Operando X-Ray Absorption Spectroscopy (XAS) Observation of Photoinduced Oxidation in FeNi (Oxy)hydroxide Overlayers on Hematite (α-Fe2O3) Photoanodes for Solar Water Splitting

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Operando X-ray absorption spectroscopy (XAS) observation of photoinduced oxidation in FeNi (oxy)hydroxide overlayers on hematite ($\alpha$-Fe$_2$O$_3$) photoanodes for solar water splitting

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Abstract

A FeNi (oxy)hydroxide co-catalyst overlayer was photoelectrochemically deposited on a thin film hematite ($\alpha$-Fe$_2$O$_3$) photoanode, leading to a cathodic shift of ~100 mV in the photocurrent onset potential. Operando X-ray absorption spectroscopy (XAS) at the Fe and Ni K-edges was used to study the changes in the overlayer with potential, in dark and under illumination conditions. Potential or illumination only had a minor effect on the Fe oxidation state, suggesting that Fe atoms do not accumulate significant amount of charge over the whole potential range. In contrast, the Ni K-edge spectra showed pronounced dependence on potential in dark and under illumination. The effect of illumination is to shift the onset for the Ni oxidation because of the generated photovoltage, and suggests that holes which are photogenerated in hematite are transferred mainly to the Ni atoms in the overlayer. The increase in the oxidation state of Ni proceeds at potentials corresponding to the redox wave of Ni, which occurs immediately prior to the onset of the oxygen evolution reaction (OER). Linear fitting analysis of the obtained spectra suggests that the overlayer does not have to be fully oxidized to promote oxygen evolution. Cathodic discharge measurements show that the photogenerated charge is stored almost exclusively in the Ni atoms within the volume of the overlayer.

Introduction

Since the pioneering work of Fujishima and Honda in the early 1970’s,$^1$ photoelectrochemical (PEC) water splitting has been actively investigated for its promise to provide an elegant path for the direct conversion of intermittent solar power into storable hydrogen fuel. A notable candidate for a photoanode material that drives water photo-oxidation in PEC cells for solar water splitting is hematite ($\alpha$-Fe$_2$O$_3$), being one of the few materials to meet the key criteria of stability, abundance, low cost, and a bandgap suitable for effective sunlight absorption. However, it also comes with some serious drawbacks: low mobility of charge carriers, low lifetime of photo-generated charge carriers due to bulk recombination, surface recombination at the photoanode/electrolyte interface, and high external voltage for solar driven water splitting. To address the last two issues, a widely exploited route to improve performance is to deposit various overlayers, which significantly reduce both surface recombination and the overpotential needed for water photo-oxidation. NiFe (oxy)hydroxide based electrocatalysts are considered as favorable materials because of their inexpensive cost (abundant elements), high catalytic activity for the oxygen evolution reaction (OER), and stability under water
oxidation reaction conditions in alkaline solution. There have been many studies of NiFe (oxy)hydroxide operating as a co-catalyst overlayer on top of a photoanode. The resultant improvement in performance has been attributed to a variety of proposed mechanisms, including Fermi level unpinning, improved surface catalysis, passivation of surface defects, formation of p-n junction or storage of excess holes to prevent surface recombination. Light-modulated impedance spectroscopy on Sn-doped hematite revealed that addition of a NiFe (oxy)hydroxide overlayer caused a decrease of surface recombination as compared to the bare hematite sample, which improved sharply with potential in the vicinity of the photocurrent onset. By measuring the electronic properties of a NiFe (oxy)hydroxide overlayer on hematite in situ, using a second working electrode, Qiu et al. observed a dramatic rise in the electrical conductivity of the overlayer, spanning the Ni redox peak in the current-voltage curve, which immediately preceded the photocurrent onset. This, together with further in-situ probing of the overlayer, led to the picture that the overlayer is active for charge transfer from the hematite to the OER, only after it has been transformed to its oxidized and conductive state.

To further clarify the processes in the overlayer spectroscopically, here we present a spectroelectrochemical study of the roles of Ni and Fe sites under operative conditions of PEC water splitting using X-ray absorption spectroscopy (XAS), an element-specific probe of the local structure and oxidation state of atoms. Operando XAS, which can directly monitor changes in the oxidation state of catalytic sites in response to applied potential and/or illumination, has indeed proven to be a powerful method for investigating charge transfer processes in electrochemical and photoelectrochemical systems. Braun et al., in their pioneering operando oxygen K-edge XAS study of a bare hematite photoanode under applied potential and illumination, interpreted pre-edge features as two types of holes at the hematite/electrolyte interface, which reached maximum population in the vicinity of the photocurrent onset. A number of measurements were done on the metal absorption edge of overlayers deposited on photoabsorbers. Minguzzi et al. performed an operando XAS study on IrO$_x$ overlayer deposited on top of a hematite photoanode, at the Ir K-edge, which showed a clear oxidation of the Ir sites in response to illumination. Li et al. used high-energy-resolution fluorescence detection XAS to study ultrathin (1-3 nm) overlayers of IrO$_x$ on top of a Si photoanode. The authors observed a near-linear increase of the Ir oxidation state prior to the current onset, followed by saturation or even decrease a few hundreds of meV above the onset potential. Interestingly, these trends were completely identical for anodes which operate in light and dark conditions, aside from being shifted according to the respective onset potentials. This suggests that, for the hematite photoanode and NiFe (oxy)hydroxide overlayer system in the present study, previous operando XAS studies of NiFe (oxy)hydroxide catalysts, even without photoexcitation, could offer pertinent insights. Such (non-photo) works include recent papers by Friebel et al., Wang et al., and Drevon et al., and others. Similar to the IrO$_x$ overlayer studies, the oxidation state of Ni was found to increase prior to the onset of the OER, and saturate a few hundreds of meV after the onset. The Fe K-edge spectra, on the other hand, showed considerably less pronounced changes of oxidation state, although they were correlated with changes in Ni K-edge. Additionally, by extracting bond lengths from extended X-ray fine structure (EXAFS) measurements, Friebel et al. found that Fe is not interstitial between NiO$_2$ sheets, but rather substitutes into Ni sites in NiO$_x$ octahedra at low Fe content and additionally forms a separate $\gamma$-FeOOH phase at higher Fe content, and that the structure transforms from $\alpha$-Ni(OH)$_2$ at low potential, to $\gamma$-NiOOH upon oxygen evolution. Recent work by Morikawa et al. on $\beta$-FeOOH nanorods modified with Ni(OH)$_2$ have suggested that $\beta$-NiOOH is the active phase under OER conditions. While there have been no definite conclusions or consensus as to the precise roles of Fe and Ni in enhancing water-oxidation activity,
decrease in the activation energy for OER at Fe sites as a result of shortening of the Fe-O bond-length in NiFe (oxy)hydroxide was proposed as a possibility. In this work, we measure a hematite photoanode with an FeNi (oxy)hydroxide overlayer (with ~87 cat.% Fe), with operando XAS at the Ni and Fe K-edges, controlling both potential and dark/light conditions, and discuss the results in context of water photooxidation processes in PEC water splitting. We show the relation between the XAS results to photoelectrochemical measurements including current-voltage, and found a good correspondence between determined Ni oxidation state and cathodic discharge measurements.

**Results**

Our primary sample consisted of a heteroepitaxial Sn-doped (1 cat.%) hematite layer, deposited by pulsed layer deposition on a Nb-doped SnO$_2$ coated (0001) sapphire substrate. The deposition conditions, structure and microstructure of similar samples are reported elsewhere. An FeNi (oxy)hydroxide co-catalyst overlayer having an Fe:Ni ratio of ~7:1, to be consistent with our previous work, was deposited photoelectrochemically on the hematite layer (note that the Fe-Ni order has been reversed to reflect a majority of Fe). TEM suggested the formation of two phases, an amorphous and crystalline phase, one of which is speculated to be Fe-rich. Full characterization including SEM, TEM, XPS and AFM of similar samples, is reported in Ref. 19. A study of the effect of other Fe:Ni compositions on hematite could be a subject of future work. The thicknesses of the hematite layer and FeNi (oxy)hydroxide overlayer were estimated to be 10 and 30 nm, respectively. A bare hematite photoanode was prepared as a reference sample, under identical conditions but without an overlayer. Linear sweep voltammetry (LSV) for both photoanodes, measured in the dark and under white-light illumination with intensity of $100 \text{mW/cm}^2$ at the sample position, is presented in Figure S1. The dark current was nearly zero over the entire potential range examined. Consistent with previous reports, deposition of the FeNi (oxy)hydroxide co-catalyst overlayer led to a cathodic shift of ~100 mV in the photocurrent onset potential, whereas the photocurrent plateau remained nearly the same as for the bare hematite sample. However, unlike our previous study, a small redox peak of Ni(II)/Ni(III) appeared at 1.05 V$_{\text{RHE}}$ under illumination conditions, just before the onset potential for OER. The reason for the appearance of this peak is the relatively large thickness (~30 nm) of the FeNi (oxy)hydroxide overlayer, designed to enhance its XAS signal, which was considerably thicker than in the previous study (~2 nm).

