In this work, spectroelectrochemical techniques are employed to analyse the catalytic water oxidation performance of a series of three nickel/iron oxyhydroxide electrocatalysts deposited on FTO and BiVO$_4$, at neutral pH. Similar electrochemical water oxidation performance is observed for each of the FeOOH, Ni(Fe)OOH and FeOOHNiOOH electrocatalysts studied, which is found to result from a balance between degree of charge accumulation and rate of water oxidation. Once added onto BiVO$_4$ photoanodes, a large enhancement in the water oxidation photoelectrochemical performance is observed in comparison to the un-modified BiVO$_4$. To understand the origin of this enhancement, the films were evaluated through time-resolved optical spectroscopic techniques, allowing comparisons between electrochemical and photoelectrochemical water oxidation. For all three catalysts, fast hole transfer from BiVO$_4$ to the catalyst is observed in the transient absorption data. Using operando photoinduced absorption measurements, we find that water oxidation is driven by oxidised states within the catalyst layer, following hole transfer from BiVO$_4$. This charge transfer is correlated with a suppression of recombination losses which result in remarkably enhanced water oxidation performance relative to un-modified BiVO$_4$. Moreover, despite similar electrocatalytic performance of all three electrocatalysts, we show that variations in water oxidation performance observed among the BiVO$_4$/MOOH photoanodes stem from differences in photoelectrochemical and electrochemical charge accumulation in the catalyst layers. Under illumination, the amount of accumulated charge in the catalyst is driven by the injection of photogenerated holes from BiVO$_4^-$, which is further affected by the recombination loss at the BiVO$_4^-$/MOOH interface, and thus leads to deviations from their behaviour as standalone electrocatalysts.
**Water oxidation kinetics of nanoporous BiVO₄ photoanodes functionalised with nickel/iron oxyhydroxide electrocatalysts**

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**Abstract**

In this work, spectroelectrochemical techniques are employed to analyse the catalytic water oxidation performance of a series of three nickel/iron oxyhydroxide electrocatalysts deposited on FTO and BiVO₄, at neutral pH. Similar electrochemical water oxidation performance is observed for each of the FeOOH, Ni(Fe)OOH and FeOOHNiOOH electrocatalysts studied, which is found to result from a balance between degree of charge accumulation and rate of water oxidation. Once added onto BiVO₄ photoanodes, a large enhancement in the water oxidation photoelectrochemical performance is observed in comparison to the un-modified BiVO₄. To understand the origin of this enhancement, the films were evaluated through time-resolved optical spectroscopic techniques, allowing comparisons between electrochemical and photoelectrochemical water oxidation. For all three catalysts, fast hole transfer from BiVO₄ to the catalyst is observed in the transient absorption data. Using operando photoinduced absorption measurements, we find that water oxidation is driven by oxidised states within the catalyst layer, following hole transfer from BiVO₄. This charge transfer is correlated with a suppression of recombination losses which result in remarkably enhanced water oxidation performance relative to un-modified BiVO₄. Moreover, despite similar electrocatalytic performance of all three electrocatalysts, we show that variations in water oxidation performance observed among the BiVO₄/MOOH photoanodes stem from differences in photoelectrochemical and electrochemical charge accumulation in the catalyst layers. Under illumination, the amount of accumulated charge in the catalyst is driven by the injection of photogenerated holes from BiVO₄, which is further affected by the recombination loss at the BiVO₄/MOOH interface, and thus leads to deviations from their behaviour as standalone electrocatalysts.
Introduction

Artificial photosynthesis employing photoelectrochemical or photocatalytic systems is attracting increasing interest for the sustainable synthesis of molecular fuels and chemicals. \(^1\)–\(^4\) Metal oxides are widely studied as light absorbing materials for such solar-to-fuel systems, particularly for the challenging water oxidation reaction. \(^5\)–\(^6\) This interest is derived particularly from their stability under the highly oxidising conditions required to drive this reaction. However, the performance of such metal oxide-based photoelectrodes is generally limited by recombination losses; in particular, competing surface recombination losses (also known as back electron/hole recombination) due to the slow rate of water oxidation, can be very significant. \(^7\)–\(^12\) One widely used approach to reduce such losses is the addition of water oxidation catalyst layers on the photoanode surface, which can lead to an enhancement in performance. \(^12\)–\(^16\) However, the selection of suitable catalysts is challenging as the requirements for efficient photoanode performance is likely to be different from the requirements for efficient, dark electrocatalysis. This is because, unlike electrocatalytic systems, driven by a voltage source, photoanodes utilise photogenerated holes, which are subject to electron-hole recombination losses at the photoanode/electrocatalyst/electrolyte interfaces, substantially affecting water oxidation currents. \(^11\)\(^,\)\(^13\)\(^,\)\(^17\)–\(^19\) Thus, even for a well-understood water oxidation catalyst used as an electrocatalyst, understanding the catalyst-photoanode interaction is critical to enhance photocurrent yields in metal oxide/electrocatalyst photoanodes.

Several earth abundant and inexpensive electrocatalysts have garnered extensive attention for water oxidation, such as cobalt based CoPi, \(^20\) and Co-Fe Prussian Blue. \(^14\) Transition metal oxyhydroxides (referred to herein as MOOH) like NiOOH and FeOOH have also been coupled with BiVO\(_4\) and some of these combinations have resulted in the construction of state-of-the-art BiVO\(_4\) photoanodes, \(^13\)\(^,\)\(^15\)\(^,\)\(^21\) exhibiting remarkable photocurrent densities of 5.87 mA/cm\(^2\) at 1.23 V\(_{\text{RHE}}\). \(^15\) However, while the presence of MOOH considerably enhances the water oxidation performance of BiVO\(_4\), most notably for nanoporous electrodes, the origin of this enhancement has not been clearly elucidated to date. Crucially, it has also been observed that the performance enhancement of the BiVO\(_4\)/MOOH system using either FeOOH or NiOOH for water oxidation does not correlate with the performance of FeOOH or NiOOH, respectively, when used as electrocatalysts on FTO. \(^15\) This discrepancy complicates the optimisation of photoelectrochemical devices and highlights the need to improve our understanding of photoanode/electrocatalyst interface. \(^13\)

In this study, transient optical and spectroelectrochemical techniques are utilised to: (1) compare performances of FeOOH, NiOOH, FeOOH\(_n\)NiOOH in terms of when they are used as an electrocatalyst on a conducting substrate in neutral electrolyte; and (2) investigate how their performance changes
they are placed on BiVO$_4$ nanoporous photoanodes and need to utilise photogenerated holes for water oxidation under the same electrolyte conditions. The results obtained from this study provide insight into the role of MOOH on BiVO$_4$ in enhancing water oxidation photocurrent and in the performance differences of the three MOOH catalysts on a conducting substrate and on a BiVO$_4$ photoelectrode.

