

QUASI-SOLID DYE SENSITIZED SOLAR CELL WITH POLY (3-HEXYLTHIOPHENE) AS A HOLE CONDUCTOR

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INTRODUCTION

Dye sensitized solar cells (DSSCs) are a low cost alternative to silicon based solar cells with conversion efficiency exceeding 10% (Gratzel *et al.* 1991). The high efficient DSSCs are of photo electrochemical nature that consists of dye adsorb high band gap nanocrystalline semiconductor coated on conducting tin oxide glass as photo anode and Pt sputtered counter electrode where the capillary space of the film in between the two electrodes is filled with electrolyte containing iodine/triiodide redox couple. But these solar cells suffer from electrolyte leakage and photo corrosion problems. The replacement of the electrolyte with solid hole conductor overcomes some of these problems, so that interest has been drawn on the solid state dye sensitized solar cells which are less problematic taking over the challenge to improve their efficiency. The low efficiency of dye sensitized solid state solar cells is due to the difficulty of securing a permanent solid-to-solid contact between the surface of mesoporous high band gap semiconductor with the hole conductor deposited on top of it. Attempts has been made to fabricate dye sensitized solid state solar cells using inorganic solid hole conductors such as CuI and CuSCN (Tennakone *et al.* 2000) and organic small molecules such as 2,2',7,7'-tetrakis(N,N-di-4-methoxyphenylamino)- 9,9'-spirobifluorene (spiro-OMeTAD) as the hole transporter (Bach *et al.* 1999). The distinctive features of a solid hole conductor are their low temperature solution based deposition technique and high hole mobility. With the optimized fabrication strategies and device configurations efficiency of dye sensitized solid state solar cells has been also brought up to a level of $\sim 5\%$ using some of these hole conductors. (Zhang *et al.*2011)

During the past few years conjugated polymers have been investigated as hole transport materials in DSSCs due to their high conductivity and desired optoelectronic properties. Among those polymeric materials Poly(3-hexylthiophene) (P3HT) is an outstanding representative of this family. It possesses high hole mobility ($0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a good solubility in various organic solvents which allow solution processing of polymer on dye coated mesoporous semiconductor films of DSSCs. (Zhang *et al.*2011)

In this paper we report a dye sensitized quasi solid state solar cell fabricated using P3HT as the hole transporter. Zhang *et al.* has also reported a dye sensitized solid state solar cell of similar configuration in 2011 using P3HT as the hole conductor. But in their work electrical contact to the P3HT has been made by vacuum deposition of Ag on the photo electrode that restricts the fabrication of large area DSSCs. In our work we have used natural graphite to make the electrical contact with the P3HT layer. In addition, we have interposed an ultra thin layer of electrolyte incorporating iodine/triiodide redox couple that mediate the transfer of electrons between the two solid surfaces.

METHODOLOGY

A nanocryatalline TiO₂ film of $\sim 10 \mu\text{m}$ thick was deposited on conducting tin oxide (CTO) glass plate ($12 \Omega \text{ cm}^{-2}$) by the following method. Titanium isopropoxide 5 ml was mixed with 5.5 ml of acetic acid. The mixture was diluted with 10 ml of propan-2-ol and 5 ml of water

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was added drop wise while keeping the solution vigorously stirred. Hydrolyzed titanium isopropoxide was mixed with 0.6 g of Degussa P-25 TiO powder. Conducting glass substrates cut into the size of $1 \times 1.5 \text{ cm}^2$ were ultrasonically cleaned by immersing them in propan-2-ol, rinsed with deionized water and dried in an air stream. A cleaned CTO glass plate was placed on the surface of a hot plate heated to $120 \text{ }^\circ\text{C}$ and the viscous TiO₂ suspension is spread on the conducting surface by a dropper, allowed to dry and sintered in air at $450 \text{ }^\circ\text{C}$ for 10 min. Once the plate was cooled, the loose TiO₂ particles were blown off and the coating process and sintering were repeated several times until a film thickness of $10 \text{ }\mu\text{m}$ was formed. A nanocrystalline TiO₂ film was dyed with the Ru N3 dye by immersing the TiO₂ plates in dye solution (0.5 mM in ethanol) for 12 hours. The TiO₂ film taken out from the dye solution was rinsed with alcohol. The dried film was immersed again in a solution containing 0.05 M I₂, 0.5 M tert-butylpyridine, and 0.6 M dimethylpropylimidazolium iodide in acetonitrile. Then it was taken out and allowed to dry. After that P3HT in chlorobenzene (15 mg ml^{-1}) was spin-coated onto the dyed TiO₂ films at 3000 rpm for 30 s. Natural graphite was coated on the P3HT layer and Au or Pt coated CTO glass was pressed on it to make the back contact. The photocurrent-photovoltage measurements of the cells were recorded by a galvanostat/potentiostat coupled to a computer at 1000 Wm^{-2} light intensity.