Figure 1 illustrates the configuration of the operando XAS measurements, which were performed at the P64 beamline of PETRA III synchrotron (DESY, Hamburg, Germany). The sample was placed in a special electrochemical cell (see the SI for details), such that a thin (~200-300 µm) layer of 1 M NaOH aqueous electrolyte covered the sample surface. Potential was applied to the photoanode and the current was measured using an Ivium potentiostat in three-electrode mode, with an Hg/HgO/1M NaOH reference electrode and Pt counter electrode placed in the electrolyte. The sample was photoexcited with a high-power white LED that provided an intensity of $100 \text{mW/cm}^2$ at the sample position. For brevity, we denote this state of illumination as the "light" condition, and absence of such as "dark". Fe and Ni K-edge absorption spectra were measured in fluorescence detection mode with a 100-pixel Ge-detector (Canberra). Further details including photograph of the cell and the measurement setup, are provided in the SI (Figures S2 and S3). As a preliminary check for possible beamline damage to the sample and to ensure stability of the PEC system, successive measurements of the XAS spectrum of the bare hematite
sample near the Fe K-edge were carried out in dark, light, and back to dark conditions, at a constant potential of 1.5 V_{RHE}, where there is photocurrent. Figure S4 shows that the white line (WL) intensity decreased under light conditions, which is likely associated with partial oxidation of surface Fe sites \(^{30,31}\) that proceeds under oxygen evolution conditions.\(^{39}\) Upon removing the illumination and returning to dark conditions, the spectrum was restored to its initial dark state, demonstrating stability of the system.

**Figure 1: Schematic side view illustration of the operando photoelectrochemical XAS measurement setup.**

The procedure to monitor the evolution of oxidation states of Fe and Ni in the photoanode was as follows. The potential was set to values tracing the photocurrent pre-onset (points A, B) and post-onset (points C,D,E) regions of the LSV curve (under illumination) shown in Figure 2. A zoom-in of the dark current, presented in the inset of Figure 2, reveals a feature related to Ni redox activity,\(^{40,41}\) prior to the onset of oxygen evolution. For each potential, and for both dark and light conditions, XAS spectra were measured at both the Fe and Ni K-edges, before proceeding to the next potential. The near-edge spectra for the Fe K-edge are shown in Figures 3(a) and 3(b) for dark and light conditions, respectively. Note that all spectra presented here were normalized by the standard procedure using Athena software,\(^{42}\) according to the jump at the absorption edge, defined by the difference between the extrapolated lines fitted to the low-energy (pre-edge) and high-energy (post-edge) parts of the spectra. As is common practice, the WL intensity is described relative to this jump. We focus on the near-edge (XANES) region since most of the clear changes were observed there. Full spectra are presented in Figure S5. From Figure 3(a), the XAS spectra measured in dark, with exception of point A (at 0.53 V_{RHE}), were affected very little by the applied potential in the range applied. To highlight any differences between the spectra, the insets in Figure 3 show them subtracted by the spectrum measured at point A (0.53 V_{RHE}) in dark. All of the spectra are characterized by a shift in spectral weight to higher energies (manifested by negative valley followed by a positive peak), as compared to the spectrum measured at point A (0.53 V_{RHE}), but were otherwise independent of potential. We suggest that the spectral weight shift common to points B-E is related to the expected depletion of electrons from the surface at anodic bias.\(^{39}\) Under illumination (Figure 3b), the general trend is similar to the dark case, except for a notable increase in intensity of the WL peak for point E (1.5 V_{RHE}). No other significant potential dependence in XANES or EXAFS region (shown in Figure S5) of the spectra were detected. This result of very little (if any) oxidation of Fe atoms is generally consistent with previous reports of relatively small oxidation of Fe in FeNi
(oxy)hydroxide electrocatalysts.\textsuperscript{29-31,43} Furthermore, the contribution from the underlying hematite layer would diminish observed changes in the Fe-edge spectra originating from the overlayer. It is peculiar that the WL of the Fe K-edge under illumination slightly increases with potential, rather than decreases as might have been expected from electrocatalyst studies.\textsuperscript{29-31} In fact, it is difficult to distinguish Fe contributions coming from the FeNi (oxy)hydroxide overlayer or the hematite layer. However, we note that the trend is opposite to that observed for bare hematite in Figure S4. We speculate the origin of this effect might be a change in the geometry, or small change in the time-averaged Fe oxidation state, of the Fe sites in the overlayer as a result of a change in the oxidation state of neighboring Ni sites\textsuperscript{29,34}, or some additional effect of illumination on the overlayer that EXAFS analysis could possibly clarify, but will be investigated elsewhere. Whatever the case, the relatively small changes indicate that most of the Fe sites of the overlayer do not accumulate charge before and during OER.

![Figure 2](image.png)

**Figure 2:** LSV voltamograms measured under dark (dashed line) and light (solid line) conditions within the beamline before the XAS measurements for hematite/FeNi (oxy)hydroxide. Points A-E represent XAS measurement points taken under light condition. XAS measurements were carried out also in the dark at the same potential values. Note that we use the same labels for the corresponding potentials in dark conditions. Inset: Zoom-in of the dark current LSV.
Figure 3: Normalized Fe K-edge XANES spectra of hematite/FeNi (oxy)hydroxide under (a) dark and (b) light conditions. The measurement point, at different potentials (see Figure 2), is indicated in the legend. All of the potentials are versus RHE. All the spectra are normalized by the standard method based on the extrapolated jump at the absorption edge. The insets show the measured spectra subtracted by the spectrum measured in point A (0.53 V_RHE) in dark.

The XAS spectra at the Ni K-edge, under dark and light conditions, are presented in Figure 4, displaying markedly more pronounced changes than those observed for the Fe K-edge spectra in Figure 3. Increase
of the Ni oxidation state with increased potentials is evident from the shifts in the WL for both dark and light conditions. Notably, the oxidation state of Ni also increases in the dark (Figure 4(a)), just below the OER onset potential, at potentials encompassing with the peak at ~1.3-1.4 V (Figure 2, inset). This is not surprising, since the standard potential of the Ni(II)/Ni(III) (Ni(OH))$_2$/NiOOH redox reaction is 1.348 V.\textsuperscript{44} It is also consistent with the study of Drevon et al. who reported an edge shift prior to the OER onset in NiFe (oxy)hydroxide electrocatalysts,\textsuperscript{31} as well as Li et al. for Si photo-absorbers with Ir overlayers.\textsuperscript{28} Most of the change in the WL region occurs between the spectra recorded at points C (1.2 V$_{RHE}$, blue curve) and D (1.35 V$_{RHE}$, green curve), while the spectrum recorded at point E (1.5 V$_{RHE}$, orange curve) nearly overlaps with that recorded at point D. This indicates that the Ni oxidation begins to saturate just after the onset of OER current (Figure 2, inset), consistently with previous reports on NiFe (oxy)hydroxide electrocatalysts.\textsuperscript{29,31} Fitting of the spectra, shown below, can clarify the oxidation state trends.

Under illumination conditions (Figure 4(b)), the WL shift is even more pronounced. The most noticeable change in the XANES region is observed between the spectra recorded at points B (1 V$_{RHE}$, red solid curve) and C (1.2 V$_{RHE}$, blue curve), near the onset potentials of Ni photo-oxidation and prior to water photo-oxidation (at ~1.2 V$_{RHE}$) observed in the LSV curve measured under illumination. The spectral shift begins to stabilize around point D (1.35 V$_{RHE}$). Comparison of the light and dark spectra at each potential (Figure S5) clearly shows that starting at point C (1.2 V$_{RHE}$) illumination shifts the WL position to higher energies. This is likely a result of photogenerated holes injected from the hematite layer into the FeNi (oxy)hydroxide overlayer. Indeed, most of the photogenerated holes produced in the photoanode originate in the hematite layer, made evident from the greater optical absorption in the hematite layer.\textsuperscript{16,19,45} In contrast to the hole injection under illumination, conduction band electrons are the responsible for charge transfer in dark, in case of n-type Sn-doped hematite photoanodes.\textsuperscript{46} Combining the results obtained in dark and light conditions, it follows that both electrons and holes can be transferred between the hematite layer and the FeNi (oxy)hydroxide overlayer. The transfer of the photogenerated holes to the overlayer also suppresses surface recombination,\textsuperscript{4,18} as was also suggested by IMPS measurements for similar samples.\textsuperscript{19}
Figure 4: Normalized Ni K-edge XANES spectra for hematite/FeNi (oxy)hydroxide under (a) dark and (b) light conditions. The measurement point, at different potentials (see Figure 2), is indicated in the legend. All of the potentials are versus RHE. All the spectra are normalized by the standard method based on the extrapolated jump at the absorption edge. Normalized Ni K-edge XANES spectra for NiO, β-NiOOH and Ni standards used for the fitting are also presented in panel (a). Inset: Zoom-in of the WL region.

To clarify the trend of the average Ni oxidation state as a function of applied potential under dark and light conditions, we fit each of the measured spectra to a sum of XAS spectra of Ni, Ni(OH)$_2$, β-NiOOH and γ-NiOOH, as standards for the Ni(0), Ni(II), Ni(III) and higher (>Ni(III)) oxidation states, respectively.
These standards were selected based on the most stable phases in the Pourbaix diagram of Ni under the measurement conditions (not considering the presence of Fe).\textsuperscript{47} $\gamma$-NiOOH is known to have a mixed Ni(III)/Ni(IV) oxidation state,\textsuperscript{48} and therefore can be used as a standard for higher oxidation states. The relative weights of the components were obtained by a least-squares fitting routine using the Levenberg-Marquardt method. The fitting method and results, and choice of standards, are described in more detail in the SI. The normalized XAS spectra of these standards are plotted in Figure 4(a). A Ni standard was used for the fitting process because a pre-edge feature was observed in all of the spectra at $\sim$8335 eV, which is a typical signature of metallic nickel (Ni(0)).\textsuperscript{49} Subsequent to the XAS measurements, SEM EDS analysis showed the presence of metallic Ni on the electrical contact clips to the sample (Figure S6 in SI), which may have contributed to the observed spectra. It was also determined from fitting that the metallic Ni contribution of the spectra was largely independent of potential or light. Therefore, assuming a constant contribution from the connectors, all the spectra were fitted simultaneously while keeping the metallic Ni fraction to be a shared parameter among all the spectra. The resultant fit curves are shown in Figure S7.

