Direct observation of the chemical transformations in $BiVO_4$ photoanodes upon prolonged light-aging treatments

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Abstract: Exposing $BiVO_4$ photoanodes to light-aging treatments is known to produce a significant photocurrent enhancement. Until now, the interpretation given to this phenomenon has been associated to the formation of oxygen vacancies and little has been reported about chemical changes in the material. Here, we demonstrate the chemical segregation of Bi species toward the surface upon light-aging treatment, which takes place with the concomitant formation of intra-band gap states associated to the oxygen vacancies. We further demonstrate that these intra-band gap states are photoactive and generate photocurrent under infra-red excitation. These results highlight the importance of understanding light-induced effects while employing multinary metal oxide photoelectrodes.

Introduction

Photoelectrocatalysis (PEC) has emerged as an attractive route to store solar energy involving photoelectro-oxidation and photoelectro-reduction processes. To date, most of the PEC applications developed have been mainly focused either on water splitting to obtain molecular hydrogen[1] or on the reduction of CO_2 to C1 and C2 derivatives.[2] However, there is a growing interest to exploit alternative reactions to obtain compounds with higher added-value for the chemical industry.[3,4] Among the different transformations proposed, the PEC oxidation of primary alcohols to the corresponding aldehydes or acids has attracted significant attention.[5,6],[7],[8] $BiVO_4$ is a promising material for the development of PEC devices, mainly due to its suitable band gap (2.4 eV), which allows visible light absorption (up to 516 nm)[9] leading to a theoretical photocurrent of ~7.5 $mA{\cdot}cm^{-2}$ under 1 sun illumination.[10] Furthermore its band structure (i.e. the position of the valence and conduction bands) leads to large photovoltages for driving organic transformations.[11–13] In contrast, the low electron mobility has been identified as the main bottleneck for the PEC performance of this material.[14,15]

The crystal structure of $BiVO_4$ is composed by Bi^{3+} and V^{5+} cations in coordination with O^{2-}.[16] During structural arrangement, the inherent formation of structural defects takes place and their concentration can be controlled by either modifying the synthetic conditions[17] or by post-synthetic treatments.[18,19] The most common defects in this material are oxygen vacancies (OV_s), which are the result of removing O atoms from the lattice.[20–22] It has been shown that these OV_s have a huge impact on the PEC behavior of different photoanodes for the oxygen evolution reaction (OER).[23–26] Specifically, the effect of OV_s on $BiVO_4$ for OER is based on the ability of these defects to increase the bulk carrier concentration and conductivity.[27] Furthermore, an excessive density of OV_s has been correlated to the decrease of performance.[28] The formation of OV_s also creates intra-band gap states, mainly related to V species, where the electrons are located closer to the conduction band.[29] These new electronic states lead to enhanced light absorption and have been related to the reduction of the nearby vanadium atoms from V_{ov}^{5+} to V_{ov}^{4+}.[30] The attempts to directly excite these intra-band gap states associated with oxygen vacancies in $BiVO_4$ have been limited, and only a recent study by Selim et al. reports the use of a transient infrared light to modulate the electrical response of the photoanode.[30] Consequently, infrared excitation of OV_s could clarify the role of these chemical defects on the PEC performance of $BiVO_4$.

On the other hand, prolonged light-aging treatments have been reported to improve the PEC performance of $BiVO_4$ towards OER. Trzésniewski *et al*. showed the enhancement of both photocurrent and photovoltage for undoped and uncatalyzed $BiVO_4$ photoanodes due to a process the authors refer as photocharging (10 hours under illumination at open-circuit conditions).[31] Similar results were reported by Li *et al*. after 20 hours of curing under UV illumination.[32] In both studies, the authors attributed the increase in photocurrent to the reduction of surface recombination processes as a consequence of the decrease of the defect sites at the surface.[33] The effects of the light-aging treatments were also analyzed by Liu *et al*. using Intensity Modulated Photocurrent Spectroscopy (IMPS).[34] The authors found that after three hours of light treatment, a complex interaction between charge transfer and surface

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recombination takes place, dominating the suppression of surface recombination at more positive applied potentials. More recently, Feng *et al*. reported the beneficial effects of a photoetching treatment, consisting of 10 minutes illumination at open circuit conditions. This treatment revealed that short illumination periods generates OV_s at the surface, which double the $BiVO_4$ photocurrent due to the significant enhancement of the charge separation efficiency.[35] All these studies demonstrated that short periods (10 min – 20 hours) of light-aging preferentially modify the $BiVO_4$ surface; however, illumination periods longer than 30 hours have not been reported yet.

