Influence of hole transport and thermal reactions in photo-driven water oxidation kinetics on crystalline TiO₂

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Photo-hole-driven and thermal reaction steps during water oxidation on TiO_2 compete, with holes dominating only at low light intensity where their transport is rate controlling.

Key words

Photo-driven water oxidation kinetics, Hole transport, Thermal steps, Reaction rate, TiO2

Abstract

The requirement that photogenerated holes accumulate to drive the rate limiting step is thought to cause slow water oxidation by TiO_2 to form O_2 , however detailed kinetics studies that directly establish the connection between photoabsorption and surface reactions have not been reported.

In this work, we use physically realistic kinetics models of photo-driven water oxidation on TiO₂ to evaluate how hole generation, bulk diffusion, surface mobility and reaction are coupled. The calculations show that hole formation and diffusion in the bulk crystal dominate O₂ formation at low intensity, resulting in an apparent high order dependence of the O₂ production rate on holes. As intensity increases, the water splitting reaction becomes nearly independent of it because of a buildup of intermediates that can only react thermally. Although it is believed that high hole mobility is a requirement for hole accumulation, a comparison of predicted to observed surface species indicates that immobilized holes dominate surface reactivity. The primary surface reaction sites are predicted to involve oxygen atoms that bridge two Ti atoms, supplied with OH formed by water dissociation on Ti sites. Because of the similarity among photocatalytic water oxidation mechanisms on diverse metal oxide semiconductors, which have generally low hole mobilities, the findings from this work may be relevant to them as well. If so, manipulations of hole mobility and accelerating the rate of thermal steps may provide a general pathway for improving water oxidation efficiency.

1 Introduction

The solar photon-driven oxygen evolution reaction (photo-OER) is a half-reaction of the overall water splitting process, in which four absorbed photons are required to form O₂: $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ (1) It is particularly challenging to achieve the high efficiency needed for the overall reaction to be

energetically sustainable due to its multi-step nature.¹⁻³ Some researchers believe that the inefficient utilization of photogenerated holes in photocatalytic and photoelectrochemical water oxidation processes is the root cause of poor efficiency.⁴⁻⁶ Several critical factors have been

identified. (1) High recombination rates between holes and electrons that remove a considerable fraction of photogenerated holes before they can participate in oxidation reactions. (2) Surface defects and impurities that trap photogenerated holes and prevent them from reaching the reaction sites.^{7, 8} (3) Intrinsic material limitations such as low light absorption and poor charge mobility that hinder the effective generation, transport and utilization of holes.^{9, 10} (4) Photodegradation of the photoabsorber caused by unutilized holes, reducing its stability and effectiveness in water splitting.^{11, 12}

There is another factor that can control rates which has not been strongly considered so far for photo-OER: not all reaction steps in the catalytic mechanism involve hole dynamics, depending instead on thermal energy. Key thermal steps include unimolecular decomposition of surface intermediates to release H⁺ and O₂, and bimolecular coupling steps to form the final O-O bond. Those thermal steps can dominate the overall rate of a photo-driven reaction, which has recently been identified in a kinetics modeling study of photo-OER using a molecular dyecatalyst diad.¹³ These considerations raise the question: do thermal steps only affect photo-OER in molecular systems or are they also important on the surfaces of inorganic photocatalytic and photoelectrocatalytic materials? Photo-OER on TiO₂ is a useful model system to address this question because of the extensive literature on it and numerous proposals for favored reaction pathways based on diverse, detailed experiments and theory.¹⁴⁻¹⁷ This literature enables construction of a physically-based and chemically detailed stochastic reaction-diffusion kinetics computational model that can provide insights to factors controlling photo-OER.

Theoretical studies of photo-OER on TiO_2 have examined the mechanism and identified some of the key steps facilitated by holes using their free energies. There are significant differences in the conclusions reached in those works. Liu et al.¹⁸ proposed that O-O coupling occurs via an O⁻ and surface hydroxyl on the same Ti atom at a bridging oxygen site. Imanishi et al.¹⁹ proposed that O-O coupling occurs via surface O and hydroxyl radicals on neighboring Ti atoms via a bridging oxygen site. Wang et al.²⁰ proposed that the water oxidation mechanism proceeds via holes oxidizing negatively charged intermediates and that the mechanism involves 2 parallel pathways beginning at a Ti row or bridging O at the TiO₂ surface. Of these only the study by Wang et al. reports a set of energies that is sufficiently complete to calculate rate coefficients for each step in the mechanism and perform kinetic modeling.²⁰ Their theoretical and microkinetic calculations indicated that the low concentration of photo-holes on TiO₂ limits the efficiency of the OER on TiO₂(110), rather than the intrinsic catalytic activity captured in the reaction barriers. They conclude that enhancing the concentration of surface-reaching holes is the most effective approach to accelerate the rate of photo-OER.

Experimental studies provide additional information on the influence of holes on the reaction. Durrant et al. investigated photo-OER for a series of metal oxides (BiVO₄, anatase TiO₂, Fe₂O₃, WO₃) by transient absorption spectroscopy (TAS),²¹⁻²⁴ which enabled the dynamics of photogenerated carriers leading to water oxidation on these oxides to be investigated.^{25, 26} They revealed a high-order dependence of photocurrent on surface hole density when the hole density is greater than some specific value. This observation led to a proposal that sequential trapping of up to 3 holes directly controls the reaction kinetics. For TiO₂, the relevant hole concentration range is reported to be $0.05 \sim 1 \text{ h}^+\text{nm}^{-2}$, integrating through the entire thickness (1000 nm) of the sample. Studies of the rate of O₂ photodesorption from single crystal TiO₂(110) surfaces during UV illumination by Yates and coworkers provides information on formation and transport of holes to the crystal surface.²⁷ It was found that desorption abruptly increases at a critical photon flux, which was attributed to the saturation of deep hole traps.