According to the fits, most of the Ni oxidized to a phase resembling $\beta$-NiOOH, but for the highest two potentials under illumination (points D and E) a $\sim$15% spectral content of $\gamma$-NiOOH was observed. This latter observation is in line with previous studies of NiFe (oxy)hydroxides, that reported formation of $\gamma$-NiOOH under overcharging conditions.\textsuperscript{50–53} The average oxidation state of Ni in the sample was calculated according to the obtained fractions of the Ni phases (+2 for NiO, +3 for $\beta$-NiOOH, and +3.6 for $\gamma$-NiOOH), excluding metallic Ni contribution. Plotted in Figure 5, the average oxidation state is overlayed on normalized LSV curves in dark and light. In the dark condition, the oxidation state of Ni is +2 up to $\sim$1.2 V$\text{RHE}$, above which it gradually increases to an average oxidation state of +2.35 at a potential of 1.53 V$\text{RHE}$, corresponding to a state-of-charge (SOC) of 35% in the transition from Ni(II) to Ni(III). For measurements under illumination, the onset of Ni (photo)-oxidation shifts to a lower potential than in dark, with the oxidation state increasing rapidly above $\sim$1 V$\text{RHE}$, corresponding to the onset of the Ni redox wave in the LSV curve, and below the onset of the OER. We note that for both light and dark conditions, the linear region of Ni oxidation increase occurs at the potentials spanning the Ni redox wave in the respective LSV curves. The Ni oxidation curves in light and dark seem similar but shifted according to the respective shift of the LSV curves, considered to be the photovoltage generated in the photoanode.\textsuperscript{54} A similar photovoltage-related shift was observed by Li et al.\textsuperscript{28} At the highest applied potential in light (1.5 V$\text{RHE}$), the average oxidation state reaches a value of +2.6, where it begins to saturate. These observations are in line with previous reports that partial oxidation and transition from the hydroxide to the oxyhydroxide phase precedes the OER and then saturates prior to the plateau region in the water photo-oxidation current.\textsuperscript{28,29,34}
Figure 5: Average oxidation state of Ni under dark (solid line with black triangles) and light (solid line with red triangles) conditions for hematite/FeNi (oxy)hydroxide, overlayed on the LSV voltamograms recorded during the XAS measurement under the same conditions (black and dashed lines for dark and light conditions, respectively). Dark and light currents were normalized by dividing by their respective currents at 1.63 V\textsubscript{RHE}.

If the observed increase of Ni oxidation state is indeed instrumental in promoting the water photo-oxidation reaction (either directly whereby the OER reaction occurs at oxidized Ni sites as suggested above, or indirectly by lowering the potential of the OER onset at the Fe site, as proposed by Friebel et al.\textsuperscript{29}), this result nevertheless implies that the FeNi (oxy)hydroxide overlayer does not need to be fully oxidized before this happens, as was also concluded from electrochemical measurements by Qiu et al.\textsuperscript{20} However, we cannot rule out the possibility that the foremost surface atoms may be fully oxidized, since the X-ray fluorescence includes contributions from many atomic layers. The observed saturation of the oxidation state not far above the onset for OER could be owing to competition for holes between Ni and water oxidation reactions. When the overlayer is charged to its active state, a portion of the holes begin to be injected into the electrolyte, while the remainder continue to cause oxidation of the overlayer. This would create a negative feedback, since if oxidized Ni enhances the OER, this increased OER will draw more holes away from further increasing its oxidation state, therefore stabilizing (saturating) it at some potential.

As a complementary investigation of how the overlayer transforms during the OER, cathodic discharge measurements were carried out for the samples with and without the FeNi (oxy)hydroxide overlayer. These measurements determine “stable charge” which does not get discharged upon removing light, but only by ramping down potential. The measurement procedure, as first proposed to monitor the surface state in TiO\textsubscript{2} photoanodes for water photo-oxidation,\textsuperscript{55} was also previously applied to study hematite photoanodes.\textsuperscript{36,56,57} The sample is first held in the electrolyte (1M NaOH) under constant potential (called the charging potential) and illumination, to facilitate filling of hematite surface states and charge the FeNi (oxy)hydroxide overlayer. In the next step, the light is turned off, and the current drops. After the
current has stabilized, the potential is swept cathodically to discharge the surface states and FeNi (oxy)hydroxide overlayer. The resulting cathodic current upon discharge is integrated over time to calculate the "stable" charge that remained after the light was turned off. A representative cathodic discharge measurement plot is shown in the Figure S10. The resultant stable charge as a function of the applied charging potential for bare hematite photoanode and hematite photoanode with the FeNi (oxy)hydroxide overlayer is plotted in Figure 6(a). The amount of stored charge in the sample with the FeNi (oxy)hydroxide overlayer is an order of magnitude higher than for the bare hematite. This is because the charge is stored only on the surface in the case of as the bare hematite photoanode, while in case of ion permeable redox active layer such as FeNi (oxy)hydroxide overlayer the charge is stored in the whole layer. A similar observation was made for a "non-stable charge" measurement of the transient currents in response to light on/off at a potential fixed to the OER onset, which is also related to stable charge. For bare hematite, a strong correlation between the photocurrent and stable surface charge curves is observed, consistent with a previous study, suggesting a direct correlation between the two processes. However, a distinctly different trend is observed for the sample with the FeNi (oxy)hydroxide overlayer. Major accumulation of charge instead coincides with the onset potential of Ni photo-oxidation which occurs prior to the onset of OER. Moreover, the stable charge curve is similar to the oxidation state curve (Figure 5). Figure 6(b) shows the interpolated average oxidation state as a function of the stored stable charge. The plot suggests linear dependence between the two parameters, supporting accumulation of the stable charge by oxidation of the Ni atoms. We note that Ni oxidation state for zero stable charge is higher than +2.6±0.1. The reason is that most of the charge accumulated at low potentials is in the form of “unstable” charge, that is removed upon switching off the light during stable charge measurements. The obtained data shows that Ni sites are oxidized by the photogenerated holes, even before the onset of water photo-oxidation. The stable charge seems to stabilize at the highest potential applied (1.5 V_{RHE}), in line with the stabilization of the Ni oxidation state obtained from the XAS measurements.
Figure 6: (a) Stable charge for bare hematite (black squares) and hematite/FeNi (oxy)hydroxide photoanodes (red circles), as a function of charging potential, overlayed on LSV measurement in matching conditions for bare hematite (black dashed line) and hematite with overlayer (red dashed line). (b) Average Ni oxidation state under illumination (obtained from XAS fitting) as a function of the stable charge for the hematite photoanode with the overlayer, interpolated from Figures 5 and 6(a).
To summarize, we have studied the effect of illumination and potential on the oxidation of the transition metal sites (Fe, Ni) in the hematite photoanode with FeNi (oxy)hydroxide overlayer. The observed change with potential for the Fe K-edge was rather small, however it was more pronounced for light than for dark conditions. This small change of the average could signify a temporary increase in the Fe oxidation state. Of great interest for future studies would be to track the possible oxidation states evolution with time, which could be connected to multiple site reactions (in this case, Ni and Fe) as recently suggested in the literature.\textsuperscript{59–61} The Ni sites were more strongly affected by both potential and illumination, consistent with previous spectro-electrochemical \textit{operando} XAS studies, including those done without photoexcitation.\textsuperscript{28–31} For both dark and light conditions we found that partial oxidation of Ni in the overlayer proceeded at potentials corresponding to the redox wave of Ni (Ni(OH)\textsubscript{2}/NiOOH), which occurs immediately prior to the onset of the OER. This is consistent with the picture of Qiu et al.\textsuperscript{20} the Ni sites need to be oxidized for effective OER activity. These observations further suggest that the main effect of light absorption is to shift the Ni oxidation to lower potentials by the photovoltage generated in the photoanode. The maximal oxidation state of Ni started to saturate and reached a value of $+2.6\pm0.1$ under illumination, and a negative feedback mechanism limiting the oxidation state was suggested. In addition, considering the dependence of the Ni K-edge on potential in dark and light, we conclude that both electrons and holes can be transferred between the hematite and FeNi (oxy)hydroxide layers. Intriguingly, the cathodic discharge measurements shared very similar characteristics to the Ni oxidation state curve (from XAS measurements), rather than the photocurrent curve as for bare hematite, showing a linear relation to phase transformations in the overlayer. We observed a greater than tenfold increase of stable charge measured for the sample with the FeNi (oxy)hydroxide overlayer, as compared to the bare hematite sample, indicating that the whole overlayer stores the charge in the Ni atoms, consistent with the XAS results. While the iron atoms did not appear to be charged on average, it does not rule out the possibility that their oxidation state could change in some temporal window in the transient response to illumination. Future advances in instrumentation could enable such dynamical measurements resolved in the temporal and/or spatial domains.

