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Studying The Significant Effect of Temperature on The Electron Transfer Rate of Ruthenium N3 Dye In Contact with CdSe Semiconductors

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Abstract

Use The electron transfer rate (ETR) of CdSe semiconductors in contact with ruthenium N3 dye was calculated based on the electron transport theory using the quantum hypothesis of the donor-acceptor model. The electron transport rate of the ruthenium compound N3-CdSe was affected based on the calculation of the rearrangement energy, polarity, strong coupling, path length, atomic density, and concentration. The electron transport rate of the electrons was also studied and evaluated. Morpholine and ethylamine (E) solvents are used to study the electron transport rate affected by reorganization energy, force coupling, and temperature, and are analysed in N3-e devices, based on the electron transport rate results. The electron transport rate results show that the rate behavior is strongly affected by temperature, redistribution energy, force coupling, and strong coupling, which limits the movement of electrons in N3-CdSe devices.The rate, which is affected by increasing temperature and bond coupling strength as well as increasing reorganization energy, greatly affects the electron transport process and determines the electronic characteristics of N3-CdSe devices. Specifically, the electron transfer rate increases with increasing temperature and coupling between the N3 dye and CdSe..This plays a key role in increasing the electron transfer rate, as an increase in strong coupling corresponds to increased electron transfer, and vice versa.

Keywords: Temperature, Electron Transfer, Ruthenium N3,CdSe.

1. Introduction

Electron transfer is the fundamental mechanism in the fields of physical chemistry, physics, and biophysics, which manifests in electricity, photosynthesis, complex chemistry and other areas of device technology and solar cells[1]. Electron transport is the primary basic reaction in photovoltaic cells, and it relies on photoinduced transport across molecular and semiconductor interfaces in devices [2].

Theoretical and practical research focuses on electron transport interactions in various devices across physics, biology, and chemistry. Marcus presented the basic classical theory of electron transport in 1950 in a simplified model. He then applied his theory to molecular systems to understand the interaction. Leading to qualitatively correct conclusions[3]. In recent years, Marcu's theory has gained considerable attention as a key element in charge transfer interactions to explain the physical properties and adaptability to different temperatures in photovoltaic applications [4]. The mechanism for transferring electrons across material interfaces is primarily aimed at improving the performance of technological devices and materials. It has received increasing attention and provided valuable insights for the development of performance enhancement devices [5]. Electron transport in dye-sensitized solar cells (DSSCs), pioneered by Oregano and recently gained increasing attention [6].

Recently, have argued that reorganization energy is the most important parameter in electron transport reactions for the reorganization of energy levels in devices. Electron transport occurs in multi-junction devices in various device technologies[7].Contact molecules with semiconductor interfaces have been used in many devices such that solar cells, and electronic devices [8]. Furthermore, the dye molecules are affected by the semiconductor potentials, causing the conduction band to shift either up or down, preventing electronic recombination at the interface, which depends on the electronic properties of light absorption at the LUMO level[9].

In fact, semiconductors possess a wide range of properties, from conductivity to insulation, and are used as the basis for many solar cell technologies. Ruthenium N3 has superior light absorption and electron transfer capabilities to the conduction band, thus improving overall device efficiency. This compound shows great potential in improving the solar energy collection efficiency of dye-sensitized solar cells (DSSCs) [11]. Cadmium selenide (CdSe) is an inorganic material belonging to the group II-VI semiconductors, and has become one of the best materials in the solar cell industry thanks to its n-type conductivity and band gap of 1.74 electron volts at room temperature [12]. CdSe material highlights the potential for improving the performance of solar cells for indoor applications, as it features higher carrier mobility, a wide band gap, and a higher absorption coefficient, making it an attractive candidate for use in solar cells [13]. As a result of the challenges of quantum theory in electron transport and the increasing interest in the effect of potentials on the rate of electron transport from the donor state to the acceptor state, numerous researchers have developed and contributed electron transport theory (ETT) based on theoretical analytical process as well as computer simulation methods and experimental [14].

In this paper, we investigate the effect of temperature on the electron transport reaction rate from the excited state of the N3 dye to the conduction band in CdSe semiconductors.

