

Charge Transport in Dye_Sensitized solar cells

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Abstract

A quantum mechanical model used to study, the electron transfer reaction for the titanium dioxide TiO_2 , tin dioxide SnO_2 , and Indium tin oxide ITO semiconductor and the redox thiopyronine (Tp) molecule dye. Theoretical method was adapted to calculate the coupling matrix element coefficient for semiconductor /dye state and the rate constant of electron transfer reaction. The calculated results of rate constant were compared with experimental and theoretical results show good agreement with these results.

انتقال الشحنة في الخلية الشمسية للصبغة المتحسسة ضوئيا

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الخلاصة

استخدام أنموذج ميكانيك كمي لدراسة تفاعل الانتقال الالكتروني لشبه موصل لثنائي اوكسيد التيتانيوم وثنائي اوكسيد القصدير واوكسيد الانديوم ألتن وجزيئات صبغة الثايوبايروناين. اعتمدت طريقة نظرية لحساب معامل عناصر المصفوفة المزدوجة لحالة الشبه الموصل صبغة وثابت معدل الانتقال الالكتروني. نتائج الحسابات لثابت الانتقال الالكتروني وقورنت مع النتائج العملية والنظرية وأظهرت تطابق جيد مع تلك الحسابات.

Introduction

Electron transfer reactions are fundamentally important in biology and technology (1), because of the complexity of electron transfer in biological systems. Many simple compounds were synthesized to look into its detailed mechanism (2).

The natural photosynthetic process involves the extremely efficient capture of solar energy, energy transfer, electron transfer, which ultimately reaches the reaction center where the reactions of various substrates take place (3).

Electron transfer between dyes and colloidal semiconductor plays a vital role in silver halide photography, electro photography, and more recently in solar energy cells (4).

Electron transfer dynamics at the sensitizer semiconductor nanoparticle interface have been intensely studied in recent years(5). The striking feature of dye-sensitized cells is the mechanism by which energy is absorbed from photons. In the solar cells photons are absorbed by dye molecules. then transported to the current collector via semiconductor (6), this is in contrast to traditional pn-junction solar cells where photons are absorbed by the semiconductor itself exciting electrons in the valence band to enable promotion into the conduction band ,excited dye molecules inject electrons into the wide band gap semiconductor (6). In this work have been studied the electron transfer reaction in thiopyroine Tp dye. The chemical formula ($C_{16}H_{18}ClN_{25}, 3H_2O$) and titanium dioxide (TiO_2), tin dioxide (SnO_2), and indium tin oxide ITO semiconductor at acetonitrile solvent.

Theory

A quantum mechanical description of the electronic and vibrational dynamics involved in the electron transfer can be achieved using simplified model of the interface(7). Consider two electron state $|D\rangle$, and $|A\rangle$ which represent the electron donor and acceptor sites of the electron

transfer system in solvent respectively. The two state are coupled to each other (Via) the electronic coupling coefficient.

Under the weak coupling assumption, the rate constant k_{et} for the electron transfer from a single electronic state of the semiconductor to dye molecules, which includes both the effect of electron tunneling and nuclear reorganization energy can be expressed using the Fermi golden rule. Electronic state to electronic state transition (8).

$$k_{et} = \frac{4\pi^2}{h^2} |V|^2 FC \dots\dots\dots [1]$$

Here FC is the Franck Condon factor, V is the electronic coupling matrix element and h is plank's constant,

A common classical expression for the Franck Condon factor is given by (8).

$$FC = (4\pi\lambda k_B T)^{-\frac{1}{2}} e^{-\frac{(\lambda+\Delta G)^2}{4\pi k_B T}} \dots[2]$$

Where λ is the reorganization energy, and ΔG is the free energy change of the reaction under the prevailing conditions of temperature, when a continuum at donor or acceptor levels is involved in the electron transfer, as is the case in semiconductor dye interface, the rate constant for electron transfer can then be written as (9).

$$k_{et} = \frac{4\pi^2}{h^2} (4\pi\lambda k_B T)^{-\frac{1}{2}} e^{\left[\frac{-\lambda}{4k_B T} (\pi k_B T |V|^2 \left(1 - \frac{\pi^2 k_B T}{4\pi} \right)) \right]} \dots\dots[3]$$

Where k_B is the Boltzmann's constant, and T is the absolute temperature.