Results and Discussion

Nanoporous BiVO$_4$ photoanodes used in this study were prepared using previously reported methods with one modification (see Supporting Information for details),$^{13}$ which was decreasing the film thickness (from ~750 to ~450-500 nm). This was necessary to increase the transparency of the BiVO$_4$ photoanodes, which is critical for the spectroscopic methods used in this study. As a result, the photocurrent obtained in this study with thinner BiVO$_4$ photoanodes is lower than that previously reported.$^{13}$ However, this decrease did not affect our comparison of the interactions of BiVO$_4$ with various MOOH electrocatalysts.

The FeOOH, NiOOH, FeOOHNiOOH electrocatalysts were synthesised as previously reported by anodic deposition on FTO to examine electrocatalytic function$^{22}$ and on BiVO$_4$ to examine photoelectrocatalytic function.$^{13}$ The trend in the photoelectrochemical enhancements between the three electrocatalysts upon when deposited on nanoporous BiVO$_4$ has previously been reported.$^{13}$

When deposited on FTO, the thicknesses of the FeOOH and NiOOH electrocatalysts were determined to be ~ 80 nm.$^{22}$ The FeOOHNiOOH, which was prepared by sequential deposition of FeOOH and NiOOH layers, was ~120 nm thick.$^{22}$ When deposited onto BiVO$_4$, the thickness of the catalyst layer was < 5 nm for FeOOH or NiOOH and < 10 nm for FeOOHNiOOH (increasing the thickness of the electrocatalyst layer on BiVO$_4$ is not favourable for photocurrent generation$^{13}$). We note that NiOOH in this study was deposited, as previously, in an electrolyte that was not rigorously free of Fe impurities, and the NiOOH contained a trace amount of Fe (~1 at %).$^{22}$ Thus, hereafter, NiOOH will be denoted as Ni(Fe)OOH.

All investigations presented herein were performed at pH 7 as the current work aims to better understand the high performance of BiVO$_4$/MOOH photoanodes reported previously at this pH.$^{13}$ While MOOH electrocatalysts are typically used in basic conditions, MOOH-coupled photoanodes that are not stable in strongly basic conditions, such as BiVO$_4$, are often used in (near) neutral conditions to optimise system stability.

At pH 7, the three MOOH electrocatalysts studied herein exhibit similar electrochemical water oxidation performances, as can be seen in the steady-state current voltage ($I-V$) plots shown in Figure
The similar overall performance at pH 7 differs from that observed under alkaline media (pH 13), where the catalytic onset potential for FeOOH is anodically shifted by 70 mV compared with Ni(Fe)OOH and FeOOHNiOOH. All the presented studies for NiOOH and FeOOHNiOOH and their photoanode counterparts were obtained after the in situ regeneration of NiOOH from Ni(OH)$_2$, using an activation procedure detailed previously, as Ni(OH)$_2$ forms over time when the electrodes are not in use (see Supporting Information for details). This activation process is referred to herein as the (0/+)$^a$ oxidation process.

When these catalysts are deposited on top of BiVO$_4$ photoanodes remarkable enhancements in the photoelectrochemical water oxidation performance are observed in comparison to the unmodified nanoporous BiVO$_4$ photoanode (Figure 1b). To understand the origin of this performance enhancement upon MOOH addition, transient optical and spectroelectrochemical techniques were employed to compare the water oxidation and recombination kinetics of the Ni/Fe oxyhydroxide water oxidation electrocatalysts when used either as electrocatalyst or when deposited on BiVO$_4$ photoanodes.

**Figure 1.** Electrochemical and photoelectrochemical performance of FeOOH, FeOOHNiOOH as electrocatalyst and when functionalised on BiVO$_4$ photoanodes at pH 7. (a) Steady state J-V curves for FeOOH (red), FeOOHNiOOH (blue) and Ni(Fe)OOH (green); These were recorded by measuring the steady state current at different applied potential under atmospheric conditions. Inset: schematic representation of the different electrocatalyst samples studied in this work. Red represents a Fe-based group, and green represents a Ni-based group. (b) Linear Sweep Voltammetry (LSV) under chopped light (1 sun equivalent, 365 nm LED, back irradiation) for BiVO$_4$/FeOOH (red), BiVO$_4$/FeOOHNiOOH (blue), BiVO$_4$/Ni(Fe)OOH (green) and un-modified BiVO$_4$ (black). All measurements were conducted in 0.1 M phosphate buffer. The J - V curves were recorded using a 10 mV/s scan rate.

Firstly, the optical and kinetic characteristics of the electrocatalysts when deposited on FTO were analysed. The optical changes during the sample activation (0/+)$^a$ oxidation process to convert Ni(OH)$_2$
to NiOOH for both Ni(Fe)OOH and FeOOH NiOOH electrocatalyst samples are shown in Figure S2.\textsuperscript{22–25} It is observed that Ni(Fe)OOH accumulated more (0/+\,\,) compared with FeOOH NiOOH. Since Ni(Fe)OOH and FeOOH NiOOH both contain similar amounts of NiOOH,\textsuperscript{22} this result suggests that as the Fe content increases, the oxidation of Ni(OH)\textsubscript{2} to NiOOH becomes more difficult. This is consistent with previous literature where the shift in the oxidation of Ni(OH)\textsubscript{2}/NiOOH to more anodic potentials has been correlated with the increase in Fe content.\textsuperscript{24,26}

![Graphs showing kinetics of water oxidation under electrochemical conditions by the FeOOH, FeOOH NiOOH and Ni(Fe)OOH electrocatalysts.](image)

**Figure 2.** Kinetics of water oxidation under electrochemical conditions by the FeOOH, FeOOH NiOOH and Ni(Fe)OOH electrocatalysts. (a) Normalised ΔOD spectra of the MOOH(++) species and their corresponding extinction coefficient for FeOOH (red), FeOOH NiOOH (blue) and Ni(Fe)OOH (green). The spectra are obtained by subtracting the spectra after activation from the spectrum at 1.81 $V_{RHE}$. (b) Water oxidation reaction time constants ($\tau$, solid circles, top panel) and the applied potential (bottom panel) as a function of the accumulated MOOH(++) density. (c) The TOF for O$_2$ evolution (solid circles, left axis) against the applied potential, plotted together with the current density (open circles, right axis). All measurements were taken in 0.1 M phosphate buffer (pH 7). Same colours used in (a), (b) and (c).