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Supporting information for Operando X-ray absorption spectroscopy (XAS) observation of photoinduced oxidation in FeNi (oxy)hydroxide overlayers on hematite (α-Fe₂O₃) photoanodes for solar water splitting

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*Email: Sample preparation

Two heteroepitaxial hematite photoanodes were prepared. The hematite films were deposited by pulsed laser deposition (PLD) following a recipe reported previously by our group.¹ The films were deposited from a 1 cat% Sn-doped Fe₂O₃ ceramic target onto a c-plane (001) oriented sapphire substrate coated with a transparent Nb:SnO₂(100) layer, that was also deposited by PLD using the previously reported recipe.¹ The thickness of the hematite film, controlled by number of the laser pulses in PLD, was ~10 nm.

FeNi (oxy)hydroxide layer was deposited onto one of the hematite photoanodes by photoelectrochemical deposition.² The exact parameters of the deposition along with layer characterization using AFM, TEM, XPS are reported elsewhere.³ The deposition time was 75 min, corresponding to a thickness of ~30 nm.

Photoelectrochemical measurements

Prior to XAS measurements, the photoelectrochemical performance of the bare hematite and hematite with FeNi (oxy)hydroxide overlayer photoanodes was characterized using a "Cappuccino cell" photoelectrochemical cell⁴ in the standard three-electrode setup. The aperture area was 0.11 cm². An Hg/HgO/1M NaOH electrode (RE-61AP, ALS-Japan) was used as a reference electrode and a platinum wire coil as a counter electrode. The measured potentials were converted to the RHE scale, using the Nernst equation. The measurements were carried out using a CompactStat potentiostat (Ivium
Technologies). A 1M NaOH aqueous solution (pH 13.6) was used for all the measurements. Linear sweep voltammetry (LSV) measurements were carried out in a sweep rate of 10 mV/s. A broad band LED (Mightex, glacier white 6500K, GCS-6500-15-A0510) was used as a light source. LSV and surface discharge measurements were conducted under $100 \frac{mW}{cm^2}$ illumination intensity. This light source was used for all of the measurements reported in this work.

![Graph](image)

**Figure S1:** LSV voltamograms measured under dark (dashed line) and light (solid line) conditions for the bare hematite sample, and light (dash-dotted line) for the sample after deposition of the FeNi (oxy)hydroxide overlayer. The light intensity was calibrated to $100 \frac{mW}{cm^2}$. 
**Operando XAS measurement cell and setup**

Operando X-ray absorption spectroscopy (XAS) measurements were conducted with the samples in photoelectrochemical cells similar to the one reported in reference 1. The cells are presented in Figure S2. The top cell was prepared by heat sealing of thin polypropylene film with polypropylene frame, while the bottom was prepared using mylar membrane on silicon frame. The bottom cell was replaced by the top one in the middle of the measurement due to small leak found in the cell. The measurements were carried out using the three-electrode setup as mentioned above. For the XAS measurements, the illuminated area and area exposed to the electrolyte could not be controlled precisely, but was estimated to be ~0.4 cm$^2$ for the current density calculation in Figure 2.

![Figure S2: Photoelectrochemical cells for the operando XAS measurements.](image-url)
**X-ray absorption spectroscopy (XAS) setup**

*Operando* XAS measurements were performed at the P64 beamline at PETRA-III, Hamburg, Germany. The measurements were conducted in fluorescence detection mode under ambient pressure, using 100 element HPGe detector (Canberra). Energy calibration of the Si(111) monochromator was performed using Fe and Ni metal foils. The incident flux on the sample was \( \sim 10^{12} \) photons/s. Six thirty-minute long scans were performed for each operation point A-E (see Figure 2 in the article) for both dark and light conditions. The data points due to Bragg reflections of the heteroepitaxial thin films and the sapphire substrate were manually removed and the data was linearly interpolated in the corresponding regions. A photograph of the measurement setup is presented in Figure S3.

*Figure S3: Operando XAS setup on site. Main components of the beamline and the measurements setup are indicated in the image.*
XAS stability (dark-light-dark)

Preliminary measurements using a bare hematite photoanode were performed prior to the operando XAS measurements on the hematite photoanode with the overlayer. The measurements were carried out to confirm the reproducibility of the beamline and check that no beam damage is induced to the sample. Figure S4 shows a sequence of dark, light and back to the dark measurements at a potential of 1.5 $V_{\text{RHE}}$. The obtained spectra show that the dark measurements were precisely reproduced, confirming reliability of the measurement setup.

**Figure S4:** XAS stability measurement for bare hematite sample. The measurements of the XAS spectrum near the Fe K-edge were carried out in dark, light, and back to dark conditions, at a constant potential of 1.5 $V_{\text{RHE}}$. 
**Figure S5:** Full EXAFS K-edge spectra of (a) Fe and (b) Ni under dark (solid line) and light (dashed line) conditions under potentials corresponding to points A-E in Figure 2 of the article. The potentials (with respect to the RHE) are presented at the bottom of the figures.
SEM and EDS analysis

After the XAS experiment, the photoelectrochemical cell compounds and other peripheral components attached to the cell were investigated to find the origin of the observed metallic Ni signature. By using SEM (Zeiss Ultra-Plus HRSEM) EDS (Oxford SDD) analysis, it was found that the metallic alligator clip that are was used to connect the photoanode to the potentiostat are composed of iron and nickel alloy. The obtained EDS spectrum is presented in Figure S6. During the spectra acquisition the microscope operated at 10 kV. Spectra acquisition was set to 600s.

![Figure S6: EDS spectra of the metallic connector used at the XAS measurements.](image-url)
XANES fitting

Figure S7: XANES measured spectra (red) and the fitting (blue), using Ni, Ni(OH)$_2$, β-NiOOH and γ-NiOOH standards, as described in the article. The measurement conditions are specified in each plot (the specified potentials are vs. the RHE).

We chose to use the specified components for the final fitting as the mentioned phases are nominally the most likely to be present during the measurements. However, we also checked the fitting quality using NiO instead of Ni(OH)$_2$ as a standard, and found that the fitting quality improved, as shown below. We nevertheless decided to use Ni(OH)$_2$, as the hydroxide phase is the most stable in aqueous electrolyte under the measurement conditions, according to the Pourbaix diagram for Ni (not considering the presence of Fe). We would like to emphasize that the qualitative results were not
affected by changing the standard and/or modifying the energy fitting range, thus the main conclusions of the manuscript would remain the same.

To estimate the error-bars in the average oxidation state, we varied the component spectra used in the fittings, as well as the energy ranges in the fits, which resulted in several different oxidation state curves, and used the standard deviation in these curves for the error-bar. The variations were:

A) **Base Spectra: Metallic Ni, Ni(OH), β-NiOOH, γ-NiOOH (conditions used in the article)**
   - Energy Range: 8325-8380 eV

B) **Base Spectra: Metallic Ni, Ni(OH), β-NiOOH (without including γ-NiOOH)**
   - Energy Range: 8325-8380 eV

C) **Base Spectra: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)\(_2\) with NiO)**
   - Energy Range: 8325-8380 eV

D) **Base Spectra: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)\(_2\) with NiO)**
   - Energy Range: 8345-8370 eV (reduced energy range: especially cutting before WL)

E) **Base Spectra: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)\(_2\) with NiO)**
   - Energy Range: 8325-8360 eV (reduced energy range: especially cutting after WL)

The fits are plotted in Figure S8. To gauge the variations in fittings, we compare the fitting results at the highest potential in light conditions, by tabulating the percent of each component, after subtracting the metallic Ni contribution, and the relative χ\(^2\) values of the fittings, and the average Ni oxidation states, shown in Table S1. A plot comparing the oxidation states vs. potential for the different fittings is presented in Figure S9.

**Table S1: Comparison of various fitting conditions (specified above).**

| Fitting Conditions (refer to text above) | Ni(OH)\(_2\) or NiO 1.53 V\text{RHE}, light | β-NiOOH 1.53 V\text{RHE}, light | γ-NiOOH 1.53 V\text{RHE}, light | χ\(^2\) of fit | Avg. Ni oxidation state 1.53 V\text{RHE}, light |
|----------------------------------------|-----------------------------------------------|---------------------------------|---------------------------------|---------------|---------------------------------------------|
| A                                      | 50%                                           | 33%                             | 17%                             | 41            | 2.63                                        |
| B                                      | 30%                                           | 70%                             | N/A                             | 29            | 2.77                                        |
| C                                      | 24%                                           | 74%                             | 2%                              | 28            | 2.77                                        |
| D                                      | 16%                                           | 65%                             | 19%                             | 8.6           | 2.96                                        |
| E                                      | 21%                                           | 68%                             | 11%                             | 35.6          | 2.86                                        |
Figure S8: The data (red) and the different fitting variations (A-E) as explained in the text above.
Figure S9: The resultant average Ni oxidation states corresponding to the various fits in Figure S8.
Cathodic discharge measurement procedure

Figure S10 shows the response of the current when the potential is swept during the cathodic discharge measurement. The sample is first held in the electrolyte (1M NaOH) under constant potential and illumination for 60s. In the next step, the potential is held at the same value while the light is turned off, resulting in a drop of the current, as shown in the figure. After the current has stabilized, the potential is swept cathodically to discharge the photoanode and then swept back to the original value. The back-and-forth sweep is performed 3 times to ensure full discharge. The resulting cathodic current upon the first discharge is integrated over time to calculate the “stable” charge that remained after the light was turned off. The integrated area of the second discharge peak (shown in the inset) is subtracted from the first peak to account for the dark current.

