# Charge Transfer Dynamics in Aqueous Dye-Sensitized Photoelectrochemical Cells: Implications for Water Splitting Efficiency

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**Supporting Information** 

**ABSTRACT:** Water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) utilize molecular species for light-harvesting and water oxidation in order to store solar energy as hydrogen fuel. To engineer these devices for better performance, research has centered around suppressing charge recombination at the semiconductor-sensitizer interface and developing better catalysts for water oxidation. Yet it remains quantitatively unknown how much DSPECs can benefit from these improvements. We use a simplified photoanode process to model the charge transport dynamics in DSPECs under surface reaction-limiting conditions. By combining intensity-



modulated photocurrent spectroscopy (IMPS) and numerical simulations, we explore in detail how electron transport and recombination rates as well as the sensitizer regeneration rate affect the steady-state photocurrent and the charge carrier concentration distribution. Numerical simulations confirm that fast electron diffusion in the semiconductor, a slow interfacial charge recombination rate, and rapid catalysis of water oxidation can improve the incident-photon-to-current-efficiency of DSPECs. The benefit, however, is largely compromised by the low charge injection efficiency, a problem that has not yet been fully appreciated. These simulations indicate that the best-known water oxidation catalysts are already adequate and that improvements in light harvesting and injection yields are the most important challenges for designing higher-performance WS-DSPECs.

# INTRODUCTION

Water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) integrate wide band gap semiconductors with molecular components to achieve solar-to-fuel conversion.<sup>1-3</sup> The introduction of molecular species offers great flexibility in the design of light absorbers and catalysts, and in principle, the same thermodynamic limit of ~32% efficiency of semiconductor-based solar-fuel systems also applies to WS-DSPECs.<sup>4</sup> However, the best reported WS-DSPECs perform far below this limit.<sup>5</sup> Although catalysis of the kinetically demanding four-electron oxidation of water is responsible for part of the energy loss, a more significant energy penalty arises from the low quantum yield of the photoanode, which results from recombination processes during charge collection.<sup>6</sup> A quantitative analysis of the electron transport and recombination processes in WS-DSPECs is therefore important for understanding the practical limits of efficiency and optimizing device performance.

Through a series of photoelectrochemical and transient spectroscopy experiments, we have previously explored and established a kinetic framework for understanding the transient photocurrent behavior of WS-DSPECs. Using rate constants derived from transient photovoltage decay experiments, Swierk et al.<sup>7</sup> constructed a kinetic model that was able to fit the

photocurrent-time behavior in a typical WS-DSPEC chronoamperometric experiment. The model points out that, as the photocurrent decays (over a period of tens of seconds), the concentrations of oxidized dye molecules and trapped electrons slowly increase, eventually reaching a photostationary state. However, this simple model did not include the electron transport and recombination properties in the TiO<sub>2</sub> mesoporous network, which are known to govern the performance of conventional power-generating DSSCs (dye-sensitized solar cells). The dynamic response of DSSCs, including photoelectron generation, electron diffusion in TiO<sub>2</sub>, and electron recombination with nonaqueous redox shuttles, has been explored extensively in DSSCs by intensity-modulated photocurrent spectroscopy (IMPS).<sup>8-10</sup>

In IMPS, a sinusoidal modulation of light intensity is superimposed on the steady-state light illumination. This induces photocurrent modulation in the photoelectrode. The phase shift caused by charge transport processes conveys information about electron diffusion and recombination rates. While IMPS has brought significant advances to our

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fundamental understanding and to the optimization of DSSCs, it has not yet been applied to WS-DSPECs. In DSSCs, the competition between electron diffusion in TiO<sub>2</sub> and electron recombination with the oxidized redox mediator (such as  $I_3^{-}$ ) determines the overall efficiency. In contrast, the water oxidation reaction, because of its slow kinetics, is typically the limiting factor in WS-DSPECs. In this work, we seek to explore with IMPS the electron transfer kinetics in DSPECs in the surface-kinetic limiting case (mimicking slow water oxidation conditions). This is achieved by adding a oneelectron donor molecule at low concentration. We construct a kinetic model describing the interplay between electron diffusion, recombination, and hole transfer to solution species, which is also simulated by using numerical methods. Our numerical analysis evaluates four strategies for optimizing the device performance: increasing the yield of charge injection by the photoexcited dye; increasing the rate of electron diffusion in the nanocrystalline semiconductor film; suppressing charge recombination at the sensitizer-semiconductor interface; and integrating the device with catalysts that have high turnover frequency.

