also displayed surface La/Fe ratios of 1.2.⁴² Likewise, Stoetzing et al. found by computational simulations that LaO-rich surfaces are more reactive than FeO towards water adsorption,⁴³ which, in turn, favours the OER.

Fig. 3a shows the linear sweep voltammetry (LSV) under chopped-light illumination (AM 1.5G, 100 mW cm⁻²) of LFO as a function of different treatments. As-prepared LFO (black line) exhibits both photocathodic and photoanodic response, with

the photocurrent switching occurring at around 0.65 V vs RHE. This behaviour is commonplace among nanostructured electrodes wherein the charge separation does not occur by a space-charge field but rather by diffusion, and the p- or n-type character is ultimately determined by the delicate balance between surface charge transfer kinetics, preferential surface trapping and charge collection of one of the carriers.^{44,45} Given the low doping density of pristine LFO films and the flat band location (*see below*), it would not be conceivable to suggest that the built-in electric field developed around the p-type – n-type switching region is barely negligible, allowing diffusion mechanisms to control the PEC response. We hypothesize that, at low applied potentials (< 0.65 V), photogenerated electrons are preferentially trapped at the interface, driving, subsequently, the reduction of oxygen dissolved in the electrolyte.⁴⁴ At higher applied potentials (> 0.65 V) the drift-like charge separation induced by the increasing band bending starts to take over, resulting in the n-type behaviour associated to PEC water oxidation. To further strengthen the built-in electric field in the n-type region, bare LFO films were intentionally n-doped with oxygen vacancies, by annealing in the presence of H₂,^{46,47} coded as H-LFO. Note that the presence of the oxygen defects can be tracked by monitoring the Fe²⁺/Fe³⁺ ratio using the XPS data, since an oxygen vacancy would be compensated by the reduction of two nearby Fe³⁺ ions to Fe²⁺ to maintain the electroneutrality (see Fig. S3 and ESI for further details). In fact, an increase of the Fe²⁺/Fe³⁺ ratio from 0.15 to 0.32 is detected upon the hydrogen treatment. As a

result, this treatment doubled the photocurrent values in the n-type region (red line) reaching values of up to 0.22 mA cm^{-2} at 1.23 V vs RHE, while leaving unchanged the photocurrent switching potential and photocathodic response. In addition, photocurrent transient spikes appeared upon the treatments evidencing surface recombination. Note that the p-type photocurrents are much poorer than those observed in the n-type regime. This is expected, not only because of the small concentration (traces) of oxygen dissolved in the electrolyte, but also because holes, with lower mobility than electrons in LFO, are more likely to recombine on the way to the substrate. It is worth noting that the aforementioned p-type character of the surface LFO could impinge the photocurrent values.

Fig. 3. (a) Linear sweep voltammograms under chopped-light illumination for LFO as a function of the treatment (pristine, annealed, NFO-coated) and electrolyte (baseline corrected for H₂O₂ measurement). (b) Charge transfer (η_{surface} , full markers) and charge separation (η_{bulk} , empty markers) efficiency for LFO as a function of the treatment. The electrolyte employed was 1 M NaOH, except for the measurement coded "(H₂O₂)", which was carried out in 1 M NaOH + 0.5 M H₂O₂. All measurements were performed under an irradiance of 1 sun (AM 1.5G) using a scan rate 20 mV s^{-1} .

We next engineered the H-LFO surface by coating with NiFeO_x (NFO). The H-LFO / NFO films delivered a benchmarking photocurrent of 0.4 mA cm^{-2} at 1.23 V vs RHE without noticeable transient photocurrent spikes while the onset potential shifts up to 0.55 V vs RHE. Interestingly, the photocathodic response was completely suppressed, likely because of the passivation of surface electron traps. The incident photon-to-current efficiency (IPCE) spectra values correlate well with the increased photocurrent registered upon

subsequent treatments (Fig. S4). In addition, it is worth noting that the IPCEs' spectral response match well with E_g , whereas E_g^I appears to be inactive. This is in agreement with previous reports on ferrites like Fe₂O₃, CaFe₂O₄, ZnFe₂O₄ or CuFe₂O₄, wherein E_g^I is associated with the *d-d* transition of Fe³⁺ which results on the formation of a small polaron prone to rapid recombination since the electron – hole pairs are localized in the same transition cation.^{48,49} In addition, we determined the Faradaic efficiency for solar water oxidation of H-LFO/NFO to be $96 \pm 3 \%$ (Fig. S5).

