Theoretical Investigation on Interfacial-Potential-Limited Diffusion and Recombination in Dye-Sensitized Solar Cells

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ABSTRACT: The electron diffusion and recombination limited by interfacial potential in dye-sensitized solar cells are theoretically investigated within a potential barrier model. The dependence of diffusion coefficient $D$ and recombination rate $K$ on various parameters is examined. The $D$ and $K$ exhibit electron density dependence with three distinct regions: (i) constant region, (ii) linear region, and (iii) nonlinear region when the quasi-Fermi energy level sweeps from the lower-energy side to the conduction band edge. For a dye-sensitized solar cell operated at normal conditions, a linear-density-dependent expression for $D$ or $K$ is a reasonable approximation. The diffusion coefficient $D$ in a temperature range of 200–400 K exhibits thermally excited behavior as $D \sim \exp(-E_{act}/k_BT)$ when the potential barrier width $W$ is large enough ($\sim 4$ nm) and the corresponding activation energy $E_{act}$ is independent of quasi-Fermi energy level or electron density. The diffusion coefficient $D$ shows linear dependence on particle size. The recombination rate $K$ shows more complicated size dependence due to the competition between the pure size effect and the local electric field effect. When the quasi-Fermi energy level approaches the conduction band edge, the $K$ increases significantly with size due to the shrinkage of the potential barrier on the interface. Because of the local electric field generated by excess electrons accumulated in nanoparticles, the recombination rate $K$ is approximately proportional to $1/\varepsilon_r$ ($\varepsilon_r$ is relative dielectric constant of interfacial layer). This implies a way to suppress recombination by controlling the dielectric property of the interfacial layer. The interfacial-potential-limited diffusion and recombination are beneficial supplements to the well-established mechanisms, such as localized-state-limited diffusion (trapping and detrapping effect), chemical-reaction-limited recombination, etc., and is helpful for us to understand the operating mechanism in dye-sensitized solar cells.

INTRODUCTION

The diffusion of excess electrons in the nanocrystalline semiconductor and the recombination of electrons from the semiconductor to the electrolyte or to excited dye molecules are two crucial processes to determine the photovoltaic performance of dye-sensitized solar cells (DSCs). The two processes have been extensively investigated since the DSC was invented by O’Regan and Grätzel in 1991.1 The injected electrons from light-excited dye molecules into nanocrystalline semiconductors reach an anode electrode via a diffusion process because of the lack of macroscopic electric field in the semiconductor network permeated with high conductive electrolyte.3–4 The electrons collected by the anode provide the external circuit a current source; however, not all injected electrons can be collected, and electrons are in part lost due to the recombination. Currently, the overall conversion efficiency of DSCs has reached 11%.5,6 To achieve higher efficiency, we need to obtain a more comprehensive and intensive understanding of these key processes, such as here mentioned diffusion and recombination.

The titanium dioxide (TiO$_2$) film is popularly used as an anode electrode in DSCs. The TiO$_2$ film is usually prepared from nanocrystalline TiO$_2$ particles by sintering the paste containing such nanocrystalline particles. The diffusion coefficient is on the order of $10^{-6}$ m$^2$ s$^{-1}$ for bulk anatase,7 but it is on the order of $10^{-12} \sim 10^{-13}$ m$^2$ s$^{-1}$ for the nanocrystalline anatase film.8–10 There are two possible origins for the very lower diffusion coefficient in nanocrystalline TiO$_2$ film: one is the trapping and detrapping of electrons to/from localized states in the band gap, and the other is the scattering of potential barrier existing in the neck region between two nanocrystalline particles.11 The power-law electron density dependence has been found for the diffusion coefficient,8–10 and this is usually explained as a result of trapping and detrapping.8 For the localized (trap) states with an exponential density

$$\rho_i(E) = N_i \exp[\alpha_i(E - E_r)/k_BT]$$

a density-dependent diffusion coefficient $D$ and recombination rate $K$

$$D = D_0(n_{tot}/n_{tot,0})^{(1 - \alpha_i)/\alpha_i}$$

$$K = K_0(n_{tot}/n_{tot,0})^{(1 - \alpha_i)/\alpha_i}$$

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are derived from theoretical considerations\textsuperscript{12} and from random walk simulation.\textsuperscript{13—15} In eq 2, \(n_{el0}\) denotes a total electron density (conduction band electron density and localized electron density), and \(n_{el00}\) denotes the electron density at a reference point. Here the recombination is assumed to be limited by electron diffusion in the electrode, and hence the recombination rate also shows power—law electron density dependence. The power—law electron-density-dependent \(D\) and \(K\) have also been used in simulations of steady transport properties.\textsuperscript{16,17}