*Figure 2a* shows the optical response of the electrocatalysts. At applied potentials greater than the water oxidation catalytic onset, growth of new spectral features can be observed for each of the electrocatalysts, as shown in *Figure 2a* (and *Figure S3* for spectra as a function of applied potential). These spectral features are assigned to the generation of oxidised states that accumulate under water oxidation catalysis, referred to as MOOH(++) herein. As can be observed in *Figure 2a* (blue and red traces), the spectra of the FeOOH(++) and the FeOOH NiOOH(++) species are almost indistinguishable, with an absorption maximum between 400 – 425 nm, suggestive of the similar nature of these oxidised states. In contrast, the Ni(Fe)OOH(++) species shown in *Figure 2a* (green trace) exhibit a peak centred
at ~650 nm, indicative of a different nature of the oxidised state that forms in Ni(Fe)OOH. A similar trend for the respective spectral features of the MOOH(+) and MOOH(++) species of these three electrocatalysts, is also present at pH 13, suggesting that the catalytically active species observed under neutral and alkaline conditions are similar in nature. It is worth noting that the Ni(Fe)OOH samples were found to be relatively unstable when potentials greater than 2 V RHE were applied, leading to a loss in the optical signal and performance. This effect can be associated with the gradual dissolution of NiOOH at pH 7 under anodic bias required for water oxidation (see Supporting Information for more details, Figures S3 – S5).

To allow quantitative comparison of the oxidation of these electrocatalysts and the associated water oxidation kinetics, the extinction coefficients (ε) of the MOOH(++) oxidised species for each of the catalysts shown in Figure 2a were estimated using step-potential spectroelectrochemistry (SP-SEC), (see section D in Supporting Information for description of the method and additional data). Extinction coefficient (ε) values of ~3500 and ~3100 M$^{-1}$ cm$^{-1}$ were obtained at wavelengths of 550 nm for FeOOH and FeOOH$_2$NiOOH, and a value of ~3100 M$^{-1}$ cm$^{-1}$ was obtained at 650 nm for Ni(Fe)OOH. Using the estimated values of ε for each of the samples, the optical signal (ΔOD) shown in Figure S3 can be correlated with the density of accumulated MOOH(++) species as a function of applied potential. When combined with current densities, these data yield kinetic information on the water oxidation process, allowing the estimation of reaction time (τ) or turn over frequency (TOF) for O$_2$ evolution, as a function of MOOH(++) species. These analyses have been described in section F in the Supporting Information and have been reported previously.

The water oxidation kinetic data are plotted as a function of MOOH(++) accumulated species (Figure 2b) and also as a function of applied potential (Figure 2c).

As can be observed in Figure 2b (empty circles, bottom panel), the density of the MOOH(++) accumulated species increases with the applied potential for each of the electrocatalysts, resulting in an acceleration of the water oxidation time constants (τ) by two orders of magnitude (solid circles, top panel). For a given potential, it is also observed that Ni(Fe)OOH accumulates more MOOH(++) species than FeOOH and FeOOH$_2$NiOOH. Whilst it is apparent that both FeOOH and FeOOH$_2$NiOOH exhibit similar reaction time constants, Ni(Fe)OOH(++) states oxidise water circa an order of magnitude more slowly, when compared at equivalent densities of MOOH(++) species. The slower water oxidation kinetics of Ni(Fe)OOH(++) is also reflected in the plot of TOF (s$^{-1}$) vs applied potential (Figure 2c) which shows that at a given potential, FeOOH(++) and FeOOH$_2$NiOOH(++) both oxidise water at a similar rate, whereas the TOF (s$^{-1}$) for Ni(Fe)OOH(++) is approximately halved. Overall, while Ni(Fe)OOH(++) is able to accumulate a greater density of MOOH(++) species than FeOOH and FeOOH$_2$NiOOH, this gain is offset by slower water oxidation kinetics. As a result, the electrocatalytic performance for water
oxidation is relatively invariant for all three electrocatalyst as shown in Figure 1a and 2c. These trends are markedly different to those observed at pH 13 where Ni(Fe)OOH shows the fastest water oxidation kinetics amongst the three and, in comparison to FeOOHNiOOH, FeOOH starts accumulating charge at more anodic potentials, consistent with a later catalytic onset. However the origin of these differences with pH is beyond the scope of this study.

Next we look at the interaction between these electrocatalyst and BiVO₄ photoanodes. The poor performance of the un-modified nanoporous BiVO₄ has previously been assigned to holes accumulating at the BiVO₄ surface undergoing extensive losses due to water oxidation kinetics on BiVO₄ being slower than surface recombination. However it was not clear if the performance enhancement observed after addition of MOOH results primarily from faster water oxidation kinetics or slower surface recombination kinetics.

The enhancement observed in Figure 1b is consistent with that reported previously for these BiVO₄/MOOH combinations and is much greater than that typically found when electrocatalysts (e.g. CoPi) are deposited on dense planar BiVO₄ electrodes; such comparisons between CoPi and MOOH electrocatalysts are discussed later. Interestingly, while the three MOOH electrocatalysts show comparable performances, the BiVO₄/MOOH photoelectrodes exhibit differences in their water oxidation photocurrents (Figure 1b). In order to unravel the origin of the differences in performance enhancement upon the addition of MOOH electrocatalysts to BiVO₄, two different time-resolved optical and photoelectrochemical techniques are employed: transient absorption spectroscopy (TAS) employing short laser pulse excitation, and spectroelectrochemical photo-induced absorption spectroscopy (PIAS), employing quasi-steady state LED excitation.