With the aim of narrowing down the origin of the photogenerated carrier losses, the so-called charge transfer efficiency at the electrode/electrolyte interface (η_{surface}) and charge separation efficiency in the bulk (η_{bulk}) were calculated (Fig. 3b).^{13,50} To do so, H-LFO was first tested in the presence of H₂O₂ (Fig. 3a, grey line) as a sacrificial hole scavenger. Assuming that in the presence of this sacrificial hole scavenger all the holes reaching the surface are transferred to the electrolyte, η_{surface} is defined as $J_{\text{H}_2\text{O}_2}^0 / J_{\text{H}_2\text{O}_2}$. As observed, although the saturation value of η_{surface} was very low ($\sim 10 \%$) for the bare material, it rapidly increased with the H₂-treatment (38%) and further improved with the incorporation of NFO (60%). Admittedly, these treatments demonstrated to improve η_{surface} either by activating the catalytic process or mitigating the recombination, but were insufficient to completely override the interfacial carrier losses. The photogenerated carrier losses in the bulk can be estimated via η_{bulk} , defined as $J_{\text{H}_2\text{O}_2} / J_{\text{abs}}$, wherein J_{abs} corresponds to the maximum photocurrent density that can be delivered by the photoanode on the basis of its absorption spectra. In this case, J_{abs} was estimated to be 7.5 mA cm^{-2} (Fig. S6). Pristine LFO depicts a very poor charge separation efficiency, hitting a maximum of 2.5% at high applied potentials, which severely limits the photocurrent recorded. The H₂-treatment, however, caused η_{bulk} to increase 4-fold confirming its impact on both the bulk properties and the interface. It is worth bearing in mind that η_{bulk} remains below the values of other emerging ferrites.^{1,13} Obviously, this could be accounted for by the short minority carrier diffusion length, estimated to be $< 5 \text{ nm}$ (see ESI), that originates from the small-polaron hopping-type conduction,³⁰ together with bulk transport issues likely magnified here with respect to other ferrites. Overall, these results provide compelling evidence that both surface and bulk recombination are behind the low photocurrent response. Unfortunately, these analyses merely weigh the contribution of surface and bulk losses but cannot pinpoint the underlying limiting electronic/kinetic features of these electrodes. Identifying these parameters is key to rationally engineer the next generation of photoanodes. With this in mind, we will next focus on deciphering the role that oxygen vacancy-implantation and NFO-coating play at enhancing the performance as well as the underlying photogenerated carrier dynamics that govern the PEC response. The impact of the lattice oxygen vacancies on the bulk transport characteristics was investigated in a solid-state fashion to circumvent any interference from the electrolyte (see ESI for details).^{13,51} The conductivity in the longitudinal direction (along the nanorod) consistently increased from 9.4 to $23.1 \mu\text{S cm}^{-1}$

upon the H₂-treatment (Fig. 4a) suggesting that oxygen defects improved bulk charge transport, likely by improving the electron density as commonly reported in metal oxide photoanodes.^{46,52} This is in agreement with the studies of Miyusaki et al. wherein the deficiency in oxygen was found to enhance the hole conductivity in LFO.³⁰

Fig. 4. (a) Current vs voltage characteristics, including FTO as reference. b) iR -corrected linear sweep voltammogram of LFO and H-LFO, (inset) corresponding Tafel plot.

