ENHANCE THE PERFORMANCE OF DYE – SENSITIZED SOLAR CELLS BY DIPOLE MOLECULES

T. Jaseetharan

Department of Physical Sciences, Faculty of Applied Sciences, South Eastern University of
Sri Lanka
jaseetharan@seu.ac.lk

Abstract

Dye – Sensitized nanoporous Titanium dioxide (TiO_2) solar cell is a promising electrochemical device for cost – efficient solar power conversion. This type of solar cell consists of a nanoporous TiO_2 electrode coated with a monolayer of dye molecules, an electrolyte containing I^-/I_3^- redox couple and a platinum counter electrode. Dye molecule acts as a sensitizer and the redox couple is used to regenerate the dye molecule. The effect of dipoles on the open – circuit voltage and short – circuit current density of the dye sensitized solar cell was systematically investigated. These parameters were enhanced by 3.8 % and 25.7 % respectively, and the overall performance of the solar cell was enhanced by 23.8 %.

Keywords: Short – circuit current density, Open – circuit voltage, Sensitizer, Dipole

Introduction

Dye – sensitize solar cells are the cost – efficient electrochemical cells in the energy conversion process. This type of solar Cell was developed in 1991 by O. Regan and Gratzel. Dye-sensitized solar cell combines the optical absorption and charge separation processes by the association of a sensitizer as photon absorbing material with a wide band gap semiconductor. The photo electrode consists of a wide band gap, porous semiconductor (usually TiO_2)of high surface area semiconductor attached to the conducting substrate {Fluorine doped Tin (IV) oxide – FTO} [1, 2].

That is sensitized for the solar radiation by a dye-adsorbed on its surface. Dye molecules are attached to the semiconductor surface through the functional groups on the dye. Anchoring of the dye with TiO_2 takes place through groups like carboxylic acid and phosphoric acid. Operation of a photovoltaic cell can be generally divided into three basic steps consists light absorption, charge separation and charge collection. The power conversion efficiency of a solar cell depends on the efficiency of each of these steps and is maximized by the selection of suitable materials and cell design.

Figure 2 shows the major charge transfer and transport process in a dye-sensitized solar cell[2]. Photons are absorbed by the dye molecules and excited from HOMO (highest occupied molecular orbit) to a LUMO (lowest unoccupied molecular orbit) level (route 1), this happens on the 10^{-15} s time scale. These electrons are then injected into the conduction band of the TiO_2 (route 2) take place in 10^{-15} to 10^{-12} s.

About 60 % of the electrons are injected from the singlet state and about 40 % from the triplet state[2]. For efficient charge injection, the energy level of the dye has to be between 0.2 V and 0.3 V above the conduction band edge of the TiO_2. The corresponding injection rate constants for the singlet state in the femto second range and about one order slower for the triplet state.