The derivation of power—law electron-density-dependent diffusion coefficient \(D\) at steady state is based on an assumption that the electron transport property in the investigated system is dominated by the hopping of the localized states via extended states (conduction band states), and there were not any direct contributions from conduction band electrons.\textsuperscript{14} However, the direct contribution of the conduction band state to electron transport may not be negligible in the nanocrystalline film composed of high-crystallized nanoparticles with a mean size of \(\sim 20\) nm and good connection among them. First, it is possible for the conduction band state density to be higher than the localized state density in a nanoparticle with diameter 20 nm. The surface-to-volume ratio of a nanoparticle with a diameter of 20 nm is only about 3—6% if an atomic scale of 1—2 Å is assumed, and this value is much lower than the corresponding value for a strict nanoparticle. Therefore, the localized state density should be lower in the well-crystallized nanoparticle with a size of 20 nm. Even if an amorphous boundary layer with thickness of about 2 nm is considered, the ratio of the core atom number to total atom number still reaches about 50% in the nanoparticle with a diameter of 20 nm. Second, it is possible for the conduction band electron to tunnel through the potential barrier formed between the connected nanoparticles. It has been found that the conductivity in a microcrystalline silicon can be well described by a heterogeneous charge transport model,\textsuperscript{18} which is based on a fluctuation-induced tunneling mechanism.\textsuperscript{19}

A more powerful example to show that the extended state electron can significantly contribute to transport property is the fluctuation-induced tunneling in pressed TiO\textsubscript{2}-nanotube pellets.\textsuperscript{20} In a pellet, the contacts between TiO\textsubscript{2} nanotubes are formed by applying pressure, and the connection should not be as good as that in a TiO\textsubscript{2} film formed in a sintering process; however, the electron still can transport through the potential barrier. On the basis of the above general considerations, it is necessary to consider the tunneling contribution to electron transport in a nanocrystalline TiO\textsubscript{2} film.

There also has been some experimental evidence to show that the trapping mechanism is not adequate to interpret the relevant results. Barnes et al. have extracted exponent factor \(\alpha_i\) from the measured bias dependence of electron density and electron density dependence of \(D\) and \(K\), respectively, and three different values 0.29, 0.37, and 0.47 have been found.\textsuperscript{21} This result may indicate that the diffusion coefficient and recombination rate are not fully determined by a trapping and detrapping mechanism. Kopidakis et al. have investigated the temperature dependence of the electron diffusion coefficient in electrolyte-filled TiO\textsubscript{2} nanoparticle films and found that the dispersion parameter is temperature-independent, and this result is contrary to the prediction of trapping mechanism.\textsuperscript{22} In comparison with trapping and detrapping, the influence of the interfacial potential scattering on diffusion has not been rigorously addressed, although this possibility has already been mentioned by Cao et al.\textsuperscript{11}

The recombination occurs on the interface between the nanocrystalline semiconductor and electrolyte or excited dye molecules. If the recombination is limited by electron diffusion in the semiconductor, the recombination rate will take the same form as the diffusion coefficient.\textsuperscript{12,16,17} The recombination can occur through different channels; therefore, it naturally falls into two categories: one is direct recombination, and the other is indirect recombination where conduction band electrons react at holes via a relay of localized states. If we assume a Boltzmann form of recombination current for a localized state electron, we obtain

\[
J_r = K_i(n_i - n_{i0})
\]  

(3)

for the indirect recombination. Because the electron density \(n_i\) for localized states with a state density shown in eq 1 and the electron density \(n\) for conduction band satisfy the following equations

\[
n_i = \frac{N_i k_B T}{\alpha_i} \exp\left[\frac{\alpha_i (E_F - E_c)/k_B T}{\alpha_i (E_F - E_c)/k_B T}\right]
\]

(4)

\[
n = N_c \exp\left[\frac{(E_F - E_c)/k_B T}{(E_F - E_c)/k_B T}\right]
\]

the indirect recombination current can be rewritten in a form as

\[
J_r = K_i(n_i^{00} - n_{i0}^{00})
\]

(5)

A similar recombination current has been used in the simulation of the steady transport property by Bisquert,\textsuperscript{23} although there it was not explicitly stated that it is derived from a localized-state-mediated recombination.