To investigate if charge transfer occurs following bandgap excitation of BiVO₄, TAS was employed under an applied potential of 1.4 V_RHE. Figure 3a and b presents the TA spectra for BiVO₄ and BiVO₄/Ni(Fe)OOH and a comparison of the normalised charge carrier kinetics between un-modified BiVO₄ and the BiVO₄/Ni(Fe)OOH photoanodes. Equivalent TA spectra for the other BiVO₄/MOOH configurations are included in the Supporting Information (Figure S8). The data for BiVO₄ are similar to that reported previously, and are associated with holes accumulated at the surface. The optical signal observed at shorter wavelengths (~<50 nm) across all BiVO₄ and BiVO₄/MOOH photoanodes is dominated by a short-lived transient bleach and is indicative of the trapping of conduction band electrons into oxygen vacancy states as reported previously (we note that the magnitude of this bleaching varies between samples, mostly likely resulting from differences in oxygen vacancy density). The recovery of the bleach in the optical signal on the 1 ms timescale is concomitant with
the electron extraction from the photoanodes, after which only the longer lived optical signal for BiVO₄ holes or MOOH(++) species can be observed.⁴⁰

Figure 3. Transient absorption spectra and kinetics of BiVO₄ and BiVO₄/Ni(Fe)OOH photoanodes. (a) The transient absorption spectra showing the spectral signature of Ni(Fe)OOH(++) species in BiVO₄/Ni(Fe)OOH (top panel) and BiVO₄ (bottom panel). (b) Normalised transient absorption kinetics of BiVO₄ (black, 650 nm, h⁺) and BiVO₄/Ni(Fe)OOH (green, 650 nm, Ni(Fe)OOH(++)). All data were obtained under an applied potential of 1.4 V_RHE, using 355 nm excitation (∆300 μJ/cm²), in 0.1 M phosphate buffer.

In the case of BiVO₄/Ni(Fe)OOH (Figure 3a, top panel), a peak at 650 nm can be observed from the 10 μs TA spectra onwards, which is reminiscent of the Ni(Fe)OOH(++) species observed under electrocatalytic conditions shown in Figure 2a. This similarity in the spectral features at 650 nm suggest that both electrical and photo-induced oxidation (via surface holes from BiVO₄) generate similar Ni(Fe)OOH(++) species. The observation of this feature in the spectrum obtained at 10 μs is indicative of a significant fraction of fast hole transfer from BiVO₄ to the MOOH catalyst, which occurs within the time resolution of the measurements (< 10 μs). The spectral shape in Figure 3a (top panel) is clearly distinct from un-modified BiVO₄ (Figure 3a, bottom panel) at all timescales, indicating that holes primarily reside in the Ni(Fe)OOH catalyst layer over the timescales studied herein. Comparison of the kinetic traces presented in Figure 3b shows that Ni(Fe)OOH(++) species have a much longer lifetime than the holes in BiVO₄. Following hole transfer from BiVO₄ to the Ni(Fe)OOH layer, the accumulated Ni(Fe)OOH(++) species are spatially separated from photogenerated electrons in BiVO₄.
and therefore, surface recombination in BiVO$_4$/Ni(Fe)OOH is reduced in comparison to un-modified BiVO$_4$. Analogous conclusions can be drawn for the cases of BiVO$_4$/FeOOH and BiVO$_4$/FeOOHNiOOH, where the spectral profiles of the MOOH(++) species can be observed in the TA spectra (millisecond onwards), although charge transfer is less clear than the case of BiVO$_4$/Ni(Fe)OOH due to the similarity in the spectral signatures of holes in BiVO$_4$ and MOOH(++) species in FeOOH and FeOOHNiOOH within the probed region. In addition, the optical signature of MOOH(++) species for FeOOH and FeOOHNiOOH at early timescales (μs – ms) also overlaps with the transient bleach observed due to electron trapping in BiVO$_4$, further obscuring the detection of charge transfer at early timescales for these two cases. Nonetheless, all three catalyst-functionalised samples exhibit much longer lived signals than BiVO$_4$ alone (as seen in the TA spectra, Figure 3 and Figure S8 in the SI), indicative of catalyst deposition resulting in a substantial extension of the lifetime of photogenerated charges, attributed to slower recombination kinetics.

At early timescales (between 10 μs and 1 ms), an absorption tail at longer wavelengths (~700 – 900 nm) is present in all samples (Figure 3a and Figure S8). As this spectral signal is also present in the un-modified BiVO$_4$ photoanode, it may be indicative of photogenerated charges within BiVO$_4$. In the case of the catalyst modified samples (BiVO$_4$/MOOH), this tail absorption decays by ~1 ms without any significant concomitant change in the signal observed for the MOOH(++) species, most clearly visible for the case of BiVO$_4$/Ni(Fe)OOH (Figure 3a). Since the extinction coefficients of the MOOH(++) species are ~7-8 times larger than the hole extinction coefficient of BiVO$_4$ (420 M$^{-1}$ cm$^{-1}$)$^{28}$, any further hole transfer from BiVO$_4$ to the catalyst layer within 10 μs and 1 ms would be expected to give rise to a much larger signal observed for the MOOH(++) species. Since no increase in signal is observed, this may be indicative of recombination of photogenerated species in BiVO$_4$ that have not transferred to the catalyst layer by ~10 μs.

It is intriguing that the FeOOHNiOOH functionalised BiVO$_4$ photoanode performs better than the FeOOH counterpart (Figure 1b), despite exhibiting almost invariant kinetics for water oxidation under electrocatalytic conditions (Figure 2b). From the TA spectra (Figure S8), it appears that the signal amplitude for BiVO$_4$/FeOOHNiOOH is slightly larger than it is for BiVO$_4$/FeOOH. Taking the respective extinction coefficients of the MOOH(++) species into consideration, this would indicate that a greater amount of holes successfully transfer from BiVO$_4$ to FeOOHNiOOH in comparison to FeOOH, thus suggestive of FeOOHNiOOH being able to accumulate a greater density of MOOH(++) in comparison to FeOOH alone, when deposited on BiVO$_4$. On the other hand, the lower performance of BiVO$_4$/Ni(Fe)OOH can be explained by the slower kinetics of the Ni(Fe)OOH(++) species (as shown in Figure 2b) for the same accumulated charges. For electrochemical water oxidation, this is
compensated by the accumulation of a greater density of MOOH(++) species. However, under illumination when BiVO$_4$/Ni(Fe)OOH is used, the maximum number of charges accumulated on the Ni(Fe)OOH layer will be determined primarily by the number of photogenerated holes that are transferred to the catalyst layer. As observed in the TA spectra at early timescales, the amount of MOOH(++) accumulated on the MOOH layer is within the same order of magnitude between the three catalysts. Since water oxidation is slower on Ni(Fe)OOH in comparison to the other two catalysts for a given MOOH(++) density, there is increased scope for competing recombination processes at the BiVO$_4$/Ni(Fe)OOH interface, as reported previously.$^{18}$

![Figure 4. Comparison of normalised spectra of MOOH(++) species under electrochemical (EC) and photoelectrochemical (PEC) conditions.](image)

To examine the photoelectrochemical processes under steady-state conditions, spectroelectrochemical photoinduced absorption spectroscopy (PIAS) was employed. Unfortunately, instability of BiVO$_4$/Ni(Fe)OOH samples (Figure S6) under oxidative conditions over prolonged periods of time required for PIAS measurements precludes them from these analyses. The normalised PIAS spectra of BiVO$_4$, BiVO$_4$/FeOOH and BiVO$_4$/FeOOHNiOOH under an applied potential of 1.4 V$_{RHE}$ and 1 sun illumination are shown in Figure 4, along with the normalised spectra of the respective MOOH(++) species obtained under electrochemical conditions. The resemblance of the spectral shapes indicate
that similar species accumulate under the two catalytic conditions, which, in conjunction with the TAS data discussed above, further confirms that photoexcitation of BiVO$_4$ leads to the oxidation of the catalyst, also under PEC operation.

