



The role of solvent and structure in the kinetics of the excitons in porphyrin-based hybrid solar cells



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ABSTRACT

In this study, we investigated the rate of exciton formation and dissociation in TiO₂/Si/porphyrins hybrid solar cells in different phases. Using different porphyrin-based donors in four sets, it was found the best hybrid architectures belong to the donors containing metal and alkyl group and those exposed to the solvents. The proper kinetic of the excitonic processes in these hybrid solar cells are originated from lower affinity energy and exciton binding energy of their donors. Also, donors with the lowest energy barrier of electron injection as well as the highest excitonic Bohr radius showed that the excitons can be dissociated in the dye/semiconductors interface, easily. The analysis of the probable correlations between the molecular descriptors and kinetic parameters of the excitons presented more credible evidences about the solvent and metal effects on the photovoltaic processes. Finally, based on the other performance characters of these solar cells, it was concluded that the maximum value of the external quantum efficiency belongs to the metalloporphyrins in the solvent media.

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1. Introduction

Today, the investigation of the clean and abundant energy sources is an important subject considered by the researchers, greatly. Both fossil and nuclear fuels are of limited abundance and their use can follow a threat to humanity. Therefore, finding the best alternatives to generate electricity seems mandatory (Bobicki et al., 2012; Robertson, 2006). Obviously, designing and building the devices to convert the solar energy into more usable energy for man, such as electricity, is considered a priority in energy and environment researches (Adams and Day, 1876).

High performance and low cost solar cells are in the central of interest of using the renewable energy sources (Grätzel et al., 2012; Mohammadi et al., 2013). Each type of the photovoltaic cells, including the organic or inorganic materials and even a combination of them has its merits and drawbacks (Peters et al., 2011). The metal free organic compounds are of the significant attention in the field of renewable, sustainable energy (Al-Sehemi et al., 2013), photo excitation and photo-electrochemical processes (Tielrooij et al., 2013) due to relatively low cost, easy chemical modification, and structural flexibility (Lan and Huang, 2008; Weitz et al., 2008; Newman et al., 2004; Zaumseil and

Sirringhaus, 2007; Chen and Chao, 2005; Kaltenbrunner et al., 2012; Sun et al., 2012; Mohammadi and Wang, 2014).

Recently, it has been shown that organic and metal organic materials such as porphyrins may be good candidates to improve the performance and charge transfer (CT) processes in dye-sensitized solar cells (DSSCs) (Xu et al., 2008; Liang et al., 2007; Hagfeldt et al., 2010; Tigreros et al., 2014; Arkan et al., 2015, 2016). High dielectric constant value and good thermal stability of the inorganic semiconductors (for example; TiO₂, ZnO, CdS, CdSe, PbS and PbSe) make them as the materials with superior electric properties, while their nanoparticles present better photo-conducting and electric characters (Moon et al., 2011; Tai et al., 2010; Boucle et al., 2008). One of the methods to enhance the stability of the materials and power conversion efficiencies of the photovoltaic cells is the hybrid of the inorganic semiconductors and organic materials (Antonietta Loi and Hummelen, 2013; Cnops et al., 2014; Jeon et al., 2014).

The main processes in the mechanism of action of the hybrid solar cells include the making the excitons, excitons transfer to the interface, charge transport from the donor to the acceptor components on interface and finally charge injection to the electrodes (Chandrasekaran et al., 2011; Kisslinger et al., 2017). Some competitive processes such as recombination of the excitons in the donor and separated charges at the interfaces are able to reduce the power of the conversion efficiency (Liu, 2014). Organic materi-

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als as donors and inorganic nanoparticles as acceptors (Arici et al., 2004) can be considered as the active layer in photovoltaic devices to improve some processes such as Frenkel exciton formation (Singh, 1994; Frenkel, 1931; Narayan and Singh, 2013a, 2013b; Roncali, 2009; Kippelen and Brédas, 2009; Brédas et al., 2009), diffusion (Steinbacher et al., 2012; Yen and Selzer, 1981; Lunt et al., 2009) and dissociation (Narayan and Singh, 2013c; Silva, 2013; Deibel et al., 2010; Bansal et al., 2013).

The construction of the heterojunctions between organic small molecules and semiconductor materials for the hybrid photovoltaic applications is of interest by the researchers (Bhardwaj et al., 2012; Hu et al., 2009; Han et al., 2006; Alberio et al., 2009; Verma et al., 2009; Walsh, 2011; Yun et al., 2009; Taleatu et al., 2013; Bhat et al., 2011; Ozdal et al., 2012; Johansson et al., 2011). The selection of a proper organic dye as a sensitizer to absorb photons in the full sunlight spectrum is a challenge (Tian and Cao, 2013). A lot of studies about the hybrid solar cells were done by the researchers (Saunders and Turner, 2008; Zhou et al., 2010; Wright and Uddin, 2012) to access the appropriate inorganic/organic combinations and finally, the optimal hybrid designing. Using proper combinations of the hybrid organic/inorganic and solvents in the photovoltaic devices can promote the power conversion efficiency.

In this study, we applied several donor materials in hybrid combinations to achieve a better configuration for the hybrid solar cells. Also, we investigated the solvent effects such as methanol (MeOH: CH₃OH) and tert-butanol (t-BuOH: (CH₃)₃COH) on the performance of the hybrid solar cells. Here, the hybrid solar cells comprise of the porphyrin derivatives (organic active material) as a donor deposited on the Si/TiO₂ (nanostructured semiconductor) as an acceptor forming a heterojunction between the two materials. Porphyrins attain strong absorption in the 350–500 nm (Soret or B-band) and 550–700 nm (Q-band) regions (Inahori et al., 2009).

