

**Water Flipping and the Oxygen Evolution Reaction on  $\text{Fe}_2\text{O}_3$  Nanolayers**

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**Abstract.** Hematite photoanodes are promising for the oxygen evolution reaction,<sup>1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11</sup> however, their high overpotential (0.5-0.6 V)<sup>1</sup> for water oxidation and limited photocurrent make them economically unviable at present. The work needed to orient dipoles at an electrode surface may be an overlooked contribution to the overpotential, especially regarding dipoles of water, the electron source in the oxygen evolution reaction (OER). Here, we employ second harmonic amplitude and phase measurements to quantify the number of net-aligned Stern layer water molecules and the work associated with water flipping, on hematite, an earth abundant OER semiconductor associated with a high overpotential. At zero applied bias, the pH-dependent potentials for Stern layer water molecule flipping exhibit Nernstian behavior. At positive applied potentials and pH 13, a complete monolayer of water molecules points the oxygen atoms towards the electrode, favorable for the OER. The work associated with water flipping matches the cohesive energy of liquid water (44 kJ mol<sup>-1</sup>) and the OER current density is highest. This current is negligible at pH 5, where the work approaches 100 kJ mol<sup>-1</sup>. Our findings suggest a causal relationship between the need for Stern layer water flipping and the OER overpotential, opening avenues for lowering the latter.

**Main Text.**

Strategies to improve hematite photoanode performance include accelerating water oxidation kinetics with catalytic surface coatings,<sup>12</sup> slowing down electron–hole recombination,<sup>13</sup> chemical and structural modifications to hematite,<sup>5, 14</sup> including edge-to-face anisotropy,<sup>15</sup> and non-covalent interactions via electrolyte tuning,<sup>16</sup> all of which involve processes occurring at the electrolyte:electrode interface. One important knowledge gap that remains to be bridged is a detailed molecular understanding of the water structure and the electrostatics at hematite:electrolyte interfaces under bias and/or photoexcitation. For example, the work to orient water dipoles in the Stern layer at the interface under applied potential bias may be an overlooked contribution to the overpotential. This work, we posit, is necessary to properly align water's oxygen atom with an oxo group of the electrode's active site prior to electron transfer. Testing this hypothesis is especially important for pH conditions above the point of zero charge (e.g. pH 13, the commonly employed pH for the OER on hematite),<sup>1, 4, 7</sup> where, at zero V bias applied, the Stern layer water molecules point their protons towards the negatively charged surface, blocking line-of-sight access of water's oxygen to the active sites that eventually form at positive bias. Obtaining this work requires the quantification of two properties: the number of net-aligned Stern layer water molecules and the total interfacial potential drop across the electrolyte:electrode interface.

Important insights for water flipping can be provided by atomistic simulations,<sup>6, 17, 18</sup> but experimental benchmarks have not yet been obtained. From an experimental perspective, scanning probes<sup>19, 20</sup> have been successfully paired with finite-element analysis<sup>21</sup> and extended to individual molecules,<sup>22</sup> including water over ultraflat surfaces,<sup>23</sup> to obtain topographic information of liquid:solid interfaces, but the absolute number of net-aligned Stern layer water molecules has not yet been reported from experiments performed on electrodes. Counting how many Stern layer

water molecules point their dipoles up vs down requires an interface-selective probe that is also sensitive to the absolute dipole orientation. Experimental methods sensitive to interfacial potentials and fields include fluorescent labeling, which allows for super-resolution but is subject to bleaching within a few minutes.<sup>24</sup> Voltage-sensitive spin-,<sup>25</sup> Stark-,<sup>26, 27, 28, 29, 30, 31, 32, 33, 34</sup> or plasmonic labels<sup>35</sup> are popular spectroscopic alternative methods, especially when the probe is tethered to an electrode during potential sweeps to avoid label desorption.

Despite their surface specificity and sensitivity to interfacial potentials,<sup>36, 37</sup> nonlinear spectroscopic studies of hematite:electrolyte interfaces remain sparse,<sup>38, 39, 40</sup> given the strong absorber problem on both sides of the interface. We use atomic layer deposition (ALD)<sup>39, 40</sup> to prepare ten-nm thin Fe<sub>2</sub>O<sub>3</sub> nanolayers to overcome this issue. Our previous studies<sup>39, 40</sup> employed the 120 fs, 600 nm output of a 1 kHz optical parametric amplifier to obtain second harmonic generation signal intensities at 300 nm, well above hematite's band gap of ~590 nm. In the present work, we now probe 10-nm thin hematite layers deposited by ALD onto fluorine-doped tin oxide (FTO)-deposited float glass slides with the 80 fs, 1033 nm output of an 80 MHz ytterbium crystal-based oscillator (LightConversion Flint, 12 nm bandwidth). The conductive FTO substrate + hematite nanolayer is used as the working electrode in a standard three electrode cell configured for optical spectroscopic interrogation. We present an absolute phase determination method for internal reflection geometries and measure the SHG amplitude and phase at variable pH values and under electrochemical bias. Moreover, we evaluate the third-order nonlinear susceptibility contribution at third harmonic wavelengths of 344 nm and 550 nm, the latter accessed with a tunable near-infrared light source. We then develop an optical model to estimate the number of net-aligned Stern layer water molecules, the total electrostatic potential across the hematite:electrolyte interface, and the work associated with Stern layer water flipping.