### NUMERICAL MODELING OF IMPS

**Theory.** Our kinetic scheme for DSPECs is an adaptation of the IMPS model for nonaqueous regenerative DSSCs.<sup>8</sup> Briefly, if we consider the dye-sensitized  $TiO_2/aqueous$  electrolyte system as a quasi-homogeneous and nonscattering medium, we can use a one-dimensional electron transfer model, as shown in Figure 1a, to represent the electron transport processes in



**Figure 1.** (a) One-dimensional electrode model, where the two surfaces of the mesoporous film (thickness d) are labeled as x = 0 and x = d, respectively. (b) Proposed charge transport and recombination scheme for the DSPEC photoanode.

DSPECs. Light-induced excited electron injection from dye molecules to  $\text{TiO}_2$  is followed by diffusive transport inside the mesoporous  $\text{TiO}_2$  network toward the FTO (fluorine-doped tin oxide glass) contact. The pseudo-first-order injection rate<sup>11</sup> ( $k_1$  in Figure 1b) is on the order of  $10^9 \text{ s}^{-1}$  and we can assume that electron injection is already complete when electron

diffusion and recombination occur. Charge extraction at the FTO-TiO<sub>2</sub> interface is treated as a potential-dependent energy barrier with a rate constant  $k_{ext}$ . Meanwhile, recombination of the injected electrons with the oxidized sensitizer molecules occurs via a bimolecular recombination process with a rate constant of  $k_2$ . This bimolecular recombination, can be modeled with a reaction order of 1 under small light perturbation conditions, although it occurs with fractional orders over wider range of light intensities.<sup>12</sup> Oxidized sensitizer molecules are regenerated with a pseudo first-order rate of  $k_3$  by catalytic water oxidation in the WS-DSPEC. Here we simulate this surface oxidation process using a one-electron donor molecule (hydroquinone, HQ) in the electrolyte, for which  $k_3$  is easily adjusted by changing the concentration. The perturbation of the electrolyte composition is neglected in the IMPS experiment. Within this model, we can describe the electron generation and recombination in DSPECs by the following continuity equations:

$$\frac{\partial n(x,t)}{\partial t} = G(x,t) + D_n \frac{\partial^2 n(x,t)}{\partial x^2} - k_2 \times \operatorname{RuP}(x,t) \times [n(x,t) - n_d]$$
(1)

where *n* is the electron concentration in  $\text{TiO}_{2}$ , RuP is the oxidized sensitizer concentration,  $D_n$  is the effective diffusion coefficient of electrons, *x* is the distance from the transparent conductor back contact, and  $n_d$  is the dark electron concentration in  $\text{TiO}_2$ . G(x, t) is the generation term describing electron injection with the following expression:

$$G(x, t) = \eta \alpha I_0 e^{-\alpha x} (1 + M e^{i\omega t})$$
<sup>(2)</sup>

where  $\eta$  represents the injection yield,  $\alpha$  is the absorption coefficient of the dye-sensitized TiO<sub>2</sub> film,  $I_0$  is the steady-state illumination intensity,  $\omega$  is the angular frequency of light modulation, *i* is the imaginary unit, and *M* is the light modulation fraction. Similarly, the rate of change in concentration of the oxidized sensitizer (RuP) can be described as follows:

$$\frac{\partial \operatorname{RuP}(x, t)}{\partial t} = G(x, t) - k_2 \times \operatorname{RuP}(x, t) \times [n(x, t) - n_d] - k_3 \times \operatorname{RuP}(x, t)$$
(3)

The two boundary conditions are

$$D_{n} \frac{\partial n(x, t)}{\partial x} \bigg|_{x=0} = k_{\text{ext}}[n(0, t) - n_{\text{d}}]$$
(4)

$$\left. \frac{\partial n(x, t)}{\partial x} \right|_{x=d} = 0 \tag{5}$$

where x = 0 and x = d represent the FTO-TiO<sub>2</sub> interface and the TiO<sub>2</sub> film surface (*d* is the film thickness), respectively.

