ABSTRACT: A thorough understanding of the kinetic competition between desired water oxidation/electron extraction processes and any detrimental surface recombination is required to achieve high water oxidation efficiencies in transition-metal oxide systems. The kinetics of these processes in high Faradaic efficiency tungsten trioxide (WO₃) photoanodes (>85%) are monitored herein by transient diffuse reflectance spectroscopy and correlated with transient photocurrent data for electron extraction. Under anodic bias, efficient hole transfer to the aqueous electrolyte is observed within a millisecond. In contrast, electron extraction is found to be comparatively slow (~10 ms), increasing in duration with nanoneedle length. The relative rates of these water oxidation and electron extraction kinetics are shown to be reversed in comparison to other commonly examined metal oxides (e.g., TiO₂, α-Fe₂O₃, and BiVO₄). Studies conducted as a function of applied bias and film processing to modulate oxygen vacancy density indicate that slow electron extraction kinetics result from electron trapping in shallow WO₃ trap states associated with oxygen vacancies. Despite these slow electron extraction kinetics, charge recombination losses on the microsecond to second time scales are observed to be modest compared to other oxides studied. We propose that the relative absence of such recombination losses, and the observation of a photocurrent onset potential close to flat-band, result directly from the faster water oxidation kinetics of WO₃. We attribute these fast water oxidation kinetics to the highly oxidizing valence band position of WO₃, thus highlighting the potential importance of thermodynamic driving force for catalysis in outcompeting detrimental surface recombination processes.

INTRODUCTION

Photocatalytic water splitting is a promising strategy for sustainable fuel generation, but the limiting kinetics of the four-hole water oxidation reaction remain a key challenge to unlocking higher efficiencies.¹ Since the pioneering study on TiO₂ by Fujishima and Honda in the 1970s,² transition-metal oxides have remained among the most widely studied photoanodes for water oxidation due to their earth abundance, good aqueous stability, and facile synthesis.³ However, most such oxides, including TiO₂, α-Fe₂O₃, and BiVO₄, demonstrate sluggish water oxidation kinetics, allowing competing recombination processes to drastically lower performance.⁴–⁷ Heterojunctions, catalysts, or overlayers are then required to accelerate water oxidation kinetics and/or slow recombination, increasing cost and complexity. With a narrower band gap than TiO₂, tungsten trioxide (WO₃) can absorb a larger proportion of the solar spectrum, while maintaining a deep valence band energy to provide a large thermodynamic driving force for water oxidation.¹¹,¹² WO₃ demonstrates good photocurrent onset and is also stable at acidic pH, which allows preferential pairing with acid-stable photocathodes.¹³,¹⁴ While there exists extensive research on the semiconducting properties of WO₃, particularly with respect to photo- and electrochromic phenomena, the kinetics of water oxidation on this metal oxide remain, to the best of our knowledge, largely unexplored.¹⁵ In this study, we measure the kinetics of water oxidation and electron extraction in nanostructured WO₃ photoanodes and compare these with other metal oxide photoanode materials. We reveal how these complementary processes of charge removal from the system compete with recombination on the microsecond to second time scale and enable the achievement of photocurrent onset potentials close to flat-band without added cocatalysts.

WO₃ is often reported to have high electrical conductivity,⁵,¹⁶ leading to its frequent implementation as an electron donor in photoelectrochemical water splitting systems. Despite the potential benefit of high electrical conductivity, it remains largely unexplored as a photoanode material. A thorough understanding of the kinetic competition between desired water oxidation/electron extraction processes and any detrimental surface recombination is required to achieve high water oxidation efficiencies in transition-metal oxide systems. The kinetics of these processes in high Faradaic efficiency tungsten trioxide (WO₃) photoanodes (>85%) are monitored herein by transient diffuse reflectance spectroscopy and correlated with transient photocurrent data for electron extraction. Under anodic bias, efficient hole transfer to the aqueous electrolyte is observed within a millisecond. In contrast, electron extraction is found to be comparatively slow (~10 ms), increasing in duration with nanoneedle length. The relative rates of these water oxidation and electron extraction kinetics are shown to be reversed in comparison to other commonly examined metal oxides (e.g., TiO₂, α-Fe₂O₃, and BiVO₄). Studies conducted as a function of applied bias and film processing to modulate oxygen vacancy density indicate that slow electron extraction kinetics result from electron trapping in shallow WO₃ trap states associated with oxygen vacancies. Despite these slow electron extraction kinetics, charge recombination losses on the microsecond to second time scales are observed to be modest compared to other oxides studied. We propose that the relative absence of such recombination losses, and the observation of a photocurrent onset potential close to flat-band, result directly from the faster water oxidation kinetics of WO₃. We attribute these fast water oxidation kinetics to the highly oxidizing valence band position of WO₃, thus highlighting the potential importance of thermodynamic driving force for catalysis in outcompeting detrimental surface recombination processes.