**EXPERIMENTAL.** In order to obtain the number of net-aligned water molecules in the Stern layer and the total interfacial potential across the hematite:electrolyte interface, we employ a nonlinear optical spectrometer that provides the SHG amplitude and phase. The spectrometer is shrouded to minimize dark counts. A longpass filter (Thorlabs FELH0750) blocks any residual visible radiation with wavelength less than 750 nm. The input polarization is set to be parallel to the surface (“s-in”), and we defocus gently using a 10 cm lens pulled back by 3 cm from its focal point, delivering 200 mW of input power. We block the fundamental and any SHG from the external sample window surface using an anodized aluminum plate and direct the fundamental and the SHG signal from the electrode:electrolyte interface into a heterodyning assembly that is separately shrouded so that the dark counts measured using our photomultiplier/single photon counter assembly is minimized. We spectrally isolate the 516 nm SHG signal using a bandpass filter (Thorlabs, FBH520-40) and record its p-polarized signal intensity. The SHG amplitude and phase are obtained by interfering the signal from the sample with a local oscillator produced in a 50  $\mu$ m thin  $\alpha$ -quartz wafer as a function of rotational angle of a phase shifting unit consisting of a 1 mm fused silica plate described elsewhere.<sup>41</sup>

The hematite nanolayers are prepared as follows: commercial FTO glass substrates (part number CG-14FTO-1109, obtained from Delta Technologies, Colorado) are float glass slides onto which a few 100 nm of pyrolytic FTO are deposited by chemical vapor deposition. We prepare hematite thin films on these FTO-coating glass slides using a  $\text{Fe}(\text{Cp})_2$  and  $\text{O}_3$  process as described previously,<sup>39</sup> only slightly modified with longer exposure to  $\text{Fe}(\text{Cp})_2$  while the vacuum pump is gated from the chamber.  $\text{Fe}(\text{Cp})_2$  (Sigma, 98%) was maintained at 100°C while  $\text{O}_3$  was generated using corona discharge in ultra-high purity  $\text{O}_2$  (LG-7, Ozone Engineering) operating at 40% power. The ALD recipe is expressed as  $(t_1-t_2-t_3)_2 - (t_4-t_5)_3$ , where  $t_1$  and  $t_4$  are the dose times for  $\text{Fe}(\text{Cp})_2$

and O<sub>3</sub> precursor respectively,  $t_2$  is the exposure time for the Fe(Cp)<sub>2</sub> precursor, and  $t_3$  and  $t_5$  are N<sub>2</sub> purge periods. The complete ALD process was (6–34–80)<sub>2</sub> – (60–60)<sub>3</sub> where the  $t_1$  pulse time was 6 seconds and the  $t_2$  wait time was 34 seconds, leading to a total exposure time of 40s. The  $t_4$  O<sub>3</sub> pulse time was 60 seconds and the purge times  $t_3$  and  $t_5$  were 80s and 60s respectively. The Fe(Cp)<sub>2</sub> exposure-purge cycle was performed 2x times before exposure to three O<sub>3</sub> pulse-purge cycles. This method yielded a growth rate of ranging from 0.75 to 1.0 Å per cycle depending on the distance of the substrate from the inlet. Insufficient purging of the Fe(Cp)<sub>2</sub> precursor can produce uneven film growth on the substrate backside, which could affect spectral analysis. With sufficient purging, the backside growth rate was measured to be approximately 50% of the growth rate on the top side of the substrate. All films were deposited to a thickness of 10 nm as confirmed by ellipsometry of silicon witness samples and an optical absorption vs thickness calibration curve (please see Supporting Information Fig. S1).