The reorganization energy, λ is defined as the energy which is required for the structural reorganization of the donor, acceptor and their salvation spheres upon electron transfer. The theoretical reorganization energies may be estimated by expression (10).

$$\lambda = \frac{e^2}{8\pi\epsilon_0} \left[\frac{1}{D} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) - \frac{1}{2R} \left(\frac{n_{se}^2 - n^2}{n_{se}^2 + n^2} \frac{1}{n^2} - \frac{\epsilon_{se}^2 - \epsilon^2}{\epsilon_{se}^2 + \epsilon^2} \frac{1}{\epsilon^2} \right) \right] \dots\dots\dots[4]$$

Here ϵ_0 is the vacuum permittivity, e is the electronic charge. ϵ is the static dielectric constant of the solvent, n is the refractive index of the solvent, R is the distance between the semiconductor and dye molecule in the solvent, D is the radius of the molecule n_{se} is the refractive index of the semiconductor and ϵ_{se} is the dielectric constant of the semiconductor.

For electron transfer the value of radius of the molecule (**D**) can be estimated from the apparent molar volumes using spherical approach (11).

$$\frac{4\pi}{3} D^3 = \left(\frac{M}{N\rho} \right) \dots\dots\dots[5]$$

Where M is the molecular weight, ρ is the density, and N is an Avogadro's number. The coupling matrix elements between the semiconductor state and the dye molecule state can be formulated by expression(8).

$$|V|^2 = \left(\frac{\pi}{\beta a} \right)^{\frac{1}{2}} \left(\frac{4}{3\pi^2 \epsilon \delta} \right) \dots\dots\dots[6]$$

Here β is the exponent for decay of the square of the matrix element with distance, a is the lattice constant, δ is the multiplying factor and ϵ is the lowest energy of electron is given by (12).

$$\epsilon = \frac{3\hbar^2}{8ma^2} \dots\dots\dots[7]$$

Where $m=0.1m_e$, m_e is the mass of electron

Results

According to the theory of electron transfer in semiconductors /dye interface at solvents, the rate constant k_{et} , between semiconductor and dye at fixed distance is depending on two factors:

The reorganization energy λ (eV), and the electronic coupling matrix element V .

We have first done the calculations of values of the reorganization energy energies using Eq[4], for different semiconductor (TiO₂, SnO₂, and ITO) with thiopyronine(TP)dye interface at acetone nitrile solvent where $\epsilon = 37.5$ (13), and $n = 1.134$ (13), are the static dielectric constant and refractive index for acetone nitrile, D is the radius of thiopyronine dye can be calculated by Eq[5], with values of density $\rho = 1.7g/m^3$ (14), and molecular weight $m = 318.8$ (15), n_{se} and ϵ_{se} are the refractive index and dielectric constant for semiconductors that given in Table(1).

Assume that $R = D + 1 \text{ }^\circ\text{A}$, we can evaluate the reorganization energy λ by inserting the values of D , R , n_{se} , ϵ_{se} , n , and ϵ in Eq(4). noting the value of $\frac{e^2}{8\pi\epsilon_0} \approx 7.2eV$.

The results are summarized in Table (1).