In this work we take the mechanism reported by Wang et al.²⁰ and integrate it with a simple 1-D model for single crystal TiO₂ photophysics to simulate the full photo-OER process in this system. We have focused on evaluating the correlation of hole densities and spatial distributions and the extent of hole diffusion on the TiO₂ surface with the overall reaction rate and the kinetics. In particular, we examine the effect of hole mobility at the surface in order to assess whether freely diffusing holes result in different kinetics than holes that are stationary, for example when deep traps (which can be surface polarons) are involved. The results show that the trends with light intensity are complex, with hole formation and diffusion in the bulk crystal dominating the chemistry at low intensity, then becoming nearly independent of light intensity in the upper range where buildup of intermediates that participate in thermal reactions becomes important. Comparisons with experimental observations of a high order dependence of rate on hole concentrations suggest that the TiO₂ structure (e.g. single crystal vs nanocrystal aggregate) may play a role in the apparent kinetics.

2 Model construction and methods

Reaction-diffusion simulations are performed to generate a detailed picture of the state of the light– TiO_2 –water system as a function of space and time. Our simulated structure of surface and bulk crystalline rutile TiO_2 (110) consists of 11 compartments in a 1-D array, as shown in Figure 1(a). This structure assumes that each compartment is well-mixed. The 1st compartment (red layer) is the (110) surface of TiO_2 , where OER occurs, as illustrated in Figure 1(b-c). Its thickness is assumed to be 1 nm, too thin for there to be significant light absorption. The 10 compartments underneath it are pure crystalline TiO_2 , where light absorption, charge carrier diffusion, and charge carrier losses occur. Ideally, a computational model would be constructed

using a complete and self-consistent set of physical data and chemical mechanism details. Such a comprehensive data set is not available for photo-OER on TiO₂, accordingly we have combined data from diverse types of systems as well as made some estimates for this work as described in this section.

A. Chemical reactions on the TiO₂ surface

A detailed reaction mechanism (reaction steps and information for all rate coefficients) for the rutile phase has been reported by Wang et al.²⁰ The anatase phase is used while measuring photo-OER kinetics,²³ however a similarly detailed mechanism has not been reported for that surface. The specific surface structure of these two phases differs, however both contain the same types of atomic arrangements that are important for this reaction, namely TiO_x centers and O atoms that bridge two Ti atoms. Accordingly, we assume that the details of the chemistry on the two phases are the same for the purposes of this study. Figure 2 shows the mechanism, which involves two distinct O₂ generation pathways.²⁰ The alternative mechanisms of Liu and Imanishi et al. are shown in Electronic Supplementary Information (ESI) Figure S1 for comparison.^{18,19}



Figure 1. Details of the reaction-diffusion model framework used in this study. (a) Layout and dimensions of the 1-D model of rutile TiO_2 (110). Schematic showing photoexcitation (yellow dots) followed by charge carrier generation, trapping and diffusion for two models of hole-surface atom interactions, (b) holes move freely from surface site to surface site, where surface sites are either Ti or bridging oxygen (Model 1) and (c) holes are immobile after they are trapped on the surface by an assembly of 2 Ti and 2 O atoms to represent Ti adjacent to bridging oxygen, with a resting state of $O^{2-}_{-}Ti_{-}O^{2-}$ (Model 2).

(a) Pathway I			O-				
$H_2O \rightarrow H^+$	$\begin{array}{c} \mathbf{D}\mathbf{H}^{-} & \mathbf{H}^{+} & \mathbf{O}\mathbf{H} \\ \mathbf{T}i & 2 & \mathbf{T}i \\ \hline \end{array}$	$\xrightarrow{-H^+} \xrightarrow{O^-} \xrightarrow{H^+} \xrightarrow{I_1}$	$\xrightarrow{I}_{0} (0-0)^{2-1}$ $\xrightarrow{I}_{0} I I I -1$ $\xrightarrow{I}_{0} I I I -1$	$\xrightarrow{+\mathbf{h}^+} \xrightarrow{(\mathbf{O}-\mathbf{O})}_{\text{Ti}} \xrightarrow{\mathbf{I}}_{\text{Ti}}$	$\xrightarrow{+\mathbf{h}^+} \mathbf{O}_2 +$	2Ti	
(b) Pathway II O_{br}^{2-} C \downarrow # (7) $#$		$\begin{array}{c} \mathbf{D}\mathbf{H}^{-} & \mathbf{O}\mathbf{H}^{-} \\ \xrightarrow{+\mathbf{h}^{+}} & \mathbf{O}_{\mathbf{b}\mathbf{r}} \\ \hline \textcircled{9} & \overset{\mathbf{h}^{+}}{\#} \end{array}$	$ \begin{array}{c} H & O^{-} \\ \hline & -H^{+} & O_{br} & +H \\ \hline & 0 & & \\ \hline & & & \\ \hline & & & \\ \end{array} $	$\rightarrow O_2 + \# \frac{+H}{(1)}$	$\stackrel{\text{H}_2\text{O}}{} \stackrel{\text{H}_2\text{O}}{\underset{\#}{\overset{-\text{H}}{13}}}$	$\stackrel{+}{\longrightarrow} \stackrel{O_{\rm br}}{\underset{\#}{\overset{-H^+}{}}}$	O _{br} ^{2–}
(c) Rate constants for the 14 steps							
1) 5.88×10 ⁶	(2) 7.42×10 ¹¹	(3) 5.08×10 ⁶	(4) 6.89×10 ⁷	(5) 7.42×10 ¹¹	6 7.42×10 ¹¹	⑦ 7.42×10 ¹¹	
(8) 3.12×10 ⁶	(9) 7.42×10 ¹¹	10 5.37×10 ⁹	(11) 7.42×10 ¹¹	12 2.18×10 ¹⁵	(13) 1.65×10 ⁸	(14) 2.39×10 ⁷	

Figure 2. The photo-OER reaction scheme and rate constants on rutile TiO_2 (110) surface as described by Wang et al.,²⁰ (a) pathway I which involves only Ti atoms, and (b) pathway II which involves bridging oxygens. Ti represents the free site of Ti_{5c} (5-coordinated Titanium) on the Ti row and # represents the free site of O_{vac} on the O_{br} (bridge Oxygen) row. The two pathways are coupled by transfer of OH radicals formed in step 2 to convert bridging O⁻ to bridging OOH⁻ in step 8. (c) Rate constants of each step in (a) and (b). The bold and non-bold texts represent first-order (s⁻¹) and second-order (Lmole⁻¹s⁻¹) values, respectively.