X-ray photoelectron spectroscopy and atom probe tomography show high chemical purity in our ALD hematite nanolayers.<sup>39</sup> Supporting Information Fig. S1B-C show a depth-resolved elemental analysis indicating no fluorine in the top-most region of our 10-nm hematite layers. While the semiconducting ALD-hematite nanolayers exhibit no measurable conductivity when measured on an insulating substrate, the ALD-hematite-on-FTO-deposited glass samples show a combined resistance of a few tens to a few hundred Ohm/sq., consistent with the FTO-coated glass substrates from Delta Technologies. The samples resist delamination or corrosion, even in 0.6M salt concentration.<sup>42</sup> X-Ray photoelectron spectroscopy and grazing incidence angle X-ray diffraction are consistent with hematite (Fe/O ratio of between 0.64 and 0.73, multiplet in the Fe 2p<sub>3/2</sub> region, and major 2θ peaks at 33-35, 49, and 54 degrees).<sup>39</sup> Atomic force microscopy shows

an rms surface roughness nearly identical to that of the FTO-deposited glass slides (10 nm, please see Supporting Information Note S2).

The sample cell is described elsewhere.<sup>41</sup> Briefly, the assembly consists of custom-built PEEK-based half-cells, one holding a 1 mm-thin optical window and the other holding an ALD-hematite on FTO-deposited glass slide, both held leak tight using O-rings (FFKM perfluoroelastomer, Ace Seal). We use a sealed 4 mm diameter, 30 mm long Ag/AgCl reference electrode (SNG-ECRXACC30, redox.me) located in the same compartment as the working (ALD-hematite on FTO-deposited glass) and counter (Pt) electrodes. An inlet and outlet allow for liquid exchange using a peristaltic pump so that we can vary the pH under *operando* conditions. The electrochemical measurements are carried out with a PGSTAT302N electrochemical workstation with a SCAN250 analog linear sweep module (Metrohm).

**RESULTS AND DISCUSSION.** Fig. 1 shows the SHG signal intensity at 516 nm recorded at pH 9, pH 11, and pH 13, along with the measured current, as a function of applied potential against Ag/AgCl balanced to 1 M ionic strength with NaClO<sub>4</sub>. The SHG intensities exhibit a minimum around 0.4 to 0.5 V, with lower signal intensities produced at pH 13 when compared to pH 11 or pH 9. The measured current recapitulates that observed by others,<sup>10, 43</sup> in that no iron oxidation/reduction waves are observed and that mA cm<sup>-2</sup> current densities are observed at ~1 V applied bias in the dark. Control measurements show that the 1033 nm laser illumination does not produce a photocurrent. The FTO-containing slide produces 10 to 20 counts per 100 ms changes in the SHG intensity during the CVs, ten times smaller than the signals observed from the ALD-hematite on FTO-deposited glass samples (please see Supporting Information Fig. S4). The current produced by the FTO-deposited glass slide at +1.1V applied bias is about ten times smaller than that obtained from the ALD-hematite on FTO-deposited glass at the same applied voltage (0.8 mA

$\text{cm}^{-2}$ , again, in the dark). Changes in the amplitude and phase (obtained as described further below) with applied potential are not resolved when the FTO-deposited glass sample is probed (please see Supporting Information Fig. S4), likely due to the small SHG signal intensity changes observed in homodyne-detection.

Fig. 1B shows a representative collection of nonlinear optical interferograms recorded during a cyclic voltammogram (CV) between -0.5 and +1.4 V vs Ag/AgCl at pH 13 and 1 M  $\text{NaClO}_4$ . As a reminder, the interferograms arise from the constructive and deconstructive interaction of the SHG photons generated by the sample (the “signal”) and by a 50  $\mu\text{m}$  thin  $\alpha$ -quartz wafer (the “local oscillator”) as their relative phase at the detector is matched and mismatched using a rotating phase shifting unit. Clear changes in the amplitude and phase are observed at the various applied potentials. Fig. 1C shows the SHG amplitudes and phases obtained during CVs collected between pH 13 and pH 5 (more acidic conditions lead to FTO dissolution). The SHG phase values from our fit function (please see Supporting Information Note S3) were converted to the absolute phases relative the zero phase from the purely real SHG signal produced from a hematite-free portion of our sample. These portions were produced by using a Zn-HCl etching method on as-deposited ALD-hematite-on-FTO substrates. In short, a Kapton mask was used to create a 10 mm x 15 mm exposed window where Zn metal powder and 2M HCl were placed. The resulting reaction was allowed to proceed for 20 minutes before removing the excess reactants and rinsing with deionized water. If the window retained any conductivity, the etching process was repeated until only non-conductive glass remained. We first measured an SHG interferogram at a portion of our glass slide that was free of FTO and hematite, then translated the sample stage such that the laser beam impinged on the ALD-hematite-on-FTO-deposited glass portion of our sample in contact with air to measure an interferogram there, and finally added pH

13/1M NaClO<sub>4</sub> electrolyte using our peristaltic pump so that the optical alignment did not change and a third interferogram could be measured.