Few works have tried to analyze the influence of light-aging treatments on $BiVO_4$ using in situ spectroelectrochemical measurements. Particularly, Firet et al. employing a sequence of XPS, UV-Vis and XRS techniques[36] and Venugopal et al. using infrared spectroscopy[37] revealed a dynamic nature of the light treatments on $BiVO_4$/electrolyte interface, however, in these cases the effect of the electrolyte could mask the true effects of light into the material during the light-aging process.

In the present study, we report the effect of prolonged light treatments on the PEC behavior of $BiVO_4$ photoelectrodes for the benzyl alcohol oxidation under air conditions for 48 hours. We have selected this reaction as a model platform for more complex organic transformations, opening the door to more sustainable and environmentally friendly synthetic strategies. Morphological, structural, and electrical measurements allowed us to unravel the different chemical processes taking place in the material during the light treatment and correlate them with the changes observed in PEC response. Moreover, we show for the first time, to the best of our knowledge, steady-state photocurrent generation upon continuous infra-red excitation, confirming the photoactivity of these light-induced electronic states.

Results and Discussion

$BiVO_4$ photoanodes were prepared by electrodeposition on FTO substrates, as detailed in the Supporting Information (S.I.) and were illuminated in air to elucidate the influence of prolonged light-aging treatments for the oxidation of benzyl alcohol. Our $BiVO_4$ photoanodes were illuminated at two different light intensities (1 and 3 suns for 1LA-$BiVO_4$ and 3LA-$BiVO_4$, respectively) for 48 h while the other films were kept under dark conditions (Reference). All samples were tested using the operational conditions normally used to oxidize selectively benzyl alcohol to benzaldehyde.[6] A 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$) in CH_3CN solution served as non-aqueous electrolyte in order to avoid the competing water oxidation reaction. A UV filter was incorporated to the ozone free Xe lamp in order to avoid the singlet oxygen generation and the non-faradaic oxidation of benzyl alcohol, previously reported for a similar system.[5] **Figure 1** compares the photocurrent of 1LA-$BiVO_4$ and 3LA-$BiVO_4$ to that for the Reference, showing a performance enhancement after the light-aging treatment. Similarly, the light-aging (LA) treatment produced films with higher photocurrents towards the oxygen evolution reaction (OER) as shown in S.I., **Figure S2**. The difference in the onset potential between LA and Reference sample observed for OER and not present in ROH oxidation demonstrates the higher catalytic activity of $BiVO_4$ photoanodes towards alcohol oxidation compared to OER.

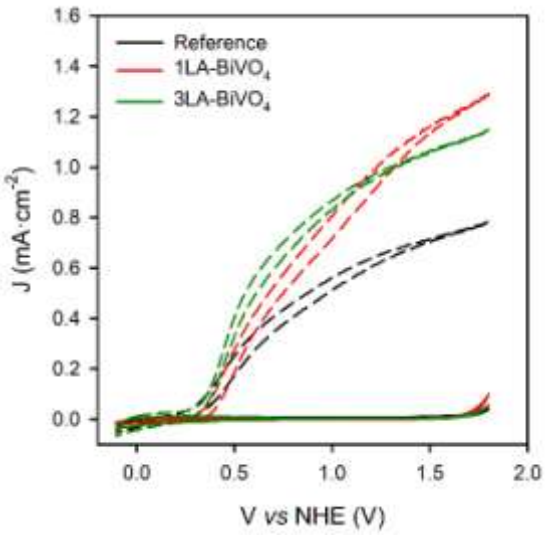

Figure 1. Cyclic Voltammograms of Reference (black), 1LA-$BiVO_4$ (red) and 3LA-$BiVO_4$ (green) photoanodes measured at 20 $mV \cdot s^{-1}$ in 0.1M benzyl alcohol in acetonitrile solution with 0.1M $TBAClO_4$ in the dark (solid lines) and under illumination (100 $mW \cdot cm^{-2}$) [dashed lines].