Prior work has emphasized the importance of surface hole mobility in determining the photo-OER rate at a given light intensity. In order to assess the influence of mobility on the chemistry, we have examined two models for photo-OER that both use the full Wang mechanism, shown in Figure 2. One is a well-mixed model (Model 1, Figure 1(b)). In this model, holes reaching the surface diffuse freely so that the kinetics are controlled only by the instantaneous total populations of the intermediates. Holes interact with intermediates on the Ti row and the O bridge. The other is a deep hole trap model (Model 2, Figure 1(c)). In this model, there is no hole diffusion after trapping at surface sites, so the kinetics are controlled by the details of local populations only. In this case the reaction sites are 4-atom clusters with two adjacent Ti atoms each connected to one O atom, represented as O²⁻ Ti Ti O²⁻. Holes are trapped by any of the 4 atoms and remain there. To form O₂ under Model 2, multiple holes are trapped and accumulate near each other. Two possible arrangements are displayed in Figure S2. One is that the two O atoms are located on the same side of the two connected Ti atoms, and the other is that the two O atoms are located on both sides of the two connected Ti atoms. These two models are designed to test the influence of surface hole mobility on the photo-OER process and how accumulation of holes close together in space influences the kinetics. The full reaction mechanism as implemented in the simulations is presented in the ESI Section 2, together with an explanation of the technique used to analyze the results of the simulations.

B. Concentrations of reactants

The total concentration of surface reactive sites is set as 4.15×10^{-3} mole·L⁻¹ for the volume of the 10^{-10} L surface compartment. Assuming 50% of the sites are Ti and 50% of the sites are O_{br}, then the initial concentrations of Ti and O_{br} are set as 2.075×10^{-3} mole·L⁻¹ for

Model 1. Since each $O^{2-}_{Ti}_{Ti}O^{2-}$ cluster in Model 2 has four reactive sites, the initial concentration of it is 25% of surface reactive sites, which is 1.0375×10^{-3} mole·L⁻¹.

C. Light absorption, charge carrier generation, diffusion and recombination

Holes and electrons are generated by absorption of light in bulk TiO₂, shown in Figure 1 as a set of 10 30 nm thick gray layers. The incident light intensity range modeled in this work is $1 \times 10^{11} \sim 1 \times 10^{18}$ photons \cdot cm⁻²s⁻¹, corresponding to $5.79 \times 10^{-5} \sim 5.79 \times 10^{2}$ mW \cdot cm⁻². This overlaps the light intensity range used in experiments and extends it to lower and higher intensities to examine trends. The total thickness of these compartments is 300 nm, which is the $1/e^{2}$ absorption depth of 365nm light. The Beer-Lambert law is used to calculate the rate coefficient for photocarrier formation in each compartment (ESI sections 3 and 4) using an estimated reflectivity of $20\%^{28-31}$ and absorption coefficient α of 10^4 cm⁻¹.^{23, 32}

Each photoabsorption event generates one electron and one hole. The charge carriers diffuse between compartments with a rate given by Fick's law, and irreversibly escape into bulk TiO_2 from the lowest compartment. Charge carrier diffusion coefficients of 1.35×10^{-3} cm²s⁻¹ for electrons and 10^{-5} cm²s⁻¹ for holes are taken based on the estimation from theoretical studies by Deskins and Dupuis.^{33, 34} In those studies, the hole diffusion coefficient varied with crystallographic orientation. Due to the differences in TiO_2 characteristics, there is no clear signature that enables us to choose a value of the hole diffusion coefficient via comparison to the experiments. However, the calculations indicate that a hole diffusion coefficient between 10^{-5} and 10^{-7} cm²s⁻¹ is a reasonable value. We performed a limited set of parallel calculations using both values, which showed that they yield similar trends in the simulation results except for the very lowest light intensities (ESI Section 4 and Table S2). We have chosen the larger value, and

do not believe that this choice has a significant impact on the conclusions we have drawn from our kinetic study.

D. Incorporation of defects and traps

The TiO₂ modeled in this study is assumed to be a perfect undoped single crystal, free of defects. While this is an unrealistic assumption, it is the simplest possible assumption for these simulations since few details are available on the TiO₂ materials used for experimental studies. We have made some limited calculations assuming that trapping of holes by defects leads to recombination and hole losses. The trap density is set as 10¹⁸ cm⁻³, as was estimated by Yates.²⁷ (ESI section 3) In our mechanism, holes are trapped by these defects. Trapped holes will undergo first-order recombination with the arriving electrons. Here, the concentration of trapped holes is assumed to be constant so it is first-order recombination. Those holes that are not trapped will undergo second-order recombination with electrons. We also examine the case where defects can trap electrons, undergoing first order recombination with arriving holes.

E. Computational methodology

The reaction-diffusion reactions were simulated using Kinetiscope,³⁵ an open-access stochastic chemical kinetics program. The stochastic method is well-suited for multiscale simulations that connect molecular-level events to experimental observables because it can accommodate a great deal of detail and very wide dynamic range of instantaneous rates.³⁶⁻³⁸ This allows a direct connection between photophysical processes such as charge carrier formation and the slower catalytic kinetics to be made. The kinetic simulation results provide information on populations of all species in the system as a function of space and time. When accurate processes

and rate coefficients are employed, stochastic chemical kinetics simulations have the advantage of producing an absolute time base for direct comparison to experimental data.