Figure 5. Comparison of kinetics under electrochemical and photoelectrochemical conditions. (a) The density of oxidising equivalents ($h^+$ for BiVO$_4$, or MOOH(++) species for catalysts) under catalytic conditions plotted against the (photo)current obtained. The reaction orders ($\beta$) for the respective electrochemical and photoelectrochemical water oxidation reactions are also shown (determined from the slope). (b) The density of oxidising equivalents plotted against the water reaction time constants ($\tau$) under photoelectrochemical conditions for BiVO$_4$ and BiVO$_4$/MOOH photoanodes. Same colours used in (a) and (b): BiVO$_4$ (black solid circles); BiVO$_4$/FeOOH (red solid circles); BiVO$_4$/FeOONiOOH (blue solid circles); FeOOH (red empty circles); FeOONiOOH (blue empty circles). All measurements were taken in 0.1 M phosphate buffer.

The optical signals obtained through PIAS and SP-SEC for the photoanodes and electrocatalyst electrodes, respectively, under catalytic conditions, were converted to the amount of oxidising equivalents for water oxidation, i.e. holes in BiVO$_4$ and MOOH(++) species in the case of the catalysts. By relating the optical signal to the concomitant current transient signals, kinetic information associated with water oxidation reaction can be analysed using rate law plots according to the following equation:

$$\log J = \log k_{WO} + \beta \log (\text{MOOH}(++)$$  

(1)
Where \( J \) is the (photo)electrochemical steady-state current density (water oxidation flux), (MOOH(++) is the density of the MOOH(++) species (in the case of un-modified BiVO\(_4\), it is the surface h\(^+\) density), \( k_{wo} \) is the water oxidation rate constant and \( \beta \) is the order of the reaction with respect to the surface density of MOOH(++) (or h\(^+\) density in BiVO\(_4\)). This analysis approach has been employed to investigate reaction kinetics on metal oxide surfaces\(^{31-33} \) and electrocatalytic systems previously.\(^{22,34} \)

Firstly, from Figure 5a, we can observe that photogenerated holes in BiVO\(_4\) follow a reaction order (\( \beta \)) of 3 for water oxidation, consistent with previous reports,\(^{31,32} \) whereas both FeOOH and FeOONiOOH operate with a \( \beta \) value of ~2 under both photoelectrochemical and electrochemical conditions at pH 7. A reaction order of ~2 for these electrocatalysts differs from that observed under alkaline conditions (\( \beta \) ~4 at pH 13),\(^{22} \) and is indicative of differences in reaction mechanisms in neutral and alkaline media. More importantly, at pH 7, the different reaction orders between BiVO\(_4\) and BiVO\(_4\)/MOOH photoanodes indicates that the water oxidation reaction proceeds via different mechanisms when driven directly by photogenerated holes in BiVO\(_4\) and by MOOH(++) species in the catalyst layer, where the MOOH(++) species are generated following hole transfer from BiVO\(_4\). Furthermore, it is apparent that similar orders of magnitude of MOOH(++) species are observed optically under both electrochemical (EC) and photoelectrochemical (PEC) conditions, consistent with the MOOH(++) species driving water oxidation in both systems, although differences in film morphology between the EC and PEC samples prevent quantitative comparison. A comparison of the reaction time constants for PEC water oxidation, shown in Figure 5b for BiVO\(_4\) and BiVO\(_4\)/MOOH photoelectrodes, indicate that no significant enhancement in water oxidation timescale is gained upon electrocatalyst deposition.

It is also striking that catalysts often employed for water oxidation, where water oxidation is observed to take place via oxidised states in the catalyst (i.e. Co-Fe based Prussian Blue), display time constants on the order of seconds.\(^{35} \) Even the popular Ni(Fe)OOH catalysts investigated under optimal alkaline conditions\(^{22} \) operate with time constants that are comparable to water oxidation by metal oxides such as BiVO\(_4\), and slower than that observed for WO\(_3\).\(^{32,36} \) Therefore it appears that the significant enhancement in photoelectrochemical performance of BiVO\(_4\) photoanodes decorated with these electrocatalysts does not originate from faster kinetics of water oxidation relative to BiVO\(_4\). Rather, the results obtained in this study suggest that the role of the catalyst layer is to decrease the kinetics of surface recombination and effectively decrease the recombination losses via fast hole transfer from BiVO\(_4\) to the catalyst layer. This spatially separates charges, and retards surface recombination losses that compete with water oxidation.
Scheme 1. Schematic illustration of electrochemical and photoelectrochemical water oxidation in MOOH electrodes and BiVO₄/MOOH photoelectrodes. (a) The electrochemically generated MOOH(++) species (blue spheres) in the activated electrocatalyst accumulate and drive water oxidation. (b) The photogenerated holes in the BiVO₄ transfer to the activated catalyst, generating MOOH(++) species (blue spheres) which then drive water oxidation. The electrons in the conduction band are collected at the back contact.

The same observations were found for Co-Fe Prussian Blue, where fast hole transfer to the catalyst layer followed by fast water oxidation kinetics led to enhanced performance. This is however, markedly different to CoPi, which exhibits water oxidation time constants (τ) that are two to three orders of magnitude slower than what is observed for BiVO₄ alone, where the enhancement in performance has been attributed to increased band-bending within the BiVO₄ that drives charge separation. It is observed that the amount of charge accumulated in CoPi under PEC conditions (when deposited on BiVO₄) is significantly lower (by two orders of magnitude) than that observed in the electrocatalyst under electrochemical water oxidation conditions at matched current densities.