Per means of example, the fitted SHG phase for the glass:air interface of the data shown in Fig. 1C was  $\varphi_{\text{fit}} = 180^\circ \pm 20^\circ$  from up to seven replicate measurements. This result means that the offset needed to obtain the absolute zero phase should be  $\varphi_{\text{offset}} = -180^\circ$  since then  $\varphi_{\text{fit}} - \varphi_{\text{offset}} = 0^\circ$ . This zero phase is expected for a transparent, non-birefringent, uncharged material such as glass, for which  $\chi^{(2)}_{\text{glass:air}} \propto E_{\text{SHG glass:air}} e^{i0^\circ}$  =purely real, which is fulfilled if the SHG phase is  $0^\circ$ . The fitted phase for the ALD-hematite-on-FTO-deposited glass portion of the sample is found to be delayed from  $180^\circ$  to  $50^\circ$ , which corresponds to an absolute phase of  $50^\circ - 180^\circ = -130^\circ$ . Adding electrolyte at pH 13 further delays the phase by  $-100^\circ$  to  $-55^\circ$ , which corresponds to an absolute phase of  $-235^\circ$  (or  $+125^\circ$ , given  $360^\circ$  symmetry) for the hematite:electrolyte interface at pH 13 and OCP.

The second-order nonlinear susceptibility should contain contributions from two sources, namely the Stern layer ( $\chi_{\text{Stern}}^{(2)}$ ) and the topmost layer of hematite's iron and oxygen atoms ( $\chi_{\text{hem}}^{(2)}$ ). Given the slight absorbance of our 10 nm thin hematite nanolayers at around 500 nm (near the SHG wavelength),  $\chi_{\text{hem}}^{(2)}$  is likely to be pre-resonant at this wavelength and needs to be isolated and quantified. To do so, we went to a condition of applied potential and pH where the surface and the space charge potentials are minimized, such that the remaining source of SHG is largely due to  $\chi_{\text{hem}}^{(2)}$ , given that waters' molecular hyperpolarizabilities should orientationally average to a zero (or close to zero)  $\chi_{\text{Stern}}^{(2)}$  value when there is no electric field across the Stern layer. We therefore proceeded to determine, with zero applied potential, the pH of zero charge (PZC, at which the total surface potential should be at or near zero) and the flatband potential,  $U_{FB}$  (at which the space charge layer potential should be at or near zero). A Mott-Schottky analysis of electrical impedance

spectroscopy (EIS) measurements that will be reported elsewhere indicates the flatband potential of our 10-nm thin nanolayers to be -0.2 V (*resp.* +0.2 V) vs Ag/AgCl at 1 M NaClO<sub>4</sub> and pH 13 (*resp.* pH 6). SHG measurements are consistent with a PZC between 5 and 7, as the SHG intensity change with ionic strength is negligible in that pH range (Fig. 1D), supporting the notion that the PZC at zero applied bias is between pH 5 and 7. Our earlier experiments on ALD-hematite deposited on fused silica (no FTO present) were consistent<sup>39</sup> with a point of zero charge of 5.5±0.3, in agreement with literature values for ‘natural’ hematite (PZC=5-7) but below those reported for ‘commercial’ (PZC=6-9) or ‘synthetic’ (PZC=7-10) hematite samples.<sup>44, 45, 46, 47, 48, 49, 50</sup> In this present work, we also determine the phase and amplitude via optical interference measurements at each pH (Fig. 1E) and at open circuit potential, finding that the change in the SHG phase is smallest between pH 5 and 7. The phase at the PZC is not zero, as it would be for a fully transparent material. Instead, our hematite nanolayers appear orange and have an absorbance of ~0.1 at the 515 nm SHG signal wavelength (please see Supporting Information Fig. S6). To obtain  $\overline{\chi_{hem}^{(2)}}$  in eqn. 1, we collected interferograms at pH 6 and pH 7 (covering the PZC range) and at an applied potential of +0.1 V and +0.2 V, covering the flatband potential range that we determined using EIS in this pH range, and find that  $\overline{\chi_{hem}^{(2)}} = 3.6 \times 10^{-22} \text{ m}^2\text{V}^{-1} \cdot e^{i\varphi_{hem}}$  with  $\varphi_{hem}=150^\circ$  to  $180^\circ$  (from replicate measurements on three different electrodes, again, relative to the zero phase from the glass:air interface). The remaining contribution to the total second-order nonlinear susceptibility,  $\chi_{tot}^{(2)}$ , at high ionic strength (1 M NaClO<sub>4</sub>), where the Debye length is less than one nanometer, is then just  $\overline{\chi_{hem}^{(2)}}$ , the second-order nonlinear susceptibility of the hematite:Stern layer interface and its associated phase,  $\varphi_{hem}$ , according to

