Hematite photoanodes were prepared by anodic electrodeposition in the presence of polyvinylpyrrolidone (PVP). PVP has been shown to alter hematite nanoparticle morphology, but has not been used before for anodic electrodeposition of thin films. Significant improvement in the water oxidation photocurrent was observed with PVP, with greater charge-collection efficiency due to a finer nanostructured morphology, and higher quantum yields for photons absorbed throughout the thickness of the hematite film from its increased porosity. Different post-deposition treatments showed distinct effects with and without PVP. Compared to electrodes dried 48 hours before annealing under N2, electrode performance was significantly reduced upon annealing in air, or annealing immediately after deposition when PVP was not used. Distinct wavelength dependence for front- versus back-side illumination, and a ~100-fold decrease in dopant density, was attributed to formation of a dead layer on the top of those electrodes with reduced photocurrent, and was avoided using PVP.

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1 M NaOH and determining the concentration from the absorbance at 450 nm.

Photoelectrochemical measurements.—Photoelectrochemical characterization was carried out using the same electrochemical setup described above, with SCE reference and Pt counter electrodes, in an electrolyte of 1.0 M NaOH (pH 13.6). Unless indicated otherwise, all potentials herein are reported versus the reversible hydrogen electrode, converted according to Equation 1:

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{pH} + E_{\text{SCe}}^0 \]  

where \( E_{\text{SCE}} \) is the applied potential vs. the SCE reference electrode, and \( E_{\text{SCe}}^0 = 0.242 \text{V} \). Current density vs. potential (\( J-E \)) curves were measured at a scan rate of 20 mVs^{-1} in the dark and under simulated sunlight (300-W Xe arc lamp with AM1.5G filter, Newport), set to 100 mW/cm² with a ThorLabs S302C thermal sensor.

The external quantum yield (EQY) was measured with a 300-W Xe arc lamp coupled to a monochromator (Cornerstone 260, Newport). Approximately 10% of the output beam was split off to a reference Si photodiode whose photocurrent was monitored by a transimpedance amplifier (PDA 750, Terahertz Technologies Inc.). The system was calibrated by replacing the PEC cell by a calibrated Si photodiode (818-UV with OD3 external attenuator, Newport). The EQY at each wavelength was calculated by Equation 2:

\[ EQY_{\text{PEC}}(\lambda) = \frac{I_{\text{PEC}}(\lambda)I_{\text{ref calib}}(\lambda)}{I_{\text{calib}}(\lambda)I_{\text{ref PEC}}(\lambda)} \times EQY_{\text{calib}}(\lambda) \]  

where \( I_{\text{PEC}}(\lambda) \) and \( I_{\text{ref calib}}(\lambda) \) are the net photocurrents as a function of wavelength for the hematite PEC cell, typically at 1.23 or 1.53 V, and for the calibrated photodiode at short-circuit, respectively, and \( EQY_{\text{calib}}(\lambda) \) is the known EQY of the calibrated photodiode. Correcting for any fluctuations in lamp output with time, \( I_{\text{PEC}}(\lambda) \) and \( I_{\text{ref calib}}(\lambda) \) are the short-circuit currents of the reference photodiode recorded during each measurement for the PEC and for calibration, respectively. EQY were not corrected for optical losses due to reflection or absorption by the electrochemical cell.

Photoelectrochemical impedance spectroscopy (EIS) was performed using a 10-mV amplitude perturbation of 50 mHz to 1 MHz under dark conditions. Impedance data were fitted to an equivalent circuit using ZsimpWin software (Ametek).

Figure 1. XRD pattern of annealed (solid, a and c) and as-deposited films (dashed, b and d), deposited with PVP (red, a and b) and without PVP (blue, c and d). Peaks due to the FTO substrate and lepidocrocite are marked with a star and L respectively, and hematite peaks are indicated by their corresponding Miller indexes.