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High conductivity in WO₃ is considered to be a result of a large density of charge carriers, caused by intrinsic oxygen vacancies, which act as n-type dopants.²³ Carrier concentrations in the range from 1 × 10¹⁷ to 1 × 10²⁵ cm⁻³ have been reported, depending on stoichiometry (WO₃ₓ).¹¹,²⁶,²⁷ Similarly, changes in the stoichiometry of single crystals have been shown to modulate electrical conductivity between 10 and 1 × 10⁻⁴ S/cm.²³ However, such deviations from stoichiometry have also been suggested to introduce chemical defects that can result in increased charge trapping, which, rather than boost performance, can often introduce additional recombination pathways.²⁸⁻²⁻³² For example, the presence of defect states in the band gap of α-Fe₂O₃ has been shown to enhance electron-hole recombination kinetics that can outcompete water oxidation.³³ In addition, high carrier densities can also result in shorter minority carrier lifetimes and thus also accelerated recombination losses.³⁴,³⁵ Water oxidation is a kinetically slow process, requiring the accumulation of multiple holes. As such, kinetic competition between water oxidation/electron extraction and surface charge recombination (sometimes called back electron−hole recombination) can severely limit the efficiency of photoelectrochemical water oxidation.³⁶⁻³⁹ Using sacrificial reagents, Amano et al. found that the size of suspended WO₃ particles affected the frequency of surface recombination with concurrent effects on oxygen evolution rate.⁴⁰ However, this competition has received limited attention to date for WO₃ photoanodes under photoelectrochemical conditions.

Reported herein is an analysis the dynamics of photogenerated charges in tungsten oxide photoanodes synthesized by chemical vapor deposition (CVD). The synthesis method generates highly oxygen-deficient monoclinic WO₃₋ₓ nano-needle structured films that are intensely blue in color, which are then annealed in air at elevated temperature to remove most of the oxygen vacancies. These photoanodes exhibit an early photocurrent onset potential (ca. 0.5 V vs reversible hydrogen electrode (RHE)) and a high Faradaic efficiency for water oxidation (>85%). The rate of water oxidation is analyzed by transient diffuse reflectance spectroscopy and transient photocurrent measurements and is found to be faster than other commonly used transition-metal oxides and much faster than electron extraction. The effect of interband defects on electron transport is then investigated. We find that electron trapping in the WO₃ needles is significant and propose a trap-mediated mechanism of electron transport to the back contact (fluorine-doped tin oxide (FTO)). To examine how the density of traps may affect this electron transport, we alter the annealing time and the needle length and find that this has profound effects on extraction time. We thus provide unique kinetic insight on the charge carriers of WO₃, a material growing in popularity for solar fuel-related applications,⁴¹⁻⁴⁵ and highlight the direct impact these kinetics have on photoelectrochemical performance.

**RESULTS**

**Sample Characterization.** Tungsten oxide samples were prepared by aerosol-assisted chemical vapor deposition (AA-CVD) according to a previously established synthesis,⁴⁶ as detailed in the Supporting Information (Methods). Figure 1a shows the cross-sectional scanning electron microscopy (SEM) image of an annealed WO₃ sample, indicating the 4 μm long needles (yellow line) on top of the dense seed layer (400 nm, red line). X-ray diffraction data confirm the crystalline monoclinic nature of these WO₃ films, with the (002) peak most prominent due to the preferential growth along this axis (Supporting Information, S1).

