

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

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### Abstract

*Dye – Sensitized nanoporous Titanium dioxide (TiO<sub>2</sub>) solar cell is a promising electrochemical device for cost – efficient solar power conversion. This type of solar cell consists of a nanoporous TiO<sub>2</sub> electrode coated with a monolayer of dye molecules, an electrolyte containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> 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<sub>2</sub>) of high surface area semiconductor attached to the conducting substrate {Fluorine doped Tin (IV) oxide – FTO} <sup>1,2</sup>.

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<sub>2</sub> 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<sup>2</sup>. 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<sup>-15</sup> s time scale. These electrons are then injected into the conduction band of the TiO<sub>2</sub> (route 2) take place in 10<sup>-15</sup> to 10<sup>-12</sup> s.

About 60 % of the electrons are injected from the singlet state and about 40 % from the triplet state<sup>2</sup>. 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<sub>2</sub>. The corresponding injection rate constants for the singlet state in the femto second range and about one order slower for the triplet state.

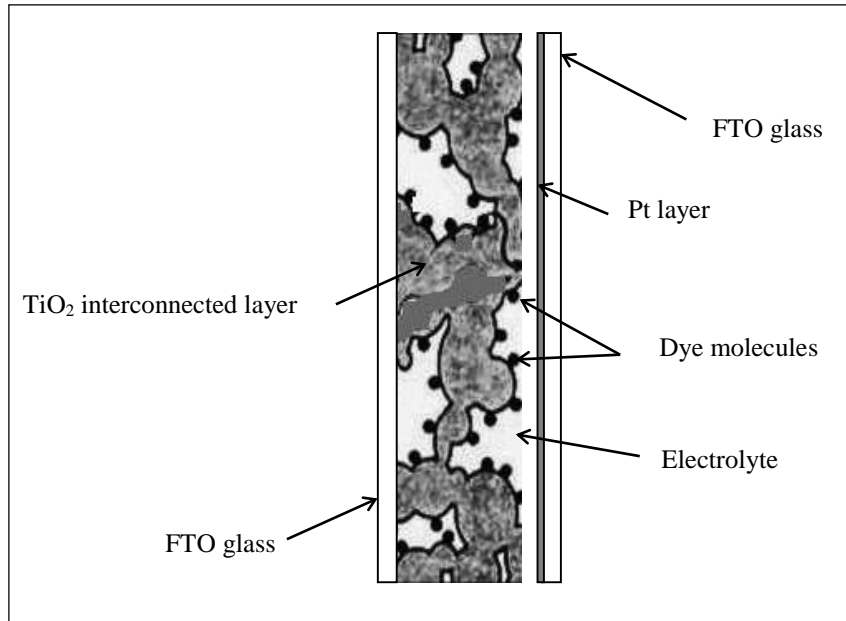


Figure 1: Structure of a typical dye-sensitized solar cell

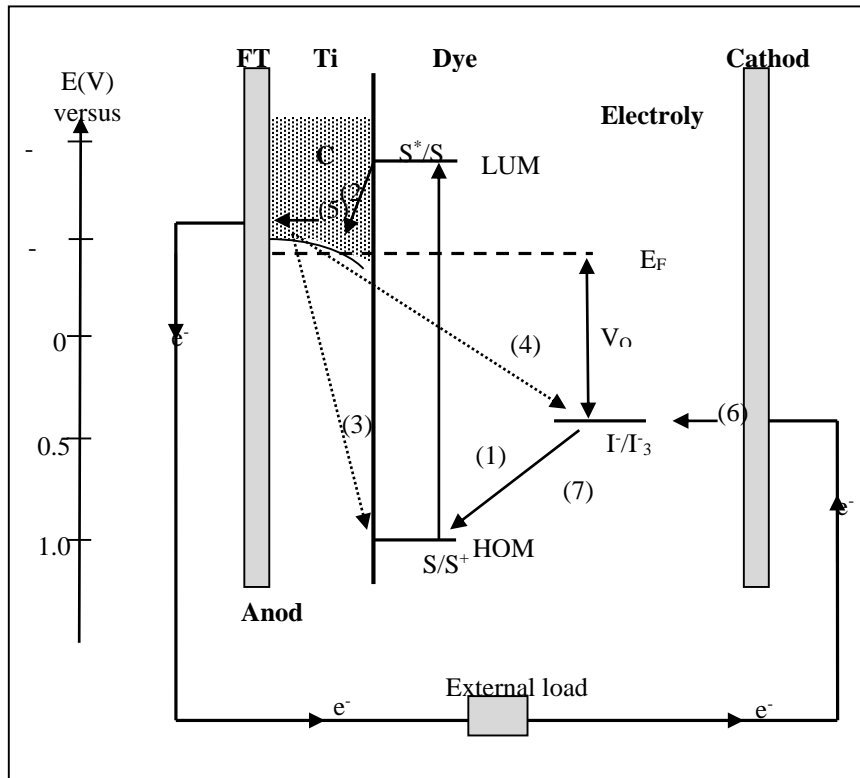


Figure 2: Energy conversion mechanism of dye-sensitized solar cells

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<sub>2</sub> 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<sup>-3</sup> second in the presence of pure solvent. The dye regeneration is faster with increasing I<sup>-</sup> 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<sup>3</sup>. The change in the surface potential induced by a self assembled monolayer or dipole molecules is given by