The reaction mechanisms for charge carrier generation and transport and for photo-OER are input as a set of reaction or diffusion steps, each having a reaction rate coefficient. All species in the system are represented by particles, each of which represents an amount of material within the simulation volume, and therefore a concentration. Concentrations and rate coefficients are used to calculate the instantaneous rates of every step, and these rates are a measure of the probability of that step taking place. Random numbers are used to select among probability-weighted events, and the total of all the probabilities is used to calculate the associated time step. After event selection, reactant and product concentrations are updated, and the reaction rates for each step are recalculated in preparation for a new event selection cycle. An advantageous feature of this method is the ability to incorporate non-chemical marker species into the mechanistic steps (ESI Section 2). These markers do not influence the kinetics, but do offer a way to examine the simulation results in greater detail than is possible using concentrations of chemical species alone. These markers can be used to count the occurrences of particular steps leading to the same products, for example, and the derivative of the cumulative marker quantities as a function of time can be used to determine the rates of those steps.^{13, 39-42}

3 Results and discussion

A. Overall photo-OER rates and photogenerated hole populations

According to Equation (1), four H^+ must be produced for every O_2 in simulations of both models to match the stoichiometry of the water oxidation process.¹⁹ This is indeed found as shown in ESI Table S3. The hole photocurrent is assumed to be only due to consumption of

holes in the catalytic reaction, and is calculated from $4 \times dO_2/dt$, where dO_2/dt is the steady-state generation rate of oxygen for each set of simulation conditions. At this point, all the species in the reaction have reached steady states, and the species concentrations as a function of time are shown in Figures S4 and S5.

The calculated hole concentrations and hole photocurrents as a function of light intensity for the range of $5.79 \times 10^{-5} \sim 5.79 \times 10^2$ mW·cm⁻² are shown in Figure 3(a). The hole concentrations are in units of h⁺nm⁻², as has been conventionally done in prior studies.²³ Here, nm² refers to sample geometric surface area, and includes the holes formed as a function of light absorption depth in the underlying crystal. In both Model 1 and Model 2 the hole photocurrent increases with increasing light intensity and then reaches saturation. The hole photocurrent generated by Model 2 is significantly larger than that of Model 1, reaching a value 30 times higher at 100 mW·cm⁻² and above. This is a consequence of specific reaction steps as will be discussed below. The total hole concentrations in the bulk crystal overlap above about 1mW·cm⁻² under both models, and continue to increase as the light intensity increases without reaching saturation, indicating the identical characteristics of the two models at this light range.

The data in Figure 3(a) are replotted to show the relationship between hole photocurrent and hole concentration in Figure 3(b), where each point corresponds to a specific light intensity. Both models show distinctive regimes. In the low total hole concentration region, the hole photocurrent increases sharply with increasing light intensity. Around 2×10^{-4} h⁺nm⁻² there is an abrupt transition in slope, with the hole photocurrent increasing more slowly as the hole concentration increases, eventually reaching saturation despite the significant increase in hole availability. There are also differences in trends between the 2 models. In the low light intensity region, Model 1 exhibits a negative slope, and Model 2 has a positive slope. This feature is the result of differences in the competition between hole trapping, surface diffusion and accumulation in these models. In Model 1 surface hole diffusion leads to formation of abundant oxidized surface species but can slow the process of accumulating oxidizing equivalents to form precursors to O₂ formation. Facile hole diffusion leads to steady state being established at a lower light intensity with a lower saturation hole photocurrent than found for Model 2. Model 2, on the other hand, constrains how oxidizing equivalents are accumulated, and this constraint strongly affects the overall kinetics.



Figure 3. Overall hole concentrations and their connection to the predicted hole photocurrent calculated from the O_2 production rate, all at steady state. (a) Total photocurrent and hole concentrations as a function of light intensity for Models 1 and 2. (b) Photocurrent as a function of hole concentration for Models 1 and 2. Apparent reaction order as a function of hole concentration calculated from equation 2 for (c) Model 1 and (d) for Model 2. The enlarged points in (b)-(d) correspond to the light intensity range marked using the dashed lines in (a). To facilitate comparison with the experiment, 0.016 h⁺nm⁻²s⁻¹ is equal to 1 mA·cm⁻².

The photogenerated hole and electron spatial distributions at steady state for Model 1 are shown in Figures 4 and 5, and those for Model 2, which are essentially identical, are presented in ESI Figures S6 and S7. At lower light intensity, most of the holes diffuse up into the crystal surface, driven by the concentration gradient formed by the surface reactions. The photocurrent from O₂ production changes very quickly as the intensity increases because holes are populating only one part of the system. As the light intensity increases, the population of holes in the full volume of the illuminated TiO₂ increases. The heat maps of hole and electron concentrations clearly show how the distribution of carriers changes with depth and light intensity. The electron distributions shown in Figures 5 and S7 are uniform and their populations are about 1% of the corresponding sub-surface (bulk) hole population.



Figure 4. (a) Photogenerated hole concentrations as a function of depth and light intensity for Model 1. Hole concentrations as a function of time and depth below the TiO₂ surface for light intensities of (b) $5.79 \times 10^{-4} \text{ mW} \cdot \text{cm}^{-2}$ (c) $2.7 \times 10^{1} \text{ mW} \cdot \text{cm}^{-2}$ and (d) $5.79 \times 10^{2} \text{ mW} \cdot \text{cm}^{-2}$.