To study the nature of the LA treatment on $BiVO_4$, we firstly analyzed the morphology and crystalline structure of $BiVO_4$ by scanning electron microscopy (SEM), see **Figures 2a**, **2b** and **Figure S3** in S.I. A clear change in the surface of the $BiVO_4$ photoanodes is observed after LA. More precisely, while the Reference $BiVO_4$ exhibits a homogenous surface (**Figure 2a**), the LA samples are characterized by the presence of several islands (region B in **Figure 2b**) formed by small nanoparticles surrounding the regular $BiVO_4$ grains. Interestingly, EDS analysis for the different samples (**Figure 2c**), revealed that, upon LA treatment, the stoichiometric Bi/V concentration ratio of the Reference $BiVO_4$ divides into Bi deficient (zone A in **Figure 2b**) and Bi enriched domains (zone B in **Figure 2b**). These observations evidence the morphological and chemical modification of the $BiVO_4$ photoanodes due to LA and are directly related to the photocurrent increase shown in **Figure 1**.

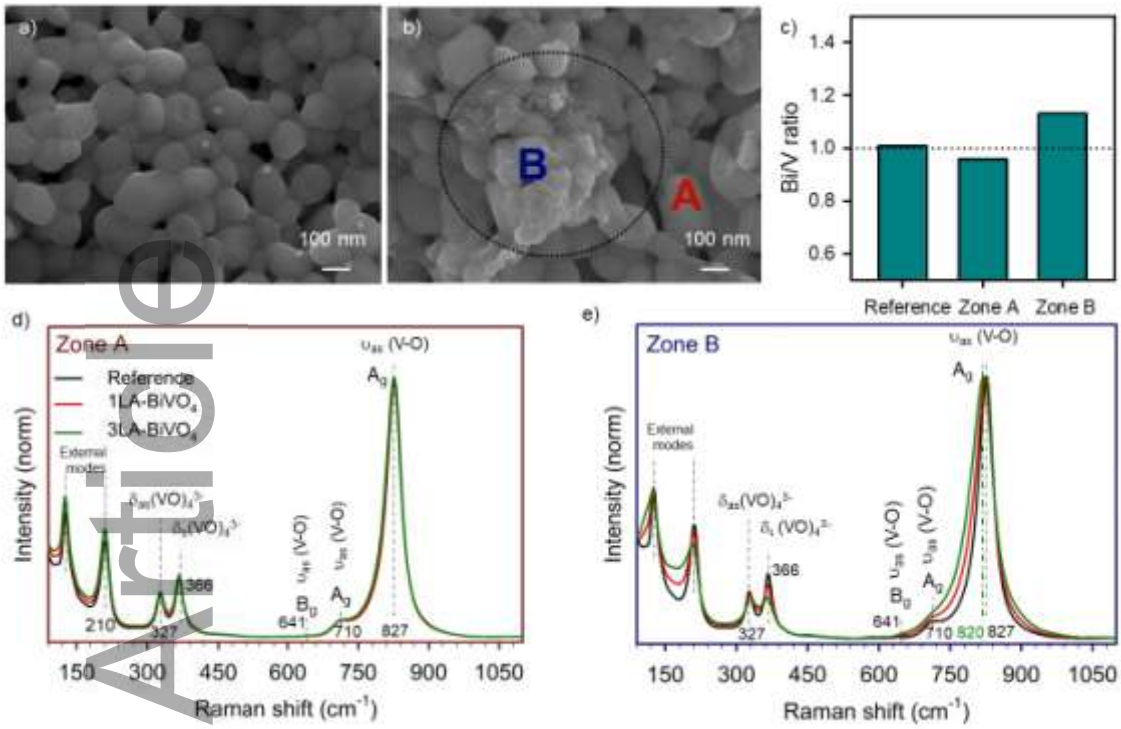

Figure 2. Top-view SEM images of (a) Reference and (b) 1LA-$BiVO_4$. (c) Bi/V concentration ratio for Reference and A and B zones measured by EDS in (b). Raman spectra of (d) Zone A and (e) Zone B.