$$\Delta V = \frac{N_s \mu \cos\theta}{\epsilon_r \epsilon_0}$$

where  $\mu$  is the dipole moment,  $\epsilon_r \epsilon_0$  is the permittivity of the organic monolayer,  $N_s$  is the surface dipole concentration and  $\theta$  is the angle between the dipole and the surface normal<sup>3</sup>. In this study, TiO<sub>2</sub> electrodes were treated with dipole molecules having different dipole moments.

## Materials and Methods

### Preparation of TiO<sub>2</sub> nanoporous electrode

TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> layer and this layer was allowed to dry in air for few minutes and sintered in 450 °C for one hour.

### Dipole treatment

TiO<sub>2</sub> 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<sub>2</sub> gas.

### Dye adsorption

Modified TiO<sub>2</sub> 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<sub>2</sub> electrodes were removed from the dye solution and were blown with N<sub>2</sub> gas.

### Preparation of counter electrode

Counter electrode solution ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) was painted on the conductive side of the cleaned FTO glass by using a brush. Then the layer was sintered at  $450^\circ\text{C}$  for 30 minutes.

### Fabrication of dye-sensitized solar cells

Photo electrode ( $\text{TiO}_2$  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  $\text{I}^-/\text{I}_3^-$  electrolyte solution was injected between the photo electrode and counter electrode.

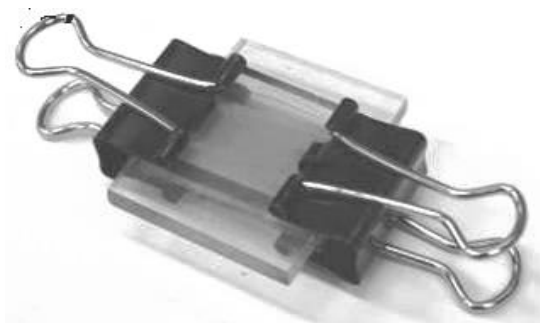


Figure 3: Fabricated dye – sensitized solar cells

### Characterizations

Absorption measurements of dye solution, benzoic acid solution, Nanoporous  $\text{TiO}_2$  electrode, surface modified  $\text{TiO}_2$  electrode, dye adsorbed  $\text{TiO}_2$  electrode and  $\text{TiO}_2$  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).