$$\chi_{tot}^{(2)} = C \cdot E_{sig} e^{i\varphi_{sig}} = \chi_{Stern}^{(2)} + \overline{\chi_{hem}^{(2)}} - \Phi(0)_{DL} \chi_{water}^{(3)} (1 + 1.5i) \pm \frac{U - U_{FB}}{d_{SC}} \chi_{SC}^{(3)} \int_{-\delta}^0 e^{i\Delta_{kzz}} dz$$

with  $\chi_{Stern}^{(2)}$ ,  $\Phi(0)_{DL}$ , and  $U - U_{FB}$  all zero at the PZC and 0.1 to 0.2 V applied. (eqn. 1).

Here, the horizontal bar indicates that hematite's second-order response is complex-valued due to partial resonance enhancement as outlined below,  $C$  is the quartz calibration factor that also includes the Fresnel coefficients ( $C$  is determined to be  $4.2 \times 10^{-22} \text{ m}^2 \text{V}^{-1}$  for our hematite on FTO-coated glass anodes, at pH 7 and OCP), and the  $\chi_{water}^{(3)}$  term accounts for the phase-matched third-order nonlinear polarization in the bulk water, as described earlier.<sup>51, 52, 53, 54, 55, 56</sup> The last term is the third-order nonlinear polarization in the space charge layer, with the difference of externally applied potential,  $U$ , and the flatband potential,  $U_{FB}$ , over the space charge layer thickness,  $d_{SC}$  (limited to the 10 nm thickness of the hematite nanolayers) multiplied into the third-order nonlinear susceptibility of the space charge layer,  $\chi_{SC}^{(3)}$ , and the phase-matching term arising in the hematite nanolayer having an effective thickness of  $\delta$ .

We now rearrange eqn. 1b by subtracting  $\overline{\chi_{hem}^{(2)}}$  from  $C \cdot E_{sig} e^{i\varphi_{sig}}$  and solve the integral on the right-hand-side by employing a lower bound of  $\delta=20$  nm, given the AFM-derived 10 nm rms roughness of our hematite nanolayers on FTO, a wave vector mismatch  $\Delta_{kz}$  of  $2.5 \times 10^7 \text{ m}^{-1}$ , and  $d_{SC}=10$  nm, according to

$$C \cdot E_{sig} e^{i\varphi_{sig}} - \overline{\chi_{hem}^{(2)}} = \chi_{Stern}^{(2)} - \Phi(0)_{DL} \chi_{water}^{(3)} (1 + 1.5i) \pm (U - U_{FB}) \chi_{SC}^{(3)} \cdot (1.9 + 0.5i) \quad (\text{eqn. 2})$$

We use water's third-order nonlinear susceptibility,  $\chi_{water}^{(3)}=1 \times 10^{-21} \text{ m}^2 \text{V}^2$  for non-resonant conditions,<sup>52, 57, 58, 59, 60, 61</sup> and the EIS-derived space charge layer thickness estimate,  $d_{SC}$ , of 10 nm. Third-order nonlinear susceptibilities of iron oxide nanolayers have been reported to be sizeable from Maker fringe measurements in transmission geometries.<sup>62, 63, 64</sup> Our own measurements of 1030 nm  $\rightarrow \lambda(\text{THG})=344$  nm (recorded at pH 13 and OCP in our internal

reflection geometry after replacing the 515 bandpass filter with a  $325 \pm 25$  nm bandpass filter, Edmund Optics 12094) indicate a few tens of counts per 100 msec, whereas the SHG signal intensity for  $1030$  nm  $\rightarrow \lambda(\text{SHG})=515$  nm is in the few hundred counts per 100 msec range. The square root of this intensity ratio ( $\sim 3$ ) is close to the one we obtain from a complementary measurement using a tunable near-infrared laser (1kHz-pumped TOPAS, 120 fs bandwidth,  $10 \mu\text{J}$  per pulse), which allows us to measure the intensity at a third harmonic wavelength ( $1500$  nm  $\rightarrow 550$  nm) that matches the second harmonic wavelength ( $1100$  nm  $\rightarrow 550$  nm, close to the  $516$  nm SHG wavelength used in our oscillator experiments described throughout this work). That latter experiment yields a square root of the THG and SHG intensity ratio at  $550$  nm of  $\sim 6$ . Both experiments indicate that  $\chi_{SC}^{(3)}$  in our  $515$  nm amplitude and phase resolved SHG experiments is on the order of  $10^{-22}$  to  $10^{-21}$   $\text{m}^2\text{V}^{-2}$ , given that  $\overline{\chi_{hem}^{(2)}} = 3.6 \times 10^{-22} \text{ m}^2\text{V}^{-1}$ .