To further analyze the morphological and chemical modifications of $BiVO_4$ photoanodes induced by LA treatment, we performed Raman spectroscopy on all samples in both zones A and B in **Figure 2b**. As depicted in **Figures 2d** and **2e**, Raman bands perfectly matched with the vibrational modes of $BiVO_4$.[38,39] Comparing the different samples, Raman bands were practically independent of LA in zone A. However, a significant band broadening is observed in zone B after LA, in particular for both the external and A_g modes. This has been previously attributed to the formation of defects, such as oxygen vacancies or hydrogen impurities.[40,41] We note that that oxygen vacancies in metal oxides can also be monitored by other techniques like electron paramagnetic resonance (EPR),[42,43] cathodoluminescence,[44] transient absorption spectroscopy (TAS)[28] and spectroelectrochemistry.[45] On the other hand, XRD measurements did not evidence any relevant modification of the crystalline structure due to LA (**Figure S4** in S.I.).

We move now to investigate the morphological transformation upon light-aging by transmission electron microscopy (TEM). Indeed, compared to the homogeneous surface of the Reference $BiVO_4$ sample (**Figure 3a**), 1LA-$BiVO_4$ evidenced the development of a thin amorphous layer, as the origin of the growth of small nanoparticles, as observed in **Figure 3b**, on the $BiVO_4$ crystallites which results in a granulated surface (**Figure 3c**). Additionally, scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM-EELS) proved the increase of Bi species on the surface of $BiVO_4$ crystallites after LA (**Figure S5** in S.I.). It is apparent from **Figure 3** that prolonged electron beam irradiation undergoes in a dramatic morphological transformation of our $BiVO_4$. Interestingly, the migration of some atomic species from the bulk to form particles at the surface could be recorded during the electron beam irradiation (the complete sequence can be visualized in the video freely available at 10.5281/zenodo.5643642) and the final morphology presented the segregation of a significant number of nanoparticles on top of the $BiVO_4$ grains (**Figures 3c** and **3d**).

To understand the nature and composition of these aggregates, we carried out a detailed HR-TEM characterization. **Figure 3e** shows the HR-TEM image of the bulk area of a $BiVO_4$ grain. The power spectrum (Fast Fourier Transform) analysis of this area (inset in **Figure 3e**) confirms the clinobisvanite $BiVO_4$ phase I112/B (s.g. 15) oriented along its [011] zone axis. However, focusing the electron beam on the segregated nanoparticles (**Figure 3f**), the power spectrum analysis clearly indicates the presence of Bi species. The results of the power spectra analysis in different areas matched with two different Bi structures: metallic Bi with hexagonal structure (R3-MH s.g. 166) oriented along [241] and [5-51] and monoclinic Bi_2O_3 oriented along [110] and [-114] zone axis, indicating the plausible chemical composition of this segregated particles (see **Figure S6** in S.I.).

We note that the electron beam in both SEM and TEM measurements is clearly different in wavelengths and intensities compared to sunlight (LA treatment). However, the morphology and presence of Bi-rich particles at the surface on the LA treated sample (**Figure S5** in S.I.) suggests that the localized structural modification induced by

LA is alike to that presented after electron beam irradiation, involving in both cases the segregation of Bi species.