Figure S10: Cathodic discharge measurement procedure. The applied potential (red line) and the resultant current (black line) versus time are shown. Inset: close up of the cathodic discharge current.

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Supporting information for Operando X-ray absorption spectroscopy (XAS) observation of photoinduced oxidation in FeNi (oxy)hydroxide overlayers on hematite ($\alpha$-Fe$_2$O$_3$) photoanodes for solar water splitting

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Sample preparation

Two heteroepitaxial hematite photoanodes were prepared. The hematite films were deposited by pulsed laser deposition (PLD) following a recipe reported previously by our group.$^1$ The films were deposited from a 1 cat% Sn-doped Fe$_2$O$_3$ ceramic target onto a c-plane (001) oriented sapphire substrate coated with a transparent Nb:SnO$_2$(100) layer, that was also deposited by PLD using the previously reported recipe.$^1$ The thickness of the hematite film, controlled by number of the laser pulses in PLD, was ~10 nm.

FeNi (oxy)hydroxide layer was deposited onto one of the hematite photoanodes by photoelectrochemical deposition.$^2$ The exact parameters of the deposition along with layer characterization using AFM, TEM, XPS are reported elsewhere.$^3$ The deposition time was 75 min, corresponding to a thickness of ~30 nm.

Photoelectrochemical measurements

Prior to XAS measurements, the photoelectrochemical performance of the bare hematite and hematite with FeNi (oxy)hydroxide overlayer photoanodes was characterized using a “Cappuccino cell” photoelectrochemical cell$^4$ in the standard three-electrode setup. The aperture area was 0.11 cm$^2$. An Hg/HgO/1M NaOH electrode (RE-61AP, ALS-Japan) was used as a reference electrode and a platinum wire coil as a counter electrode. The measured potentials were converted to the RHE scale, using the Nernst equation. The measurements were carried out using a CompactStat potentiostat (Ivium Technologies). A 1M NaOH aqueous solution (pH 13.6) was used for all the measurements. Linear sweep voltammetry (LSV)
measurements were carried out in a sweep rate of 10 mV/s. A broad band LED (Mightex, glacier white 6500K, GCS-6500-15-A0510) was used as a light source. LSV and surface discharge measurements were conducted under 100 mW/cm² illumination intensity. This light source was used for all of the measurements reported in this work.

Figure S1: LSV voltamograms measured under dark (dashed line) and light (solid line) conditions for the bare hematite sample, and light (dash-dotted line) for the sample after deposition of the FeNi (oxy)hydroxide overlayer. The light intensity was calibrated to 100 mW/cm².
Operando XAS measurement cell and setup

Operando X-ray absorption spectroscopy (XAS) measurements were conducted with the samples in photoelectrochemical cells similar to the one reported in reference 5. The cells are presented in Figure S2. The top cell was prepared by heat sealing of thin polypropylene film with polypropylene frame, while the bottom was prepared using mylar membrane on silicon frame. The bottom cell was replaced by the top one in the middle of the measurement due to small leak found in the cell. The measurements were carried out using the three-electrode setup as mentioned above. For the XAS measurements, the illuminated area and area exposed to the electrolyte could not be controlled precisely, but was estimated to be ~0.4 cm² for the current density calculation in Figure 2.

![Figure S2: Photoelectrochemical cells for the operando XAS measurements.](image-url)
X-ray absorption spectroscopy (XAS) setup

Operando XAS measurements were performed at the P64 beamline at PETRA-III, Hamburg, Germany. The measurements were conducted in fluorescence detection mode under ambient pressure, using 100 element HPGe detector (Canberra). Energy calibration of the Si(111) monochromator was performed using Fe and Ni metal foils. The incident flux on the sample was \( \sim 10^{12} \) photons/s. Six thirty-minute long scans were performed for each operation point A-E (see Figure 2 in the article) for both dark and light conditions. The data points due to Bragg reflections of the heteroepitaxial thin films and the sapphire substrate were manually removed and the data was linearly interpolated in the corresponding regions. A photograph of the measurement setup is presented in Figure S3.

![Operando XAS setup on site. Main components of the beamline and the measurements setup are indicated in the image.](image)

**Figure S3:** Operando XAS setup on site. Main components of the beamline and the measurements setup are indicated in the image.
XAS stability (dark-light-dark)

Preliminary measurements using a bare hematite photoanode were performed prior to the *operando* XAS measurements on the hematite photoanode with the overlayer. The measurements were carried out to confirm the reproducibility of the beamline and check that no beam damage is induced to the sample. Figure S4 shows a sequence of dark, light and back to the dark measurements at a potential of 1.5 V<sub>RHE</sub>. The obtained spectra show that the dark measurements were precisely reproduced, confirming reliability of the measurement setup.

![Image](image_url)

*Figure S4: XAS stability measurement for bare hematite sample. The measurements of the XAS spectrum near the Fe K-edge were carried out in dark, light, and back to dark conditions, at a constant potential of 1.5 V<sub>RHE</sub>.*
Figure S5: Full EXAFS K-edge spectra of (a) Fe and (b) Ni under dark (solid line) and light (dashed line) conditions under potentials corresponding to points A-E in Figure 2 of the article. The potentials (with respect to the RHE) are presented at the bottom of the figures.
SEM and EDS analysis

After the XAS experiment, the photoelectrochemical cell compounds and other peripheral components attached to the cell were investigated to find the origin of the observed metallic Ni signature. By using SEM (Zeiss Ultra-Plus HRSEM) EDS (Oxford SDD) analysis, it was found that the metallic alligator clip that are was used to connect the photoanode to the potentiostat are composed of iron and nickel alloy. The obtained EDS spectrum is presented in Figure S6. During the spectra acquisition the microscope operated at 10 kV. Spectra acquisition was set to 600s.

Figure S6: EDS spectra of the metallic connector used at the XAS measurements.
XANES fitting

Figure S7: XANES measured spectra (red) and the fitting (blue), using Ni, Ni(OH)$_2$, β-NiOOH and γ-NiOOH standards, as described in the article. The measurement conditions are specified in each plot (the specified potentials are vs. the RHE).

We chose to use the specified components for the final fitting as the mentioned phases are nominally the most likely to be present during the measurements. However, we also checked the fitting quality using NiO instead of Ni(OH)$_2$ as a standard, and found that the fitting quality improved, as shown below. We nevertheless decided to use Ni(OH)$_2$ as the hydroxide phase is the most stable in aqueous electrolyte under the measurement conditions, according to the Pourbaix diagram for Ni (not considering the presence of Fe). We would like to emphasize that the qualitative results were not affected by changing
the standard and/or modifying the energy fitting range, thus the main conclusions of the manuscript would remain the same.

To estimate the error-bars in the average oxidation state, we varied the component spectra used in the fittings, as well as the energy ranges in the fits, which resulted in several different oxidation state curves, and used the standard deviation in these curves for the error-bar. The variations were:

A) **Base Spectra**: Metallic Ni, Ni(OH), β-NiOOH, γ-NiOOH (conditions used in the article)
   **Energy Range**: 8325-8380 eV

B) **Base Spectra**: Metallic Ni, Ni(OH)$_2$, β-NiOOH (without including γ-NiOOH)
   **Energy Range**: 8325-8380 eV

C) **Base Spectra**: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)$_2$ with NiO)
   **Energy Range**: 8325-8380 eV

D) **Base Spectra**: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)$_2$ with NiO)
   **Energy Range**: 8345-8370 eV (reduced energy range: especially cutting before WL)

E) **Base Spectra**: Metallic Ni, NiO, β-NiOOH, γ-NiOOH (replacing Ni(OH)$_2$ with NiO)
   **Energy Range**: 8325-8360 eV (reduced energy range: especially cutting after WL)

The fits are plotted in Figure S8. To gauge the variations in fittings, we compare the fitting results at the highest potential in light conditions, by tabulating the percent of each component, after subtracting the metallic Ni contribution, and the relative $\chi^2$ values of the fittings, and the average Ni oxidation states, shown in Table S1. A plot comparing the oxidation states vs. potential for the different fittings is presented in Figure S9.

***Table S1: Comparison of various fitting conditions (specified above).***

| Fitting Conditions (refer to text above) | Ni(OH)$_2$ or NiO 1.53 V$_{RHE}$, light | β-NiOOH 1.53 V$_{RHE}$, light | γ-NiOOH 1.53 V$_{RHE}$, light | $\chi^2$ of fit | Avg. Ni oxidation state 1.53 V$_{RHE}$, light |
|-----------------------------------------|--------------------------------------|-------------------------------|-------------------------------|----------------|---------------------------------------------|
| A                                       | 50%                                  | 33%                           | 17%                           | 41             | 2.63                                        |
| B                                       | 30%                                  | 70%                           | N/A                           | 29             | 2.77                                        |
| C                                       | 24%                                  | 74%                           | 2%                            | 28             | 2.77                                        |
| D                                       | 16%                                  | 65%                           | 19%                           | 8.6            | 2.96                                        |
| E                                       | 21%                                  | 68%                           | 11%                           | 35.6           | 2.86                                        |
Figure S8: The data (red) and the different fitting variations (A-E) as explained in the text above.
Figure S9: The resultant average Ni oxidation states corresponding to the various fits in Figure S8.
Cathodic discharge measurement procedure

Figure S10 shows the response of the current when the potential is swept during the cathodic discharge measurement. The sample is first held in the electrolyte (1M NaOH) under constant potential and illumination for 60s. In the next step, the potential is held at the same value while the light is turned off, resulting in a drop of the current, as shown in the figure. After the current has stabilized, the potential is swept cathodically to discharge the photoanode and then swept back to the original value. The back-and-forth sweep is performed 3 times to ensure full discharge. The resulting cathodic current upon the first discharge is integrated over time to calculate the “stable” charge that remained after the light was turned off. The integrated area of the second discharge peak (shown in the inset) is subtracted from the first peak to account for the dark current.