Several reports dealing with oxide perovskite electrocatalyst have acknowledged the impact of surface oxygen vacancies on the OER catalysis,^{19,28} though this phenomenon has not been brought up yet on perovskite photoanodes. Dark LSVs of LFO and H-LFO photoanodes were recorded to interrogate the impact of oxygen defects on the electrocatalytic performance (Fig. 4b). Note that we performed an iR -correction that not only compensates for the ohmic resistance but also for the film's resistance, estimated above (Fig. 4a). As a result, dark LSVs are primarily controlled by the surface catalytic activity. Both electrodes display a steep increase of current at potentials above 1.6 V vs RHE, which corresponds to the OER. This early response, at potentials much more positive than the valence

band (see ESI for details on the energy band positions), is not unexpected and, indeed, it has been reported for several oxide photoanodes.^{13,50} This phenomenon is commonly accounted for by the presence of a large density of mid-gap states which leads to a significant current leakage at the photoanode/electrolyte interface.⁵³ Interestingly, the incorporation of surface oxygen vacancies drastically reduced the overpotential to achieve a current density of 10 mA cm⁻² by 100 mV, *i.e.*, from 1.88 V (LFO) to 1.78 V (H-LFO), while the Tafel slope decreased from 160 mV dec⁻¹ to 110 mV dec⁻¹, respectively. These Tafel plot values are within the typical range of values reported in the literature and they are supported by a simple electrochemical kinetic analysis.^{19,54} These results lead us to firmly conclude that surface oxygen vacancies activate the catalytic activity of the perovskite oxide photoanodes' interface. We hypothesize that, the surface oxygen defects favour the OER by exposing more of iron centres, presumably the redox active centres, and by reducing the adsorption energy of the reaction intermediates, as it has been argued among oxide perovskites electrocatalysts.^{19,28}

Next, a series of spectroelectrochemical techniques were deployed to unravel how NFO activates the H-LFO photoanode toward the solar water oxidation. Photoelectrochemical impedance spectroscopy (PEIS) was utilized first to determine the basic bulk electronic properties of bare H-LFO photoanodes. Assuming, with caution, the validity of the Mott–Schottky (MS) model, we obtained a flat band (V_{fb}) potential of around 0.43 V vs RHE (see ESI), which matches quite well with that reported by Peng et al., although in that case the authors reported a photocurrent onset severely delayed beyond 1.23 V vs RHE.³³ In a broader context, this estimated V_{fb} is very promising, being amongst the lowest when compared with state-of-the-art ferrite photoanodes such as ZnFe₂O₄ (0.64 V vs RHE),³⁶ α -Fe₂O₃ (0.45–0.6 V vs RHE)⁵⁵ or CuFe₂O₄ (0.7 V vs RHE).⁵⁰ Likewise, MS analysis brought out a relatively low donor concentration (N_D) of 7.32×10^{17} cm⁻³, when compared with metal oxides such as α -Fe₂O₃,⁵⁶ CuFe₂O₄⁵⁰ or BiVO₄.⁵⁷ This value directly impacts on the depletion width, which is calculated to reach values of *ca.* 90 nm at 1.2 V vs RHE (see ESI), that is, the diameter of the LFO nanorods. These findings suggest that the nanorods would be near to fully depleted although withstanding a rather weak space-charge field, even upon doping with oxygen vacancies, which will limit the charge separation.

To interrogate how the interfacial electronic structure is affected by NFO, the density of surface states (DOSS) was plotted as a function of the applied bias (Fig. 5, see ESI for details). In all cases, the DOSS was fitted to a Gaussian function and the corresponding total density of surface states (N_{SS}) was extracted from the integration of the Gaussian function. Interestingly, the DOSS changes drastically with the incorporation of NFO. In fact, whereas H-LFO displays a single broad DOSS band ranging from 0.8 V to 1.1 V vs RHE, the deposition of NFO causes the appearance of two distinct bands extending from 0.65 V to 0.85 V vs RHE and from 0.95 V to 1.05 V vs RHE, respectively. It must be borne in mind that PEIS does not reveal the actual potential of the surface accumulated holes. To determine the actual energy distribution of the DOSS,