The direct recombination limited by chemical reaction is usually described by using a kinetic theory. In a typical DSC with \(I_3/\Gamma^+\) as the redox pair, if we suppose the recombination is controlled by the elementary single-electron reaction

\[
\Gamma^+ + e^- \rightarrow I_3
\]

(6)

the recombination current \(J_r\) obeys the following equation

\[
J_r = k_c(n_e n_{i1}^{1/2} n_i^{1/2} - \bar{n}_e n_{i1}^{1/2} \bar{n}_i^{1/2} \bar{n}_1^{-3/2})
\]

(7)

where \(n_e\) and \(n_i\) are electron density in the semiconductor, \(I_3\) concentration in electrolyte, and \(\Gamma^+\) concentration in electrolyte, respectively; \(\bar{n}_e\) denotes the corresponding value in the equilibrium state, and \(k_c\) is a constant related to the kinetic coefficient of the controlling reaction and equilibrium constants of other elementary reactions.\textsuperscript{24} In the situation with high concentrations of \(\Gamma^+\) and \(I_3\), the variation of \(n_{i1}\) and \(n_i\) with \(n_e\) is negligible, so usually a Boltzmann form of recombination

\[
J_r \approx K(n_e - \bar{n}_e)
\]

(8)

is obtained.

It should be mentioned here that there exist some other possible mechanisms to make the direct recombination deviate from linear dependence on electron density. Fisher et al. assumed a different chemical reaction procedure, and a quadratic form was obtained.\textsuperscript{8} In addition to the limitation of the chemical reaction, an interfacial potential may be a determinant factor for the direct recombination in some situations, e.g., with a strong interfacial potential or with a rapid chemical reaction.

In this paper, we focus our attention on the influence of interfacial potential barrier on the electron diffusion and recombination, which has not been well addressed in the literature. A potential barrier model is used to model the influence of
interfacial potential on diffusion and recombination. The formulas to calculate diffusion coefficient and recombination rate are developed by using thermodynamical statistics on diffusion current and recombination current within the potential barrier model. The dependence of diffusion coefficient and recombination rate on various parameters, such as electrical field will be generated to meet with the requirement of the potential barrier. The dependence of diffusion coefficient and recombination rate on various parameters, such as electron density, grain size, potential barrier height, and width, are examined and discussed in combination with relevant experimental results.

■ THEORY

Interfacial-Potential-Barrier Limited Diffusion. As mentioned in the Introduction section, the interfacial potential barrier is formed in the neck region between nanocrystalline grains. Figure 1 shows a schematic diagram for the interfacial potential barrier. The motion of the electron is described by a Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)$$

with a potential

$$V(x) = \begin{cases} 0, & x < 0 \\ U, & x \in [0, W] \\ 0, & x > W \end{cases}$$

Here $m$ is the effective mass of the conduction band electron, and $U$ and $W$ are the height and width of the potential barrier.

According to quantum mechanics, the transmission probability for an electron with energy $E$ through the barrier is

$$T(E) = \left[ 1 + \frac{U^2}{4E(U-E)} \sinh^2(\lambda W) \right]^{-1}$$

where

$$\lambda = \sqrt{\frac{2m(U-E)}{\hbar^2}}$$

The current from the left crystalline grain to the right crystalline grain is

$$J_{L-R} = \frac{2}{L^2} \sum_{k} T(E_k) \frac{\hbar^2}{m} f_{E_L}^0(E_k) \left[ 1 - f_{E_R}^0(E_k) \right]$$

where $f_{E_L}^0(E)$ is the Fermi–Dirac distribution function; $E_k$ is conduction band energy; $\vec{k}$ is wavevector; and $E_k$ satisfies the following energy dispersion relation

$$E_k = \frac{\hbar^2 k^2}{2m} \left( k_x^2 + k_y^2 + k_z^2 \right)$$

Analogously, the current from the right to the left is

$$J_{R-L} = \frac{2}{L^2} \sum_{k} T(E_k) \frac{\hbar^2}{m} \left[ 1 - f_{E_L}^0(E_k) \right] f_{E_R}^0(E_k)$$

and the net diffusion current $J_d$ is equal to the difference between $J_{R-L}$ and $J_{L-R}$; therefore

$$J_d = \frac{2}{L^3} \sum_{k} T(E_k) \frac{\hbar^2}{m} \left[ f_{E_L}^0(E_k) - f_{E_R}^0(E_k) \right]$$