Therefore, it is concluded that the amount of charge that accumulates in CoPi from BiVO₄ is insufficient to drive water oxidation. This conclusion is also supported by intensity-modulated photocurrent spectroscopy (IMPS) studies which indicate that CoPi mainly serves to passivate surface defects, with no significant enhancement of water oxidation kinetics when deposited on BiVO₄ or α-Fe₂O₃. However, as conflicting studies based on dual working electrode measurements that assign water oxidation to the CoPi catalyst overlayers also have been reported, this makes the role of CoPi as a co-catalyst overlayer on semiconductor photoelectrodes difficult to determine. For the case of the MOOH electrocatalysts studied herein, although a slight discrepancy in the amount of MOOH(++)
species is also observed between the electrocatalysts and the BiVO$_4$/MOOH photoelectrodes, this difference (within an order of magnitude) is less dramatic than the case of CoPi,$^{28}$ and is more similar to the case of RuO$_x$ catalysts operating as electrocatalysts and co-catalysts on photoelectrochemical systems.$^{34}$ The charge transfer observed from BiVO$_4$ to the catalyst layer to generate MOOH($^+$) species is seen both in the transient absorption spectra and the photo-induced spectra under steady-state conditions. Additionally, as the reaction order for water oxidation for BiVO$_4$/MOOH photoanodes also differs from that of BiVO$_4$ photoanodes, it strongly indicates that water oxidation in the catalyst-decorated photoanodes studied herein is driven via MOOH($^+$) species accumulated in the catalyst layer (as illustrated in Scheme 1).

Conclusions

In this work, the electrochemical and photoelectrochemical performance of FeOOH, FeOOHNiOOH, and Ni(Fe)OOH catalysts are studied at pH 7 as standalone electrocatalysts and when added on the surface of BiVO$_4$ photoanodes. Our results demonstrate that electrocatalytic performance results from both the intrinsic reaction kinetics and the potential dependence of charge accumulation, where the latter consideration is not important under photoelectrochemical conditions. We show that while FeOOH and FeOOHNiOOH exhibit faster kinetics for water oxidation than Ni(Fe)OOH, this nickel-based catalyst is able to accumulate a larger density of oxidative MOOH($^+$). As a result, the three catalyst show a similar electrocatalytic water oxidation performances. This trade-off between accumulation and reaction kinetics hinders the selection of electrocatalysts to make junctions with photoanodes, through standard J-V characterisations.

Once deposited onto the surface of nanoporous BiVO$_4$ photoanodes, substantial improvements in the photoelectrochemical performance are observed with respect to un-modified BiVO$_4$, attributed to fast charge transfer (< 10 µs) from BiVO$_4$ to the catalyst layer, and the resultant suppressed recombination losses. However, rather surprisingly, no significant enhancement in the water oxidation time constant is observed for the BiVO$_4$/MOOH photoanodes in comparison to BiVO$_4$. Moreover, differences between the catalysts emerge in the BiVO$_4$/MOOH photoanodes, stemming from the charge accumulation within the catalyst layer being governed by the transfer of photogenerated holes from BiVO$_4$. This significantly impedes the ability of Ni(Fe)OOH to accumulate a greater amount of Ni(Fe)OOH($^+$) needed to offset its slower water oxidation kinetics, which leads to a lower performance of BiVO$_4$/Ni(Fe)OOH photoanodes in comparison to the other two configurations. On the other hand, when NiOOH is added to FeOOH as a dual-layer catalyst on BiVO$_4$, it helps accumulate more MOOH($^+$) species within the catalyst layer than FeOOH alone, resulting in a greater enhancement in the photocurrent generated by BiVO$_4$/FeOOHNiOOH photoanodes. Overall, this study
highlights the two different factors that govern the performance BiVO$_4$/MOOH photoanodes and need to be considered when selecting electrocatalysts for applications in photoelectrochemical systems: (1) the number of charges that can be accumulated within the catalyst layer; and (2) how fast these charges can oxidise water to compete with recombination processes.

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Supporting information

Water oxidation kinetics of nanoporous BiVO$_4$ photoanodes functionalised by nickel/iron oxyhydroxide electrocatalysts

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Experimental Details

a. Electrocatalysts Preparation:

The experimental procedure for the preparation of FeOOH, Ni(Fe)OOH and FeOOHNiOOH electrocatalysts deposited on FTO have been detailed previously. We note that the thickness of FeOOH on FTO used in this study (~80nm) is significantly thinner than that in our previous work (~350 nm), while those of Ni(Fe)OOH are comparable in both studies. As the electrical conductivity of FeOOH is low, the thickness of FeOOH can considerably affect the electrocatalytic properties of FeOOH. This is why the performance of Ni(Fe)OOH was better than that of the thicker FeOOH in our previous study while the performance of the thinner FeOOH in this study is comparable to that of Ni(Fe)OOH.

b. Photoanodes preparation

BiVO₄ film preparation: The nanoporous BiVO₄ electrodes used in this study were based on the previously reported method with only one modification, which is the decrease in charge passed during the deposition of BiOI (from 0.13 C/cm² to 0.06 C/cm²). This is to prepare thinner BiVO₄ electrodes (from ~700 nm to 450-500 nm) that are transparent enough for the spectroscopic methods used in this study. The lateral dimensions of the BiVO₄ electrodes prepared in this study were 1 × 1.2 cm.

![Figure S1. SEM images of nanoporous BiVO₄ films used in this study, of film thickness ~450-500 nm.](image)

Photodeposition of catalysts: The mechanisms of FeOOH and NiOOH photodeposition were reported previously. A 0.1 M FeSO₄·7H₂O (Sigma-Aldrich, 99%) aqueous solution (pH ~ 4.3 as prepared and N₂ purged for 30 min before deposition) and a 0.1 M NiSO₄·6H₂O (Sigma-Aldrich, 98%) aqueous solution (pH adjusted to 6.8–7.0 using a 0.070 M NaOH (Sigma Aldrich, 97%) aqueous solution) were used for FeOOH and NiOOH photodeposition on BiVO₄ electrodes, respectively. Photodeposition was conducted in an undivided three-electrode cell using BiVO₄ electrode as the WE, Ag/AgCl (4 M KCl) as the RE and a platinum CE. A 300 W Xe arc lamp (Ushio, UXL-302-O) with an AM 1.5G filter was used as the light source. The light was back-illuminated on the BiVO₄ WE and the intensity was set to 1 mW/cm². For FeOOH photodeposition on BiVO₄, a constant potential of 0.23 V vs Ag/AgCl (4 M KCl) was applied to pass 30 mC/cm² with gentle stirring. For NiOOH photodeposition on BiVO₄, an open circuit potential of the BiVO₄ electrode in dark (ca. 0 V vs Ag/AgCl (4 M KCl)) was applied to pass 28.6 mC/cm² with gentle stirring. The resulting BiVO₄/FeOOH and BiVO₄/Ni(Fe)OOH films were rinsed with DI water and dried with a gentle stream of air. In order to prepare BiVO₄/FeOOH NiOOH electrode, photodeposition of NiOOH was carried out on the BiVO₄/FeOOH film using the same conditions.
described above. A total charge of 30 mC/cm² and 28.6 mC/cm² were passed for the FeOOH and NiOOH deposition, respectively. When depositing FeOOH and NiOOH on BiVO₄ in a row, BiVO₄/FeOOH was dried in air for at least 3 h before NiOOH photodeposition. Finally, the resulting BiVO₄/FeOOH NiOOH films were rinsed with DI water and dried with a gentle stream of air. The samples were transparently masked to give an exposed sample area between 0.13 – 0.2 cm².