2. Materials and Methods

2.1.Theory

The rate of electron transport in N3-CdSe device is [15]

$$|T|^2 = \sum \frac{2\pi t}{\hbar} |\langle C_{RC} \rangle|^2 \rho_{RC}(E_R - E_C)) \quad \textbf{(1)}$$

Where ħ is the Planck constant divided on 2π,t is time , C_{RC} is strong coupling and $\rho_{RC}(E_R - E_C)$ is the density function and E_R and dye E_C are energies in CdSe semiconductor and N3 dye. The density as function of reorganization energyΛ_C^R(eV), and driving potential ΔU^0 ,it is given by [16].

$$\langle \hat{\boldsymbol{\rho}}_{\boldsymbol{D}} \rangle = \frac{e^{-\frac{(\Lambda_C^R + \Delta U^0)^2}{4\Lambda_C^R k_B T}}}{\sqrt{4\pi\Lambda_C^R k_B T}} \quad \textbf{(2)}$$

Where k_B is the Boltzmann constant and T is temperature and driving energy $\Delta U^0 = \mathrm{E_c} - \mathrm{Q^o}$,where $\mathrm{E_c}$ is conduction band and chemical potential for N3 dye $\mathrm{Q^o}$ [17]. The electron transport rate of electronic transfer writes as.

$$|T|^2 = \frac{2\pi t}{\hbar} \sum |\langle C_{RC} \rangle|^2 \rho_{RC}(E_R - E_C)\, dE \quad \textbf{(3)}$$

Inserting **Equation (2)** in **Equation (3)** and introduces the Fermi density in system to results

$$|T|^2 = \frac{2\pi t}{\hbar} \int \frac{e^{-\frac{(\Lambda_C^R + \Delta U^0)^2}{4\Lambda_C^R k_B T}}}{\sqrt{4\pi\Lambda_C^R k_B T}} |\langle C_{RC} \rangle|^2 \rho_{RC}(E_R - E_C)) \mathrm{F_{(E)}} dE \quad \textbf{(4)}$$

The effective density of state in N3/CdSe system is [18].

$$\rho_{RC}(E_R - E_C)) = \rho_R(E) \langle \hat{\boldsymbol{\rho}}_{\boldsymbol{D}} \rangle \rho_C^{-2/3} \frac{\boldsymbol{l_C}}{(\frac{6}{\pi})^{1/3}} \quad \textbf{(5)}$$

where $\rho_R(E)$ is the electronic density of the CdSe, l_C is the length and ρ_C is the atomic density of the CdSe. The **Equation (4)** in **Equation (5)** to produce.

$$|T|^2 = \frac{2\pi t}{\hbar}\int \frac{e^{-\frac{(\Lambda_C^R+\Delta U^0)^2}{4\Lambda_C^R k_B T}}}{\sqrt{4\pi\Lambda_C^R k_B T}}|\langle C_{RC}\rangle|^2\rho_R(E)\rho_C^{-2/3}\frac{l_C}{(\frac{6}{\pi})^{1/3}}\mathrm{F}_{(\mathrm{E})}dE \quad \textbf{(6)}$$

The electron transport rate proportional to time t by[19]

$$T_{RC} = \frac{|T|^2}{t} \quad \textbf{(7)}$$

The **Equation (6)** inserts in **Equation(7)** to obtain.

$$T_{RC} = \frac{2\pi}{\hbar}\int \frac{e^{-\frac{(\Lambda_C^R+\Delta U^0)^2}{4\Lambda_C^R k_B T}}}{\sqrt{4\pi\Lambda_C^R k_B T}}|\langle C_{RC}\rangle|^2\rho_R(E)\rho_C^{-2/3}\frac{l_C}{(\frac{6}{\pi})^{1/3}}\mathrm{F}_{(\mathrm{E})}dE \quad \textbf{(8)}$$

The integral in **Equation(8)** results to density of electrons in CdSe [20]

$$\int \rho_R(E)\mathrm{F}_{(\mathrm{E})}dE = [\rho_R] \quad \textbf{(9)}$$

Insert **Equation (9)** in **Equation(8)** to reduce.