We now convert eqn. 2 into the properties we seek, namely  $\chi_{Stern}^{(2)}$  (the nonlinear susceptibility of the Stern layer species, largely  $\text{H}_2\text{O}$ , with  $<10\%$  counter ions) and  $\Phi(0)$  (the total interfacial potential drop across it). To this end, we collect  $Re$  and  $Im$  of eqn. 2 and find

$$\Phi(0) = -\left[C \cdot E_{sig,norm} e^{i\varphi_{sig}} - \chi_{hem}^{(2)} e^{i\varphi_{hem}} - 0.5 \cdot \chi_{SC}^{(3)} \cdot (U - U_{FB})\right] / 1.5 \chi_{water}^{(3)} \quad (\text{eqn. 3a}) \text{ and}$$

$$\chi_{Stern}^{(2)} = C \cdot E_{sig,norm} e^{i\varphi_{sig}} - \chi_{hem}^{(2)} e^{i\varphi_{hem}} + \Phi(0) \chi_{water}^{(3)} - 1.9 \chi_{SC}^{(3)} (U - U_{FB}) \quad (\text{eqn. 3b})$$

Here again we use the following parameters:  $C = 4.2 \times 10^{-22} \text{ m}^2\text{V}^{-1}$ ,  $\overline{\chi_{hem}^{(2)}} = 3.6 \times 10^{-22} \text{ m}^2\text{V}^{-1} \cdot e^{i\varphi_{hem}}$  with  $\varphi_{hem}=150^\circ$  to  $180^\circ$  relative to the  $0$  phase of the glass:air interface,  $\chi_{water}^{(3)}=1 \times 10^{-21} \text{ m}^2\text{V}^2$ ,  $U_{FB}=-0.2$  V vs Ag/AgCl at pH 13, and  $\chi_{SC}^{(3)}$  is on the order of  $10^{-22}$  to  $10^{-21} \text{ m}^2\text{V}^{-2}$ . We employ pH 7 at OCP as the reference state for which we determined our calibration factor  $C$  and to which we normalize the SHG amplitudes in the form of  $E_{sig,norm}$ .

Fig. 2A shows the total surface potential,  $\Phi(0)$ , and the Stern layer second-order nonlinear susceptibility,  $\chi_{Stern}^{(2)}$ , at pH 13. The total surface potential is slightly negative at OCP, consistent with surface potentials around -0.1 to -0.2 V at elevated pH that were reported for various hematite crystal faces using electrochemical and modeling means.<sup>65</sup> At +0.6 V applied bias, the total surface potential crosses zero V to become positive, increasing up to ~+400 mV at +1.4 V applied bias. The  $\chi_{Stern}^{(2)}$  values, in turn, are positive for negative applied potentials up to 0 V applied, beyond which they turn negative, consistent with the flipping of the Stern layer water molecules from a “protons toward the electrode” to a “protons away from the electrode” configuration:  $\chi_{Stern}^{(2)}$  values of water molecules pointing their protons away from bulk water are positively signed, as observed in heterodyne-detected vibrationally resonant sum frequency generation spectroscopy studies<sup>37, 66</sup>,<sup>67</sup> and in angle-resolved non-resonant second harmonic scattering experiments.<sup>60</sup> We then employ our previously established equation<sup>41, 57</sup> to estimate the number of net-aligned Stern layer water molecules,  $\mathcal{N}_{\downarrow} = \chi_{Stern}^{(2)} \cdot \varepsilon \varepsilon_0 (10^4 \text{ cm}^2 \text{ m}^{-2} \alpha^{(2)})^{-1}$ , where we use a Stern layer water permittivity  $\varepsilon$  of 1.77 to 2,<sup>68</sup>  $\varepsilon_0$  is the vacuum permittivity, and  $\alpha^{(2)} = 5.3 \times 10^{-52} \text{ C m}^3 \text{ V}^{-2}$  is an estimate for the second-order molecular hyperpolarizability of pure liquid water.<sup>58, 59</sup> Given our 1 M aqueous solution of NaClO<sub>4</sub>, we expect some amount of counter ions to be present in the Stern layer, but the dominant species is H<sub>2</sub>O.