The roughness factor of the thin, nanoporous BiVO₄ film used in this study was determined to be 20 based on the mass of BiVO₄ contained in the thin film and the specific surface area of nanoporous BiVO₄ (31.8 m²/g) reported in our previous study.² Using the roughness factor of BiVO₄ and the estimated amount of catalyst deposited (assuming 100% Faradaic efficiency of the charge passed during photodeposition), the thicknesses of FeOOH, Ni(Fe)OOH, and FeOOHNiOOH catalyst layers on the nanoporous BiVO₄ electrode were calculated to be 3 nm, 4 nm, and 7 nm, respectively.

c. Instrumentation

**Electrochemical set-up:** Electrochemical experiments were carried out using an Autolab potentiostat (PGSTAT 101) and a typical three-electrode configuration with a platinum mesh as counter electrode, an Ag/AgCl electrode (saturated KCl) as reference and the electrocatalysts as working electrode. A 0.1 M phosphate buffer (pH 7) was used as the electrolyte in all experiments. The measured values (vs Ag/AgCl) were then converted to potentials against the reversible hydrogen electrode (RHE) using the Nernst equation:

\[
V_{\text{RHE}} = V_{\text{Ag/AgCl}} + V_{\text{Ag/AgCl}}^0 + 0.059 \cdot p\text{H}
\]

with \(V_{\text{Ag/AgCl}}^0\) (saturated KCl) = 0.199 V

**Spectroelectrochemical experiments:** Spectroelectrochemistry (SEC), i.e. optical absorption as a function of applied potential, was measured by fitting the spectroelectrochemical cell in a Cary 60 UV-Vis spectrometer (Agilent Technologies). The measured data is generally presented as spectroelectrochemical difference spectra (ΔO.D.), which are generated by subtracting a reference spectrum (usually at the OCP or water-oxidation onset) from the absorption data obtained under conditions of interest (e.g. higher applied potentials). The technique is explained in detail by Pastor et al.⁴

**Step-Potential Spectroelectrochemistry (SP-SEC):** We used this technique to estimate the extinction coefficient of the doubly oxidized species. This technique, has been reported by us previously,¹ uses an electrochemical pump and an optical probe. The electrochemical pump (step-potential) is carried out by applying a squared (ON/OFF) voltage (potential difference) until steady-state conditions are reached. The effect of the applied potential on the electrocatalyst was monitored using light from a 100 W tungsten lamp, equipped with an Oriel cornerstone 130 monochromator. The transmitted probe light was filtered by several band pass and long pass filters (Comar Optics) and detected by a silicon photodiode (Hamamatsu S3071). Collected photons were converted to a voltage signal, sent to an amplifier (Costronics) and recorded by an oscilloscope (Tektronics TDS 2012c) and with a DAQ card (National Instruments, NI USB-6211) on the timescale of ms - s. Simultaneously, the extracted current was monitored using a Palmsense3 potentiostat. All data were acquired by a home-programmed LabView software.

**Transient Absorbance Spectroscopy (TAS)** The microsecond-second transient absorption decays were recorded using laser excitation pulses (6 ns) at 355 nm generated from a Nd:YAG laser (Big Sky Laser Technologies Ultra CFR Nd:YAG laser system, 6 ns pulse width, and 0.5 Hz). A liquid light guide with a diameter of 0.5 cm was used to transmit the laser pulse to the sample. The probe light source was a tungsten lamp (Bentham IL1 tungsten lamp), and the probe wavelength was selected using a
monochromator (OBB-2001 dual grating, Photon Technology International) placed prior to the sample. Transient absorption data was collected with a Si photodiode (Hamamatsu S3071). The information was passed through an amplifier box (Costronics) and recorded using a Tektronics TDS 2012c oscilloscope (microsecond to millisecond timescale) and a DAQ card (National Instruments, USB-6211) (millisecond to second timescale). The data was processed using home-built software based on Labview. The decays observed are the average between 16 and 32 averages laser pulses.

As the area of the probed beam (0.28 cm$^2$) used to measure the change in the optical density was larger than the exposed area of the sample to the electrolyte, this was accounted for by dividing the raw data by the fractional area: $\frac{\text{Area of sample exposed area}}{\text{Area of probed area}}$.

**Spectroelectrochemical Photo-Induced Absorption Spectroscopy (PIAS):** Spectroelectrochemical Photo-induced absorption spectroscopy (PIAS) allows long-lived photogenerated species to be monitored under pseudo steady-state conditions. During these experiments, the sample was illuminated with light pulses (approximately 5 s on/5 s off), provided by a 365 nm LED (pump light). The change in absorbance was recorded using a probe light, which consisted of a tungsten lamp (Bentham IL1 tungsten lamp), and the probe wavelength was selected using a monochromator (OBB-2001, Photon Technology International) placed prior to the sample. Several long pass and band pass filters (Comar Instruments) were used to attenuate the pump light arriving at the detector. Transmitted photons were collected with a Si photodiode (Hamamatsu S3071). The signal was recorded with a DAQ card (National Instruments, USB-6211) without amplification.