Figure S10: Cathodic discharge measurement procedure. The applied potential (red line) and the resultant current (black line) versus time are shown. Inset: close up of the cathodic discharge current.

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Operando X-ray absorption spectroscopy (XAS) observation of photoinduced oxidation in FeNi (oxy)hydroxide overlayers on hematite (α-Fe₂O₃) photoanodes for solar water splitting

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Abstract

A FeNi (oxy)hydroxide co-catalyst overlayer was photoelectrochemically deposited on a thin film hematite (α-Fe₂O₃) photoanode, leading to a cathodic shift of ~100 mV in the photocurrent onset potential. Operando X-ray absorption spectroscopy (XAS) at the Fe and Ni K-edges was used to study the changes in the overlayer with potential, in dark and under illumination conditions. Potential or illumination only had a minor effect on the Fe oxidation state, suggesting that Fe atoms do not accumulate significant amount of charge over the whole potential range. In contrast, the Ni K-edge spectra showed pronounced dependence on potential in dark and under illumination. The effect of illumination is to shift the onset for the Ni oxidation because of the generated photovoltage, and suggests that holes which are photogenerated in hematite are transferred mainly to the Ni atoms in the overlayer. The increase in the oxidation state of Ni proceeds at potentials corresponding to the redox wave of Ni, which occurs immediately prior to the onset of the oxygen evolution reaction (OER). Linear fitting analysis of the obtained spectra suggests that the overlayer does not have to be fully oxidized to promote oxygen evolution. Cathodic discharge measurements show that the photogenerated charge is stored almost exclusively in the Ni atoms within the volume of the overlayer.

Introduction

Since the pioneering work of Fujishima and Honda in the early 1970’s,¹ photoelectrochemical (PEC) water splitting has been actively investigated for its promise to provide an elegant path for the direct conversion of intermittent solar power into storable hydrogen fuel.² A notable candidate for a photoanode material that drives water photo-oxidation in PEC cells for solar water splitting is hematite (α − Fe₂O₃), being one of the few materials to meet the key criteria of stability, abundance, low cost, and a bandgap suitable for effective sunlight absorption.³ However, it also comes with some serious drawbacks: low mobility of charge carriers, low lifetime of photo-generated charge carriers due to bulk recombination, surface recombination at the photoanode/electrolyte interface, and high external voltage for solar driven water splitting.⁴⁵⁶ To address the last two issues, a widely exploited route to improve performance is to deposit various overlayers, which significantly reduce both surface recombination and the overpotential needed for water photo-oxidation.⁷⁻⁹ NiFe (oxy)hydroxide based electrocatalysts are considered as favorable materials because of their inexpensive cost (abundant elements), high catalytic activity for the oxygen evolution reaction (OER),¹⁰ and stability under water oxidation reaction conditions in alkaline solution.¹¹
There have been many studies of NiFe (oxy)hydroxide operating as a co-catalyst overlayer on top of a photoanode. The resultant improvement in performance has been attributed to a variety of proposed mechanisms, including Fermi level unpinning, improved surface catalysis, passivation of surface defects, formation of p-n junction or storage of excess holes to prevent surface recombination. Light-modulated impedance spectroscopy on Sn-doped hematite revealed that addition of a NiFe (oxy)hydroxide overlayer caused a decrease of surface recombination as compared to the bare hematite sample, which improved sharply with potential in the vicinity of the photocurrent onset. By measuring the electronic properties of a NiFe (oxy)hydroxide overlayer on hematite in situ, using a second working electrode, Qiu et al. observed a dramatic rise in the electrical conductivity of the overlayer, spanning the Ni redox peak in the current-voltage curve, which immediately preceded the photocurrent onset. This, together with further in-situ probing of the overlayer, led to the picture that the overlayer is active for charge transfer from the hematite to the OER, only after it has been transformed to its oxidized and conductive state.

To further clarify the processes in the overlayer spectroscopically, here we present a spectr electrochemical study of the roles of Ni and Fe sites under operative conditions of PEC water splitting using X-ray absorption spectroscopy (XAS), an element-specific probe of the local structure and oxidation state of atoms. Operando XAS, which can directly monitor changes in the oxidation state of catalytic sites in response to applied potential and/or illumination, has indeed proven to be a powerful method for investigating charge transfer processes in electrochemical and photoelectrochemical systems. Braun et al., in their pioneering operando oxygen K-edge XAS study of a bare hematite photoanode under applied potential and illumination, interpreted pre-edge features as two types of holes at the hematite/electrolyte interface, which reached maximum population in the vicinity of the photocurrent onset. A number of measurements were done on the metal absorption edge of overlayers deposited on photoabsorbers. Minguzzi et al. performed an operando XAS study on IrO{x} overlayer deposited on top of a hematite photoanode, at the Ir K-edge, which showed a clear oxidation of the Ir sites in response to illumination. Li et al. used high-energy-resolution fluorescence detection XAS to study ultrathin (1–3 nm) overlayers of IrO{x} on top of a Si photoanode. The authors observed a near-linear increase of the Ir oxidation state prior to the current onset, followed by saturation or even decrease a few hundreds of meV above the onset potential. Interestingly, these trends were completely identical for anodes which operate in light and dark conditions, aside from being shifted according to the respective onset potentials. This suggests that, for the hematite photoanode and NiFe (oxy)hydroxide overlayer system in the present study, previous operando XAS studies of NiFe (oxy)hydroxide catalysts, even without photoexcitation, could offer pertinent insights. Such (non-photo) works include recent papers by Friebel et al., Wang et al., and Drevon et al., and others. Similar to the IrO{x} overlayer studies, the oxidation state of Ni was found to increase prior to the onset of the OER, and saturate a few hundreds of meV after the onset. The Fe K-edge spectra, on the other hand, showed considerably less pronounced changes of oxidation state, although they were correlated with changes in Ni K-edge. Additionally, by extracting bond lengths from extended X-ray fine structure (EXAFS) measurements, Friebel et al. found that Fe is not interstitial between NiO{2} sheets, but rather substitutes into Ni sites in NiO{8} octahedra at low Fe content and additionally forms a separate γ-FeOOH phase at higher Fe content, and that the structure transforms from α-Ni(OH){2} at low potential, to γ-NiOOH upon oxygen evolution. Recent work by Morikawa et al. on β-FeOOH nanorods modified with Ni(OH){2} have suggested that β-NiOOH is the active phase under OER conditions. While there have been no definite conclusions or consensus as to the precise roles of Fe and Ni in enhancing water-oxidation activity, decrease in the
activation energy for OER at Fe sites as a result of shortening of the Fe-O bond-length in NiFe (oxy)hydroxide was proposed as a possibility. In this work, we measure a hematite photoanode with an FeNi (oxy)hydroxide overlayer (with ~87 cat.% Fe), with operando XAS at the Ni and Fe K-edges, controlling both potential and dark/light conditions, and discuss the results in context of water photo-oxidation processes in PEC water splitting. We show the relation between the XAS results to photo-electrochemical measurements including current-voltage, and found a good correspondence between determined Ni oxidation state and cathodic discharge measurements.

Results

Our primary sample consisted of a heteroepitaxial Sn-doped (1 cat.%) hematite layer, deposited by pulsed layer deposition on a Nb-doped SnO$_2$ coated (0001) sapphire substrate. The deposition conditions, structure and microstructure of similar samples are reported elsewhere.$^{36}$ An FeNi (oxy)hydroxide co-catalyst overlayer having an Fe: Ni ratio of ~7:1, to be consistent with our previous work,$^{19}$ was deposited photoelectrochemically on the hematite layer (note that the Fe-Ni order has been reversed to reflect a majority of Fe). TEM suggested the formation of two phases, an amorphous and crystalline phase, one of which is speculated to be Fe-rich. Full characterization including SEM, TEM, XPS and AFM of similar samples, is reported in Ref. 19. A study of the effect of other Fe: Ni compositions on hematite could be a subject of future work. The thicknesses of the hematite layer and FeNi (oxy)hydroxide overlayer were estimated to be 10 and 30 nm, respectively. A bare hematite photoanode was prepared as a reference sample, under identical conditions but without an overlayer. Linear sweep voltammetry (LSV) for both photoanodes, measured in the dark and under white-light illumination with intensity of $\sim$100 mW cm$^{-2}$ at the sample position, is presented in Figure S1. The dark current was nearly zero over the entire potential range examined. Consistent with previous reports,$^{9,18,37}$ deposition of the FeNi (oxy)hydroxide co-catalyst overlayer led to a cathodic shift of $\sim$100 mV in the photocurrent onset potential, whereas the photocurrent plateau remained nearly the same as for the bare hematite sample. However, unlike our previous study,$^{19}$ a small redox peak of Ni(II)/ Ni(III) appeared at 1.05 V$_{RHE}$ under illumination conditions, just before the onset potential for OER. The reason for the appearance of this peak is the relatively large thickness ($\sim$30 nm) of the FeNi (oxy)hydroxide overlayer, designed to enhance its XAS signal, which was considerably thicker than in the previous study ($\sim$2 nm).