Results and Discussion

Film structure and morphology.—The XRD patterns of as-deposited films indicate the growth of amorphous lepidocrocite (\( \gamma \)-FeOOH) on the FTO glass during anodic deposition (Fig. 1, traces 1a and 1c). Although others report annealing at a lower temperature with a longer dwell time, we found that annealing at 550°C for 1 hour gave ambiguous XRD patterns, tentatively attributed to a mixture of amorphous maghemite (\( \gamma \)-Fe₂O₃) and hematite. After annealing at 650°C, in all cases diffraction patterns indicate pure hematite.

Comparing films deposited in the presence of PVP and without it, relative peak intensities of annealed films varied, in particular the [110] orientation, which indicates preferential growth along that axis and significantly increases hematite’s conductivity. However, these variations were not consistent among different samples, and Lotgering analysis of peaks intensities did not reveal a statistically significant difference correlated to electrode preparation. Annealing in air or annealing immediately after deposition did not significantly alter diffractograms (See Supplemental Material, Fig. S1).

Addition of PVP to the electrolyte reduced the electrodeposition current density, likely due to the greater electrolyte viscosity and thus reduced mass transfer and/or due to the complexion of PVP with the iron oxide surface. Therefore, to produce electrodes with comparable film thicknesses, the total charge passed per unit area of FTO was monitored, typically resulting in 50% longer deposition times with PVP for the same total charge (Fig. S2). Films synthesized with and without PVP with equal charge passed per unit area were indistinguishable by UV-visible absorption spectroscopy, both showing a clear onset of absorption at 600 nm (Fig. S3), consistent with a bandgap of 2.1–2.2 eV. The higher absorbance at energies above the bandgap with increasing deposition times indicates growth of thicker films, although significant light scattering precludes quantitative comparison.

SEM images reveal that anodic electrodeposition results in highly uniform hematite thin films. Although the overall morphology of the films is similar, as shown in Figs. 2a–2b, the size of features decreases by ~25% for films made with PVP, significantly increasing the interfacial surface area (vide infra). Cross-sectional views indicate equal thickness for films with and without PVP (Figs. 2c–2d), but show that films with PVP are more porous, with a more uniform distribution of...
voids throughout the thickness of the film. SEM further indicates that a greater total charge passed during deposition results in thicker films, ranging from 0.5 to 1.5 μm, and images show a coarsening of features at longer deposition times (Fig. S4). In addition, for electrodes prepared without PVP annealing immediately after deposition and annealing in air both resulted in formation of numerous defect regions in the morphology of the electrode surface, but these non-uniform areas were not observed with PVP, nor if electrodes were dried 48 hours before annealing under N2 (Fig. S5).

The roughness factor, as determined by adsorption of a monolayer of Orange II dye, using an area of 40 nm2 per molecule,33 was increased on average by 75% with the addition of PVP during iron oxide film deposition. Depending on film thickness, the ratio of the real surface area compared to geometric area ranged from 9.5 to 31 without PVP, and from 16 to 52 with PVP. In both cases, the roughness factor reached a maximum as film thickness increased, and then decreased due to the coarsening observed at the longest deposition times.

PVP could alter the hematite morphology by a specific surface interaction with the FeOOH surface during the anodic deposition,28,30,31 which would likely result in anisotropic growth, but oriented crystal growth was not observed by XRD. Alternatively, in a more random incorporation process, PVP in the electrolyte may get kinetically trapped within the film as Fe2+ is oxidized to Fe3+ and precipitates onto FTO, increasing film porosity when PVP is subsequently burned off during the annealing step.22 The increased viscosity of the deposition solution with added PVP reduces mass transfer to the electrode surface, and it may be that the decreased iron oxide deposition rate results in the improved film morphology. Zandi et al. found that lowering the deposition potential resulted in electrodes with greatly reduced photoactivity, both with and without PVP. Others have reported similar findings for hematite electrodes prepared by hydrothermal synthesis from FeCl3.38,40