Samples were also characterized by X-ray photoelectron spectroscopy (XPS). The XPS spectra of WO₃ samples before and after annealing indicate the films are of similar purity, with adventitious carbon the only detectable impurity (Figure S2b). The W 4f peaks in the unannealed, blue sample show significant shoulders at lower binding energy as a result of a large number of W⁵⁺ species present, which can be directly correlated with oxygen vacancies (Figure S2c). The proportion of W⁵⁺ to W⁶⁺ analyzed with this surface-sensitive technique is ~30%. Figure 1b shows that after annealing in air at 500°C for 2 h, the number of these reduced states is dramatically decreased to ~10% of the tungsten atoms probed. Photographs of the annealed and unannealed samples are given in Figure S2a.
Photoelectrochemical Water-Splitting Performance. The current−voltage characteristics of annealed WO3 were examined by linear sweep voltammetry under chopped simulated 1 sun irradiation from the front side (EE), as shown in Figure 2. As highlighted in Figure S3, the dark current was negligible over the voltage range examined, as was the photocurrent for the unanneled sample. As shown in Figure 2, the photocurrent reaches a plateau at \( \sim 1.23 \text{ V}_{\text{RHE}} \) (\( \sim 0.4 \text{ mA/cm}^2 \)), and the onset potential (ca. 0.5 \text{ V}_{\text{RHE}}) is only \( \sim 100 \text{ mV} \) above the calculated flat-band for such nanostructured WO3.47 Unlike photoanodes of several other transition-metal oxides, there is an absence of transient spikes when the light is turned on (positive spikes) or off (negative spikes). Such photocurrent transients are indicative of current loss from recombination processes at the surface, typically the recombination of surface accumulated holes with bulk electrons, which compete with hole transfer to the electrolyte (e.g., by water oxidation).36,48 These transients are readily observed in \( \alpha-\text{Fe}_2\text{O}_3 \) and BiVO4, for which this recombination can be a significant loss pathway.49,50 The early photocurrent onset observed for the WO3 needles combined with the lack of transient current spikes suggests that there is very little such surface recombination occurring, which may be a result of slower surface recombination or a faster reaction of accumulated holes, as we discuss further below. Oxygen evolution was measured with a calibrated Clark electrode as detailed in the Supporting Information. Figure S4 demonstrates the high Faradaic efficiencies obtained, which were consistently between 85 and 90%. We note this to be higher than a large proportion of the Faradaic efficiency values reported in the literature for this material.15,25,39 This high Faradaic efficiency may be related to the high crystallinity of the WO3 needles and/or preferential crystal orientation, reported by others to be significant.40,51 Further analysis on this aspect is, however, beyond the scope of this kinetic study.

Dynamics of Electrons and Holes. Transient diffuse reflectance spectroscopy (TDRS) measurements were performed on the microsecond to second time scale to monitor the kinetics of photogenerated charges under water oxidation conditions (see Supporting Information for details). Previous studies have shown that WO3 exhibits two main spectral features: a broad transient signal centered at \( \sim 800 \text{ nm} \) that, by use of chemical scavengers, has been assigned to photoexcited electrons around the conduction band and a hole signal, which may be probed below 550 nm.52 The transient diffuse reflectance (TDR) spectra for the WO3 needles in this work, Figure 3a, are in agreement with these previous assignments. The stronger electron absorbance signal spans most of the visible spectrum down to \( \sim 550 \text{ nm} \). Monitoring the electrons at 800 nm, we observe a long-lived transient signal that decays by \( \sim 1 \text{ s} \) (black trace, Figure 3b). The transient photocurrent (TPC) was measured simultaneously and integrated to give the extracted electron density as a function of time delay (dashed blue trace, Figure 3b). On the one hand, by comparing the TDRS electron signal at 800 nm with the integrated TPC signal, it is clear that the integrated TPC signal rises as the 800 nm signal decays, supporting the assignment of the 800 nm TDRS signal to WO3 electrons. On the other hand, the hole signal,
monitored at 500 nm, presents a much faster decay, implying faster kinetics for the hole reaction with the electrolyte. Given the high Faradaic efficiency exhibited by this photoanode, this hole reaction can be assigned primarily to water oxidation. If we take approximate half-times for these decays with respect to the signal amplitude at 10 μs, \( t_{1/2} \) (electrons) is \( \sim 10 \) ms, and \( t_{1/2} \) (holes) is \( \sim 0.5 \) ms. These values indicate that holes react an order of magnitude faster than electrons are extracted by the external circuit. As will be highlighted in more detail in the following sections, this time scale of water oxidation is much faster than those observed for other commonly studied transition-metal oxides.8,10,53

