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Accurate analysis of electron transfer from quantum dots to metal oxides in quantum dot sensitized solar cells

Mohammad Javad Fahimi [a], Davood Fathi [a,*], Mehdi Ansari-Rad [b]

[a] School of Electrical and Computer Engineering, Tarbiat Modares University (TMU), P.O. Box 14115-194, Tehran, Iran
[b] Department of Physics, University of Shahrood, Shahrood, Iran

HIGHLIGHTS

- Electron transfer rate in quantum dot sensitized solar cells (QDSSCs) is analyzed.
- Maximum electron transfer rate is obtained for CdTe-SnO_2 combination.
- Optimum diameter of QD is 2-5 nm, depending on the metal oxide-QD combination.
- Removal of the structural disorders increases the value of electron transfer rate.
- The obtained results could be used as a guide for the future design of QDSSCs.

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ABSTRACT

Electron transfer rate from quantum dot (QD) to metal oxide (MO) in quantum dot sensitized solar cells (QDSSCs) has an important role in the efficiency. In this work, we analyse the electron transfer rate from CdSe, CdS and CdTe QDs to TiO_2, ZnO and SnO_2 MOs by extending the related equations with considering various effects, based on the Marcus theory. In this regard, the effects of QD diameter, QD–MO spacing, the crystalline defects, temperature, and the reorganizational energy, on the electron transfer rate are investigated. The results show that, the maximum electron transfer rate is achieved for CdTe QD with the mentioned three MOs. Moreover, in order to direct the designer to reach the appropriate QDs–MOs combinations for obtaining the maximum electron transfer rate, the average electron transfer rate for various combinations is calculated. For the verification of simulation method, a part of work has been compared with the previous experimental and theoretical results, which indicates the correctness of our simulation algorithm.

1. Introduction

Photovoltaic cells (PVs) have had an increasingly growing market in terms of technological and economic aspects, in recent years. PVs are typically classified into three groups including first, second, and third generations [1], where the quantum dot solar cells (QDSCs) are considered among the third generation cells and involve the efficiency boost capability up to 44% and also low cost [2,3]. QDSCs in turn, are classified into four groups: hetero-junction, Schottky barrier, Perovskite, and QDSSCs [4]. QDSSCs still have the efficiency as low of 6–7% and the researchers' effort to enhance this efficiency has own significant importance [5]. These cells usually consist of the light absorber material (QD), the semiconductor as the collector of electrons with a large band gap (MO), the electrolyte, the counter and photo electrodes [6]. Nowadays, QDs are of great importance because of two important features: (1) the band gap tuning with the change of size, and (2) the multiple exciton generation for an incident photon [7–9]. Regarding sensitive materials widely used as QDs for the light absorption, we can refer to PbS, CdS, CdTe, and CdSe where their usage goes back to 1990 [3,10]. Also the large band gap semiconductors such as TiO_2, SnO_2, and ZnO can be used to collect electrons [11].

Electron transfer plays important role in materials science, biology, and chemistry [12,13]. The efficiency of a solar cell depends on three parameters: the short circuit photocurrent J_{sc}, the open circuit photovoltage, and the fill factor. The electron transfer rate from the light absorbing material to the electron collector semiconductor is one of the parameters enhancing J_{sc}, and as a result, the efficiency of cell will be promoted [6]. According to our investigations, there are some works conducted on the electron

* Corresponding author. Fax: +98 21 82884325.
E-mail address: d.fathi@modares.ac.ir (D. Fathi).

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transfer from QD to the MO in QDSSCs which are briefly mentioned here. In [14,15], the electron transfer rate from CdSe QD to three TiO_2, ZnO, and SnO_2 MOs in a QDSSC with a porous structure has been studied by taking into account the effect of QD diameter. In [16], the multiple electron transfer from CdSe QD to ZnO MO, which is a prerequisite for successful utilization of multiple exciton generation for photovoltaics, has been studied. The effect of morphology of ZnO on the electron transfer rate to CdSe has been studied in [17]. In [18], the theory of tuning electron transfer rates through molecular bridges in QD sensitized oxides has been discussed, which the related results could be used in QDSSCs. Also in [19], the hole/electron transfer dynamics in a CdSe QD sensitized by pyrogallol red molecule has been analyzed and studied. For further investigations, we tried to extract the related equations of electron transfer rate and observe the various effects induced by different parameters on this rate.

The results we have obtained in this work, include the effects of QD diameter, temperature, the crystalline defects of MOs, the reorganizational energy, and QD–MO spacing, on the electron transfer rate for three QDs (CdS, CdTe, and CdSe) and three MOs (TiO_2, SnO_2, and ZnO). Also to provide insights into the design to achieve the maximum electron transfer rate, we have calculated the average electron transfer rate for real condition (QDs distributed randomly on MO with sizes varying in the range of 2–6 nm) for the mentioned three QDs and three MOs. To ensure accuracy of the results, some obtained results concerning the effect of QD diameter on the electron transfer rate were compared with those reported in [14,15], where a high consistency between the two sets of results were observed.