**Photoelectrochemical performance.**—To compare photoelectrochemical performance of the hematite photoanodes, current density vs. potential (J-E) curves were measured in the dark and under simulated AM1.5G solar illumination (Fig. 3). With PVP and without electrodes show a similar photocurrent onset potential at ~0.9 V, but across a nearly ten-fold variation in charge deposited, electrodes synthesized with PVP showed significantly increased photocurrents, particularly at shorter deposition times (Fig. 4). At the oxygen evolution potential, addition of PVP resulted in an average ~30% improvement in photocurrents, increasing for the thinnest films. A similar trend is observed at higher overpotential, but the improvement was not as significant the greater the charge passed during deposition (Fig. S6), and in all cases photocurrents decreased at longer deposition times.

These trends are consistent with the observed variations in interfacial surface area for the electrodes.

For electrodes made both with and without PVP, over the course of two hours under AM1.5 illumination photocurrents were perfectly stable, and neither showed any signs of degradation or side reactions (Fig. S7), indicating that the increased photocurrent with PVP is not due to the oxidation of residual PVP or its byproducts on the electrode surface.

The effect of PVP concentration in the deposition solution on electrode photocurrents shows a relatively weak dependence on concentrations above 2% by mass (Fig. S8). At concentrations over 7%, the very high viscosity of the deposition solution made degassing it by bubbling N2 problematic. The effect of the polymeric size of PVP used during deposition shows only a slight increase of photocurrent with molecular mass (Fig. S9). Because of this, an average molecular mass of PVP of 360,000 and concentration of 3.6% (corresponding to ~100 μM) was used unless noted otherwise.

**J-E curves** were measured by illuminating in two orientations, from the Fe2O3 side of the electrode (front) and through the FTO substrate (back). For all N2-annealed electrodes, back-side illumination decreased the photocurrent (Fig. 5a), due in part to reflection off the glass substrate and the absorption of UV photons by the FTO film. However, the difference between front- and back-side illumination was more pronounced for electrodes made without PVP, as seen in Fig. 4. Without PVP, currents dropped by 25–70% going from front- to back-side illumination, whereas with PVP the drop was ~20% for all but the thickest electrodes. The smaller and more consistent drop across film thicknesses indicates that PVP improves charge collection for photons absorbed throughout the film’s thickness. For electrodes made without PVP, holes generated too far from the electrolyte interface are not collected. The wavelength dependence of the photocurrent further supports this interpretation, as discussed below. This suggests that the greater film porosity with PVP allows the electrolyte to penetrate further into the film, although this effect is lost at longer deposition times where features are coarsened (Fig. S4).

**Annealing in air vs. N2.**—In contrast to other reports using anodic electrodeposition to produce hematite photoanodes,23,26,30,37 films herein were typically annealed under N2(g) rather than air. Annealing in air at 650 °C resulted in electrodes with greatly reduced photoactivity, both with and without PVP. Others have reported similar findings for hematite electrodes prepared by hydrothermal synthesis from FeCl3.38,40 Debate continues regarding the exact nature of the mechanism and how oxygen vacancies affect electrode performance. Freitas et al. propose that N2 annealing improves the catalytic efficiency of
Effect of annealing immediately after deposition.—Electrodes that were deposited without PVP and annealed in N₂ immediately after deposition, rather than first drying at 60°C for 48 hours, gave very similar results to air-annealed electrodes (that were dried). For electrodes made without PVP, foregoing the drying step caused a near total loss of front-side photocurrent (Fig. 5c). As was observed for annealing in air, these too showed much higher photocurrents by back-side illumination than front-side. In contrast, for electrodes made with PVP annealed immediately, results were more typical, with substantial photocurrents in both illumination orientations and front-side greater than back-side. This is consistent with the highly uniform films made with PVP and the appearance of numerous defects in the electrode surface morphology when made without PVP and annealed immediately (Fig. S5), suggesting the defective regions are responsible. On the other hand, no defective regions were observed for air-annealed electrodes made with PVP, but in that case performance still suffered, indicating a second effect due to O₂.