Now let $E_F^0 = E_F$ and $E_F^\pm = E_F + \delta E_F$, then

$$J_d = \frac{2}{L^3} \sum_{k} T(E_k) \frac{\hbar^2}{m} \frac{\partial f_{E_L}^0(E_k)}{\partial E_F} \delta E_F$$

where $n$ is electron density in conduction band, and it can be calculated from

$$n = \frac{2}{L^3} \sum_{k} f_{E_L}^0(E_k)$$

Considering $J_d = -D((\partial n)/(\partial x))$ and $(\partial n)/(\partial x) = -(\partial n)/L$, we obtain

$$D = L \left[ \sum_{k} T(E_k) \frac{\hbar^2}{m} \frac{\partial f_{E_L}^0(E_k)}{\partial E_F} \right]^{-1}$$

Because the volume of the nanocrystalline grain is much larger than that of the unit cell, the summation on $k$ in the above equation can be replaced by the integration on energy $E$. So finally we obtain the formula

$$D = L \int \frac{T(E) f_{E_L}^0(E) dE}{\sqrt{8m} \int E^{1/2} \frac{\partial f_{E_L}^0(E)}{\partial E} dE}$$

for the calculation of coefficient $D$.

Interfacial-Potential-Barrier Limited Recombination. When a semiconductor material contacts with electrolyte, a local electrical field will be generated to meet with the requirement of...
The electrochemical balance, and a potential difference across the semiconductor/electrolyte interface is established. For a junction formed from bulk semiconductor and metal, a depletion layer with a micrometer scale of thickness is usually generated. For a nanoscaled semiconductor, the local electric field is negligible if only a depletion approximation is considered. However, finally the electrochemical balance is always realized in a semiconductor/electrolyte system, otherwise the electrons would flow from a region with high electrochemical potential energy to a region with lower electrochemical potential energy. For a cylinder with radius of 10 nm, a charge density with scale of 0.1 e/nm³ is needed to yield a 1 V potential difference between the center and the side. So the nanoscaled semiconductor must be in an overionized state compare to depletion, and then a local electrical field is generated to establish electrochemical balance. Because the energy level of the surface state is higher than the valence band energy, the electrons on surface states are first lost during the process of realizing electrochemical balance. Hence it can be anticipated that the built-in field in semiconductors is highly localized near the interface. Such localized potential distribution at the interface has been confirmed by an analysis of in situ surface conductance in n-CdS/electrolyte.

In a realistic semiconductor/electrolyte system, the concrete form of interfacial potential may be very complicated. The disorder and defects in the boundary layer, the absorbed ions, and polarization of absorbed molecules on the interface should also contribute to the interfacial potential. As a study based on the model, we use a square potential barrier to model the inhibition of recombination by interfacial potential (see Figure 2). In this paper, cylindrical geometry is used to model the column formed from connected TiO₂ particles. This is equivalent to assuming that the TiO₂ particles have been merged into one continuous column, and the fluctuation of the radius along a column axis is neglected. A similar simplification has also been adopted in a two-dimensional model for photovoltage and photocurrent in DSC. The other possible choice is spherical geometry, in which the spherical characteristic of the nanoparticle remains and an overlapping factor must be introduced to describe how much volume is overlapped together between two adjacent particles. The spherical geometry is suited to the case where the size of the neck region is far smaller than the size of the nanoparticle. The form of electric potential distribution and the ratio of surface to volume are dependent on the adopted geometry. However, we will see there are no essential differences between the two geometries. To keep the model as simple as possible, we adopt cylindrical geometry.

With an accumulation of excess electrons (injected from dye molecules) in the nanocrystalline particle, the local electric field generated by the excess electrons is not negligible. Supposing the density of excess electrons is n and these electrons distribute uniformly in the core of the TiO₂ cylinder, we can calculate the corresponding potential field by using Gauss theorem and obtain total potential energy as

\[
V(x) = \begin{cases} 
-\frac{e^2nR^2}{4\varepsilon_0\varepsilon_r} & (x \leq R) \\
U - \frac{e^2nR^2}{4\varepsilon_0\varepsilon_r} \ln(x/R) & (x \in [R, R + W]) \\
0 & (x > R + W) 
\end{cases}
\]  

(21)

where U and W are the height and width of square potential barrier in the equilibrium state, respectively; n is excess electron density; R is cylindrical radius; ε₀ is vacuum permittivity; and ε_r is the relative dielectric constant of the interface layer (here the core layer is assumed to have the same dielectric constant). If spherical geometry is used, the potential energy has a form as \(-e^2n/6\varepsilon_0\varepsilon_r\) for \(x \leq R\) and \(U + [e^2nR^2/(6\varepsilon_0\varepsilon_r)] - [e^2nR^2/(3\varepsilon_0\varepsilon_r)]\) for \(x \in [R, R + W]\), respectively, and the shrinkage of potential barrier is about 2/3 of the shrinkage in cylindrical geometry.