Hole Kinetics in Water and Propylene Carbonate. To further examine the rapid water oxidation kinetics evident from the TDRS decay at 500 nm in Figure 2, the same kinetic measurement was repeated in inert organic solvent (propylene carbonate). As seen in Figure 4 (red trace), when there is no water present, a longer-lived transient signal is observed at 500 nm. This trace still decays within the time scale of the measurement due to some oxidation of the solvent and/or other recombination processes. When a small percentage of water (pH 1 electrolyte) is added to the electrolyte, the rate of signal decay is increased, thus confirming that the fast decay observed at 500 nm is due to surface holes reacting with water. Although the poor miscibility of water in propylene carbonate limits our comparisons to low water concentrations, a clear trend of increasing rate with increasing water content is observed, with the 100% aqueous electrolyte displaying the fastest oxidation kinetics.

Kinetics of Electron Transport. To further investigate the relatively slow electron extraction kinetics shown in the 800 nm TDRS and TPC data in Figure 3, a series of transient diffuse reflectance decays were recorded at a range of potentials, along with integrated transient photocurrent signals, to determine the effect of applied bias (Figure 5a). With progressively larger anodic bias, the magnitude of the initial optical and final extracted charge signals increase simultaneously. The rise in these signal amplitudes indicates an increase in the density of photogenerated long-lived electrons that can be extracted from the film into the external circuit. This can be rationalized as a consequence of greater band bending in the material under higher bias, creating a larger space charge layer to separate charges and thus a higher yield of electrons. In other words, the magnitude of the optical signal directly correlates with the number of electrons that remain in the electrode after any ultrafast bulk recombination occurs. In Figure 5b, we plot the correlation between our initial optical TDRS assay of long-lived electrons (green triangles) and our integrated photocurrent assay of extracted electrons (blue circles) versus applied potential. The close agreement between these two assays indicates that, despite the slow electron extraction kinetics, the electrons observed on these time scales are still extracted reasonably efficiently by the external circuit; that is, relatively few of the electrons monitored on the micro- to second time scales studied herein are recombining on this time scale. This is in agreement with the early photocurrent onset and lack of transient spikes observed in the chopped \( J \sim V \) curve (Figure 2). If we consider the extracted charge density at both 50 ms (Figure 6b, pink squares) and 1 s (blue circles), we observe a small difference at low bias indicative of modest back electron–hole recombination losses. Back electron–hole (surface) recombination occurs over long time scales as a result of charge accumulation at the electrode–electrolyte interface. This buildup of charge draws electrons in the opposite direction of normal current flow, diminishing the total charge collected. By 1.15 \( V_{\text{RHE}} \) a large enough field is maintained to successfully prevent this slow time scale recombination process. This “surface recombination turnover” potential is lower than for \( \alpha \)-Fe2O3 and BiVO4 photoanodes8,36,34,55 most probably due to the faster competing water oxidation reaction kinetics reported above. Applied potentials of at least 1.15 \( V_{\text{RHE}} \) result in increased charge extraction with time, as the majority of electrons are collected.

Figure 5c,d gives, respectively, the normalized optical and photocurrent (without integration) transients for a series of applied biases. We note that increasing bias results in longer-lived optical signals and slower charge extraction kinetics. This could be a result of improved charge separation, although, as mentioned, there is little recombination at these time scales, as most charges are extracted. Alternatively, and more likely, these slower kinetics under stronger anodic bias could result from increased trapping of charges with larger bias, resulting in hindered transport. It is widely acknowledged that WO3 has a large propensity to form electronic defects within the band gap.24,29,56 With the conduction and valence band energies pinned at the electrolyte interface, increases in applied potential could empty, and thus make available for electron trapping, an increasing density of unoccupied shallow defect states within the space charge layer. This would slow extraction, as electrons would encounter a greater number of progressively deeper states with increasing positive bias. This is analyzed further in the discussion section below.