J-E Curves with H₂O₂ as a hole scavenger.—To better understand the effect of using PVP and N₂-vs.-air annealing, J-E curves were also measured in 1 M NaOH with 0.5 M H₂O₂ added as a hole scavenger in order to distinguish between a change in charge-carrier generation and/or collection efficiency versus interfacial electron-transfer kinetics. As shown in Figure 6, for all electrodes with appreciable photoactivity the onset of photocurrent shifted negative 400 mV, to 0.5–0.6 V, and its rise was more immediate, as expected from the more rapid H₂O₂ oxidation kinetics.

For air-annealed electrodes, front-side illumination in H₂O₂ still generated negligible photocurrent, but the back-side photocurrent was three times larger than without H₂O₂ (Fig. 6b), though still less than for those annealed under N₂. This suggests a combination of both reduced catalytic activity at the surface and decreased charge-carrier transport efficiency with air annealing. Interestingly, the onset potential for these electrodes’ photocurrent onset was further shifted ~80 mV negative compared to N₂-annealed electrodes. Assuming rapid interfacial kinetics, this shift may indicate reduced surface recombination, or perhaps a shift in flatband potential, although the latter is not supported by our EIS results, as discussed below.

Electrodes deposited without PVP and annealed immediately behaved much like those annealed in air, with negligible front-side current with or without H₂O₂, and a three-fold improvement in back-side photocurrent with H₂O₂ (Fig. 6c). But with PVP they behaved as those annealed under N₂, with comparable net photocurrents with or without H₂O₂, and higher front- versus back-side photocurrents. It is as yet unclear how PVP acts to offset the deleterious effect of annealing immediately.

External quantum yield.—To better understand the variations in J-E curves, the EQY (or IPCE) was measured, as shown Fig. 7. For all electrodes, integration over all wavelengths of the product of the EQY and spectral irradiance of the AM1.5 solar spectrum yields good agreement with photocurrents measured by J-E curves (within 10%).
Figure 6. Net photocurrent calculated from light minus dark J-E curves measured in 1.0 M NaOH and 0.5 M H2O2 for electrodes annealed (a) in N2, (b) in air, and (c) immediately following deposition (i.e. without drying for 48 hrs at 60 °C). Electrodes deposited with PVP are shown red, without in blue; front side illumination indicated by dashed, and back by solid lines.

Electrodes dried and annealed under N2.—As expected, electrodes deposited with PVP and annealed under N2 showed higher quantum yields than those without PVP (Fig. 7a). Despite variations in magnitude, all these electrodes showed a similar profile, reaching a maximum EQY at 370 nm with a shoulder to 550 nm, and with front-side illumination giving higher yields than back-side, as expected from J-E curves.

The EQY results for these electrodes are fully consistent with a standard model where charge carrier collection is limited by a short hole-diffusion length. Under back-side illumination, for a film thicker than the diffusion length and with low porosity, as higher energy photons are more strongly absorbed, electron-hole pairs are generated closer to the FTO-hematite interface and are more likely to recombine before reaching the electrolyte interface, decreasing the EQY. Correspondingly, under front-side illumination high-energy photons are absorbed closer to the electrolyte interface, resulting in a higher EQY. In contrast, lower energy photons have a greater penetration depth and are absorbed more uniformly throughout the film. Meanwhile, electrolyte permeates throughout a highly porous nanostructured film, and charge-carrier collection is instead limited by the dimensions of individual nanoparticles, with negligible difference expected for front- versus back-side illumination at all wavelengths.