In the semiclassical limit, the transmission probability is given by \(T = e^{-2\sigma}\), where

\[
\sigma = \frac{1}{\hbar} \int_a^b \sqrt{2m[V(x) - E]}dx
\]  

(22)

In the above equation, a and b are the two classical turning points where \(V(x) = E\). Supposing the quasi-Fermi energy level in semiconductor is \(E_F\) and the redox energy level in electrolyte is \(E_{redox}\) we obtain the net current passing through the boundary barrier to electrolyte as

\[
J_t = \frac{2}{L^3} \sum_k T(E_k) \frac{|\hbar |k_x|}{m} [f_{E_F}(E_k) - f_{E_{redox}}(E_k)]
\]  

(23)

directly from eq 16, and the factor \(L^3\) should be understood as volume of nanocrystalline grain. Let

\[
J(E_F) = \frac{2}{L^3} \sum_k T(E_k) \frac{|\hbar |k_x|}{m} f_{E_F}(E_k)
\]  

(24)

then \(I_t = J(E_F) - J(E_{redox})\).

Introducing \(P(E) = J(E) = \int_0^E T(x)dx\) and replacing the summation on wavevector \(k\) with integral on energy \(E\),
we obtain

\[
J(E_F) = \frac{4\pi m_e}{\hbar^3} \int_0^\infty P(E)f_{\text{F}}(E)dE \tag{25}
\]

The recombination rate \( K \) can be evaluated from \( J(E_F) \) by using the relation

\[
\left[ J(E_F) - J(E_{\text{redox}}) \right] \cdot S = K(n - n_0) \cdot V \tag{26}
\]

where \( S \) and \( V \) are surface area and volume for a cylinder with a unit length. So finally we obtain recombination rate \( K \) as

\[
K = \frac{2\left[ J(E_F) - J(E_{\text{redox}}) \right]}{R(n - n_0)} \tag{27}
\]

If spherical geometry is used and the overlapping between spheres is neglected, the corresponding \( K \) is obtained by multiplying a factor 3/2 at the right side of the above equation.

**RESULTS AND DISCUSSION**

**Diffusion Coefficient** \( D \). Figure 3 shows the typical dependence of diffusion coefficient \( D \) on electron density \( n \) or quasi-Fermi energy level \( E_F \). The diffusion coefficient \( D \) sequentially experiences three distinct regions: constant, linear, and nonlinear region when \( E_F \) is increased from \(-1.0 \) to \( 0.1 \) eV. When \( D \) falls into the linear region, we introduce a linear coefficient \( C_D \) to describe the dependence and write \( D \) as

\[
D = D_0 + C_D(n - n_0) \tag{28}
\]

where \( n_0 \) and \( D_0 \) are electron density and diffusion coefficient at \( E_F \approx -0.4 \) eV. Because \( C_D \) is a small quantity, we can extend this relation into the whole region of \( E_F < 0 \).

Figure 4 shows the dependence of \( D_0 \) and reduced linear coefficient \( C_D/D_0 \) on potential barrier parameters. The diffusion coefficient \( D_0 \) sensitively depends on potential barrier height \( U \) and width \( W \), and it decreases rapidly with \( U \) and \( W \). A potential barrier with height \( U = 0.3 - 0.5 \) eV and width \( W = 2 - 4 \) nm is enough to yield a diffusion coefficient as low as \( 10^{-8} \) m² s⁻¹, which is a typical value observed in experiment. Contrary to the \( D_0 \) value, the reduced linear coefficient \( C_D/D_0 \) is maintained at a value with scale of \( 10^{-26} \) m⁻³. This means that a 2-fold variation of \( D \) will be obtained only if the electron density \( n \) reaches \( 10^{26} \) m⁻³. For anatase TiO₂, the effective mass of the conduction band electron \( m = 1.0 \) mₑ (mass of electron)²⁸ and this yields an electron density \( n = 1.9 \times 10^{25} \) m⁻³ at \( E_F = 0 \) (at the conduction band edge). So this 2-fold variation is almost impossible to realize in a DSC operated at a normal condition. On the basis of the above consideration, we can conclude that the nonlinear
behavior on \( n \) in the potential-barrier-limited diffusion coefficient can be safely neglected in DSC.