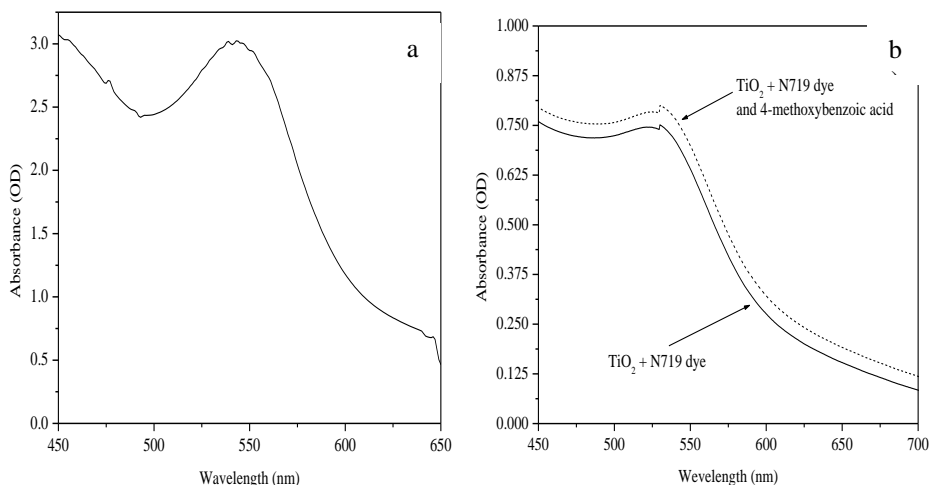


Figure 4: Current – voltage characterization

## Results and Discussion

Figure 5: UV – VIS absorption spectrum of the (a) 0.3 mM N719 dye solution (b) dye-adsorbed surface modified  $\text{TiO}_2$  layers and dye- adsorbed unmodified  $\text{TiO}_2$  layer. (All

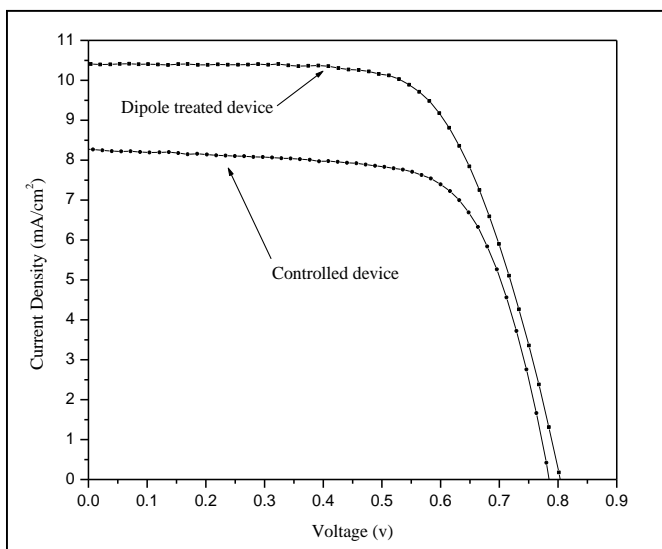
modified and unmodified TiO<sub>2</sub> layers were dipped in to the 0.3 mM dye solution for 24 hours)



**Figure 5: UV – VIS absorption spectrum**

Dipole modified dye-adsorbed TiO<sub>2</sub> electrodes show the similar absorption nature of the unmodified dye-adsorbed TiO<sub>2</sub> 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<sup>-2</sup> (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 <sub>OC</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	Efficiency (%)
Controlled (TiO <sub>2</sub> /dye/electrolyte/Pt)	0.78	8.26	4.45
TiO <sub>2</sub> /dye + dipole molecule/electrolyte/Pt	0.81	10.38	5.51
<b>Improvement</b>	<b>3.8 %</b>	<b>25.7 %</b>	<b>23.8 %</b>

The open-circuit voltage is the difference between the Fermi level of TiO<sub>2</sub> and the potential of the redox couple<sup>4</sup>. 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<sub>2</sub> and shifted the Fermi level (E<sub>F</sub>) toward the vacuum level (away from the redox potential level E<sub>redox</sub>). Increase in the energy difference between the E<sub>F</sub> and E<sub>redox</sub> would increase the open-circuit voltage. And also dipole moment of the 4-methoxybenzoic acid molecule decreases the overlap of the TiO<sub>2</sub> states with oxidized species of the electrolyte, which results in a lower recombination and a higher photocurrent as described<sup>5</sup>.

## 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<sub>2</sub> in dye-sensitized solar cells depending on the direction of dipole based on the functional group of the dipole molecule.

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