With PVP, the smaller nanoparticle feature size reduces the distance charge carriers must travel to reach the interface and increases the interfacial surface area, increasing the collection efficiency at all wavelengths compared to those made without PVP. In addition, the use of PVP increases film porosity, which accounts for the smaller drop in photocurrent going to back-side illumination with PVP, as well as the wavelength dependence of EQY measurements.

For all electrodes illuminated from the back, strong absorbance by the FTO below 300 nm, with a shoulder extending to 400 nm (Fig. S3), causes the EQY to go to zero in this region. At longer wavelengths, ~15% of incident photons are lost to absorption by the substrate, or reflection off it. By dividing the EQY by the fraction of
light transmitted through the FTO glass at each wavelength, the EQY can be corrected to take these losses into account (Fig. S10). For the thinnest films, with or without PVP, this correction in EQY shows no significant difference between front versus back illumination, indicating fairly uniform charge-carrier collection efficiency throughout the films’ thickness. However, for thicker films made without PVP, the corrected back-side EQY is significantly lower than for front-side at wavelengths below 450 nm, indicating these photons are absorbed too far from the electrolyte interface to be collected efficiently. Use of PVP increases porosity, allowing the electrolyte to penetrate more fully into the hematite film, and thus improves collection near the FTO by decreasing the length charge carriers must diffuse before reaching the interface.26,36, such that optical transmission losses from the substrate entirely account for the difference in front- versus back-side photocurrents for all but the thickest films.

**Electrodes annealed immediately or in air.**—Electrodes annealed in air (with or without PVP, Fig. 7b), and electrodes annealed immediately made without PVP (Fig. 7c), the front-side EQY was negligibly small at all wavelengths, consistent with J–E curves. Multiplying traces by 50 for easier comparison reveals that the front-side EQY for those electrodes reaches a local maximum at 570 nm. Note that for electrodes made with PVP that were annealed immediately, in Fig. 7c, front- and back-side EQY curve profiles were not substantially different from the typical behavior shown in Fig. 7a. For all electrodes, irrespective of preparation method, the back-side illuminated EQY show the same characteristic profile, although the EQY in visible portion of the spectrum (the shoulder at ~550 nm) was diminished for those electrodes that gave negligible front-side photocurrents.

If annealing immediately, or in air, caused a loss of photocurrent due to shorter charge-carrier diffusion lengths, according to the standard model invoked above, under front-side illumination one would expect to see higher yields for UV/blue photons with negligible yields to the red, and conversely, lower yields to the blue and higher yields to the red by back-side. Yet, this is exactly the opposite of what is observed. In the UV, front-side illumination results in a 1–2 order-of-magnitude decrease in yield compared to back-side illumination. At wavelengths approaching the energy of the bandgap the difference diminishes, observed as a local maximum in the EQY at 570 nm for front-side illumination. In other words, for these electrodes, front-side illumination effectively reduces to zero the yield of higher energy photons that are absorbed closest to the electrolyte interface. The much higher back-side EQY in the UV region indicates charge collection is more efficient closer to the FTO interface, likely due to doping by Sn. Since yields are overall still much lower for back-side illumination, it suggests formation of a dead or inactive layer on top of the electrode from which no holes are collected. For front-side illumination, with a dead layer ~100 nm thick, all high-energy photons would be absorbed within it, yielding essentially no current. Only photons with the longest penetration depth, closest to the bandgap energy, would escape the dead layer. With back-side illumination, for a porous film, photons absorbed in the active layer closer to the FTO interface could still yield holes able to reach the electrolyte. Such an effect accounts for the peak in EQY observed at 570 nm via front-side illumination, and the more substantial yield in the UV with depressed yield in the visible region with back-side illumination.