Figure 5 shows the dependence of \( D \) on temperature. A linear \( \log(D) \) against \( 1/T \) with two distinct temperature regions, \( T < 200 \) K and \( T > 200 \) K, respectively, is found. From eq 20 we know that the temperature dependence of \( D \) stems from the Fermi-Dirac distribution function \( f \). Because the numerator and the denominator in eq 20 show different temperature behavior, \( D \) exhibits a two-temperature-region characteristic. When the temperature is low, the variance of \( ((\partial f)/(\partial E)) \) with temperature is more significant than that of \( f \) itself, so the linear dependence of \( \log(D) \) on \( 1/T \) for \( T < 200 \) K is mainly contributed by the \( 1/T \) term. This can be understood from a physical viewpoint as follows: the diffusion coefficient \( D \) is a measure of diffusion current under the same electron density gradient; however, the effective electron density gradient decreases with temperature because of the dispersive factor \( \sqrt{E} \), so the \( D \) increases with temperature. When temperature is high enough, the tunneling current will significantly increase with temperature because the tunneling probability increases with energy. Because the slope for \( T < 200 \) K is much lower than that for \( T > 200 \) K, the diffusion at low temperature can be regarded as a temperature-independent tunneling.

The linear behavior of \( \log(D) \) against \( 1/T \) with two distinct temperature regions is independent of quasi-Fermi energy, and almost “parallel” lines are obtained for different \( E_F \) values (see panel (a) in Figure 5). The temperature dependence is sensitive to the barrier width \( W \) (see panel (b) in Figure 5), and the dependence for \( T > 200 \) K becomes more significant with the increase of \( W \). When the potential barrier width \( W \) is large enough (\( \sim 4 \) nm), a linear \( \log(D) \) against \( 1/T \) for \( T > 200 \) K is obtained. The linear behavior of \( \log(D) \) against \( 1/T \) is usually interpreted by using a classical concept on activation energy as \( D \sim \exp(-E_{act}/k_B T) \). Although the diffusion coefficient itself depends on potential barrier height \( U \), the slope of \( \log(D) \) against \( 1/T \) for \( T > 200 \) K is almost a constant for different \( U \) values (see panel (c) in Figure 5). The temperature dependence of the diffusion coefficient in the range of 200–400 K has been investigated in experiment by Kopidakis et al., and a linear relation \( \log(D) \sim 1/T \) for \( T > 200 \) K has been found. It has been argued that the temperature dependence of the diffusion coefficient found in experiment can not be explained by using the trapping and detrapping mechanism, but the experimental result can be well explained by our theoretical calculation based on the interfacial potential limited diffusion.

Because the diffusion coefficient in a realistic DSC can not be measured at low temperature due to electrolyte, currently there are not any experimental data below 200 K. However, this is not a problem for a conventional solid film. Similar temperature behavior of conductivity has indeed been observed in micro-crystalline silicon and in TiO\(_2\)-derived nanotube pellets, and a similar tunneling mechanism has also been employed to interpret the temperature behavior. In our model calculation, only potential barrier tunneling is considered. In previous works, the fluctuation-induced tunneling is used to interpret the temperature-dependent conductivity. The difference between the fluctuation-induced tunneling and the conventional tunneling is that the tunneling probability for an electron through potential barrier in the former is effectively enhanced because the barrier is narrowed and lowered due to the equivalent electric field corresponding to thermal fluctuation. When the potential is narrow or lower, the fluctuation-induced tunneling will lead to a similar result as anticipated by using a sole tunneling mechanism. In our work, the height of the potential barrier is lower by about 0.3–0.4 eV, so the thermal excitation is comparable with the potential barrier height and leads to a temperature-dependent diffusion.

The potential-barrier-limited diffusion coefficient linearly depends on nanocrystalline grain size (see eq 20). Nakade et al. examined the size dependence of the diffusion coefficient and found that \( D \) obeys a scaling of \( L^{2/3} \) rather than \( L \). We have re-examined their data and find that \( D \) obeys a linear scaling rather than \( L \) and \( L^{2/3} \) (see Table 1). This result indicates that the interfacial potential may dominate the diffusion process in their samples.