the photovoltage (quasi-Fermi levels splitting) generated by the photoanode must be added to the potential at which DOSS are detected by PEIS. It is worth noting that the first band is centred around the photocurrent onset in both photoanodes. This suggests that it corresponds to the build-up of surface holes that precedes the water oxidation reaction, typically in the form of high-valent metal (iron)-oxo complexes.^{55,58} Analysis of these DOSS reveals that N_{SS} reaches values of $(3.7 \pm 0.1) \times 10^{15} \text{ cm}^{-2}$ and $(3.7 \pm 0.2) \times 10^{15} \text{ cm}^{-2}$ for the bare and coated H-LFO film, respectively. Note that the surface considered for the calculation was corrected by the roughness to define more accurately the DOSS. These values are high enough to cause Fermi level pinning (FLP) ($> 10^{12} \text{ cm}^{-2}$),⁵⁹ which could account for the observed delay in the photocurrent onset with respect to V_{fb} . Aside from the surface recombination involving the reactive intermediate species tracked by PEIS, we cannot rule out the presence of additional surface recombination pathways linked, for instance, to intrinsic surface trap states.⁶⁰ The fact that we could not find evidence of them by using rapid-scan cyclic voltammetry, as previously shown for other metal oxides,^{36,58} points to a very fast trapping-recombination phenomenon, if existing.

appears to be homogeneously dispersed over the surface, as confirmed by probing the Raman spectra and energy-dispersive X-ray spectroscopy (EDX) on different spots (see ESI for details). The “earlier” DOSS could, however, be associated to holes accumulated either at NFO or at H-LFO’s surface. On the one hand, photogenerated holes could be quickly injected into the NFO and carry out the OER at its surface. The catalytic activity of NFO could account for the shift of the photocurrent onset and DOSS.⁶¹ On the other hand, NFO could act as a passivating agent, interacting with interfacial traps and suppressing the surface recombination, while the OER still occurs at the H-LFO’s surface, or more specifically, at the surface regions passivated by the NFO. The outcome will be as well a negative shift in the onset potential.⁶² Deciphering which one of these scenarios prevails is of utmost importance to understand what limits the performance on LFO photoanodes.

Fig. 5. Energy distribution of density of surface states (DOSS) extracted from the impedance response recorded under 1 sun illumination. DOSS profiles were fitted with Gaussian functions.

Proceeding further on the analysis of Fig. 5, NFO-coated films display a “late” DOSS, with a N_{SS} value of $(7.5 \pm 0.1) \times 10^{14} \text{ cm}^{-2}$. The existence of two distinct DOSS bands in the presence of NFO bears out the fact that two types of surface reacting holes with different oxidation potential are driving the water oxidation. The fact that the “late” DOSS resembles the one observed in the bare films led us to conclude that it corresponds to holes accumulated at bare H-LFO’s surface. Note that the porous nature of NFO renders some of the underlying surface of H-LFO virtually unchanged upon the coating. Indeed, no significant differences were detected between the relative electrochemically active surface area of bare and NFO-coated LFO (see ESI for further details). We note as well that NFO

To nail down the role of NFO, we next turned to interrogate the interfacial carrier dynamics at the photoanode/electrolyte interface. Fig. 6a,b shows the intensity-modulated photocurrent spectroscopy (IMPS) Nyquist plots obtained at different applied potentials for bare and NFO-coated H-LFO. Overall, the response features two well-defined semicircles with the characteristic high- (HFI) and low-frequency intercept (LFI) with the real axis. Briefly, HFI is proportional to the flux of holes arriving to the interface, and thus, it connects directly to the band bending developed within the material, whereas LFI correlates with the amount of holes that are ultimately injected into the electrolyte.⁵⁵ In the absence of NFO, HFI barely changes at low applied bias (< 0.8 V) but increases at higher potentials reaching saturation at 1.2 V vs RHE. This sluggish variation of HFI agrees well with the presence of a strong FLP at the nearby of the photocurrent onset, which is mitigated at increasing applied bias. Likewise, LFI rises with potential owing to the increased density of surface accumulated holes. Strikingly, the incorporation of NFO causes HFI and LFI to increase readily in all the potential range, providing compelling evidence for the suppression of the FLP. By assuming a phenomenological model (see ESI), the rate constant for charge transfer (k_{tran}) and recombination (k_{rec}) at the photoelectrode/electrolyte interface were estimated as a function of the applied potential. At first glance, the incorporation of NFO slightly decreases k_{tran} while causing k_{rec} to plunge. Firstly, in the absence of NFO, k_{tran} gradually increases with the applied potential, from 62 s⁻¹ to 135 s⁻¹, which is common sign of FLP.⁶³ Coating with NFO reprograms k_{tran} to remain virtually unchanged in all the potential range, providing compelling evidence of the suppression, at least partially, of the FLP, and to yield a lower average value (slower reaction). Secondly k_{rec} , decreases with