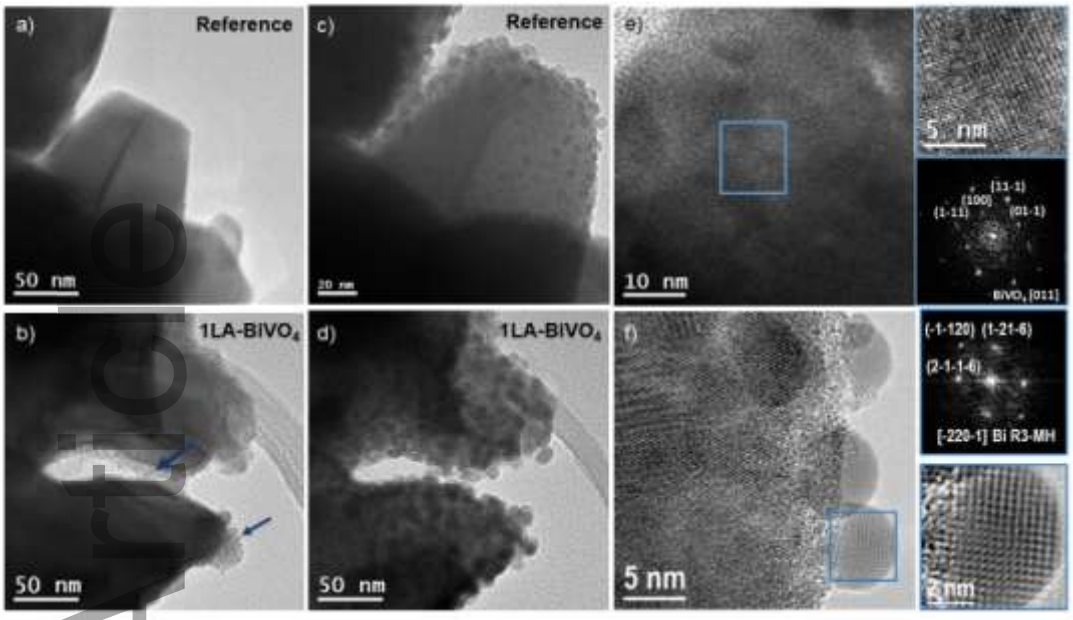

Figure 3. TEM images **(a) - (b) before and** (c) - (d) after electron beam irradiation. (a) and (c) correspond to the Reference and (b) and (d) correspond to the 1LA-$BiVO_4$, demonstrating **that the $BiVO_4$ morp**hology transforms during either light or electron beam irradiation. (e) and (f) HR-TEM and power spectra images of bulk and surface **$BiVO_4$** grains respectively after electron beam irradiation.

Summarizing, we have shown by different spectroscopic and microscopic techniques, that LA induces OV_S and a Bi segregation process. These processes have been reported previously in different studies, where BiVO4 has undergone prolonged exposure to light, including light treatments studies at open circuit conditions and stability tests under operational conditions.[18,25,31,33,35,36,46] In all cases different morphological and compositional processes take place at the electrode in different electrolytes and in different structures of BiVO4 converging in a higher proportion of Bi compared to V.

Now, we turn to investigate plausible mechanistic insights of the effect of LA on the functional performance of the photoanodes (as showed in **Figure 1**). To this end, we perform Impedance Spectroscopy (IS) measurements under illumination to extract Nyquist plots, at different potentials, relevant for the selective oxidation of benzyl alcohol to benzaldehyde. **Figure 4a** shows one of the experimentally obtained Nyquist plot and the selected equivalent circuit (inset) used to fit the data, which has been generally employed for different metal oxide photoanodes.[47] This equivalent circuit is commonly used to separate the contribution of bulk and surface processes in the photoanodes.[33] The elements employed are: R_s (series resistance), C_{bulk} (bulk capacitance), R_{bulk} (bulk resistance), R_{ct} (charge transfer resistance) and C_s (surface capacitance). The obtained capacitances and resistances as a function of the applied potential are reported in **Figures S7** and **S8** in S.I.

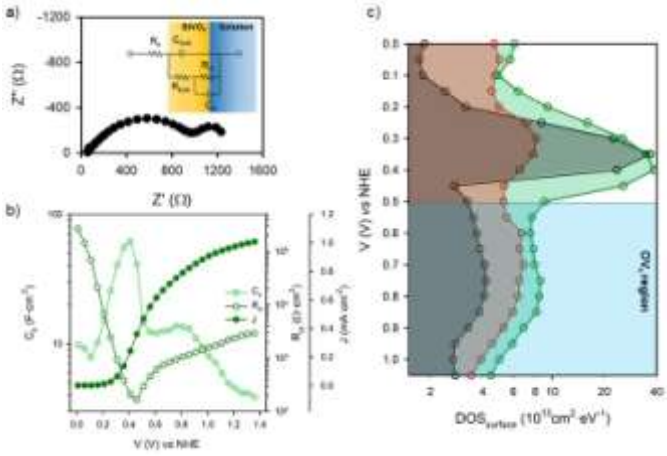

Figure 4. (a) Nyquist plot of Reference sample and selected equivalent circuit to fit the experimental data of the Reference and LA samples. (b) Surface capacitance (C_s), charge transfer resistance (R_{ct}) and photocurrent (J) of Reference $BiVO_4$. (c) Density of surface states as a function of applied potential. Reference (Black), 1LA-$BiVO_4$ (Red) and 3LA-$BiVO_4$ (Green). Measurements were performed under illumination, in 0.1 M benzyl alcohol oxidation conditions.