In this section, we have discussed the dependence of diffusion coefficient on various model parameters, such as Fermi energy level, barrier height, barrier width, temperature, and particle size. Since the electron diffusion in the interfacial potential barrier model is realized via a tunneling through a barrier, it is necessary to give a discussion on the origin of the potential barrier between the connected nanocrystalline particles. It has been confirmed that there exists an amorphous transition region with a thickness of \( 1–3 \) nm between nanocrystalline TiO\(_2\) particles, and the mismatching energy between the differently oriented lattice planes is released by the formation of this transition region. In addition to the mismatching, the defects may be introduced into the transition region during the preparation of TiO\(_2\) film; e. g., the atom vacancy may be generated in the neck region after the organic material in the paste is burned off. Our calculation results indicate that the diffusion coefficient with a magnitude of about

<table>
<thead>
<tr>
<th>size (nm)</th>
<th>( D ) ((10^{-8} \text{ m}^2 \text{ s}^{-1}))</th>
<th>( D/\text{L}^{2/3} ) (au)</th>
<th>( D/\text{L} ) (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.33</td>
<td>9.6</td>
<td>0.90</td>
</tr>
<tr>
<td>19</td>
<td>0.78</td>
<td>9.1</td>
<td>1.7</td>
</tr>
<tr>
<td>32</td>
<td>1.2</td>
<td>2.9</td>
<td>1.9</td>
</tr>
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*See the Table 2 in ref 26.*
10\(^{-8}\) m\(^{2}\) s\(^{-1}\), which is consistent with experimental result, is obtained with potential parameters \(U = 0.3 – 0.5\) eV and \(W = 2 – 4\) nm. Here the potential barrier width agrees well with the thickness (1–3 nm) of the amorphous transition region observed in experiment.\(^{31}\) To generate linear dependence of \(\log(D)\) on \(1/T\) in the range of 200–400 K, the potential-barrier width must reach 4 nm, and this is slightly larger than 3 nm. Considering the complication and divergence in experiments, the potential barrier with a width of 4 nm may exist in reality.

**Recombination Rate \(K\).** Figure 6 shows typical electron density dependence of recombination rate \(K\). The \(K\) has density dependence similar to \(D\), and it also sequentially demonstrates constant, linear, and nonlinear behavior when quasi-Fermi energy level \(E_F\) is increased from –1.0 to 0.1 eV. The main difference is that a one-order lower electron density is required for \(K\) entering nonlinear region. We can also introduce a coefficient \(C_K\) to describe the linear dependence as

\[
K = K_0 + C_K(n - n_0)
\]

where \(n_0\) and \(K_0\) are electron density and recombination rate at \(E_F \approx -0.45\) eV. Because \(C_K\) is a small quantity, we can extend this relation into the whole region of \(E_F < -0.1\) eV.

Figure 7 shows the dependence of \(K_0\) and reduced linear coefficient \(C_K/K_0\) on potential barrier parameters. The \(K_0\) decreases with potential barrier height \(U\) and width \(W\) because the probability of an electron passing through the barrier decreases with \(U\) and \(W\). A potential barrier with height about 1.0 eV and width of 2–3 nm yields a recombination rate of 1–10\(^{8}\) s\(^{-1}\). Currently there have not been any direct experimental data for the boundary layer thickness of a TiO\(_2\) nanoparticle in a vacuum or in an electrolyte. If we assume that the thickness of the boundary layer of the nanoparticle surrounded by an electrolyte has the same scale (1–3 nm) as the amorphous transition region between two connected nanoparticles,\(^{31}\) the estimated potential-barrier width of 2–3 nm is a reasonable result. The reduced linear coefficient \(C_K/K_0\) increases with barrier width and decreases with barrier height due to the exponential characteristic of transmission probability. Because the \(C_K/K_0\) has a scale of 10\(^{-25}\) m\(^{2}\), the recombination rate will drastically increase when \(E_F\) approaches the conduction band edge. So, the nonlinear electron density dependence of the recombination rate is not negligible.