Figure 5. (a) Photogenerated electron concentrations as a function of depth and light intensity for Model 1. Electron concentrations as a function of time and depth below the TiO₂ surface for light intensities of (b) $5.79 \times 10^{-4} \text{ mW} \cdot \text{cm}^{-2}$ (c) $2.7 \times 10^{1} \text{ mW} \cdot \text{cm}^{-2}$ and (d) $5.79 \times 10^{2} \text{ mW} \cdot \text{cm}^{-2}$.

The data in Figure 4 help to explain the trends seen in Figure 3. Such trends, especially those for the apparent reaction order in Figures 3(c) and 3(d) are often interpreted as evidence of a change in surface reaction mechanism as a function of light intensity. We wish to emphasize that all simulations were performed using a single mechanism as described in ESI Section 2. Here, the change in apparent order reflects only the strong variations in photo-generated hole distributions as a function of light intensity. Because of the photo-OER reaction occurring on the

surface, holes are consumed rapidly and the large concentration gradients shown in Figure 4(a) promote hole diffusion toward it. Small changes in light intensity therefore have a large effect on the surface reaction rate.

The observation for both models that there are different photocurrent regimes with light intensity is consistent with Yates et al.'s analysis of the photodesorption rate of O_2 from TiO₂. In their work, O_2 is formed from the decomposition of the oxide caused by second-order recombination of photogenerated electrons and holes.²⁷ They observed both slow and fast O_2 photodesorption, with an abrupt transition between the slow and fast rates occurring as light intensity increased. They interpreted the transition point (approximately 0.01 mW·cm⁻² estimated from the reported incident photon flux) as a signal that hole traps are saturated in the TiO₂ crystal. In the present simulations, at this incident power density the overall photocurrents in both models are just starting to transition from their low light intensity to their higher light intensity trends (Figure 3(b), 1~10 h⁺nm⁻²s⁻¹).

The surface hole concentrations shown in Figure 4 are around 10^{17} h⁺cm⁻³ for both models and do not change much with changes in light intensity. Beneath the surface, bulk hole concentrations decrease with increasing depth because of light attenuation at each light intensity, and increase overall with increasing light intensities. We can calculate the absorbance of surface and bulk holes in Δ mO.D. (ESI section 4, Figure S3, Table S2) using the absorption coefficient reported by Durrant et al. for comparison to their measurements.²³ As shown in ESI Figure S3(a) we find that the calculated hole concentrations are about 1000 times lower for a given light intensity than the measured ones. ESI Figure S3(b) shows the calculated absorbance in Δ mO.D. is 1 to 2 orders of magnitude smaller and increases more rapidly than the experimental results. The experimental absorbance starts to flatten with intensity at 28 mW·cm⁻² while the simulated

absorbance continues to increase. This suggests that there are many more holes present in the experimental sample than is predicted by the simulations for a perfect crystal, and that their population reaches a maximum as a function of light intensity.

Each photoabsorption event produces electrons and holes in equal number, and both carriers diffuse freely throughout the system with a rate given by Fickian diffusion kinetics. The main sink for holes is the reacting surface, while the main sink for electrons is at the bottom of the simulated crystal from which they are lost by diffusion away from the illuminated region. We can examine the calculated electron flux for comparison to the measured photocurrent to Durrant's paper²³ because the loss rate of electrons by diffusion is what would be measured as a current extracted by the applied potential. We compare the measured photocurrent at 57.9 $mW \cdot cm^{-2}$ to the electron flux calculated using this intensity from simulations with two hole diffusion coefficients, 10^{-5} cm²s⁻¹ and 10^{-7} cm²s⁻¹. The calculated electron flux is 77 e⁻nm⁻²s⁻¹ (1 mA·cm⁻²) when the hole diffusion coefficient is 10^{-5} cm²s⁻¹, and 17 e^{-1} mm⁻²s⁻¹ (0.27) $mA \cdot cm^{-2}$) when the hole diffusion coefficient is $10^{-7} cm^2 s^{-1}$. This net flux reflects the balance between formation, diffusion, accumulation in the solid and loss to recombination. Both of these values are close to the experimental photocurrent value of 25 $e^{-nm^{-2}s^{-1}}(0.5 \text{ mA} \cdot \text{cm}^{-2})$ at the same light intensity,²³ and much smaller than the photocurrent calculated from the simulated O₂ production rate (about 9 mA \cdot cm⁻², ESI Table S2). This large value reflects the fact that holes segregate to the surface and drive a high reaction rate there. In the experiment, a potential is applied so that all electrons can be collected. In the calculations, there is no way to lose electrons and it is possible that the ~ 10 times lower experimental current density is attributable to unrecognized inefficiencies in the measurements. In sum, the simulations indicate that the electron currents and the O₂ production currents are not necessarily equivalent because of the

multiple factors influencing them, which will be discussed in more detail at the end of this section.

The data in Figure 3(b) can be analyzed for comparison to experimental observations using the rate law proposed by Durrant et al.:²⁴

$$J^{\rm ph} = k_{\rm WO} (h_{\rm s}^{+})^{\alpha}, \tag{2}$$

where J^{ph} is a photoelectrochemical assay of the flux of water oxidation with the unit of $h^+\text{nm}^{-2}\text{s}^{-1}$, h_{s}^+ is the surface holes concentration with the unit of $h^+\text{nm}^{-2}$, α is the apparent order of the reaction with respect to the hole concentration and k_{WO} is the corresponding effective water oxidation rate constant in the unit of $\text{nm}^{2\alpha-2}$ s⁻¹. From this equation,