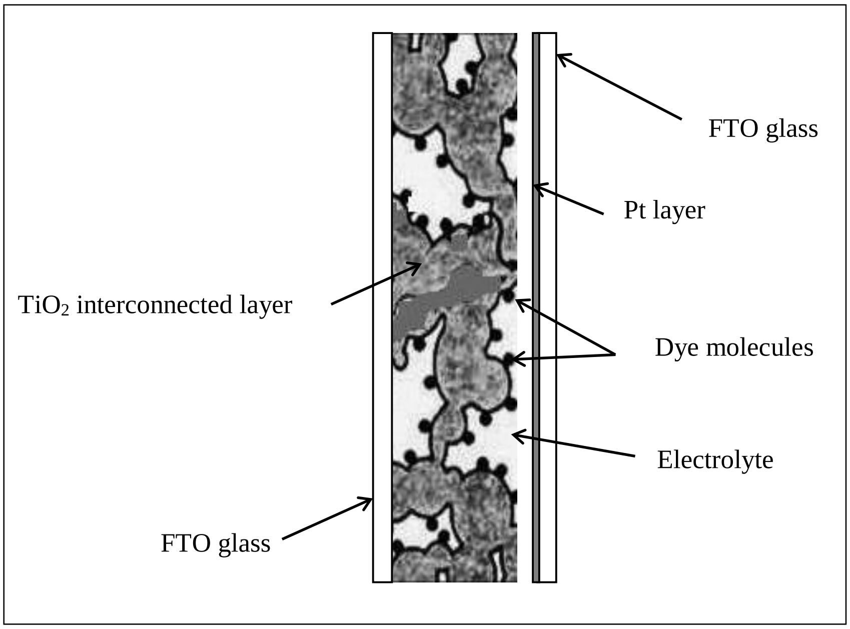

Figure 1: Structure of a typical dye-sensitized solar cell

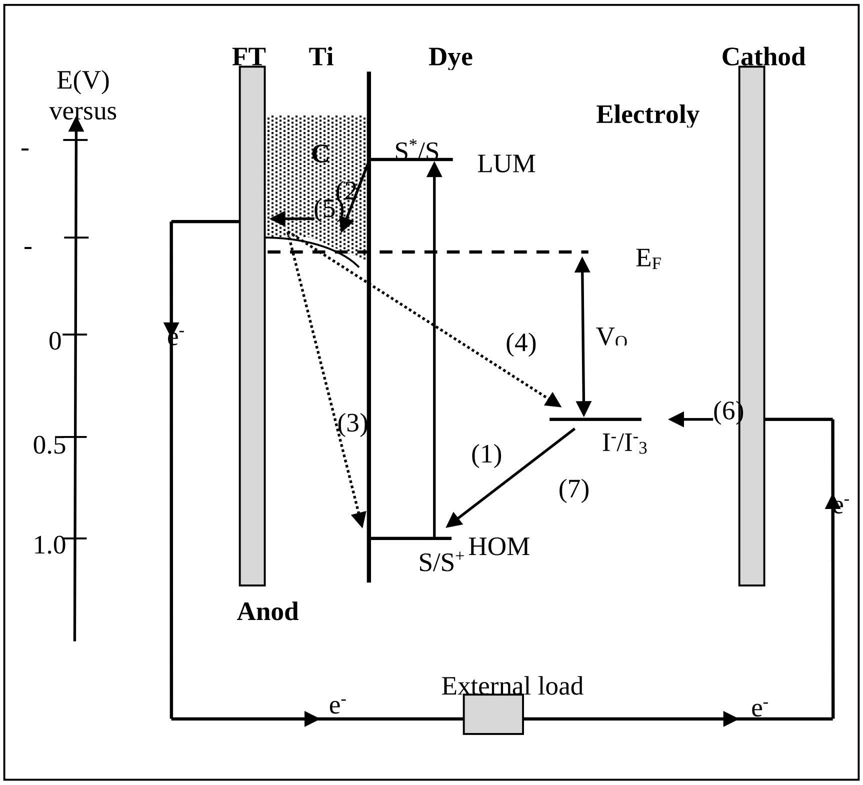

Figure 2: Energy conversion mechanism of dye-sensitized solar cells

Then the electrons transport through the interconnected nanoporous network towards the back contact where they are collected and pass through the external circuit (route 5) occurs on a ms to s time scale. The electron transport through the nanoporous TiO_2 is by diffusion and is relatively slow. After passing through the external circuit, electrons return to the system to regenerate the electrolyte components (route 6) that were used to regenerate the dye molecules (route 7), hence completing the circuit. The sensitizing dye regeneration is the determining step for the performance of the solar cells. In dye-sensitized solar cells, dye regeneration is determining step for the performance of the solar cell. The life time of the dye cation can be as long as 10^{-3} second in the presence of pure solvent. The dye regeneration is faster with increasing I^- concentration and the life time of the excited dye.

Due to the adsorption of organic molecules having different dipole moments to the semiconductor surfaces, the electronic properties of the semiconductor such as band bending, electron affinity and work function are modified[3]. The change in the surface potential induced by a self assembled monolayer or dipole molecules is given by

$$\Delta V = \frac{N_S \ \mu \ Cos\theta}{\varepsilon_r \varepsilon_0}$$

where μ is the dipole moment, $\varepsilon_r\ \varepsilon_o$ is the permittivity of the organic monolayer , N_S is thesurface dipole concentration and θ is the angle between the dipole and the surface normal[3]. In this study, TiO_2 electrodes were treated with dipole molecules having different dipole moments.

Materials and Methods

Preparation of TiO_2 nanoporous electrode

TiO_2 electrodes were fabricated by doctor blade technique. 2 cm x 1 cm size of Fluorine doped Tin Oxide (FTO) glass plates (Dyesol, Australia) were cleaned using acetone and then cleaned using isopropanol several times. After that the FTO glasses were blown with N_2 gas while annealed. Conducting sides of the FTO glasses were identified using an Ohm meter. The cleaned conducting FTO glasses were placed which its conducting side up.

Two edges of the glass were covered by scotch tape. Then small amount of TiO_2 paste was added on the glass plate and paste was quickly dragged across the surface of the FTO glass using a uniform glass rod. Then the scotch tape was carefully removed without scratching the TiO_2 layer and this layer was allowed to dry in air for few minutes and sintered in 450 ˚C for one hour.