In the hybrid systems, the energy level alignment at the acceptor/donor interfaces controls the charge generation step. Therefore, to recognize a proper configuration for the hybrid solar cells, the analysis of the energy level alignment of hybrid materials is essential. Especially, finding the correlation between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of the materials with the photovoltaic parameters is useful to understand the cases affection on photovoltaic processes of the cells.

We investigated the mechanism of the hybrid solar cell performance, TiO₂/Si/porphyrins, by the analysis of the energy level alignment of the hybrid materials through the mathematical and computational approaches. The charge transfer, rate of excitons formation and dissociation were studied. Moreover, the role of the solvent media, electrophilicity (ω) and electron affinity (EA) of the donors on the excitons formation and dissociation were investigated, too. Finally, the external quantum efficiency (EQE) of these hybrid solar cells was investigated. We believe that a knowledge of the electronic processes in the DSSC is helpful in designing of the efficient hybrid solar cells.

2. Theory and computational methods

To investigate the charge transfer processes in TiO₂/Si/porphyrins hybrid solar cells, we theoretically analyzed the excitons formation and dissociation on the donor/acceptor interface. Also, optimizing the structures of porphyrin donors, p-2H-P, p-Zn-P and p-alkyl-Zn-P; set 1, m-2H-P, m-Zn-P, m-Mg-P and m-Ca-P; set 2, o-2H-P and o-Zn-P; set 3 and CN-b-P and CN-m-P; set 4 (in the gas, MeOH and t-BuOH phases) was performed by the density functional theory (DFT) (Hohenberg and Kohn, 1964) method at the B3LYP/6-31G(d,p) level using the Gaussian 09 program pack-

age (Frisch et al., 2009). Their electronic and excited state properties were investigated by the time-dependent DFT (TD-DFT) (Zhang et al., 2012) on the six lowest states of the spin-allowed singlet-singlet of the porphyrins at the B3LYP/6-311G++(d,p) level of theory.

Since LUMO and HOMO levels are important to understand and describe the electronic transitions and natural bond orbital (NBO) analysis (Reed et al., 1988), we attended them, greatly. Moreover, quantum reactivity indices such as the electrophilicity index, ω , and the electronic chemical potential, μ , were investigated to better understand the electron transfer dynamics and the rate of the excitons formation and dissociation in these hybrid solar cells.

3. Results and discussion

3.1. Exciton dynamics in the hybrid solar cell

Since nowadays molecular modeling methods and particularly quantum chemistry are noteworthy for the interpretation of processes involved in the solar cells and even predicting of novel hybrid combinations, we analyzed the kinetics of excitons in the acceptor/donor interfaces via these methods. In this research, the porphyrin derivatives are used as the efficient donor materials due to their favorable properties in photovoltaic applications. The general structure of the porphyrin derivatives was shown in Fig. 1. The combination of Si/TiO₂ as the acceptor was selected because of the proper charge.

In hybrid solar cells, the sensitizer absorbs the solar energy and the excitons are generated in the donor component. Afterward they diffuse on the donor/acceptor interface and finally are dissociated there (Lyons and Monkman, 2005). In this section, the details of processes such as the exciton formation, excitonic binding energy and rate of exciton formation and dissociation for all sets of the porphyrin derivatives were investigated, using their corresponding interaction operators, transition matrix element and Fermi's golden rule. Finally, the external quantum efficiency (EQE) consists of all these parameters was studied.

3.1.1. Exciton formation

Upon illumination, electron and hole (e-h) are excited on the donor component. Due to electron excitation to the LUMO and staying the hole in the HOMO, an exciton is formed by the strong coulomb interactions between the electron and hole in an organic material with low dielectric constant ($\epsilon = 3-4$) (Narayan and Singh, 2015, 2012). The generation of such excitons is considered as the Frenkel type because of the weak electronic intermolecular interactions in the organics (Narayan and Singh, 2013a). The singlet binding energy between excited electron and hole is expressed through Eq. (1) (Singh and Shimakawa, 2003):

$$E_B = \frac{(\alpha - 1)^2 \mu_x e^4 k^2}{2\alpha^2 \hbar^2 \epsilon^2} \quad (1)$$

where ϵ is dielectric constant of the donor component, \hbar is reduced Planck's constant, ϵ_0 is vacuum permittivity, $k = (4\pi\epsilon_0)^{-1} = 9 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$, e is electronic charge, μ_x is reduced mass of exciton and α is a material dependent constant which shows the ratio of coulomb and exchange interactions between excited electron and hole. In organic materials, the effective masses of electrons and holes are equal with the free electron mass, m_e . Therefore, according to $m_e^* = m_h^* = m_e$ giving $\mu_x = 0.5m_e$ (Narayan and Singh, 2012). Singlet excitonic binding energy (E_B) of the porphyrins using the NBO analysis and TD-DFT computations can be calculated by Eq. (2) (Kim et al., 2012):

$$E_B = E_{g,\text{elec.}} - E_{g,\text{opt.}} = (E_{\text{LUMO}} - E_{\text{HOMO}}) - E_{0-0} \quad (2)$$

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