the applied bias in both bare and NFO-coated LFO, owing to the strengthening of the space-charge field within the film. It is worth noting that the slope of k_{rec} vs E plot increased from 0.7 to 1.4 s⁻¹ V⁻¹ supporting the mitigation of the FLP. However, we note that this slope is still far below the value expected for an ideal semiconductor liquid junction (16.5 s⁻¹ V⁻¹),⁶⁴ likely because of the weak space-charge field in the material. More importantly, k_{rec} drastically drops with NFO from, for instance, 210 s⁻¹ to 50 s⁻¹ (at 1.2 V vs RHE) indicating the partial suppression of surface recombination. Overall, the drastic slowdown of the surface recombination and charge transfer, the later expected to radically accelerate in the presence of an electrocatalyst, confirms NFO's prime role as passivation.^{62,63} We note that recently, Wang and co-workers reported the role of NFO as passivating agent when deposited on hematite photoanodes.⁶² It is worth mentioning that the increased k_{tran} in the bare film, with respect the NFO-coated one, could be rationally explained by the higher driving force of the surface holes in the former. The severe FLP present in the film is expected to cause a downward shift of the energy bands, this will result in an increased oxidizing power of the surface (lower quasi-Fermi level of holes) especially at high bias.⁶⁴ Open circuit measurement such as intensity-modulated photovoltage spectroscopy (IMVS) and time-resolved photoluminescence (TRPL) were performed to elucidate the carrier recombination dynamics without the interference of the electrocatalytic reaction. Fig. 6d,e show the IMVS Nyquist plots corresponding to bare and NFO-coated H-LFO. Both electrodes display a semicircle in the high-frequency range and an incomplete one in the low frequency. The high-frequency response is often considered to originate from the space charge recombination, whereas the second has been recently linked to

Fig. 6. IMPS Nyquist plots recorded for (a) H-LFO and (b) H-LFO/NFO as a function of the applied potential. Corresponding solid lines are the fitting results (see ESI). (c) Charge transfer (k_{tran}) and surface recombination (k_{rec}) for bare and NFO-coated H-LFO extracted from IMPS. IMVS Nyquist plots obtained for (d) bare and (e) NFO-coated H-LFO. All measurements were performed in 1 M NaOH under an irradiance of 1 sun (AM 1.5G). (f) Time-resolved photoluminescence (TRPL) decay of an H-LFO thin film electrode. The sample was excited at 340 nm. The fitting was carried out using a double exponential function.

Fig. 7. (a) Extended chronoamperometry of H-LFO (red line) and H-LFO/NFO (blue line) recorded under chopped-light illumination (1 sun) at 1.23 V vs. RHE using 1 M NaOH as electrolyte. H-LFO (red line) was annealed again in the presence of H_2 after completing the stability test, and subsequently, it was subjected to the chronoamperometry test, herein coded as " H_2 -reannealed". (b) Curve fitted Fe $2p_{3/2}$ spectra for as-prepared LFO and H-LFO, before and after the stability test, including the estimated Fe^{2+}/Fe^{3+} ratio according to Biesinger et al. (see ESI for details)⁹⁶. (c) Proposed mechanism of oxygen intercalation into H-LFO photoanodes. (c.1) As-prepared H-LFO includes oxygen vacancies (O_{vac}) (and the corresponding nearby Fe^{2+}) throughout the surface and bulk. (c.2) Under illumination, surface O_{vac} on high-valent iron, i.e., accumulating photogenerated holes, will be the preferred site of adsorption of OH^- from the electrolyte. After being deprotonated, the O^{2-} could either undergo oxidation⁹⁵ to produce oxygen or (c.3,4) diffuse into the structure (blue arrows) along the octahedral edges filling eventually a bulk O_{vac} and causing the oxidation of the two neighboring Fe^{2+} centers to Fe^{3+} to compensate the negative charge uptake.