The steady-state condition can be achieved when  $\frac{\partial n(x,t)}{\partial t} = 0$ ,  $\frac{\partial RuP(x,t)}{\partial t} = 0$ , and M = 0. Under small light perturbation conditions, the time-dependent electron and oxidized sensitizer concentrations can be represented by the following forms:

$$n(x, t) = n_0(x) + u_1(x)e^{i\omega t}$$
(6)

$$\operatorname{RuP}(x, t) = \operatorname{RuP}_{0}(x) + u_{2}(x)e^{i\omega t}$$
(7)

where  $n_0$  and  $RuP_0$  are the steady-state concentrations of electrons in  $TiO_2$  and oxidized sensitizer molecules,

respectively.  $u_1$  and  $u_2$  are the modulated components of n and RuP, respectively.

The AC component of the photocurrent is

$$j(\omega) = qD_{n} \frac{\partial u_{1}(x, t)}{\partial x} \bigg|_{x=0}$$
(8)

where q is the elementary charge. In a practical measurement, the frequency-dependent photocurrent measured in the external circuit will be attenuated by the *RC* time constant due to the series resistance (*R*) and double layer capacitance (*C*) from the electrode and electrolyte, given by

$$A(\omega) = (1 + i\omega RC)^{-P} \tag{9}$$

where P defines the exponent of the RC attenuation. In DSSCs, P is usually 1, but in our experiments with DSPECs, as will be shown later, P shows a strong dependence on the electrolyte ionic strength and a value of 2.4 is necessary for satisfactory data fitting. The measured photocurrent in response to the light perturbation is then defined by

$$\varphi_{\rm imps}(\omega) = j(\omega)A(\omega) \tag{10}$$

The above equations were solved numerically using COMSOL Multiphysics.<sup>13</sup> The main difference between this model (eqs 1-10) and that of ref 8 is that we treat interfacial charge recombination as a bimolecular process that is first order in both RuP and electron concentrations.

**Fitting Algorithm.** Initial guesses (Table S1) of  $k_2$ ,  $k_3$ , and  $D_n$  were estimated from published data, as discussed below. With a dye surface coverage of 70 nmol/cm<sup>3</sup> and a film thickness of 3  $\mu$ m,<sup>12</sup> we calculated a sensitizer molecule volume density of  $1.4 \times 10^{19}$  cm<sup>-3</sup>. The observed time scale of the recombination reaction involving  $k_2$  spans from  $10^{-3}$  to  $10^{-6}$  s,<sup>14</sup> and thus, the lower limit of  $k_2$ , a bimolecular recombination rate, ranges from  $10^{-16}$  to  $10^{-13}$  cm<sup>3</sup>·s<sup>-1</sup>. The first-order regeneration rate constant ( $k_3$ ) is in the range of  $10^0-10^1$  s<sup>-1</sup>.<sup>15</sup> The electron diffusion coefficient ( $D_n$ ) in mesoporous TiO<sub>2</sub> is on the order of  $10^{-5}$  cm<sup>2</sup>·s<sup>-1</sup>,<sup>10</sup> with a strong dependence on the electron injection level. These initial values were fed into MATLAB codes for optimization using the *fminsearch* function, in which each iteration consisted of individual and sequential searches of  $k_2$ ,  $k_3$ , and  $D_n$ , with a termination tolerance of  $10^{-3}$  relative to the experimental Nyquist plots. These iterations were repeated three times to approach global minima.