Dipole treatment

TiO_2 nanoporous electrode was immersed in to the 0.1 mM of 4-methoxybenzoic acid solution for 3 hours at room temperature. The electrode was removed from the respective solutions followed by blowing the electrode with N_2 gas.

Dye adsorption

Modified TiO_2 electrodes were immersed into the 0.3 mM of N719 [cis-diisithiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)dye solution for 24 hours. Then the dye-adsorbed TiO_2 electrodes were removed from the dye solution and were blown with N_2 gas.

Preparation of counter electrode

Counter electrode solution ($H_2PtCl_6.xH_2O$) was painted on the conductive side of the cleaned FTO glass by using a brush. Then the layer was sintered at 450 ˚C for 30 minutes.

Fabrication of dye-sensitize solar cells

Photo electrode (TiO_2 electrode with benzoic acid derivatives and dye) and the counter electrode were assembled with coated sides together and the plates were clamped together without rub or slide the plates as shown in the figure 3. Liquid I^-/I_3^- electrolyte solution was injected between the photo electrode and counter electrode.

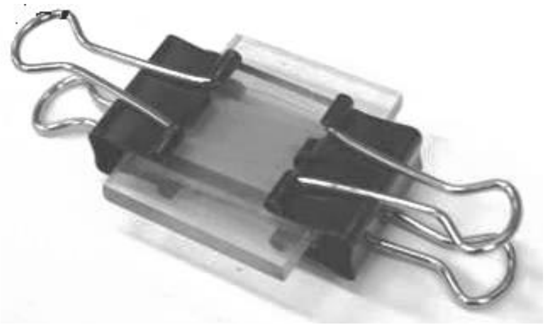

Figure 3: Fabricated dye – sensitized solar cells

Characterizations

Absorption measurements of dye solution, benzoic acid solution, Nanoporous TiO_2 electrode, surface modified TiO_2 electrode, dye adsorbed TiO_2 electrode and TiO_2 electrodes with adsorbed dye & benzoic acid were done by using JascoV-570 UV/VIS/NIR Spectrophotometer. Current - voltage characterization is one of the most important methods to find the efficient solar cell. In this study, this measurement of each dye-sensitized solar cell was done in dark condition and under the illumination of the solar simulator (Science tech) with AM 1.5 spectral filter using a computer controlled source meter unit (Keithley-2400 model).

Figure 4: Current – voltage characterization

Results and Discussion

Figure 5: UV – VIS absorption spectrum of the (a) 0.3 mM N719 dye solution (b) dye-adsorbed surface modified TiO_2 layers and dye- adsorbed unmodified TiO_2 layer. (All

modified and unmodified TiO_2 layers were dipped in to the 0.3 mM dye solution for 24 hours)

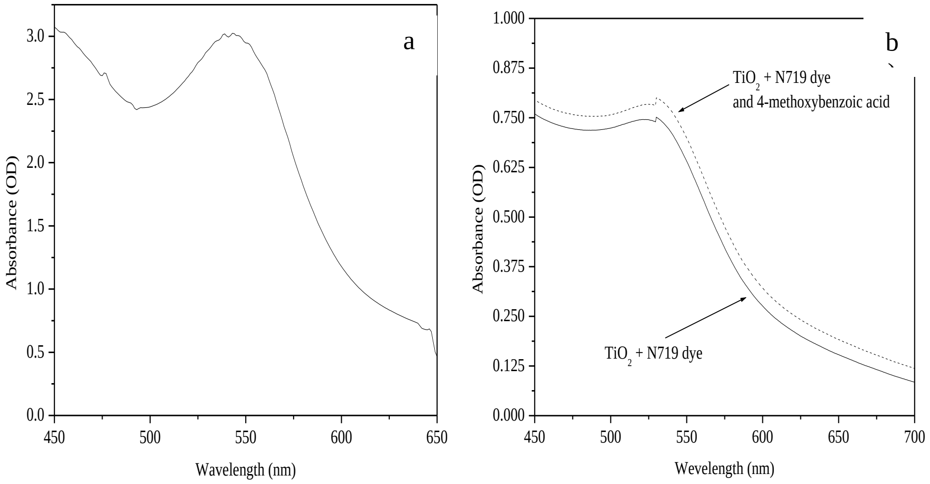

Figure 5: UV – VIS absorption spectrum

Dipole modified dye-adsorbed TiO_2 electrodes show the similar absorption nature of the unmodified dye-adsorbed TiO_2 electrode as depicted in the figure 5(b). All types of photo electrodes show the better absorption in the visible region due to the adsorption of the N719 dye.