$$T_{RC} = \frac{2\pi}{\hbar}|\langle C_{RC}\rangle|^2\frac{1}{\sqrt{4\pi\Lambda_C^R k_B T}}e^{-\frac{(\Lambda_C^R+\Delta U^0)^2}{4\Lambda_C^R k_B T}}\rho_C^{-2/3}\frac{l_C}{(\frac{6}{\pi})^{1/3}}[\rho_R] \quad \textbf{(10)}$$

The reorganization energy of system is [21].

$$\Lambda_C^R(eV) = \frac{e^2}{8\pi\varepsilon_\circ}\left[\frac{1}{r}\left[\frac{1}{n^2}-\frac{1}{\varepsilon}\right]-\frac{1}{2D_{D-S}}\left[\left(\frac{n_{Sem}^2-n^2}{n_{Sem}^2+n^2}\right)\left(\frac{1}{n^2}\right)-\frac{\varepsilon_{Sem}^2-\varepsilon^2}{\varepsilon_{Sem}^2+\varepsilon^2}\frac{1}{\varepsilon^2}\right]\right] \quad \textbf{(11)}$$

where e is electron charge**,** ε_0 is permittivity of free space,r_D and D_{D-S} are radius of N3 or CdSe and distance between N3 and CdSe, $n_{Sem}^2$and S_{sem} are s the refractive index and dielectric constant of the semiconductor,n and S are the optical and statistical dielectric constant of solvents. The radius of the dye molecule is [22].

$$r(nm) = \left(\frac{3}{4\pi}\frac{m}{N\rho}\right)^{\frac{1}{3}} \quad \textbf{(12)}$$

Where m is the molecular weight, N_A is Avogadro's number, and ρ is the mass density.

2.2. Materials

To study the photovoltaic N3 dye contact with CdSe based Dye-Sensitized Solar Cells (DSSCs), we can focus on physical properties for both materials. The physical properties of N3 dye and CdSe are listed in **Tables 1** and **2.**

Table 1. The general properties of N3 dye[23, 24] .

Full name of Dye	**Cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)**
Chemical formula	[C26H16N6O8RuS2]
Molar Mass	705.64 g/mol [23]
Density	1.7 - 1.9 g/cm³ [24]
Melting point	> 300°C
HOMO	-5.75 eV (vs. Vacuum)
LUMO	-3.75 eV (vs. Vacuum)
Calculated radius	5.3964 Å
Chemical potential	2

Table 2. Characteristic of cadmium selenide [25, 26] .

Properties	**Cadmium selenide(CdSe)**
Molecular Weight	191.23 g/mol
Crystal Structure	Wurtzite (Hexagonal)
Lattice Constant	a = 4.30, c = 7.01Å
Dielectric Constant	9.7 or 9.4
Band Gap	1.74 eV
Density	5.81 g/cm³
Melting Point	1268 °C
Melting Point	1268 °C
Radii	3.44799

3. Results

An electron transfer rate calculation depends on quantum donor-acceptor model used for in N3 dye contact with CdSe, it presents using two: Morpholine and E Ethyleneoamine solvents depends on the transition energy, it tends to play main key in limited electron transfer rate from the excited N3 dye to conduction band of CdSe using MATLAB program. Reorganization energy$\Lambda_C^R(eV)$ can calculate using **Equation (11)** by taken the radii of N3 dye and CdSe that's calculate using **Equation (12)** using the molecular weight $705.64\frac{\text{g}}{\text{mol}}, 19.23\frac{\text{g}}{\text{mol}}$ with mass density $1.36\ \text{g}/cm^3, 5.81\ \text{g}/cm^3$ of N3 dye and CdSe to results $5.93\ A^0$, and 3.44Å, respectively.The reorganization energy contribution can estimate due to **Equation (11)** for the N3-CdSe -device by taking the refractive index (n) and **(ε)**dielectric constant for Morpholine and E Ethyleneoamine solvents from the **Table 3** with taken the radii 5.93Å and 3.44 Å for N3 and CdSe , refractive index and dielectric constant of the semiconductor cadmium selenide and the distance between N3 and CdSe ,results list in **Table 4.**

Table 3. The refractive index and dielectric constant for common used solvents[27] .