Incident photon to current efficiency (IPCE) measurements were conducted at 1.23 \( V_{\text{RHE}} \) with front and back irradiation to probe whether slow electron extraction is limiting performance (Supporting Information, Figure S5a). With FTO absorption accounted for in both cases, higher efficiencies were obtained when the needles were irradiated from the back (36% vs 22% at 350 nm), with charges generated closer to the extraction point. This correlates with the slow extraction times observed by TDRS and suggests that the small amount of surface or back electron–hole recombination observed (Figure 5) has some effect on performance. The trend in IPCE also agrees with the
relatively large diffusion length of holes (150 nm) in WO$_3$, which has previously been reported to be significantly larger than for other popular metal oxides (e.g., ∼4 nm in α-Fe$_2$O$_3$), sometimes larger than the depletion width.\cite{Ye2008,Chen2014} Since the WO$_3$ needles are ∼100 nm in diameter, holes may readily diffuse to the surface regardless of whether the electrode is irradiated from the front or the back. IPCE data were also collected over longer wavelengths to confirm that any absorption from oxygen vacancies does not contribute to enhanced visible light harvesting (Figure S5b).

**WO$_3$ Modifications.** To aid confirmation of the cause of such slow electron extraction kinetics, various alterations were made to the WO$_3$ needles. The first was to grow shorter needles (2 μm) through modification of the same AA-CVD synthesis.\cite{Stenger2010} As is apparent in Figure 6a, the shorter WO$_3$ needles give a faster optical electron signal decay (blue line) and earlier charge extraction kinetics (dashed lines), indicating that electron extraction is kinetically limited by electron transport through the WO$_3$ needles. Front and back IPCE are more comparable for these shorter needles, as the electron transport distance has been reduced (Figure S6).

The second modification was to anneal the as-synthesized blue WO$_{3-x}$ needles in air for a longer period of time. We already confirmed through XPS that annealing in air reduces the number of oxygen vacancies (Figure S2b vs Figure 1b). Similarly, observations in literature show that the converse approach of annealing under oxygen-poor atmosphere (hydrogen or argon) increases the number of oxygen vacancies,\cite{Bauer2016} which may act as electron trap sites.\cite{Ye2017} Although the nature of any trap sites discussed herein have not been probed directly, it is reasonable to assume that these would be associated with oxygen vacancies as evidenced by our XPS measurements (Figure 1b) and the wealth of data on WO$_3$.\cite{Zhou2014,Stenger2010,Stenger2010b} Figure 6b compares the electron decay of a long needle sample annealed in air at 500 °C for 2 h to one annealed for 12 h, and thus with a reduced population of oxygen vacancies. This subtle change in oxygen vacancy density was determined by an increase in sub-bandgap polaron absorption (Figure S7), as previously reported in the literature.\cite{Stenger2010b,Chen2011,Chen2013} As can be observed, the half-lifetimes of both the TDRS and photocurrent decays are reduced for the sample that was annealed for a longer period of time, consistent with the idea of trap states associated with oxygen vacancies slowing electron extraction.

**Comparisons with Other Transition-Metal Oxides.** We finally compare the kinetics of water oxidation and electron extraction reported herein for WO$_3$ with other transition-metal oxides frequently employed as photoanodes for water splitting.

In Figure 7a, the transient optical signal for water oxidation by surface holes is compared between transition-metal oxides commonly studied as photoanodes for water oxidation. Often considered the kinetic bottleneck of photoelectrochemical water production, the transition-metal oxides show a wide range of rates.

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**Figure 5.** (a) TDR decays at 800 nm and the integrated transient photocurrent at a range of different applied potentials (0.7−1.6 V$_{\text{RHE}}$). (b) The initial magnitude of the optical signal (▲), and the extracted charge measured at 50 ms (■) and at the end of the measurement, 1 s (●). (c) Normalized optical decays shown in (a). (d) Normalized transient photocurrents for the same applied potentials.
splitting, the oxidation of water occurs on the time scale of 100 ms to seconds for titania (TiO₂), hematite (α-Fe₂O₃), and bismuth vanadate (BiVO₄) but is significantly faster for the WO₃ needle sample under similar applied bias. This trend can largely be correlated with the depth of the valence band (Figure 7b), with WO₃ displaying the most positive valence band energy and thus the largest thermodynamic driving force for water oxidation.