Figure 1 illustrates the configuration of the operando XAS measurements, which were performed at the P64 beamline of PETRA III synchrotron (DESY, Hamburg, Germany).$^{38}$ The sample was placed in a special electrolyte cell (see the SI for details),$^{26}$ such that a thin (~200-300 μm) layer of 1 M NaOH aqueous electrolyte covered the sample surface. Potential was applied to the photoanode and the current was measured using an Ivium potentiostat in three-electrode mode, with an Hg/HgO/1M NaOH reference electrode and Pt counter electrode placed in the electrolyte. The sample was photoexcited with a high-power white LED that provided an intensity of $\sim$100 mW cm$^{-2}$ at the sample position. For brevity, we denote this state of illumination as the “light” condition, and absence of such as “dark”. Fe and Ni K-edge absorption spectra were measured in fluorescence detection mode with a 100-pixel Ge-detector (Canberra). Further details including photograph of the cell and the measurement setup, are provided in the SI (Figures S2 and S3). As a preliminary check for possible beamline damage to the sample and to ensure stability of the PEC system, successive measurements of the XAS spectrum of the bare hematite sample near the Fe K-edge were carried out in dark, light, and back to dark conditions, at a constant potential of 1.5 V$_{RHE}$, where there is photocurrent. Figure S4 shows that the white line (WL) intensity
decreased under light conditions, which is likely associated with partial oxidation of surface Fe sites\textsuperscript{30,31} that proceeds under oxygen evolution conditions.\textsuperscript{39} Upon removing the illumination and returning to dark conditions, the spectrum was restored to its initial dark state, demonstrating stability of the system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic side view illustration of the operando photoelectrochemical XAS measurement setup.}
\end{figure}

The procedure to monitor the evolution of oxidation states of Fe and Ni in the photoanode was as follows. The potential was set to values tracing the photocurrent pre-onset (points A, B) and post-onset (points C,D,E) regions of the LSV curve (under illumination) shown in Figure 2. A zoom-in of the dark current, presented in the inset of Figure 2, reveals a feature related to Ni redox activity,\textsuperscript{40,41} prior to the onset of oxygen evolution. For each potential, and for both dark and light conditions, XAS spectra were measured at both the Fe and Ni K-edges, before proceeding to the next potential. The near-edge spectra for the Fe K-edge are shown in Figures 3(a) and 3(b) for dark and light conditions, respectively. Note that all spectra presented here were normalized by the standard procedure using Athena software,\textsuperscript{42} according to the jump at the absorption edge, defined by the difference between the extrapolated lines fitted to the low-energy (pre-edge) and high-energy (post-edge) parts of the spectra. As is common practice, the WL intensity is described relative to this jump. We focus on the near-edge (XANES) region since most of the clear changes were observed there. Full spectra are presented in Figure S5. From Figure 3(a), the XAS spectra measured in dark, with exception of point A (at 0.53 V\textsubscript{RHE}), were affected very little by the applied potential in the range applied. To highlight any differences between the spectra, the insets in Figure 3 show them subtracted by the spectrum measured at point A (0.53 V\textsubscript{RHE}) in dark. All of the spectra are characterized by a shift in spectral weight to higher energies (manifested by negative valley followed by a positive peak), as compared to the spectrum measured at point A (0.53 V\textsubscript{RHE}), but were otherwise independent of potential. We suggest that the spectral weight shift common to points B-E is related to the expected depletion of electrons from the surface at anodic bias.\textsuperscript{39} Under illumination (Figure 3b), the general trend is similar to the dark case, except for a notable increase in intensity of the WL peak for point E (1.5 V\textsubscript{RHE}). No other significant potential dependence in XANES or EXAFS region (shown in Figure S5) of the spectra were detected. This result of very little (if any) oxidation of Fe atoms is generally consistent with previous reports of relatively small oxidation of Fe in FeNi (oxy)hydroxide electrocatalysts,\textsuperscript{29-31,43} Furthermore, the contribution from the underlying hematite layer would diminish observed changes in the Fe-edge spectra originating from the overlayer. It is peculiar that the WL of the Fe K-edge under
illumination slightly increases with potential, rather than decreases as might have been expected from electrocatalyst studies$^{29-31}$. In fact, it is difficult to distinguish Fe contributions coming from the FeNi (oxy)hydroxide overlayer or the hematite layer. However, we note that the trend is opposite to that observed for bare hematite in Figure S4. We speculate the origin of this effect might be a change in the geometry, or small change in the time-averaged Fe oxidation state, of the Fe sites in the overlayer as a result of a change in the oxidation state of neighboring Ni sites$^{29,34}$, or some additional effect of illumination on the overlayer that EXAFS analysis could possibly clarify, but will be investigated elsewhere. Whatever the case, the relatively small changes indicate that most of the Fe sites of the overlayer do not accumulate charge before and during OER.

Figure 2: LSV voltamograms measured under dark (dashed line) and light (solid line) conditions within the beamline before the XAS measurements for hematite/FeNi (oxy)hydroxide. Points A-E represent XAS measurement points taken under light condition. XAS measurements were carried out also in the dark at the same potential values. Note that we use the same labels for the corresponding potentials in dark conditions.Inset: Zoom-in of the dark current LSV.
Figure 3: Normalized Fe K-edge XANES spectra of hematite/FeNi (oxy)hydroxide under (a) dark and (b) light conditions. The measurement point, at different potentials (see Figure 2), is indicated in the legend. All of the potentials are versus RHE. All the spectra are normalized by the standard method based on the extrapolated jump at the absorption edge. The insets show the measured spectra subtracted by the spectrum measured in point A (0.53 V<sub>RHE</sub>) in dark.

The XAS spectra at the Ni K-edge, under dark and light conditions, are presented in Figure 4, displaying markedly more pronounced changes than those observed for the Fe K-edge spectra in Figure 3. Increase of the Ni oxidation state with increased potentials is evident from the shifts in the WL for both dark and light conditions. Notably, the oxidation state of Ni also increases in the dark (Figure 4(a)), just below the
OER onset potential, at potentials encompassing with the peak at \(\sim 1.3-1.4\) V (Figure 2, inset). This is not surprising, since the standard potential of the Ni(II)/Ni(III) (Ni(OH))\(_2\)/NiOOH redox reaction is 1.348 V.\(^4\) It is also consistent with the study of Drevon et al. who reported an edge shift prior to the OER onset in NiFe (oxy)hydroxide electrocatalysts\(^3\), as well as Li et al. for Si photo-absorbers with Ir overlayers.\(^2\) Most of the change in the WL region occurs between the spectra recorded at points C (1.2 \(V_{\text{RHE}}\), blue curve) and D (1.35 \(V_{\text{RHE}}\), green curve), while the spectrum recorded at point E (1.5 \(V_{\text{RHE}}\), orange curve) nearly overlaps with that recorded at point D. This indicates that the Ni oxidation begins to saturate just after the onset of OER current (Figure 2, inset), consistently with previous reports on NiFe (oxy)hydroxide electrocatalysts.\(^2\)\(^9\)\(^3\)\(^1\) Fitting of the spectra, shown below, can clarify the oxidation state trends.

Under illumination conditions (Figure 4(b)), the WL shift is even more pronounced. The most noticeable change in the XANES region is observed between the spectra recorded at points B (1 \(V_{\text{RHE}}\), red solid curve) and C (1.2 \(V_{\text{RHE}}\), blue curve), near the onset potentials of Ni photo-oxidation and prior to water photooxidation (at \(\sim 1.2\) \(V_{\text{RHE}}\)) observed in the LSV curve measured under illumination. The spectral shift begins to stabilize around point D (1.35 \(V_{\text{RHE}}\)). Comparison of the light and dark spectra at each potential (Figure S5) clearly shows that starting at point C (1.2 \(V_{\text{RHE}}\)) illumination shifts the WL position to higher energies. This is likely a result of photogenerated holes injected from the hematite layer into the FeNi (oxy)hydroxide overlayer. Indeed, most of the photogenerated holes produced in the photoanode originate in the hematite layer, made evident from the greater optical absorption in the hematite layer.\(^1\)\(^6\)\(^1\)\(^9\)\(^4\)\(^5\) In contrast to the hole injection under illumination, conduction band electrons are the responsible for charge transfer in dark, in case of n-type Sn-doped hematite photoanodes.\(^4\)\(^6\) Combining the results obtained in dark and light conditions, it follows that both electrons and holes can be transferred between the hematite layer and the FeNi (oxy)hydroxide overlayer. The transfer of the photogenerated holes to the overlayer also suppresses surface recombination,\(^4\)\(^1\)\(^8\) as was also suggested by IMPS measurements for similar samples.\(^1\)\(^9\)
Figure 4: Normalized Ni K-edge XANES spectra for hematite/FeNi (oxy)hydroxide under (a) dark and (b) light conditions. The measurement point, at different potentials (see Figure 2), is indicated in the legend. All of the potentials are versus RHE. All the spectra are normalized by the standard method based on the extrapolated jump at the absorption edge. Normalized Ni K-edge XANES spectra for NiO, β-NiOOH and Ni standards used for the fitting are also presented in panel (a). Inset: Zoom-in of the WL region.