$$\log J^{\rm ph} = \log k_{\rm WO} + \alpha \log h_{\rm s}^+ \tag{3}$$

and, rearranging,

$$\alpha = \log J^{\rm ph} / \log h_{\rm s}^+ \tag{4}$$

The apparent reaction order α is shown in Figures 3(c) and (d). In general, α is extremely large at low light intensities, gradually decreasing to a value of ~0 when high light intensity is high (the O₂ production rate reaches saturation). A reaction order of 2~3 occurs for both models in a narrow intensity range, where hole concentration is in the range of $2 \times 10^{-4} \sim 4 \times 10^{-4}$ h⁺nm⁻². The data in Figures 3(c) and (d) are quite different from experimental results that showed a constant apparent reaction order of 2~3 over the range of 0.27~57.9 mW·cm⁻².²³ Specifically, over the range of hole densities examined (0.05~1 h⁺nm⁻²), a third-order dependence was observed in alkali electrolyte, while a second-order dependence was observed under both neutral and acidic conditions. However, in the calculations far fewer holes are present in the TiO₂ bulk during the water oxidation reaction than are observed experimentally²³ and the apparent high order rate dependence occurs at much lower light intensities. This suggests that the physical properties of the samples studied in the experiments have a very different influence on the chemistry compared to perfect crystals.

There are several possible factors responsible for the overall difference in photo-OER kinetics between calculations and experiments.

1. In the experiments, oxygen vacancies resulting in n-type character provide abundant hole traps and excess electrons that contribute to overall charge carrier populations. This conclusion can be directly assessed. In our calculations, we only consider the charge generated by light and ignored the electrons generated by doping – their populations will be low at the surface of an n-type semiconductor. As a test, we introduce traps with a concentration of 1×10^{18} cm⁻³ (in the range estimated by Thompson and Yates²⁷), and simulate photo-OER at three selected light intensities to study how charge carrier recombination at the defects affects the chemistry. The results are shown in ESI Table S4, which demonstrate that the concentrations of the three types of surface holes and the generation rate of O₂ do not change significantly when defects are specifically introduced. Also shown in ESI Figures S8 and S9 is the location of recombination events as a function of depth below the surface for both models calculated by experimental data. The fraction of holes lost near the surface is negligible for the first-order recombination (holes lost by recombination with trapped electrons) and second-order recombination. Only loss of trapped holes to first order recombination with electrons is significant, with the highest probability (~8% of all holes) at depths of 150-250 nm and only a few recombination events (~2%) at the surface. The above results show that recombination at defects does not have a large influence on hole concentrations and photocurrent at the surface.

- 2. Experimentally, hole absorbance as a function of light intensity increases much faster than the corresponding photocurrent, indicating that there is hole accumulation in the sample overall.²³ In addition, a higher light intensity is required for the transfer of holes from the bulk to the surface for chemical reactions. The regime that is not intensity dependent is predicted by the calculations but not observed experimentally. The reason for higher hole concentrations must be connected to sample properties but how is not clear. One possible explanation is that the polycrystallinity of the samples used in the experiments can result in significant internal scattering that will increase light absorption relative to perfect crystals. This has been identified by simulations of dye photophysical measurements on both ZrO₂ and TiO₂ photoanodes for dye-sensitized solar cells.³⁹
- 3. Because we assume an ideal sample, the influence of band bending on charge populations is not directly included. The thickness of space charge layer is estimated as 20 nm in experiments, but this is likely to be higher as potential increases.²³ However, it is unclear what a space charge layer width means for a sample whose surface rms roughness is ~20 nm on top of ~10 nm rms rough FTO. How the space charge layer evolves under illumination must be connected to the population changes shown in Figures 4 and 5, but further comparisons are not possible without modeling more realistic crystals.

Although there are significant differences between the experimental and calculated results, we do observe a regime in the perfect crystal where apparent higher order kinetics appear. It is not caused by the holes at the surface, but by the distribution of the holes in the bulk. There is no evidence that the kinetics are governed by steps of higher order dependence on holes involving surface reactive sites.

B. Surface hole populations

Three types of holes are tracked in our model: surface free holes, surface trapped holes, and bulk holes. Total hole populations are shown in Figure 4, and the concentrations of specific types of surface holes as a function of light intensity are shown in Figure 6. In Model 1 (Figure 6(a)), the total concentration of trapped holes on the surface, which are the Ti-OH and Ti-OO⁻-Ti intermediates in the photo-OER reaction, gradually decreases by 1.5×10^{17} h⁺cm⁻³ as the light intensity increases. This reflects the shift in populations of reactive intermediates on the surface from hole traps to species that can only react thermally, as discussed in section D below. At the same time, the concentrations of bulk holes and surface free holes increase. The concentration of the bulk holes is about 1 order of magnitude higher than that of surface free holes, where the concentration of bulk holes is the sum of the steady-state hole concentration of the 10 bulk layers (entire sample 300 nm) as shown in Figure 4. Similar trends are found for Model 2 (Figure 6(b)).



Figure 6. Calculated concentrations of three types of holes as a function of light intensity, (a) Model 1 and (b) Model 2.

Our simulations cover the light intensities from very low to high, forming a detailed picture of the relationship between photocurrent (O₂ production rate) and hole concentrations. A higher order dependence as observed experimentally appears in a narrow range of light

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intensities (Figure 3(b)). The mechanistic origin of a higher order dependence can be evaluated using the simulations. One possibility is that the photocurrent depends on specific hole populations involved in well-defined reaction steps, including the trapping species Ti-OH and Ti-OO⁻-Ti, with an overall apparent high order. Plots of the relationship between the concentrations of the three types of holes and photocurrent (ESI Figure S10) show primarily a first-order dependence, however.