# EXPERIMENTAL SECTION

The dye-sensitized electrodes used for IMPS were prepared on FTO by a published procedure.<sup>12</sup> The molecular sensitizer we used was bis(2,2'-bipyridine)(4,4'-diphosphonato-2,2'bipyridine)ruthenium(II) bromide (RuP).<sup>16</sup> All photoelectrochemical measurements were carried out using an Autolab potentiaostat (PGSTAT128N) in a three-electrode electrochemical cell with a Pt wire as the counter electrode and a Ag/ AgCl (3 M NaCl) electrode as the reference electrode. A 470 nm LED light (LDC470, Metrohm) provided the illumination. The light intensity modulation was realized through an Autolab LED driver controlled by the poteniostat with the AC amplitude set to 10% of the DC level. The electrolyte was aqueous 0.1 M sodium acetate/acetic acid (pH 4.7) unless otherwise noted. A small amount of hydroquinone was added to the solution as an electron donor to render the sensitizer regeneration process the photocurrent-limiting factor, mimicking the kinetically demanding photoelectrochemical water oxidation reaction. Electrochemical impedance spectroscopy (EIS) was conducted with an Autolab potentiostat (PGSTAT128N, with FRA32 M module) in 0.1 M NaAc/ HAc (pH 4.7) and 3 mM HQ at an applied bias of 0.3 V versus Ag/AgCl. The light intensity was 4.1 mW/cm<sup>2</sup> (470 nm). The applied frequency ranged from 2000 to 1 Hz with a voltage perturbation of 5 mV.

# RESULTS AND DISCUSSION

**Simulation Parameters.** Typical values for parameters used in eqs 1-10 are shown in Table 1.  $\alpha$  was calculated by

Table 1. Simulation Parameters Used to Calculate IMP0053

name	expression	unit	description
α	2200	$cm^{-1}$	absorption coefficient of the sensitized film
η	0.35	1	electron injection yield
$I_0$	$9.7 \times 10^{15}$	$cm^{-2} \cdot s^{-1}$	incident photon flux (DC)
$D_{\rm n}$	$(6.74 \pm 0.25) \times 10^{-6}$	$cm^2 \cdot s^{-1}$	electron diffusion coefficient
$n_{\rm d}$	10 <sup>5</sup>	cm <sup>-3</sup>	dark electron density in TiO <sub>2</sub>
$k_{\text{ext}}$	100	$\text{cm} \cdot \text{s}^{-1}$	charge extraction rate at FTO/TiO <sub>2</sub> interface
$k_2$	$(2.88 \pm 0.12) \times 10^{-15}$	$cm^3 \cdot s^{-1}$	electron recombination rate to oxidized dyes
<i>k</i> <sub>3</sub>	9.13 ± 0.19	s <sup>-1</sup>	dye regeneration rate from oxidizing electron donors
M	0.1	1	AC modulation percentage
RC	10 <sup>-3</sup>	s	RC time constant
Р	2.4	1	RC exponent

normalizing the UV–vis absorbance of the dye-sensitized TiO<sub>2</sub> film to the film thickness. A typical electrode has an absorbance of about 0.66 at 470 nm. With a film thickness of 3  $\mu$ m (determined by scanning electron microscopy), we calculated  $\alpha$  to be 0.66/3  $\mu$ m<sup>-1</sup> = 2200 cm<sup>-1</sup>.

The yield for initial electron injection  $\eta$  from excited sensitizer molecules to TiO<sub>2</sub> nanoparticles is close to unity in nonaqueous DSSCs. However, in aqueous WS-DSPECs,  $\eta$ shows a strong dependence on the pH of the electrolyte, because the flat-band potential of metal oxides shifts with pH.<sup>17</sup> Using time-resolved THz spectroscopy, Swierk et al.<sup>18</sup> found that  $\eta$  dropped to about 1/3 when the pH increased from 1 to 6.8. Here we used a typical value of 0.35.

The incident photon flux at 470 nm,  $I_0$ , was calculated from the incident light power  $I'_0$  according to the following formula:

$$I_0(\text{cm}^{-2} \cdot \text{s}^{-1}) = \frac{I'_0(\text{mW} \cdot \text{cm}^{-2})}{1240(\text{V} \cdot \text{nm}) \times 1.602 \times 10^{-19}(\text{C})} \times 470(\text{nm})$$
(11)

 $k_{\text{ext}}$  describes the electron extraction rate at the FTO-TiO<sub>2</sub> interface. In the experiment, the potential we applied to FTO was 0.3 V versus Ag/AgCl, a sufficiently positive bias to efficiently drive electrons through FTO-TiO<sub>2</sub> interface. Therefore,  $k_{\text{ext}}$  was given a value large enough to not limit the IMPS spectra. We confirmed that a value of 100 cm/s for  $k_{\text{ext}}$  met this requirement (Figure S1 in Supporting Information).