Figures 4b and **S7a** show the presence of two peaks at 0.35 V and 0.75 V vs NHE, for the surface capacitance (C_s light green empty circles in **Figure 4b**) of all tested samples. The peak at 0.35 V is coincident with the valley of the R_{ct} (dark green empty circles in **Figure 4b**), and both features take place at the same potential associated to the benzyl alcohol oxidation onset (dark green full cycles). A similar behavior has been already observed in different metal oxides, where a surface capacitance peak is observed just before the onset

for OER. This behavior on hematite photoanodes was assigned to charge transfer controlled by surface state charging associated to intermediate species in the reaction process.[47] Consequently, we suggest that ROH oxidation is controlled by a surface state, which dictates the hole transfer process from the electrode to the substrate. We note that this DOS is lower for the 1LA-$BiVO_4$ sample compared to the Reference material. A more detailed study of the influence of this surface capacitance on the photoelectrooxidation of benzyl alcohol remains beyond the scope of the present work.

On the other hand, the broader peak at 0.75 V vs NHE either in C_s and C_{bulk} is assigned to the V^{4+}/V^{5+} redox process, which has previously been related to the presence of OV_s in $BiVO_4$ films.[33,48,49] The presence of this peak in the reference sample suggests the intrinsic formation of this defects during the crystallization step.

Considering the C_s, the energetic distribution of these surface states, $g(E_{Fn})$ or DOS, can be estimated by equation 1

$$C_s = q \cdot g(E_{Fn}) \qquad \text{(eq. 1)}$$

where q is the elementary charge (1.6×10^{-19} C). **Figure 4c** shows that the calculated DOS associated to OV_s scales with the irradiation intensity, confirming the increase of the V^{4+} species during the light-aging process as mentioned previously in Raman. This result confirms the modification of the electronic environment of $BiVO_4$ during the LA. These observations are consistent with the results reported by Feng et al.[35] although, the higher concentration of OV_s, reflected on the bulk capacitance suggests that prolonged LA affects not only the bulk but also the surface of the film. Such higher OV_s concentration could also be responsible for the slightly lower photocurrent density found for the 3LA-$BiVO_4$ sample in **Figure 1**. This is supported by the detrimental role of a "too high" concentration of OV_s in $BiVO_4$ photoanodes as suggested in references,[23,41] which is also consistent with a recent report by Corby et al. in which an excessive concentration of OV_s could be negative for the PEC performance of WO_3 photoanodes,[28] suggesting that this effect may be general for metal oxide photoelectrodes. Furthermore, we have performed a long light aging treatment for 3 weeks (LT-1LA-$BiVO_4$, **Figure S9** in SI), which compared to 1LA-$BiVO_4$ leads to an increased DOS of OV_s, and lower photocurrent, also in good agreement with this hypothesis. Collectively, our observations also suggest the possibility that above certain levels, Bi segregation at the surface of the $BiVO_4$ could impede the charge transfer of holes to the solution. In this case, the Bi species on the surface of $BiVO_4$ could operate as a blocking layer for surface states as shown in **Figure S7** in S.I.

Finally, to confirm the generation of new intra-band gap electronic states associated with OV_s in $BiVO_4$, we used an infra-red (IR) continuous-wave laser as light source to extract steady-state photocurrents for the oxidation of benzyl alcohol. Upon sub-bandgap excitation, photocurrent generation can only be due to the activation of intra-bandgap transitions in the semiconductor material (see **Figure S10** in SI). This approach, to the best of our knowledge, uses for the first-time infrared radiation (980 nm, 1.26 eV) to selectively excite the trapped electrons from the intra-bandgap states to the conduction band. **Figure 5a** shows the IR chopped chronoamperometry measurements for Reference and 3LA-$BiVO_4$ samples at 0.8 V vs NHE. The measured photocurrent stems from the excitation of the intra-bandgap states. The highest photocurrent of the 3LA-$BiVO_4$ sample is fully consistent with its increased density of intra-bandgap states, associated with OV_s (**Figure 5b**). Surprisingly, the photocurrent of the 3LA-$BiVO_4$ sample almost doubled compared to that for the Reference (from ~50 to ~90 nA cm^{-2}). This is in excellent agreement with the equivalent increase of the DOS (from ~4 to ~$8 \cdot 10^{13}$ cm^2 eV^{-1}) associated to OV_s (**Figure 4c**).