To calculate the average electron transfer rate from QD to MO, two methods including the tunneling between two spheres and the Marcus theory can be used [14,15], where the latter was used in the present work. The electron transfer rate from QD to MO is typically in the range of 10^{10}–10^{12} s^{-1}, which depends on the type and size of both QD and MO [5]. The Marcus theory is widely used for the electron transfer reactions [13]. One of the important parameters required for the calculation of energy transfer rate is the system free energy, which depends on the difference between conduction band edges of QD and MO. For this purpose, to relate the band gap to QD diameter, methods such as the effective-mass approximation, the tight binding method, the k.p method, etc. can be used [20], where we have used the effective-mass approximation method in our work.

The obtained results related to the effect of QD diameter on the electron transfer rate, for three QDs and three MOs, will direct the solar cell designer to consider the average distribution of QD diameter in the structure as the position of peak in the electron transfer rate vs. diameter characteristics (see Section 3.1), where the maximum electron transfer rate will be achieved with this selection.

This paper is organized at the continuation as follows: In Section 2, the theory and structure of QDSSCs and also the governing relations of their performance, from the viewpoint of electron transfer rate from QDs to MOs, are presented. In Section 3, the results of analyses performed on the performance of QDSSC structure in terms of the electron transfer rate from QDs to MOs, which briefly mentioned above, will be presented. Also in this section, some of the obtained results are verified with the reported experimental works in the literature. Finally in Section 4, the conclusion and a summary of research conducted in our work will be provided.

2. Theory

The structure studied in this work is a QDSSC where MO nanoparticles are deposited on a working electrode in an electrolyte medium in which QDs are sensitized. Fig. 1 shows the schematic drawing of studied structure in which the electron transfer mechanism from QDs to MOs and the diagram of conduction and valence band edges are represented. In this figure, QDs and MOs are assumed spherical. The QDs diameters are considered in the range of 2–6 nm and the MOs diameters are assumed to be 20 nm, which these values are in agreement with the reported experimental results.

The electron transfer rate from an individual QD to a bulk MO can be calculated using the functional form of many-state Marcus model [14,15]

$$k_{ET} = \frac{2\pi}{\hbar}\int_{-\infty}^{+\infty} \rho(E)\,|\bar{H}(E)|^2 \frac{1}{\sqrt{4\pi k_B T}} e^{-\frac{(\lambda+\Delta G+E)^2}{4\lambda k_B T}} dE \quad (1)$$

where $\hbar$ is the reduced Plank's constant, k_B is Boltzmann's constant, $\rho(E)$ is the MO density of states (DOS), The reorganization energy, λ, takes on values ~0.1–1 eV in aqueous solutions [21], and $\bar{H}(E)$ is the electronic coupling matrix element which can be expressed as [13,22]

$$\bar{H}(E) = H_0 \exp\left[-\gamma\frac{R-R_0}{2}\right] \quad (2)$$

where H_0 is the donor/acceptor electronic coupling matrix element at van der Waals separation R_0 and γ is a constant determining the rate of falling off H_0 with distance. The value of γ is in the range of 0.8 – 1.2 $Å^{-1}$ where we have assumed equal to 1 $Å^{-1}$ in our work. ΔG is the total system free energy which is combination of electronic energy, $\Delta G_{electronic}$, coulombic energy, $\Delta G_{coloumb}$, and

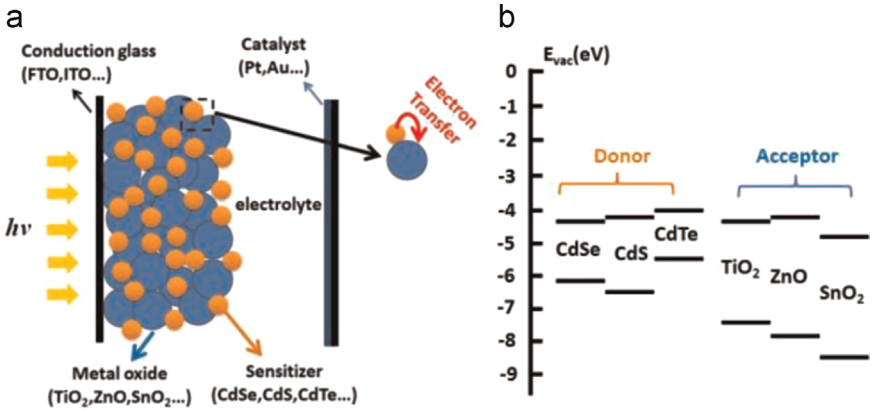

Fig. 1. Schematic drawing of studied QDSSC structure (a) with the representation of electron transfer from CdSe, CdS, CdTe QDs to TiO_2, ZnO, SnO_2 MOs, (b) the diagram of conduction and valence band edges for donors (QDs) and acceptors (MOs).