We also compared the electron extraction kinetics, observed both optically and by integrated photocurrent transients, of the WO₃ needles studied herein to TiO₂ needles of similar length (Figure 8a).65 Clearly, the electron extraction is much faster for the TiO₂ sample, with a reduction in half-life of the decay from ~20 to ~1 ms. With dense samples for ease of synthesis, Figure 8b gives a similar comparison of charge extraction for WO₃ versus dense TiO₂, α-Fe₂O₃, and BiVO₄. Once again, we observe the slowest extraction times for the WO₃ sample, finding it similar to α-Fe₂O₃, which is known to have low conductivity across such thicknesses when undoped (~500 nm).21,66,67 This strongly suggests that slow electron transport is an intrinsic property of WO₃. As proposed above, this is most likely related to its propensity to become oxygen-deficient, forming vacancies that can trap charges.28,68

## DISCUSSION

In the majority of photoelectrochemical systems examined for water oxidation, the water oxidation reaction itself is considered the kinetically limiting step, whereas the extraction of the majority carrier (electrons) is comparatively fast.10,69,70 However, in this work on WO₃ photoanodes, we find the converse to be true. Direct analysis of the transient photocurrent alongside the correlating optical decay of the electron signal has highlighted the extraction of electrons to be particularly slow, slower than the rate of water oxidation (Figure 3b). Rather surprisingly, we find evidence that holes in these nanostructured samples react faster at the electrolyte interface than for any other transition-metal oxide we have previously investigated (Figure 7a), with an optical half-lifetime under bias of less than a millisecond \((t_{1/2}(h^+) \approx 0.5 \text{ ms})\). Such rapid decay of hole signals in WO₃ has been observed previously by Cristino et al. but was assigned to nonfaradaic oxidation processes rather than water oxidation.39 Water oxidation was confirmed to be the dominant...
oxidation process at the surface of our WO3 needles through oxygen evolution measurements yielding greater than 85% Faradaic efficiency.

The importance of fast water oxidation kinetics is most apparent in the early onset of the photocurrent for this material (Figure 2), requiring a much smaller overpotential for water oxidation compared to α-Fe2O3 and BiVO4.10,76 In the case of α-Fe2O3, it has been suggested that the requirement for overpotentials as large as 0.6 V above flat-band are the result of poor water oxidation kinetics,48,54,72 necessitating the use of cocatalysts to lower the onset potential.46,73,74 In this study, the earlier onset of WO3, presented herein and observed by others,11 correlates with faster water oxidation kinetics. Rapid reaction kinetics at the interface allow an increased proportion of holes that reach the surface to perform useful chemistry over competing back electron–hole recombination processes. This is true for our WO3 nanoneedles without the need for cocatalysts or passivating overlayers. As shown in Figure 7b, the valence band edge is more positive in WO3 than in BiVO4, α-Fe2O3, and TiO2,2,17,19,64,75 which may explain the origin of the faster water oxidation kinetics observed, given the excess thermodynamic driving force then available for the reaction to occur on WO3. This relationship between valence band depth and kinetics has been proposed in other work10,76 and would then suggest that there exists a valence band energy dependence on photocatalytic water oxidation that is analogous to the overpotential dependence often found in electrocatalytic water oxidation systems. The high crystallinity of the sample, the preferential growth orientation of the needles, or effects of pH on the water oxidation mechanism may also contribute to the faster kinetics observed for our WO3, though further investigation on these aspects is beyond the scope of this study.

In stark contrast to the hole kinetics, when a similar comparison is made between WO3 electron dynamics and those of other transition-metal oxides, we find that WO3 displays slower electron extraction (Figure 8). This difference in extraction time is as large as an order of magnitude when comparing TiO2 and WO3 needles and is still evident when comparing the dense films, demonstrating that slow electron extraction is a property of WO3. Considering that good electron conductivity is often presented as a promising feature of WO3,5,14,16 this result was surprising. It suggests that the main benefit of adding WO3 as an electron transport layer in various heterojunctions is to aid charge separation and thus increase charge carrier lifetime, rather than rapidly transport electrons to the contact. Irradiated from the front, we observe that longer WO3 needles have a slower charge extraction than shorter needles (Figure 6a), confirming that the issue is related to transport through the material, rather than interfacial defects at the contact. We propose that this slow electron extraction is due to the trapping of electrons below the conduction band and suggest that the mobility of electrons is thereby reduced. The negative correlation of rate of extraction with increasing anodic bias (Figure 5c,d) supports a trap-mediated transport mechanism. As the anodic bias is increased, an increasing number of progressively deeper states below the conduction band are emptied and thus become accessible to trap photoexcited electrons. With greater applied bias, both the density and the depth of these available electron traps in the space charge layer increases. It follows that the electron extraction is slowed because electrons trap and detraps to reach the back contact, effectively hopping through the needle. This model is consistent with the observation that shorter needles have a faster extraction time, as the distance to the contact is reduced, and so fewer trapping/detrapping steps are required. The fitting of the TDR electron decay to a stretched exponential gives further analytical grounding that supports this transport mechanism, as it indicates the dispersive time range in which electrons are extracted due to multiple trapping steps (Figure S8).77 This trapping and detrapping form of transport has previously been explored with stretched exponential functions or power law decays in other metal oxide-based systems.78,79 It has also been tentatively proposed by Lindquist’s group,30 and is consistent with the presence of interband states in WO3 as confirmed in other studies.29,60 As previously acknowledged, tungsten trioxide has a large propensity to form numerous oxygen vacancy defects.56,58,68,80 It is therefore highly probable that these chemical defects form the interband states responsible for trapping electrons. This is supported herein by the improvement in extraction time observed when the WO3 is subjected to prolonged annealing in air (Figure 6b); with increased opportunity provided for oxygen to permeate the
WO$_3$ structure and fill/remove such oxygen vacancies, longer annealing results in fewer trap sites to hinder the transport of electrons to the contact. Furthermore, the lack of photocurrent in the unannealed sample (Figure S3b) suggests that excessive concentrations of oxygen vacancies trap electrons so strongly and impede the charge carrier mobility to such an extent that most charges recombine. A model of electron dynamics for WO$_3$ needles is summarized in Scheme 1.