the interfacial recombination (involving reactive intermediate species).^{55,62,65} A first-order electron lifetime can be calculated from the angular frequency at the minimum of the Nyquist plot ($\tau_n = 1/2\pi f_{min,IMVS}$), yielding values of 13.2 ms and 15.6 ms, for bare and NFO-coated H-LFO photoanodes. As expected, the surface passivation of NFO would mitigate the FLP and hence afford a stronger space-charge field upon illumination under open circuit potential (OCP) that could lengthen the lifetime. Admittedly, these extremely long lifetimes are in stark contrast with the low photocurrents recorded. We, therefore, hypothesize that IMVS is accessing the dominant, but slow, recombination process presents within its scope, whereas major carrier losses are missed at earlier stages.

To probe the recombination kinetics at shorter timescales TRPL of H-LFO was recorded at 450 nm (Fig. 6f). Note that the steady-state PL spectrum of H-LFO exhibits a broad emission band spanning from 400 to 550 nm centred at 450 nm, corresponding to the band-edge emission, as well as a weak band centred at about 750 nm (excited at 550nm), which has not been reported before and likely relates to the surface-state emission involving mid-gap trap states (Fig. S11). TRPL displays an abrupt decay with an average lifetime of only about 1.8 ns. Such a fast decay reflects a rapid annihilation of photogenerated carriers and provide compelling evidence of significant carrier losses early on upon the light absorption. Notably, the TRPL signal barely changed after coating with NFO (results not shown) reinforcing the notion that the decay is primarily governed by bulk-related recombination pathways. We hypothesize that bulk

recombination processes at the nanosecond timescale, and even shorter,⁶⁶ likely related to characteristic small polaron formation, could reduce severely the amount of free carriers and contribute to the low η_{bulk} described before.

Finally, with a better understanding on the parameters that dictate the PEC response set in place, we evaluated the operational stability of the photoanodes. The photocurrent delivered by both bare and NFO-coated H-LFO at 1.23 V vs RHE decreases steadily over time, losing by about 80 % of its value after 1 day (Fig. 7a). Intriguingly, despite the drop of photocurrent, H-LFO appears to be chemically stable in the electrolyte. For instance, no changes were noticeable neither at first sight nor using XRD, and the absorption spectrum and XPS spectra upon soaking the electrodes in concentrated NaOH solution (10 M) for 3 days remain virtually unchanged (Fig. S12). Interestingly, we noticed a drop in the surface oxygen vacancies content upon the stability test. Fig. 7b displays the XPS Fe 2p spectra of as-prepared LFO and H-LFO before and after the stability test (see ESI for further details on the band assignment). Note that we did not detect any change in the La/Fe ratio neither by XPS nor by other techniques such as EDX or ICP-MS (see ESI for details). It is worth noting that the Fe^{2+}/Fe^{3+} ratio decreased from 0.32 to 0.21 after the long-term chronoamperometry test, reaching a value similar to the one of pristine LFO (0.15). This provides compelling evidence that the refilling of oxygen vacancies is occurring in parallel to PEC water oxidation. In fact, the recovery of the photocurrent by repeating the hydrogen treatment (green line) further corroborates that