As the area of the probed beam (0.28 cm$^2$) used to measure the change in the optical density was larger than the exposed area of the sample to the electrolyte, this was accounted for by dividing the raw data by the fractional area: $\frac{\text{Area of sample exposed area}}{\text{Area of probed area}}$. 
A. Electro catalyst activation process

The anodic electrodeposition methods used in this study produced FeOOH and Ni(Fe)OOH films. While FeOOH is stable in air, black NiOOH gradually changes to transparent Ni(OH)\(_2\) in air when it is not anodically protected. Therefore, Ni(Fe)OOH and FeOOHNiOOH samples were activated before the optical and electrochemical experiments in order to convert Ni(OH)\(_2\) in these samples to NiOOH. This process oxidises the Ni\(^{II}\)(OH)\(_2\) to the higher valence NiOOH, leading to a strong absorption assigned to metal-to-oxygen charge transfer transition. To do this, the potential was swept from the open circuit potential of the sample to 1.5 V vs. the Ag/AgCl RE (scan rate = 10 mV/s) five times.\(^1\) The conversion of Ni(OH)\(_2\) to NiOOH could be confirmed visually by the return of the black colour. The same activation procedure was also used for catalysts deposited on BiVO\(_4\) photoanodes.

![Image of spectra](image)

**Figure S2.** Spectra of MOOH(+) species after sample activation. (a) Differential UV-Vis absorbance spectra (OD\(_\text{after activation} - \text{OD before activation}\)) for Ni(Fe)OOH (green) and FeOOHNiOOH (blue); (b) Normalised ΔOD spectra.
B. SEC: Spectra of MOOH(++) species under electrochemical water oxidation

Figure S3. Differential UV-Vis spectra of the catalytic species at different applied potentials. The ΔOD was estimated by subtracting the absorbance at the catalytic onset from more positive applied potentials for (a) FeOOH, (b) FeOOHNIOOH and (c) Ni(Fe)OOH.

C. NiOOH deactivation

Figure S4. SEM images of a Ni(Fe)OOH (a) before and (b) after a bulk electrolysis of 2 h applying 2 V_{RHE}. The red circle indicates bare FTO observed after the experiment.
Figure S5. Degradation of Ni(Fe)OOH films at high applied potentials (> 2 V\textsubscript{RHE}). (a) UV-Vis spectra from 1.6 V\textsubscript{RHE} (red) to 2 V\textsubscript{RHE} (yellow-orange) and to 2.2 V\textsubscript{RHE} (green). (b) LSV before (red) and after (orange) the experiments shown in part (a).

Figure S6. Stability of BiVO\textsubscript{4}/Ni(Fe)OOH. (a) Chopped chronoamperometry under 1 sun at 1.41 V\textsubscript{RHE} and (b) chopped LSV under 1 sun before (grey) and after (black) the chronoamperometry presented in Figure S5a.
D. Extinction coefficient estimation

The extinction coefficient of all the second oxidized species were estimated using the SP-SEC technique, reported previously. We monitored the changes in absorbance when a voltage step is applied. The recorded optical data is proportional to the population of the oxidized states at the applied potential (Figures S6 a, c, e). Simultaneously, the corresponding current is measured with an increase of current at the high applied potential and a reductive spike once the potential is turned to a lower one. The latter corresponds to the reduction of the accumulated oxidized states at the high potential region. The integration of these reductive currents allow us to quantify the electrons used to reduce the oxidized states. Using the Lambert-Beer law ($\text{Equation S2}$) we can estimate the corresponding extinction coefficients by plotting $\Delta\text{OD}$ against the electrons extracted (Figures S6 b, d, f). The slope of the corresponding graphs yields the $\varepsilon$ in cm$^2$/number of e$^-$, which can be transformed to M$^{-1}$cm$^{-1}$ as detailed:

\text{Equation S2} \quad A = \varepsilon \times c \quad \text{where } A \text{ = Absorbance at a particular wavelength, } \varepsilon \text{ is the extinction coefficient and } c \text{ is the concentration in electrons per cm}^2.

\[
5.8 \times 10^{-18} \frac{\text{cm}^2}{\text{no of e}^-} \times 6.022 \times 10^{23} \frac{\text{no of e}^-}{1 \text{ mol e}^-} \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} = 3500 \text{ M}^{-1}\text{cm}^{-1}
\]
Figure S7. SP-SEC of electrocatalysts to estimate the extinction coefficients of MOOH(++) species.
(a) SP-SEC for FeOOH from 1.72 V_{RHE} to the desired potential (up to 1.91 V_{RHE}) where the top panel shows the optical data at 550 nm, and the bottom panel shows the current density. (b) Plot of the optical signal at 550 nm against the charge density.
(c) SP-SEC for FeOOH NiOOH from 1.64 V_{RHE} to the desired potential (up to 1.81 V_{RHE}) where the top panel shows the optical data at 550 nm, and the bottom panel shows the current density. (d) Plot of the optical signal at 550 nm against the charge density.
(e) SP-SEC for Ni(Fe)OOH from 1.72 V_{RHE} to the desired potential (up to 1.91 V_{RHE}) where the top panel shows the optical data at 650 nm, and the bottom panel shows the current density. (f) Plot of the optical signal at 650 nm against the charge density.
E. Transient absorption spectroscopy

Figure S8. Transient absorption spectra (dark to light colours representing spectra at 10 μs – 100 μs – 1 ms – 10 ms – 100 ms – 1 s) of (a) BiVO₄/FeOOH and (b) BiVO₄/FeOOHNiOOH. All measurements were obtained under 1.4 V_{RHE} applied bias, at pH7. The samples were excited at 355 nm (300 μJ cm⁻²).

Figure S9. Normalised TA spectra at 10 ms for BiVO₄ (black), BiVO₄/FeOOH (red), BiVO₄/FeOOH NiOOH (blue) and BiVO₄/Ni(Fe)OOH (green).
F. **TOF (s\(^{-1}\)) and \(\tau\) (s) calculation from measured \([++]\) state densities and electrochemically measured water oxidation current densities.**

In order to calculate these parameters we need the number of accumulated \([++]\) (cm\(^{-2}\)), which are derived from the conversion of the obtained ΔOD using the extinction coefficient. On the other hand the current density data (A/cm\(^2\)) can be transformed into number of electrons/s using the electron charge (1.60 \times 10^{-19} \text{ Coulombs}).

For TOF calculation we consider that to produce one molecule of oxygen 4 oxidized species are needed

**Equation S3.** \(\text{TOF (s}^{-1}) = \frac{\text{number of electrons} \times \text{s}^{-1}}{4 \, [++]}\)

\(\tau\) is the lifetime of the oxidized species MOOH(++)

**Equation S4.** \(\tau (\text{s}) = \frac{[++]}{\text{number of electrons} \times \text{s}^{-1}}\)

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