The *RC* time constant was determined by electrochemical impedance spectroscopy (EIS) under illumination conditions. A typical Nyquist plot is shown in Figure S2. The data were fitted to a Randles circuit (Figure S2, inset). The *RC* time constant used for numerical modeling was 1 ms.

Numerical values of  $D_n$ ,  $k_2$ ,  $k_3$ , and P were optimized based on the fitting algorithm described earlier. A successful fit (shown in Figure 2) produced the values of  $D_{n}$ ,  $k_2$ ,  $k_3$ , and P presented in Table 1.



Figure 2. IMPS Nyquist plot (a) and Bode plots (b) for a RuPsensitized  $TiO_2$  electrode in aqueous 0.1 M sodium acetate/acetic acid and 3 mM HQ at an applied bias of 0.3 V vs Ag/AgCl. The light intensity was 4.1 mW/cm<sup>2</sup> (470 nm). Blue and orange represent experimental and simulated data, respectively. The standard errors of the experimental data are smaller than the plot symbols.

We noticed that the shape of the measured IMPS Nyquist plots showed a strong dependence on the ionic strength of the electrolyte (Figure S3, left). As we deliberately added NaClO<sub>4</sub> solution to increase the ionic strength, the IMPS Nyquist plots distorted toward the upper-left part. Although the underlying mechanism is unknown, it may be related to the interfacial electric field at the TiO<sub>2</sub>/dye/electrolyte interface, which is subject to change with ionic strength.<sup>19,20</sup> We can reproduce this effect in simulation by modulating the parameter *P* (Figure S3, right). IMPS measured in a solution of 0.1 M sodium acetate/acetic acid and 3 mM HQ required a *P* value of 2.4 for a satisfactory fitting.

**Steady-State Concentration Profile.** With the sets of parameters in Table 1 known, we calculated the concentration profiles of injected electrons and oxidized sensitizer molecules inside the TiO<sub>2</sub> film. As shown in Figure 3, the injected electrons  $(n_0)$  are depleted toward the FTO interface (x = 0), and the concentration of oxidized sensitizer molecules (RuP<sub>0</sub>) is highest there, since light penetrates into the film from the FTO side. Note that the RuP<sub>0</sub> concentration exceeds  $n_0$  throughout the film. The reason is that the concentration of HQ used in the experiment was limited so that dye regeneration, instead of electron diffusion in TiO<sub>2</sub> in conventional DSSCs, becomes the current-limiting factor. This mimics the kinetic bottleneck (catalysis of water oxidation) in WS-DSPECs.

Influence of  $I_0$ ,  $D_n$ ,  $k_2$ , and  $k_3$  on IMPS. The IMPS model presented above enables us to understand how individual processes influence the spectra by manipulating the corresponding parameters. Keeping all other values unchanged in



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**Figure 3.** Semilog plots of concentration profiles for injected electrons  $(n_0)$  and oxidized sensitizer molecules  $(\text{RuP}_0)$  inside the TiO<sub>2</sub> film under steady-state illumination. Incident light is from the FTO substrate side (x = 0).

Table 1, we simulated the steady-state concentration profiles, steady-state current density, IMPS Nyquist and Bode plots at different light intensities (Figure 4), diffusion coefficients, charge recombination rates, and dye regeneration rates (Figures 5 and S4).



**Figure 4.** Simulated steady-state current density (a), steady-state concentration profiles (b), IMPS Nyquist (c), and Bode (d) plots at various light intensities. The orange arrows indicate the direction of increasing light intensity.

In Figure 4a, the photocurrent density increases with light intensity, but not linearly. This nonlinearity can be understood by considering that the rate-limiting step in the electron transfer scheme (Figure 1) is the dye regeneration step, which is constrained by the fixed concentration of HQ. The concentrations of both RuP<sub>0</sub> and  $n_0$  increase with increasing light intensity (Figure 4b), indicating that more electrons are injected and more oxidized sensitizer molecules reside at the TiO<sub>2</sub> surface. Except for scaling the data in the positive direction, the light intensity did not affect the general shape of the IMPS plots (Figure 4c,d).