As evidenced in the bias dependence study (Figure 5a,b), we find, depending upon applied bias, that the majority of electrons observed on these microsecond to second time scales are eventually extracted, negating the possibility that a slow, trap-mediated recombination is predominantly being monitored. The lack of substantial recombination losses observed in the electron kinetics across these time scales (0.01 ms to 1 s) is supported by consideration of the internal quantum efficiencies obtained for the longer and shorter WO$_3$ needles (Figure S6), which remain similar under front illumination, despite the difference in electron extraction times shown in Figure 6a. Modest back electron−hole (surface) recombination is observed for anodic potentials close to flat-band; however, this is readily removed by applied potentials greater than 1.15 V versus RHE. The lower back electron−hole recombination losses compared to other metal oxide photoanodes such as BiVO$_4$ and Fe$_2$O$_3$ are most likely due to the faster water oxidation kinetics by WO$_3$ holes, as discussed above, which will result in less hole accumulation at the surface under conditions of steady-state photoelectrochemical water oxidation. However, the extensive electron trapping and associated slow electron transport kinetics observed for the WO$_3$ photoanodes studied herein can be expected to lead to internal resistance losses, which will limit the fill factor of the $J−V$ curve in a tandem cell device. Given the relatively efficient electron extraction observed for these WO$_3$ photoanodes, we can conclude that ultrafast bulk recombination is the most probable factor limiting device internal quantum efficiency.

In summary, we have shown our WO$_3$ needles to be rapid water oxidation photoanodes, with high Faradaic efficiency and faster hole injection into the electrolyte than in other commonly studied transition-metal oxide photoanodes. These rapid water oxidation kinetics improve catalytic performance by suppressing competing surface recombination and enabling photocurrent onset close to flat-band without added cocatalysts; we propose that the kinetics correlate with the depth of the valence band. The extraction of electrons, by comparison, is observed to be particularly slow, which we assign to trapping of electrons into vacant defects below the conduction band. We propose that these trap sites are unoccupied oxygen vacancy states which form the primary intrinsic dopants in the material. Annealing for longer in air therefore increased the rate of charge extraction by reducing the number of oxygen vacancies. We thus conclude that the density of intrinsic chemical defects, such oxygen vacancies, can have a significant effect on charge transport through nanostructured WO$_3$, with potential implications for other heavily doped materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b08852.

The SI includes material synthesis, physical characterization, details of electrochemical and optical experiments, as well as XPS, IPCE and UV-Visible absorbance spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

*j.durrant@imperial.ac.uk.

ORCID®

Sacha Corby: 0000-0001-7863-5426
Laia Françàs: 0000-0001-9171-6247
Michael Sachs: 0000-0001-9775-9336
Andreas Kafizas: 0000-0002-2382-4639
James R. Durrant: 0000-0001-8353-7345

Notes
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References
(1) Hurst, J. K. Science 2010, 328, 315.
(3) Roger, I.; Shipman, M. A.; Symes, M. D. Nature Reviews Chemistry 2017, 1, 1.