Table(1): The Reorganization energy λ (eV) for semiconductor thiopyronine(Tp) dye in Acetonitrile.

system	Refractive index(n)	Dielectric constant ϵ	Reorganization energy λ (eV)
TiO ₂ /Tp dye	2.5[16]	86 [16]	0.69134166
SnO ₂ /Tp dye	1.94[17]	4.175 [18]	0.770660433
ITO/ Tp dye	2.05[17]	4 [17]	0.749030112

The coupling matrix element coefficient can be calculated by using Eq(6)

The lowest energy ϵ of electron is calculated by Eq[7], with lattice constant $a=3^\circ\text{A}$, $M = 0.913 \times 10^{-31}$ ($m = 0.1$ mass of electron, and $\hbar = h/2\pi$ results is $\epsilon = 0.03185 eV$

Inserting the exponent for decay $\beta=1^\circ\text{A}$, the multiplying factor $\delta = 2.5 eV$, and ϵ in Eq[6], we get value of coupling matrix element $|V|^2 = 0.011007|eV|^2$

Next, we can evaluate the rate constant of electron transfer by substituting the results of λ and V in expression (3), the results are listed in Table (2).

Table(2) : Rate of electron transfer constant k_{et} between Thiopyronine Tp dye and TiO_2 , SnO_2 and ITO Semiconductor at acetonitrile solvent.

System	Reorganization energy $\lambda(\text{eV})$	Rate constant of ET $k_{et} \text{ sec}^{-1}$
TiO_2/Tp	0.69134166	$1.600925364 \times 10^{10}$
SnO_2/Tp	0.770660433	3.409356258×10^9
ITO/Tp	0.799030112	4.222008679×10^9

Discussion

The theoretical model to describe electron transfer in semiconductor /dye at solvent system in this paper is based on quantum mechanics to calculate the rate constant when the coupling coefficient of matrix element is smaller than $k_B T$ where $k_B T$ is the Boltzmann constant and T is the absolute temperature.

The transfer of electron occurs from semiconductor to dye through the tunneling between donor $|D\rangle$ and acceptor $|A\rangle$ states, when assuming continuum at donor and acceptor level .The electron transfer rate constant for TiO_2/Tp , SnO_2/Tp , and ITO/Tp , at acetonitrile solvent system studied and calculated using Eq [3]. The rate constant of all system which is of order of 10^9 in unit eV/sec . The results is in agreement with the experimental results for semiconductor /dye system (20-21), that shown in table(3). The difference between the results of rate constant for TiO_2/Tp , SnO_2/Tp , and ITO/Tp interface is due to different values of the reorganization energies .That means the electron acceptor state of SnO_2 is more delocalized than that of ITO and TiO_2 . As mentioned that the calculated electron transfer rate constant for TiO_2/Tp interface

is longer than that of ITO/Tp and SnO_2/Tp respectively.

The difference between the calculated results of the reorganization energies for TiO_2/Tp , SnO_2/TP , and ITO/Tp dye system in acetonitrile solvent may be due to effect of the refractive index and dielectric constant, However, these factors which would make the reorganization energy of SnO_2/Tp dye system longer than ITO/Tp and TiO_2/Tp of the dye system respectively.

Table(3): Theoretical calculation results for k_{et} compared with experimental and theoretical value .

System	Experimental values of k_{et}	Theoretical values k_{et}
Si/Viologen	0.6[20] ,1.6[21]	1.9[8]
In/ Me_2Fe	1~2 [21],0.084[4]	1.1[8]
TiO_2/Tp	-----	1.600(our result)
SnO_2/Tp	-----	0.3409(our result)
ITO/Tp	-----	0.422(our result)

Conclusion

Although the quantum mechanical model is good approximate, it does provide area reasonable description for electron transfer at semiconductor/dye interface of solvent system.

Although, we comparing the rate constant and the reorganization energy results in Table (2), that the rate constant in TiO_2/Tp system is better than ITO/Tp and SnO_2/Tp , this indicate, the electron is more delocalized in SnO_2 than ITO and TiO_2 .

In summary, It appears that the transfer of electron in TiO_2 is more active than SnO_2 and ITO for same dye, this indicate the electron transfer reaction occurs near the semiconductor conduction valence band edge and molecule levels dye.

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