We observe from Figure 5a that the steady-state photocurrent density increases logarithmically with the electron diffusion coefficient in TiO<sub>2</sub>. Faster diffusion of injected electrons results in a lower concentration of  $n_0$  and a higher concentration of RuP<sub>0</sub> (Figure 5b). The simulated IMPS plots (Figure S4a,b) also scale positively with the electron diffusion coefficient. Materials with high electron diffusion coefficients usually require high crystallinity. Rutile TiO<sub>2</sub> nanowire arrays,



**Figure 5.** Simulated current densities (a, c, e) and charge-carrier concentration profiles (b, d, f) at different  $D_n$  (a, b),  $k_2$  (c, d), and  $k_3$  (e, f). The orange arrows indicate the directions of increasing parameter values.

for example, have been reported to possess an electron diffusion coefficient that is 2 orders of magnitude larger than that of mesoporous  $\text{TiO}_2$  nanoparticle films.<sup>10</sup> If we use a  $D_n$  of  $10^{-4}$  cm<sup>2</sup>·s<sup>-1</sup> in Table 1 while keeping other parameters unchanged, the calculated IPCE (470 nm) can roughly double from 6.4% to 13.0%.

In Figure 5c, we observe that increasing the recombination rate  $k_2$  leads to a logarithmic decrease in photocurrent density. Faster recombination also lowers the concentrations of  $n_0$  and RuP<sub>0</sub> (Figure 5d) and shrinks the modulated photocurrent in IMPS plots (Figure S4c,d). Minimizing charge recombination at the semiconductor-sensitizer interface can be realized through core/shell structure designs. Varying the TiO<sub>2</sub> shell thickness over a SnO<sub>2</sub> core, Gish et al.<sup>21</sup> successfully extended the charge-separation lifetime from tens of microseconds to several milliseconds; similar observations were also reported by Knauf et al.<sup>22</sup> If the charge recombination from TiO<sub>2</sub> to oxidized sensitizer molecules can be slowed by just 1 order of magnitude, the IPCE of the photoanode can increase from 6.4% to 14.3% (using  $10^{-16}$  cm<sup>3</sup>/s for  $k_2$  in Table 1).

In Figure 5e, the dye regeneration rate  $k_3$  was varied, simulating faster catalytic water oxidation. Increasing  $k_3$  leads to a logarithmic increase in photocurrent density. Faster dye regeneration lowers the concentration of RuP<sub>0</sub> as expected, and more electrons are accumulated in TiO<sub>2</sub>, as suggested by the  $n_0$ levels (Figure 5f). More dramatic changes (Figure S4e,f) were observed in the IMPS simulations. The apex frequency of the lower semicircle increased with  $k_3$ , and at  $k_3 = 50$  s<sup>-1</sup>, the lower semicircle disappeared and seemed to merge into the upper semicircle. This one semicircle feature at large  $k_3$  resembles the IMPS Nyquist plots of DSSCs, where fast dye regeneration takes place. The best molecular catalysts for water oxidation reported in the literature turn over the reaction at a rate greater than 300 s<sup>-1</sup>.<sup>23</sup> Plugging this number into the model ( $k_3$  in Table 1), we calculated an IPCE as large as 14.6%.

The above simulations help to predict IPCE values as a function of kinetic parameters and point out directions for future optimization of WS-DSPECs. TiO<sub>2</sub> with faster electron diffusion can be designed, for example, by using crystalline TiO<sub>2</sub> nanowire arrays. This reduces electron accumulation under steady-state conditions and allows more oxidized sensitizer molecules to persist for the catalytic water oxidation reaction. Lowering the rate at which injected electrons recombine with oxidized sensitizer molecules allows more electrons to be collected and provides more oxidized sensitizer molecules for the oxidation reaction. This can be achieved experimentally by using a core-shell structure. Accelerating the surface oxidation reaction, by using more efficient catalysts, is crucial for the faster regeneration of oxidized sensitizer molecules, lowering the recombination loss of injected electrons. When the best measured values of  $D_{n}$ ,  $k_{2}$ , and  $k_{3}$ noted above are used at the same time into the numerical model, we calculate an IPCE of 16.9%. Note that this number is the highest IPCE the model predicts, because it matches the ratio of injected electrons (integrating eq 2 over the entire film) to the incident photon flux, suggesting that every injected electron contributes to photocurrent. Upon illumination, the photoanode absorbs 48.3% of the incident photons  $(\eta_0 = \int_0^d \alpha e^{-\alpha x} = 48.3\%);$  the low electron injection yield  $(\eta$ = 0.35) compromises the IPCE (maximum IPCE =  $\eta_0 \times \eta$  = 16.9%). Therefore, we conclude here that despite all the collective efforts of suppressing interfacial charge recombination and designing better catalysts, we can only further improve the IPCE by about 10% (Figure 6), because low electron-injection yield has not yet been recognized as the most important bottleneck for high-performance WS-DSPECs.