Solvents	Refractive index	Dielectric constant
Morpholine	1.4545	7.33
E Ethyleneoamine	1.4513	12.90

Table 4. Results of the reorganization energy $\boldsymbol{\Lambda_{RZ}(eV)}$for charge transport at RuN3- CdSe.

Solvents	Refractive index	dielectric constant	$\boldsymbol{\Lambda_C^R(eV)}$
Morpholine	1.4545	7.33	0.35090
E Ethyleneoamine	1.4513	12.90	0.42893

The rate of electron transfer T_{RC} has been calculated as a function of the reorganization energyΛ_C^R,density carrier $[\rho_R]$, strong coupling$|\langle C_{RC}\rangle|$, band energy E_c ,chemical potential Q^o, length and atomic density $\rho_C^{-2/3}$ using **Equation (10)** for the N3-CdSe device by took the transition energyΛ_C^R from the **Table (3)** for N3-CdSe device , band gab **eV** of CdSe and the potential Q^o (eV) of N3 dye, $l_C = 3A, [\rho_R] = 3.45518 \times 10^3 cm^{-3}$, $1.9291 \times 10^4 cm^{-3}$and $3.3274\times 10^4 cm^{-3}$, for T=300,305 and 310K with $C_{RC} = [0.5,0.75,1,1.25,1.5,1.75,2,2.25,2.5, 2.75,3,3.25,3.5,3.75,4]\ x10^{-6}$ eV/taken MATLAP program . Results list in Tables (5) (6) and (7) for N3-CdSe device at three temperatures T=300,305 and 310 K.

Table 5. Results rate of electron transfer rate$\boldsymbol{T_{RC}(\frac{cm^{-4}}{Sec})}$ for N3- CdSe devices at 300K

$\boldsymbol{\langle C_{RC}\rangle x10^{-6}}$ eV/ state	Carrier concentration $\boldsymbol{\rho_R(E)3455.1826\frac{1}{cm^3}}$	
	Morpholine	E Ethyleneoamine
0.5	5.207E+11	3.064E+11
0.75	1.172E+12	6.894E+11
1	2.083E+12	1.226E+12
1.25	3.254E+12	1.915E+12
1.5	4.686E+12	2.758E+12
1.75	6.378E+12	3.753E+12
2	8.331E+12	4.902E+12
2.25	1.054E+13	6.205E+12
2.5	1.302E+13	7.660E+12
2.75	1.575E+13	9.269E+12
3	1.874E+13	1.103E+13
3.25	2.200E+13	1.295E+13
3.5	2.551E+13	1.501E+13
3.75	2.929E+13	1.724E+13
4	3.332E+13	1.961E+13

Table 6. Results rate of electron transfer rate $\boldsymbol{T_{RC}}(\frac{cm^{-4}}{Sec})$ for N3- CdSe devices at 310 K

$\langle C_{RC}\rangle$x10^{-6} eV/ state	Carrier concentration $\rho_R(E)$ 1.9291× $10^4 \frac{1}{cm^3}$	
	Morpholine	E Ethyleneoamine
0.5	2.868E+12	1.724E+12
0.75	6.453E+12	3.878E+12
1	1.147E+13	6.894E+12
1.25	1.793E+13	1.077E+13
1.5	2.581E+13	1.551E+13
1.75	3.514E+13	2.111E+13
2	4.589E+13	2.758E+13
2.25	5.808E+13	3.490E+13
2.5	7.171E+13	4.309E+13
2.75	8.676E+13	5.214E+13
3	1.033E+14	6.205E+13
3.25	1.212E+14	7.282E+13
3.5	1.405E+14	8.445E+13
3.75	1.613E+14	9.695E+13
4	1.836E+14	1.103E+14

Table 7. Results rate of electron transfer rate $\boldsymbol{T_{RC}}(\frac{cm^{-4}}{Sec})$ for N3- CdSe devices at