To clarify the trend of the average Ni oxidation state as a function of applied potential under dark and light conditions, we fit each of the measured spectra to a sum of XAS spectra of Ni, Ni(OH)$_2$, β-NiOOH and γ-NiOOH, as standards for the Ni(O), Ni(II), Ni(III) and higher (>Ni(III)) oxidation states, respectively. These
standards were selected based on the most stable phases in the Pourbaix diagram of Ni under the measurement conditions (not considering the presence of Fe). 47 γ-NiOOH is known to have a mixed Ni(III)/Ni(IV) oxidation state, 48 and therefore can be used as a standard for higher oxidation states. The relative weights of the components were obtained by a least-squares fitting routine using the Levenberg-Marquardt method. The fitting method and results, and choice of standards, are described in more detail in the SI. The normalized XAS spectra of these features are plotted in Figure 4(a). A Ni standard was used for the fitting process because a pre-edge feature was observed in all of the spectra at ~8335 eV, which is a typical signature of metallic nickel (Ni(0)). 49 Subsequent to the XAS measurements, SEM EDS analysis showed the presence of metallic Ni on the electrical contact clips to the sample (Figure S6 in SI), which may have contributed to the observed spectra. It was also determined from fitting that the metallic Ni contribution of the spectra was largely independent of potential or light. Therefore, assuming a constant contribution from the connectors, all the spectra were fitted simultaneously while keeping the metallic Ni fraction to be a shared parameter among all the spectra. The resultant fit curves are shown in Figure S7.

According to the fits, most of the Ni oxidized to a phase resembling β-NiOOH, but for the highest two potentials under illumination (points D and E) a ~15% spectral content of γ-NiOOH was observed. This latter observation is in line with previous studies of NiFe (oxy)hydroxides, that reported formation of γ-NiOOH under overcharging conditions. 50–53 The average oxidation state of Ni in the sample was calculated according to the obtained fractions of the Ni phases (+2 for NiO, +3 for β-NiOOH, and +3.6 for γ-NiOOH), excluding metallic Ni contribution. Plotted in Figure 5, the average oxidation state is overlaid on normalized LSV curves in dark and light. In the dark condition, the oxidation state of Ni is +2 up to ~1.2 V \text{RHE}, above which it gradually increases to an average oxidation state of +2.35 at a potential of 1.53 V \text{RHE}, corresponding to a state-of-charge (SOC) of 35% in the transition from Ni(II) to Ni(III). For measurements under illumination, the onset of Ni (photo)-oxidation shifts to a lower potential than in dark, with the oxidation state increasing rapidly above ~1 V \text{RHE}, corresponding to the onset of the Ni redox wave in the LSV curve, and below the onset of the OER. We note that for both light and dark conditions, the linear region of Ni oxidation increase occurs at the potentials spanning the Ni redox wave in the respective LSV curves. The Ni oxidation curves in light and dark seem similar but shifted according to the respective shift of the LSV curves, considered to be the photovoltage generated in the photoanode. 54 A similar photovoltage-related shift was observed by Li et al. 28 At the highest applied potential in light (1.5 V \text{RHE}), the average oxidation state reaches a value of +2.6, where it begins to saturate. These observations are in line with previous reports that partial oxidation and transition from the hydroxide to the oxyhydroxide phase precedes the OER and then saturates prior to the plateau region in the water photo-oxidation current. 28,29,34
If the observed increase of Ni oxidation state is indeed instrumental in promoting the water photo-oxidation reaction (either directly whereby the OER reaction occurs at oxidized Ni sites as suggested above, or indirectly by lowering the potential of the OER onset at the Fe site, as proposed by Friebel et al.\textsuperscript{29}), this result nevertheless implies that the FeNi (oxy)hydroxide overlayer does not need to be fully oxidized before this happens, as was also concluded from electrochemical measurements by Qiu et al.\textsuperscript{20} However, we cannot rule out the possibility that the foremost surface atoms may be fully oxidized, since the X-ray fluorescence includes contributions from many atomic layers. The observed saturation of the oxidation state not far above the onset for OER could be owing to competition for holes between Ni and water oxidation reactions. When the overlayer is charged to its active state, a portion of the holes begin to be injected into the electrolyte, while the remainder continue to cause oxidation of the overlayer. This would create a negative feedback, since if oxidized Ni enhances the OER, this increased OER will draw more holes away from further increasing its oxidation state, therefore stabilizing (saturating) it at some potential.

As a complementary investigation of how the overlayer transforms during the OER, cathodic discharge measurements were carried out for the samples with and without the FeNi (oxy)hydroxide overlayer. These measurements determine “stable charge” which does not get discharged upon removing light, but only by ramping down potential. The measurement procedure, as first proposed to monitor the surface state in TiO\textsubscript{2} photoanodes for water photo-oxidation,\textsuperscript{55} was also previously applied to study hematite photoanodes.\textsuperscript{36,56,57} The sample is first held in the electrolyte (1M NaOH) under constant potential (called the charging potential) and illumination, to facilitate filling of hematite surface states and charge the FeNi (oxy)hydroxide overlayer. In the next step, the light is turned off, and the current drops. After the current
has stabilized, the potential is swept cathodically to discharge the surface states and FeNi (oxy)hydroxide overlayer. The resulting cathodic current upon discharge is integrated over time to calculate the “stable” charge that remained after the light was turned off. A representative cathodic discharge measurement plot is shown in the Figure S10. The resultant stable charge as a function of the applied charging potential for bare hematite photoanode and hematite photoanode with the FeNi (oxy)hydroxide overlayer is plotted in Figure 6(a). The amount of stored charge in the sample with the FeNi (oxy)hydroxide overlayer is an order of magnitude higher than for the bare hematite. This is because the charge is stored only on the surface in the case of as the bare hematite photoanode, while in case of ion permeable redox active layer such as FeNi (oxy)hydroxide overlayer the charge is stored in the whole layer. A similar observation was made for a “non-stable charge” measurement of the transient currents in response to light on/off at a potential fixed to the OER onset,37 which is also related to stable charge58. For bare hematite, a strong correlation between the photocurrent and stable surface charge curves is observed, consistent with a previous study,58 suggesting a direct correlation between the two processes. However, a distinctly different trend is observed for the sample with the FeNi (oxy)hydroxide overlayer. Major accumulation of charge instead coincides with the onset potential of Ni photo-oxidation which occurs prior to the onset of OER. Moreover, the stable charge curve is similar to the oxidation state curve (Figure 5). Figure 6(b) shows the interpolated average oxidation state as a function of the stored stable charge. The plot suggests linear dependence between the two parameters, supporting accumulation of the stable charge by oxidation of the Ni atoms. We note that Ni oxidation state for zero stable charge is higher than +2.6±0.1. The reason is that most of the charge accumulated at low potentials is in the form of “unstable” charge, that is removed upon switching off the light during stable charge measurements.37,58 The obtained data shows that Ni sites are oxidized by the photogenerated holes, even before the onset of water photo-oxidation. The stable charge seems to stabilize at the highest potential applied (1.5 V\text{RHE}), in line with the stabilization of the Ni oxidation state obtained from the XAS measurements.
Figure 6: (a) Stable charge for bare hematite (black squares) and hematite/FeNi (oxy)hydroxide photoanodes (red circles), as a function of charging potential, overlayed on LSV measurement in matching conditions for bare hematite (black dashed line) and hematite with overlayer (red dashed line). (b) Average Ni oxidation state under illumination (obtained from XAS fitting) as a function of the stable charge for the hematite photoanode with the overlayer, interpolated from Figures 5 and 6(a).
To summarize, we have studied the effect of illumination and potential on the oxidation of the transition metal sites (Fe, Ni) in the hematite photoanode with FeNi (oxy)hydroxide overlayer. The observed change with potential for the Fe K-edge was rather small, however it was more pronounced for light than for dark conditions. This small change of the average could signify a temporary increase in the Fe oxidation state. Of great interest for future studies would be to track the possible oxidation states evolution with time, which could be connected to multiple site reactions (in this case, Ni and Fe) as recently suggested in the literature.\textsuperscript{59-61} The Ni sites were more strongly affected by both potential and illumination, consistent with previous spectro-electrochemical \textit{operando} XAS studies, including those done without photoexcitation.\textsuperscript{28-31} For both dark and light conditions we found that partial oxidation of Ni in the overlayer proceeded at potentials corresponding to the redox wave of Ni (Ni(OH)\textsubscript{2}/NiOOH), which occurs immediately prior to the onset of the OER. This is consistent with the picture of Qiu et al.\textsuperscript{20} the Ni sites need to be oxidized for effective OER activity. These observations further suggest that the main effect of light absorption is to shift the Ni oxidation to lower potentials by the photovoltage generated in the photoanode. The maximal oxidation state of Ni started to saturate and reached a value of +2.6±0.1 under illumination, and a negative feedback mechanism limiting the oxidation state was suggested. In addition, considering the dependence of the Ni K-edge on potential in dark and light, we conclude that both electrons and holes can be transferred between the hematite and FeNi (oxy)hydroxide layers. Intriguingly, the cathodic discharge measurements shared very similar characteristics to the Ni oxidation state curve (from XAS measurements), rather than the photocurrent curve as for bare hematite, showing a linear relation to phase transformations in the overlayer. We observed a greater than tenfold increase of stable charge measured for the sample with the FeNi (oxy)hydroxide overlayer, as compared to the bare hematite sample, indicating that the whole overlayer stores the charge in the Ni atoms, consistent with the XAS results. While the iron atoms did not appear to be charged on average, it does not rule out the possibility that their oxidation state could change in some temporal window in the transient response to illumination. Future advances in instrumentation could enable such dynamical measurements resolved in the temporal and/or spatial domains.

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