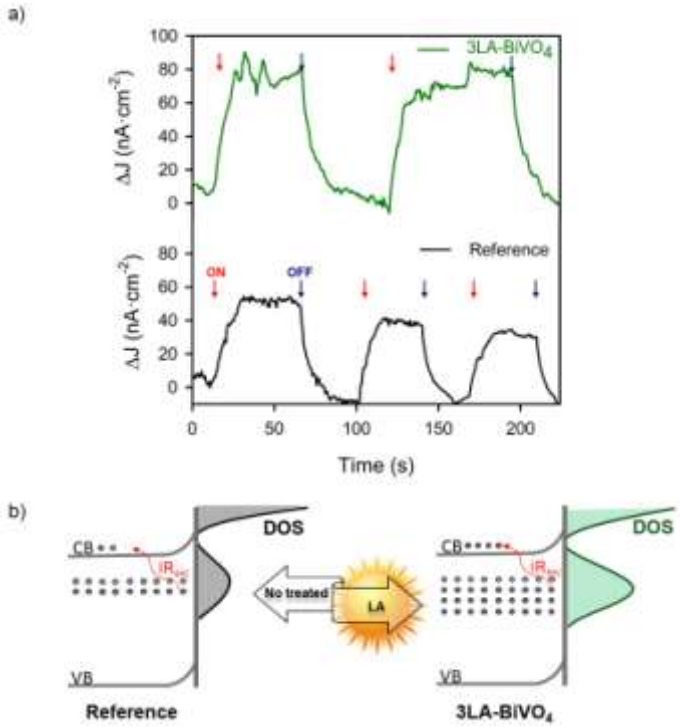

Figure 5. (a) Infra-red (IR) chopped chronoamperometry measurements of Reference (Black) and 3LA-$BiVO_4$ (green). (b) Band diagrams representation of the fresh and light-aged treated $BiVO_4$ samples.

We note that, although surface reduction of $BiVO_4$[50] and the increase of surface Bi species[25,51] have been previously reported, both effects have been characterized either after or during operando conditions and, consequently, they were attributed to vanadium dissolution.[37] On the contrary, the light-aging treatments and the structural characterization performed here take place in the absence of electrolyte. Therefore, the bismuth-rich surface observed is a direct consequence of the incidence of light on $BiVO_4$. Moreover, we demonstrate the correlation between the segregation of small Bi-rich nanoparticles and the formation of new intra-bandgap states associated to oxygen vacancies. The photoactivity of these intra-

bandgap states observed under infra-red illumination opens new perspectives for the development of competitive $BiVO_4$ photoanodes.

Conclusion

Herein, we have investigated the effect of prolonged light-aging on $BiVO_4$ photoanodes, providing a direct observation of the chemical and structural modifications after light-aging treatments. We showed that light-assisted treatments under air conditions led to the chemical transformation of the material, being more pronounced upon increased light intensity used during LA. Electrical, PEC and HR-TEM characterizations allowed assigning the chemical transformations observed to the segregation of Bi species on top of $BiVO_4$ grains, leading to the formation of new intra-bandgap states associated to oxygen vacancies. Moreover, effective photocurrent generation from these intra-bandgap states was demonstrated by infra-red light excitation, confirming the formation of oxygen vacancies during the light-aging treatment and their implications on the generation of infra-red photocurrent. These results highlight the importance of understanding the light-induced effects while employing multinary metal oxide photoelectrodes either for OER or for the synthesis of high added-value chemicals.

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Keywords: $BiVO_4$ • light aging treatments • Bi segregation • oxygen vacancies •

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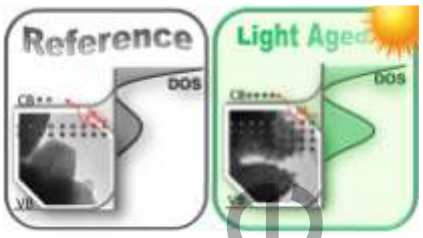

Prolonged light treatments over $BiVO_4$ photoanodes under air conditions induces Bi segregation in the surface, new intra-band gap states, as well as the formation of oxygen vacancies