$\langle C_{RC}\rangle$x10^{-6} eV/ state	Carrier concentration $\rho_R(E)$ 3.3274× $10^4 \frac{1}{cm^3}$	
	Morpholine	E Ethyleneoamine
0.5	4.926E+12	2.979E+12
0.75	1.108E+13	6.703E+12
1	1.970E+13	1.192E+13
1.25	3.078E+13	1.862E+13
1.5	4.433E+13	2.681E+13
1.75	6.034E+13	3.649E+13
2	7.881E+13	4.766E+13
2.25	9.974E+13	6.032E+13
2.5	1.231E+14	7.447E+13
2.75	1.490E+14	9.011E+13
3	1.773E+14	1.072E+14
3.25	2.081E+14	1.259E+14
3.5	2.414E+14	1.460E+14
3.75	2.771E+14	1.676E+14
4	3.152E+14	1.906E+14

4. Discussion

The results show that the reorganization energy is affected by the polarity of the solvents, and depends on the dielectric constant and refractive index of both CdSe and the two solvents, morpholene and ethyleneamine, in the N3/CdSe apparatus, where the energy increases with decreasing refractive index and increasing dielectric constant .

The calculated data indicate that the highest reorganization energy was 0.42893 electron volts for ethyleneamine, compared to the lowest reorganization energy of 0.35090 for morpholine. The rate of electron transfer, at 300 K at concentration 3.45518×10^3 cm^{-3} with taken driving force, the rate of the Morpholine solvent was highest than E Ethyleneoamine solvent used in the N3/CdSe device, where the value of electron transfer rates reached 3.332×10^{13} at the $l_C(3A)$ and strong coupling 4×10^{-6} eV state . By comparing the two solvents in the N3/CdSe device for the same strong coupling power, it is shown that a decrease in solvent transfer energy leads to a higher electron transfer rate, and the electron transfer rate increases with increasing strong coupling power state and decreasing transfer energy.

On the other hand, the electron transfer rate shows increase with increasing temperature compared to the rate at 300 K with the same coupling strength. However, the rate increased with increasing coupling strength and decreasing transfer energy. the N3/CdSe device have large rate with Morpholine solvent than device with E Ethyleneoamine solvent as results to suitable energy levels.

The results of electron transfer indicated that rate increases by increases temperature 310 k and increases the strong coupling state . Furthermore, the electron transfer rate reaches to highest value in 310 K and strong coupling $\times 10^{-6}$ eV.

Results of electron transfer in two solvents, indicates that electron transfer rate increased when the temperature was increased and the reorganization energy decreased, which show the transfer of electron increases with more energy by heat in the N3-CdSe device and the results could be shown that the N3-CdSe device with Morpholine solvent have the best electron transfer rates.

The electron transfer rate of N3 dye upon contact with CdSe increases with temperature, due to the increased kinetic energy of the electrons and the decreased rearrangement energy, as described by Marcus theory. However, increasing the temperature can also improve the efficiency of electron injection from the N3 dye into the conduction band of CdSe.

This indicates a low energy band gap for cadmium selenide (1.74 eV), and various bonds, have been used in the solvent-mediated synthesis of cadmium selenide.

5. Conclusion

In conclusion, the highest electron flow rate can be obtained based on the quantum donor-acceptor model when using solvents with low transfer energy and high temperature. The rate of electron transfer was greatly affected by increasing temperature and decreasing transfer energy for both the solvents and the N3/CdSe device. In N3-CdSe device, it founds that the rate of electron increases as the reorganization energy decreases and the strong coupling force increased. As a result of the high temperatures, electrons cross the interface between the excited N3 dye and the conduction band in CdSe, affecting charge transfer rates. As they increase, the electron transfer dynamics become more sensitive to temperature, leading to improved recombination and increased rate of injection of electrons from N3 dye into the CdSe. The N3-CdSe device with morpholine solvent was preferred by approximately 1.7 times compared to the ethylenediamine E solvent.

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Conflict of Interest

The author declares no conflicts of interest.

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Ethical Clearance

As a theoretical study with no human or animal subjects, ethical approval was unnecessary.

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