**Electrochemical impedance spectroscopy.**—To further elucidate the factors affecting electrode performance, EIS analysis was performed by fitting impedance data under dark conditions to a simplified Randles circuit (Fig. 8a, inset) from 0.1 Hz to 100 kHz as a function of applied potential. By plotting the inverse square of the capacitance, $C_{sc}$, versus applied potential, $E$, a Mott-Schottky (MS) plot can be used to determine the dopant density and flatband potential of a semiconductor electrode, according to Equation 3:

$$\left( \frac{A}{C_{sc}} \right)^2 = \frac{2}{q\varepsilon \varepsilon_0 N_D} \left( E - E_{fb} - \frac{kT}{q} \right)$$

where $A$ is the surface area of the electrode, $q$ is the elementary charge, $\varepsilon$ is the dielectric constant of the semiconductor, $N_D$ is the dopant density, $E_{fb}$ is the flatband potential, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature. Values used for the dielectric constant of undoped hematite vary,26,36,40 and the value of 32 is used herein, although the choice of value would not alter the conclusions drawn here.

MS analysis assumes a planar electrode surface and that surface states are not involved. While these criteria are not necessarily rigorously fulfilled for the electrodes tested herein, MS plots nonetheless show a clear linear regime and reveal striking differences between electrodes annealed under varying conditions (Fig. 8). Extrapolating fits of the linear region (0.9–1.4 V, $R^2 \geq 0.998$) to the abscissa gives values of $E_{fb}$ in the range of 0.50–0.63 V. These values are in general agreement with the values obtained from the onset of the photocurrent in H$_2$O$_2$ solution (Fig. 6), and with other reports.26,41,42 Here however, electrode preparation method had no significant effect on $E_{fb}$ within the error.

On the other hand, as seen comparing Figs. 8a and 8b, much steeper MS slopes were calculated for electrodes annealed in air, corresponding to $N_D = 1 \times 10^{18}$ cm$^{-3}$, over two orders of magnitude less than the value of $2 \times 10^{20}$ cm$^{-3}$ found for electrodes annealed under N$_2$. This difference is likely due to oxygen vacancies that are lost when annealing in the presence of O$_2$.40 Similarly, a much lower dopant density of $2 \times 10^{18}$ cm$^{-3}$ was calculated for electrodes annealed immediately after deposition without PVP, although the use of PVP increases $N_D$ to $1 \times 10^{20}$ cm$^{-3}$ (Fig. 8b). It is unclear why immediate
annaling would decrease $N_d$, nor why PVP counteracts this effect, although it likely results from PVP’s suppression of defects in the film morphology. The electrodes with very low $N_d$ values also gave charge transfer resistance values, $R_\tau$, that were 3–4 times higher at 1.2 V (1–1.2 MΩ vs. 300 kΩ), but that trend is reversed at potentials above 1.4 V, consistent with the higher current in dark $J-E$ curves. For all electrodes, the series resistance, $R_s$, values were constant at all potentials as expected, ranging from 10–30 Ω.

Higher dopant densities can lead to improved charge carrier mobility, higher carrier concentrations, or enhanced charge separation and temperature (to control morphology, as well the effect of atmo-

Conclusions

In conclusion, we have shown that the use of PVP during the anodic deposition of thin films leads to both increased porosity and surface area due to a finer nanostructured morphology that improves charge-carrier collection throughout the films’ thickness, and thus leads to significantly higher photocurrents to drive the oxygen evolution reaction in hematite water-splitting photoelectrochemical cells. We are currently investigating what additional gains are possible with the use of PVP by further optimizing deposition conditions (time, potential, and temperature) to control morphology, as well the effect of atmosphere with a very brief but high-temperature annealing step others have reported as being beneficial.26

For hematite electrodes annealed in air, we observed a nearly complete loss of photocurrent under front-side illumination, but a more substantial back-side photocurrent. We propose this distinct behavior is due to formation of an inactive layer on the top surface of the electrode with a ~100-fold drop in dopant density due to loss of oxygen vacancies and that is offset by Sn-doping in the vicinity of the FTO substrate. Similar results were obtained for films annealed without an initial drying step, although here only when PVP was not used. The exact nature of the dead layer and how PVP prevents its formation is being further investigated.

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