C. Competition between Ti and bridging oxygen catalytic pathways as a function of hole mobility

As shown in Figure 2, there are two pathways that can produce oxygen. Using the simulated photocurrents for each pathway, we can distinguish their contributions to the total photocurrent in Models 1 and 2 as shown in Figure 7. In Model 1, pathway I contributes most of the photocurrent (99.75%), and pathway II only accounts for 0.25%: pathway I is favored when surface hole diffusion is fast. Because pathway II requires transfer of OH radicals formed in pathway I, the dominance of pathway I indicates that the OH transfer process between 2 surface sites (Ti and bridging O) is sluggish. If, however, there is no surface hole diffusion as assumed in Model 2, pathway II produces much more photocurrent than pathway I with a transition to 98.5% of the total photocurrent at high light intensity. This is a consequence of requiring that hole trapping involves adjacent sites, so that the coupling between steps 2 and 8 looks much more like a unimolecular rearrangement than transfer of a free OH. We can compare this finding to the microkinetics simulation results of Wang et al.²⁰ using the same photo-OER mechanism and assuming only mobile surface holes, similar to our Model 1 but without including the TiO₂ photophysics. While the overall trend in reaction rate with hole concentration is similar to ours (Figure 3(a)) including a transition to a plateau in rate around 10^{-4} h⁺nm⁻², their predictions

regarding the balance between pathways I and II are different. They predict that the competition between the two parallel pathways depends on the hole concentration in TiO₂, with pathway I dominating at low hole concentrations, and pathway II occurring at a similar rate to pathway I at high hole concentrations. Looking at Figures 3 and 4, it is clear that the surface concentration of holes is nearly constant as a function of light intensity at a value of about 10⁻⁴ h⁺nm⁻², as opposed to the total concentration of holes in the system which does vary. We predict that under Model 1 pathway I is strongly dominant under all light intensities, in good agreement with the value of about 100:1 found by Wang et al. for our predicted surface hole concentration.²⁰ It is clear that kinetic modeling of photo-driven systems must be done with care because the influence of charge carrier transport may not always be neglected.



Figure 7. The fraction of photocurrent in the two pathways for Models 1 and 2.

D. Surface intermediate populations and reaction pathways

The simulations generate a complete time history of all surface species present during the reaction for both Models as shown in Figure 8. In pathway I of Model 1, the concentrations of Ti-O⁻, Ti-OH and Ti-H₂O increase sharply with the increase of light intensity at first, then

transition to near-constant values when the light intensity is greater than 1 mW·cm⁻². In contrast, the concentrations of the three species Ti-OH⁻, Ti-OO⁻-Ti, and Ti-OO²⁻-Ti continually decrease as light intensity increases. The concentrations of these species vary widely, from 10^{-8} to 10^{-3}



Figure 8. The populations of different intermediates under the entire studied range of light intensity in mole L^{-1} , where the surface volume is considered to be a surface region with a 1 nm thickness: (a) Model 1 Pathway I, (b) Model 1 Pathway II, (c) Model 2 Pathway I, and (d) Model 2 Pathway II.

mole·L⁻¹. In pathway II of Model 1, the concentration of #-O_{br}⁻ is by far the dominant species on the surface and does not change with light intensity. This species is also a major intermediate under Model 2, however #-O_{br}OH⁻, #-O_{br}O⁻ and #-O_{br}²⁻ are also important. The predicted intermediate distributions can be compared to experimental observations of infrared absorptions during photo-OER on TiO₂ in contact with aqueous base. Assignments for the peak at 838 cm⁻¹ peak is Ti-OOH and the shoulders at 928 and 812 cm⁻¹ are surface peroxo and Ti-OO-Ti respectively.⁴³ A report for this reaction at neutral pH by Roberts et al.⁴⁴ note that the spectrum is pH-dependent, and that the 812 cm⁻¹ feature is not present in pure water, which is the simulation condition used here. They assign the band at 838 cm⁻¹ (834 cm⁻¹ in their measurements) to the O-O stretch of an adsorbed Ti-OOH⁻ species. This assignment is consistent with our prediction of a buildup of this intermediate under Model 2, pathway II (Figure 8(d)), and suggests that less mobile surface holes may dominate the overall reaction. Wang et al. assigned the peak to a Ti-OO⁻ species in pathway I.²⁰ In our simulations this species is also present in Model 1, however only at low light intensities. We have calculated total coverages of oxo, peroxo, superoxo, hydroperoxo and hydroxy intermediates as a function of light intensity from the simulation results as shown in ESI Table S5 and Figure S11.

The rates of different types of reactions for Model 1 and Model 2 are shown in Figure 9, including proton loss, hole trapping, and thermal reactions such as O-O coupling, OH radical transfer and O₂ release. The rates of these processes track the overall photo-OER rate as shown by the hole photocurrent in Figure 3. Proton loss to form a negatively charged product is the fastest process under all conditions, followed by hole trapping by Ti-OH⁻ in pathway I. All other reactions have nearly equal rates and are uniformly slower than proton loss. By themselves, the rates do not provide clear information on which reaction steps most strongly influence the overall photo-OER rate or why the photo-OER rate saturates with light intensity. Consideration of the populations of intermediates in Figure 8 provides insight. They show that the intermediates that build up in pathway I are ones that need a hole to react at low light intensity, and ones that must undergo a thermal reaction at high light intensity e.g. TiO⁻-TiO⁻ coupling and loss of OH from Ti-OH. Adsorbed water becomes an important surface species, indicating that heterolytic

dissociation of it to form a proton and Ti-OH⁻ is also relatively slow at high light intensity. Under pathway II, #-O_{br}⁻ dominates at all light intensities for both models. This is because it can only react if an OH radical is supplied to it. In Model 1, which is well-mixed, this is a secondorder reaction that depends nonlinearly on reactant concentrations. In Model 2, OH transfer is a unimolecular rearrangement, which has more favorable kinetics. Indeed, pathway II is dominant for Model 2 because of relatively facile OH transfer to a bridging O⁻. The buildup of #-O_{br}⁻ indicates that formation of that species is faster than the OH transfer step at any hole mobility condition however. Roberts et al. have noted that loss of a proton from surface Ti-OOH intermediates, which is a thermal process, is a slow step that controls the overall rate of reaction.⁴⁴ The present work provides additional evidence that thermal processes are very important, and provide additional insights to how they are involved in this complex mechanism.