the loss of oxygen vacancies is the prime culprit of the H-LFO deactivation. We note that Liu et al. proposed as well the refilling of the oxygen vacancies in $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3.6}$ to account for the deterioration of its dark electrocatalytic response after long periods of operation, although to the best of our knowledge this phenomenon has not been reported yet among photoelectrodes. Indeed, doping with oxygen defects is a common practice among metal oxides such as $\alpha\text{-Fe}_2\text{O}_3$ or ZnFe_2O_4 to enhance the performance, but the lattice oxygen content remains unaltered after long operation periods.^{36,67} Likely, the characteristic high oxygen diffusivity and structural flexibility of the oxide perovskite to accommodate mobile oxygen ions within the lattice account for this unexpected behavior.⁶⁸ We hypothesize that the re-incorporation of oxygen in the oxygen-deficient structure starts with the adsorption of OH^- from the electrolyte, that is the first step of the OER (Fig. 7c). Note that we assumed that LFO performs the OER via the conventional adsorbate evolution mechanism as reported elsewhere,²⁸ which, unlike the lattice oxygen mechanism found to occur in other oxide perovskite,¹⁸ it proceeds via the sequential surface adsorption and transformation of OH^- into O_2 .⁶⁹ Under illumination, OH^- binds to the reactive sites, *i.e.*, iron centres that accumulate photogenerated holes (Fe^{4+}),^{58,70} preferentially via the oxygen vacancies (Fig. 7c.1). Next, this adsorbed OH species could either undergo a series of oxidative transformations to release O_2 (OER process) or simply deprotonate and incorporate into the lattice (refilling oxygen vacancies, Fig. 7c.2). Given the high ionic mobility assisted by the oxygen vacancies, the oxygen ion diffuses rapidly into the lattice allowing for this same mechanism to re-start. As a result, the newly incorporated oxygen fills a vacancy while neighbouring Fe^{2+} centres re-oxidize to Fe^{3+} to compensate the negative charge of oxygen consuming holes photogenerated within the material. This phenomenon accounts for the non-ideal faradaic efficiency ($< 100\%$) since part of the photogenerated holes are used to re-oxidize the lattice rather than the water. It is, thus, not unreasonable to expect the gradual filling of both bulk and surface oxygen vacancies while the solar water oxidation occurs. The progressive decrease in photocurrent could be thus ascribed to the gradual loss of doping density and preferential adsorption sites (surface oxygen defects). We note that the presence of NFO did not improve the stability of the system, *i.e.*, oxygen still incorporates in the structure under operation. This further supports the notion that the OER takes place preferentially at the oxide perovskite surface.

Conclusions

In this work, we addressed the current bottleneck in the performance of LFO photoanode by seizing upon a novel electrode nanostructure in combination with post-engineering treatments as well as by parsing the electronic and catalytic characteristics that govern the performance. Our LFO nanorod array-type electrode delivered photocurrents up to 0.4 mA cm^{-2} at 1.23 V vs RHE with an onset of 0.55 V vs RHE, thus, establishing a new benchmark performance for LFO-based PEC

water oxidation. We found that inducing oxygen defects not only improved the carrier transport throughout the film, but specially activated the interface towards the OER leading to a substantial drop of the Tafel slope. Additionally, further engineering the interface by depositing NFO demonstrated to mitigate the deleterious surface recombination as confirmed by IMPS.

Admittedly, given that we determined that a photocurrent onset as low as 0.43 V vs RHE and photocurrent values as high as 7.5 mA cm^{-2} could be achievable given its V_{fb} and light absorption, the benchmark reported herein still remains modest. Our investigations to elucidate the chief performance bottlenecks, revealed the existence of major carrier losses in the bulk ($\eta_{bulk} < 10\%$) and, although, in a minor extent at the interface ($\eta_{surface} > 60\%$) in the benchmark films. Firstly, TRPL measurements brought up the fast recombination of photogenerated carriers occurring mainly in the bulk in the nanosecond, or even shorter, timescales. In addition, the weak space-charge field and the short minority carrier diffusion length estimated for this material ($< 5\text{ nm}$) posed severe challenges for an efficient charge separation. Secondly, we found that enhancing the surface catalysis and passivation was key to improve 6-fold $\eta_{surface}$, though not able to fully override the deleterious recombination. In addition, we detected a gradual refilling of oxygen vacancies under operation that deteriorated the performance steadily over time. With all this information in hand, we anticipate that further progress on LFO photoanodes depends upon strengthening the space-charge field by, for instance, combining A-site and oxygen doping, as well as on devising a conformal catalytic overlayers that take over the OER to avoid the reinsertion of the oxygen ions in the lattice. Overall, we are convinced that these findings not only represent an encouraging step change in the state-of-the-art performance for LFO photoanodes, but more importantly, set forth the key processes that constrain the activity allowing to construct a clear path to further optimize this material.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

§ The best fit to a straight line for the $(\alpha h\nu)^n$ vs. $h\nu$ plot (Tauc plot analysis) was found when assuming $n=1/2$ (indirect-allowed transition) and $n=2$ (direct-allowed transition) to assess the optical band gap near the absorption edge. Note that two spectral

regions ranging from 750–590 nm (gradual absorption increase) and 590–500 nm (steep absorption increase) were considered

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