Fig. 2A shows that the largest  $\chi_{Stern}^{(2)}$  values, at +1.4 V applied, correspond to approximately one monolayer of net-aligned water molecules ( $10^{15} \text{ cm}^{-2}$ , based on water’s density at room temperature and standard pressure) pointing their oxygen atoms towards the electrode and their protons into the bulk electrolyte. As shown in Supporting Information Fig. S7, these results change somewhat for  $\chi_{SC}^{(3)}$  values between  $4 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  and  $8 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$ , with the larger

values resulting in  $\chi_{Stern}^{(2)}$  values of  $1.5 \times 10^{-21} \text{ m}^2\text{V}^{-1}$  at +1.4 V applied. We consider these larger  $\chi_{Stern}^{(2)}$  values unreasonable as they would correspond to 5 full monolayers of water molecules flipping (the 0.7 nm Debye length at 1 M ionic strength corresponds to  $\sim 7$  water monolayers). Supporting Information Fig. S8 shows that changing the lower integration limit of the  $\chi_{SC}^{(3)}$  term in eqn. 1 from 20 nm (given the rms roughness from AFM) to 10 nm (the space charge layer thickness from the Mott-Schottky analysis of the EIS data) yields qualitatively similar (albeit somewhat smaller) values if  $\chi_{SC}^{(3)} = 8 \times 10^{-22} \text{ m}^2\text{V}^{-2}$ .

Fig. 2B shows the number of net-aligned Stern layer water molecules as a function of applied potential up to 1 V for the pH values we surveyed between pH 5 and 13. The results indicate that water flipping requires higher positive potentials at lower pH values. As shown in the inset of Fig. 2B, the total surface potential at which the same number of Stern layer water molecules points up versus down at zero applied bias (OCP) exhibits Nernstian behavior, given its pH-dependent slope of  $0.055 \pm 0.006 \text{ V pH}^{-1}$ .

The work associated with Stern layer water flipping is computed by multiplying  $\mathcal{N}_\downarrow$  by the Faraday constant and  $\Phi(0)$ , followed by division through  $1 \times 10^{15} \text{ cm}^{-2}$  (the water monolayer) and another division by Avogadro's number. Fig. 2C plots the difference of the free energy provided by the electrode potential, obtained by multiplying Faraday's constant,  $F$ , with the applied potential,  $U$ , and the work associated with Stern layer water flipping. Fig. 2C indicates that it requires the least amount of work to flip the Stern layer water molecules at the highest pH. Moreover, as the pH is increased from 5 to 13, the net work associated with water flipping decreases from one exceeding the cohesive energy of ice<sup>69</sup> by multiple tens of  $\text{kJ mol}^{-1}$  to one matching the cohesive energy of liquid water. Fig. 3D shows that it is at these high pH values that the OER current density is highest, whereas it is significantly smaller at pH 11 and 9, and even absent at the lowest pH

values studied here. Tafel slopes (please see Supplementary Note S4 and Supporting Information Fig. S5) recorded in the several potential ranges recapitulate this result as well: they are lowest when the net work to flip the Stern layer water molecules is lowest (Fig. 3D).

**CONCLUDING REMARKS.** Our work shows that nonlinear optical amplitude and phase measurements provide new insights into the surface processes involving interfacial water molecules before and during water oxidation. We separate the detected SHG response into four distinct contributions, namely the second-order nonlinear susceptibility of the Stern layer water molecules, that of the hematite surface species, the third-order nonlinear susceptibility of the diffuse layer water molecules, and that of the space charge layer within hematite. We present an optical model to provide estimates for the number of net-aligned Stern layer water molecules and the total electrostatic potential across the hematite:electrolyte interface.

The model employs well established inputs from experiment and theory with regards to  $\chi_{Water}^{(3)}$ . Using an absolute phase determination method that involves the determination of the absolute zero phase from a non-birefringent, transparent, and uncharged reference material (glass), we quantify the  $\chi^{(2)}$  of hematite,  $\chi_{hem}^{(2)}$ , and its associated phase at the point of zero charge and the flat band potential (pH 6 and +0.2 V vs Ag/AgCl at 1 M NaClO<sub>4</sub>). Estimates for  $\chi^{(3)}$  of the space charge layer,  $\chi_{SC}^{(3)}$ , are derived from third- and second harmonic generation measurements at various wavelengths. The model is then run within the upper and lower bounds of this estimate, along with two estimates for the lower integration bound of the space charge layer integral in eqn. 1 ( $\delta=10$  and 20 nm).