Figure 9. The rates of different reaction processes under the entire studied range of light intensity: (a) Model 1 Pathway I, (b) Model 1 Pathway II, (c) Model 2 Pathway I, and (d) Model 2 Pathway II.

It is interesting to compare the kinetics predictions to the thermodynamics study of the influence of photogenerated polarons on OER on TiO₂⁴⁵ using a mechanism significantly simplified compared to that of Wang.²⁰ In that study they found that polarons stabilized surface O, OH and OOH intermediates, with the OOH stabilization proposed to significantly reduce the overpotential required to drive the reaction on Ti active sites. As discussed above, a buildup of OOH-type intermediates is consistent with infrared measurements.⁴⁴ Model 2 most closely mimics the influence of polarons by forcing holes to be stationary once they are trapped by surface species, and the influence of the polarons can be assessed by comparison to Model 1. The kinetics simulations predict a buildup of hydroxo species via the Ti pathway (Pathway I) at low light intensities, whose concentrations in both models are similar (ESI Figure S11). The concentration of Ti-peroxo species from Pathway I declines rapidly at higher light intensity. Because the hydroperoxo species only builds up in bridge oxygen pathway (Pathway II), its concentration is much higher in Model 2. This buildup reflects an imbalance between hole trapping rates across both catalytic pathways. Increasing light intensity (hole formation rate) in Model 2 shifts the overall OER reaction to bridge sites (Figure 7) because hole trapping by Ti-OH⁻ to form Ti-OH (which loses OH to a bridge O site) becomes highly favored (Figure 9). This process is not favored in Model 1, in which formation of TiO⁻ and continued reaction along pathway I dominates. As the light intensity increases, the ratio of the photocurrent generated by pathway II of Model 2 to the photocurrent generated by pathway I of Model 1 increases from 1.8 to 30, as shown in ESI Figure S12. These kinetics reveal that a polaronic-type environment, where holes are not very mobile, significantly accelerates the overall photo-OER reaction rate relative to highly mobile holes. Examination of the Model 2 mechanism indicates that this

acceleration is attributable not to the presence of immobilized holes per se, but to the fact that reactants in thermal processes are adjacent to one another. The increased rates of thermal processes such as TiO⁻ coupling and OH transfer involve entirely local rearrangements rather than stabilization of intermediates. It would be of great interest to extend the thermodynamics analysis of the role of polarons to a kinetic one applicable to photocatalysis where there is no formal overpotential in order to understand in greater detail how polarons influence surface reactivity beyond whether or not they can diffuse.

4 Conclusions

This work provides a comprehensive photo-OER kinetics investigation on crystalline TiO₂ surfaces through a reaction-diffusion kinetic model. Our findings show that while the OER necessitates the accumulation of multiple oxidizing equivalents, the process does not exhibit a higher-order rate dependence on hole concentration, as the holes arrive sequentially. This nuanced understanding challenges the conventional interpretation of rate laws, highlighting the critical need for caution when extrapolating apparent rate laws to the microscopic processes that govern complex reactions such as OER, especially those involving coupled reaction-diffusion phenomena. Under low light intensity, hole formation and diffusion within the bulk crystal predominantly drive the reaction. However, as light intensity increases, the reaction becomes nearly independent of light intensity due to the buildup of intermediates requiring thermal activation to proceed. This shift in reaction kinetics underscores the importance of thermal steps, which have often been overlooked in studies focusing solely on photogenerated carriers. A controlling influence of thermal processes on a photo-driven reaction has also been identified in a computational study of a very different system, the dye-catalyst diad for water oxidation¹³ and may be more common than currently appreciated. The localized accumulation of immobilized holes has a higher OER rate than holes that are free to diffuse, making them the principal contributors to surface reactions in situations where hole mobility is restricted. This suggests the necessity of considering hole immobilization in any realistic model of catalytic processes on TiO₂.

Our study addresses three of the four factors noted in the Introduction that lead to the inefficient utilization of photogenerated holes. (1) Although it has been proposed that high recombination rates between holes and electrons can remove a considerable fraction of photogenerated holes before they can participate in oxidation reactions, this is not found in the simulations. Using the experimentally reported recombination rate coefficients, we find the losses of holes are very low with at most 8% recombined in the crystal bulk and even lower at the surface. This indicates that the losses do not significantly compete with the surface chemistry. (2) Surface defects and impurities have been proposed to trap photogenerated holes and prevent them from reaching the reaction sites. We have found that the introduction of bulk defects into the model has little or no effect on the hole concentration and surface hole photocurrent. There are many hole traps (Ti sites and bridge oxygen sites) all over the surface; it is unclear what other types of defects would be important and further information on their kinetic properties would be valuable. (3) Intrinsic material limitations such as low light absorption and poor charge mobility are thought to hinder the effective generation, transport and utilization of holes to the TiO₂ surface. In fact, the present work reveals that the low mobility of holes on the surface promotes a high reaction rate. At very low light intensities, where holes collect preferentially at the surface, bulk hole transport is indeed rate controlling. This research provides new insights into the fundamental mechanisms of photocatalytic water splitting on TiO₂. Because of the similarity of the photo-OER chemistry across metal oxide catalysts, the findings from this work may also apply to them. By careful management of the interplay between charge carrier dynamics in the semiconductor and thermal processes, it may be possible to improve their photocatalytic water splitting performance.

Data availability

The data supporting this study is available within the main text, associated ESI and Zenodo (https://zenodo.org/records/13324071).

Author contributions

Conceptualization: FAH. Investigation (calculations): PW, GB, FAH. Formal Analysis, Validation, Visualization, Writing: all authors. Funding acquisition: FAH.

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Conflicts of interest

There are no conflicts of interest to declare.

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