**Figure 6.** Color map of numerically calculated IPCE values obtained by varying  $D_{n}$ ,  $k_{2}$ , and  $k_{3}$ .

The kinetic model presented here, however, fails to simulate accurately the IMPS spectra measured at low electron donor concentrations (Figure S5), where the radius of the lower semicircle is large (relative to that of the upper semicircle). Decreasing  $k_3$  in the model can enlarge the lower semicircle in the IMPS spectra, but only to some extent. One possible

explanation is that the kinetic picture we have modeled here requires a minimum value of  $k_3$  that can drive the electron transport in the TiO<sub>2</sub> film under diffusion-limited conditions. We also note the differences in the IMPS spectra collected at the same electron donor concentration (3 mM HQ, Figure 2 and Figure S5), which implies that there may be significant variation in the kinetic parameters for photoanodes prepared even under the same conditions. It is worth noting that the use of one-electron donors to simulate a four-electron reaction does not account for some processes in the WS-DSPEC, such as electrons scavenging by the catalyst or by photogenerated O<sub>2</sub>. Nevertheless, our model can provide an upper limit of the performance of a photoanode in which water oxidation is as facile as HQ oxidation.

# CONCLUSIONS

Understanding the electron transport properties in WS-DSPECs is essential for estimating the limits of their efficiency and for guiding attempts to optimize their design. Here we have extended an earlier model of DSPECs using intensitymodulated photocurrent spectroscopy to include electron diffusion in the TiO<sub>2</sub> film. Using hydroquinone (HQ) as the electron donor, we simplified the charge transfer in DSPECs to three processes: (1) electron diffusion in  $TiO_{2}$ , (2) recombination of injected electrons with oxidized sensitizer molecules, and (3) sensitizer regeneration through oxidation of HQ. Using experimentally derived rate constants, these processes were then modeled numerically, enabling us to examine how individual kinetic factors affect the resulting photocurrent. We found that the steady-state photocurrent increased logarithmically with increasing electron diffusion coefficient  $(D_n)$ , decreasing recombination rate  $(k_2)$ , and faster dye regeneration  $(k_3)$ , although they contributed differently to the steady-state concentration profiles of injected electrons and oxidized dye molecules. The IPCE can be maximized by increasing  $D_n$  and  $k_3$  while decreasing  $k_2$ . These findings suggest that WS-DSPECs can be improved somewhat by using oxide semiconductors with higher electron diffusion coefficients, designing core-shell structures to slow down interfacial charge recombination, and by using more efficient catalysts. Including other possible recombination processes in the proposed model, such as charge recombination between injected electrons and catalyst particles as well as back electron transfer from the catalyst to the sensitizer, can in principle provide a more complete kinetic picture WS-DSPECs. With the simple model used here, our calculations suggest that the best reported values of  $D_{n}$ ,  $k_{2}$ , and  $k_{3}$  are nearly optimum for DSPECs and that the largest remaining losses arise from weak light absorption and low charge injection efficiency with the dyes that are currently used. Electrode structures that isolate dye molecules from the aqueous electrolyte, for example, by employing thin tunneling barriers,<sup>24</sup> may provide a path to improving these remaining key parameters in WS-DSPECs.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b11356.

Different initial guesses used in simulation EIS Nyquist plots and additional IMPS plots (PDF).

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#### Notes

The authors declare no competing financial interest.

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