Figure 6 displays the current density – voltage characteristics of dipole treated device with corresponding controlled device under the illumination of 100 mW cm^{-2} (with AM 1.5 spectral filter).

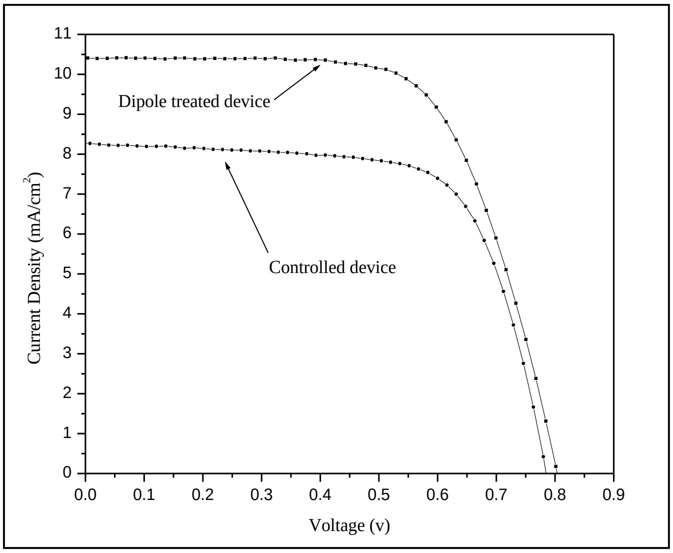

Figure 6: Current density - voltage characteristic of dye-sensitized solar cells

Table: 1 Photovoltaic parameters of the interface modified and unmodified dye-sensitized solar cells

Device	V_{OC} (V)	J_{SC} (mA cm^{-2})	Efficiency (%)
Controlled (TiO_2/dye/electrolyte/Pt)	0.78	8.26	4.45
TiO_2/dye + dipole molecule/electrolyte/Pt	0.81	10.38	5.51
Improvement	**3.8 %**	**25.7 %**	**23.8 %**

The open-circuit voltage is the difference between the Fermi level of TiO_2 and the potential of the redox couple[4]. Open-circuit voltage and short-circuit current density of the dye-sensitized solar cell are increased by the 4-methoxybenzoic acid treatment. Therefore, the dipole moment of the 4-methoxybenzoic acid molecule increased the driving force for the electron transfer from electrolyte to the surface of the TiO_2 and shifted the Fermi level (E_F) toward the vacuum level (away from the redox potential level E_{redox}). Increase in the energy difference between the E_F and E_{redox} would increase the open-circuit voltage.And alsodipole moment of the 4-methoxybenzoic acid molecule decreases the overlap of the TiO_2 states with oxidized species of the electrolyte, which results in a lower recombination and a higher photocurrent as described[5].

Conclusion

Effects of dipole molecules on the performance of the dye – sensitized solar cells were studied and the overall performance of the dye sensitized solar cell was enhanced by 23.8 %. Molecular modification can be used to change of the Fermi level of the TiO_2 in dye-sensitized solar cells depending on the direction of dipole based on the functional group of the dipole molecule.

References

1. Gratzel .M. (2004), J. Photochem. Photobiol., A, 164, 3
2. Hagfeldt, M., Grätzel, M.(1995), Chem. Rev, 95, 49.
3. Cohen, R., Kronik, L., Shanzer, A., Cahen, D., Liu, A., Rosenwaks, Y., Lorenz, J.K., Ellis, A.B. (1999), *Journal of Am. Chem. Soc.* 121, 10545.
4. Sven Ruhle, Miri Greenshtein, Chen, S.G., Alexandra Merson, Hillel Pizem, Chaim S. Sukenik, David Cahen, Arie Zaban (2005), *J. Phys. Chem. B.*109, 18907-18913.
5. Bisquert, J., Zaban, A., Greenstein, M., Mora-Sero, I.(2004), *Journal of Am. Chem. Soc.* 126, 13550.
6. Cahen, D., Hodes, G., Grätzel, M., Guillemoles, J.F., Riess, I.J.(2000), *Journal of Phys. Chem. B.* 104, 2053.
7. Kruger, J., Bach, U., Grätzel, M.(2000), *Journal of Adv. Matt.* 12, 447.
8. Ferber, J., Luthur, J.(2000), *Journal of Phys. Chem. B*. 105, 4895.

9. Bisquert, J., Garcia – Belmonte, G., Fabregat – Santiago, F.(1999), *Journal of Solid state electrochem.* 3, 337.

10. Chiatzun Goh, Shawn R. Scully, Michael D. McGehee (2007), *Journal of App. Phy*. 101, 114503.