Our results indicate that approximately one monolayer of water is net-aligned, pointing the oxygen atoms towards the surface at the highest positive potentials applied. Free energy relationships establish that the work associated with water flipping is least at the highest pH, with

a free energy gain of  $-6.1 \pm 0.1 \text{ kJ mol}^{-1} \text{ pH}^{-1}$ . The pH-dependence of the potentials at which the Stern layer water molecules start to flip at zero applied bias is Nernstian. Once the applied bias is such that the net work associated with water flipping matches the cohesive energy of liquid water, the OER takes off, as indicated by the current density increase at pH 13. At lower pH values, the net work needed to flip the Stern layer water molecules increases beyond that of the cohesive energy of ice (at pH 9), where the OER current is much smaller than at pH 13 and approaches 100  $\text{kJ mol}^{-1}$  at pH 5, where the OER current is negligible.

Like the invariance of  $\chi_{\text{water}}^{(3)}$  to pH, [salt], and surface composition,<sup>54</sup> we expect  $\chi_{\text{SC}}^{(3)}$  to be invariant with applied potential. Indeed, our own measurements show that the THG signals we obtain from our electrodes are invariant with applied potential. However, we caution that one assumption made in our optical model is perhaps not appropriate at applied potentials leading to significant oxygen evolution, namely that  $\chi_{\text{hem}}^{(2)}$  is constant. In other work that will be reported in due course we find SHG signals at  $\lambda(\text{SHG}) = 550 \text{ nm to } 570 \text{ nm}$  that grow in with applied potential, clearly indicating that  $\chi_{\text{hem}}^{(2)}$  changes, as these wavelengths correspond to the  $\lambda_{\text{max}}$  of high-oxidation state iron species (ferryl and ferrates) that form at the applied potential when the oxidation current increases parabolically (+0.6 V or so).

In sum, we report new physical insights into the structure, electrostatics, and thermodynamics of the Stern layer water molecules before and during the oxygen evolution reaction over thin hematite nanolayer anodes. Our findings suggest a causal relationship between Stern layer water flipping and the OER overpotential. We expect the approach to be useful for contributing to the understanding of the molecular origin underlying the high overpotential associated with the oxygen evolution reaction on hematite. Future work is geared towards following water flipping under conditions of visible light illumination, quantifying the wavelength

dependences of the nonlinear optical resonances under applied potential, and exploring more catalytic surfaces such as those prepared from platinum group elements.

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**CONTRIBUTIONS.** FMG conceived of the idea. RS, EM, JK, ME, YZ, ABM, MDB, KMR, and FMG designed and carried out the experiments, analyzed the data, and wrote the manuscript. MB, ME, YZ, and KMR assisted with thin film characterization and data analysis. JK and ABM prepared the thin films, measured steady state optical absorption, and assisted with electrical impedance measurements and data analysis.

**DATA AVAILABILITY.** The data supporting the findings of this study are available within the main text and the Supplementary Information and upon request to the corresponding author.

## **SUPPLEMENTARY MATERIALS**

Supplementary Notes S1-S4.

Figs. S1 to S5

Supplementary References

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**Figure Captions**

**Fig. 1.** A) SHG intensity measured at 100 ms integration time (left) and current density (right) as a function of applied potential at conditions indicated for pH 9 (light blue), 11 (dark blue), and 13 (purple). B) Interference interferogram s recorded at pH 13 and 1 M NaClO<sub>4</sub> at various applied potentials. C) SHG amplitude (left) and phase (right) as a function of applied potential at conditions indicated for pH 5 (brown), 6 (orange), 7 (green), 8 (very light blue), 9 (light blue), 11 (dark blue), and 13 (purple). D) SHG Intensity recorded at indicated pH values for low and high (0.1M) ionic strength normalized to the low ionic strength condition at a given pH. E) SHG Amplitude divided by the calibration factor,  $C = 4.2 \times 10^{-22} \text{ m}^2\text{V}^{-2}$ , vs SHG phase at open circuit potential and pH 6 at the pH values indicated.

**Fig. 2.** Total potential (green line, left ordinate), second order nonlinear susceptibility (purple line, right ordinate), and number of net-aligned Stern layer water molecules (circles, blue right ordinate) as a function of applied potential at pH 13 and 1 M NaClO<sub>4</sub>. B) Number of net-aligned Stern layer water molecules pointing their oxygen atoms towards the electrode as a function of applied potential for pH values indicated and Stern slope result (inset). Please see text for details. C) Net work associated with water flipping as a function of applied potential at indicated pH values. The dashed lines indicate the cohesive energies of water (top) and ice (bottom). D) Current density measured at pH 13, 11, and 9 (left ordinate) and Tafel slopes measured at pH 13, 11, 9, 7, 6, and 5 (right ordinate) plotted against the net work associated with Stern layer water flipping.