Figure 8 shows the size dependence of \(K\) for different quasi-Fermi energy levels \(E_F\). Due to the competition between pure size effect (see eq 27) and electrical field effect (see eq 21), \(K\) shows different size dependence for different \(E_F\). When \(E_F\) is lower, the electrical field generated by excess electrons is weak; the dependence is dominated by pure size effect; and \(K\) decreases with \(R\) because the ratio of surface area to volume of the nanoparticle decreases with \(R\). In the situation where the chemical reaction controls the recombination, the recombination \(K\) should also decrease with \(R\) since the corresponding kinetic coefficient is proportional to surface area. With the further increase of \(E_F\), more excess electrons are accumulated in nanoparticles, and the Coulomb repulsion energy among electrons is strong enough to overcome the original barrier. Alternatively, the total potential barrier is shrunk, so the recombination rate \(K\) increases with \(R\). Figure 8 shows that a drastic increase of \(K\) occurs while \(E_F\) is increased from –0.06 to –0.01 eV. The increase of \(K\) with grain
size has been observed by Nakade et al., and the effect was interpreted as a diffusion-limited recombination. In addition to the diffusion limitation, the local electric field effect may be another factor to cause the size dependence.

Because the electrical field generated by excess electrons depends on dielectric constant \( \epsilon_r \), the recombination rate \( K \) also decreases with \( \epsilon_r \). Figure 9 shows \( \epsilon_r \) dependence of linear coefficient \( C_{K0} \) and \( K \) exhibits behavior as \( 1/\epsilon_r \). Because the potential barrier is located on the interface, the parameter \( \epsilon_r \) is determined by the relevant properties of the semiconductor, dye, and electrolyte. The anatase TiO\(_2\), which is usually used as a supporting material for a photoanode electrode, has a relative dielectric constant of about 40. The acetonitrile, which is usually used as a solvent for electrolyte, has a relative dielectric constant of 37.5. So 40 may be an acceptable value for the relative dielectric constant of the barrier layer. However, there exists a large disorder in the boundary layer of nanoparticles, and the actual value may be lower than 40. The \( C_{K0} \) will drastically increase with a decreased \( \epsilon_r \) if \( \epsilon_r \) is too much lower than 40. This indicates that the control of dielectric property in the boundary layer is important to obtain a lower recombination rate.

**CONCLUSIONS**

The diffusion and recombination limited by interfacial potential is investigated within a potential barrier model. Linear dependence of diffusion coefficient \( D \) and recombination rate \( K \) on electron density \( n \) is found, while the quasi-Fermi energy level \( E_F \) is low enough. Due to the local electric field stemming from excess electron in nanocrystalline grain, the reduced linear coefficient \( C_{K0}/D_0 \) of the recombination rate constant is one order larger than that \( C_{D0}/D_0 \) of the diffusion coefficient. For anatase TiO\(_2\), \( C_{D0}/D_0 \) has a scale of \( 10^{-26} \) m\(^{-3}\) and \( C_{K} \) has a scale of \( 10^{-25} \) m\(^{-3}\). Hence, the recombination rate exhibits more sensitive density dependence than the diffusion coefficient. When the quasi-Fermi energy level \( E_F \) in the semiconductor approaches the conduction band edge, the nonlinear density dependence in \( K \) is not negligible.

The diffusion coefficient \( D \) exhibits thermally excited behavior as \( D \sim \exp(-E_{act}/k_BT) \) when the interfacial potential width \( W \) is large enough (\( \sim 4 \) nm), and the corresponding activation energy \( E_{act} \) is a constant independent of temperature and quasi-Fermi energy level. The relevant experimental phenomenon can be well interpreted by using our theoretical results.

The diffusion coefficient \( D \) linearly scales with size, but the recombination rate \( K \) shows more complicated size dependence because of the competition between pure size effect and electrical field effect. The electrical field generated by the excess electron in nanoparticles becomes stronger with the increase of electron density and leads to shrinkage of the interfacial potential barrier. Because the strength of this electric field scales with \( R^2 \), the recombination rate will significantly increase with \( R \) if the quasi-Fermi energy level approaches the conduction band edge. On the basis of our result, the size dependence found in the experiment can be well interpreted.

The recombination rate \( K \) is inversely proportional to the dielectric constant of the interface layer. The material with high dielectric constant can effectively screen the electric field generated by an excess electron in nanoparticles. This implies a way to suppress recombination by controlling the dielectric property of the interface layer.

The interfacial-potential-limited diffusion and recombination possess their unique characteristics, and they are beneficial supplements to the well-established mechanisms, such as localized-state-limited diffusion (trapping and detrapping effect), chemical-reaction-limited recombination, etc. Our result, such as electron density dependence of the diffusion coefficient, is available for the case where a semiconductor electrode is made from well-crystallized nanoparticles and can be used in relevant calculations based on diffusion equations.

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