RESULTS AND DISCUSSION

Figure 1 shows the I-V characteristics of the hetero structured TiO₂/Ru N3 Dye/P3HT dye sensitized solar cell. The device has a short circuit photocurrent of 1.0 mAcm^{-2} and open circuit photovoltage of 568 mV . The efficiency of this solid state device was found to be 0.32% and fill factor was around 0.56 which is a reasonably high value for a quasi solid state solar cell.

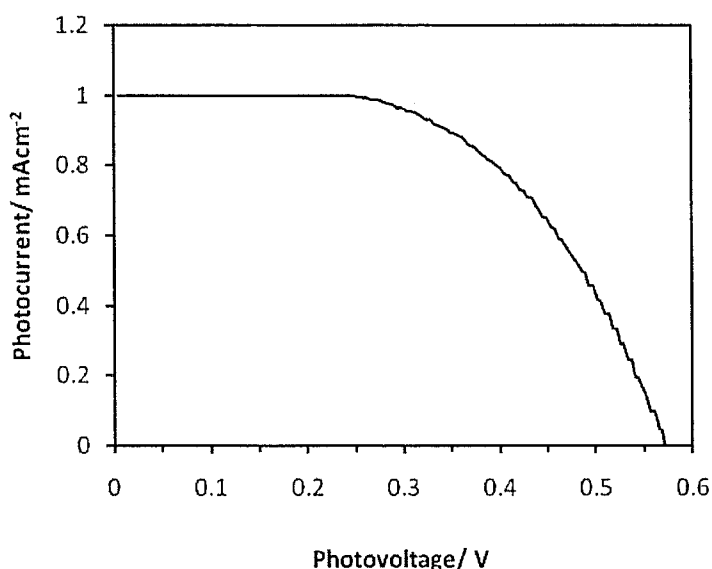


Fig. 1: I-V characteristics of TiO₂/Ru N3 Dye/P3HT dye sensitized solar cell.

The energy level diagram of TiO₂, Ru N3 dye and P3HT polymer is depicted in figure 2. It is evident from the diagram that the conduction band (CB) position of TiO₂ and energy levels of Highest Occupied Molecular Orbital (HOMO) of P3HT are located an energetically favorable manner to accept the excited electron from the dye molecule and donate an electron to the oxidized dye respectively. Since the Lowest Unoccupied Molecular Orbital (LUMO) of P3HT is at a higher energy level than the conduction band of TiO₂, injection of electron from the P3HT by absorption of visible light is also feasible. But Zhang *et al.* in their study have shown that P3HT merely operates in this kind of hetero structure as an electron donor.

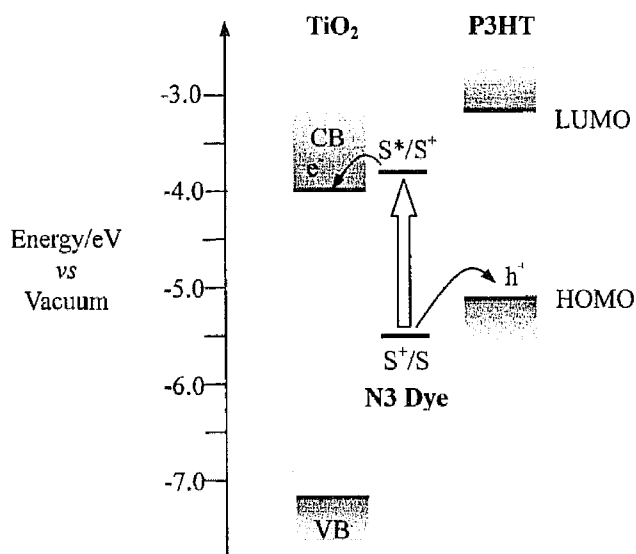


Fig. 2: Energy level diagram of TiO_2 , Ru N3 dye and P3HT.

The other important discovery in this study was the use of natural graphite to make the electrical contacts to the P3HT polymer. Without deposition of a metal such as *Al* or *Ag* by vacuum deposition, it is difficult to form an electrical contact between the P3HT layer and the counter electrode. Therefore this procedure restricts fabrication of large area solar cells and makes the assembly complicated. Depositing silver paste on P3HT by printing techniques has also failed because silver particles penetrate through the pin holes in the P3HT layer resulting short circuiting the cell. Therefore our technique of application of graphite on spin coated P3HT layer avoids those problems to bring down the manufacturing cost further down.

When the P3HT layer was deposited on TiO_2 film just after coating the dye, the photo current was rather low. But when the film is immersed in electrolytic solution containing iodine/triiodide redox couple prior to deposition of P3HT, the photocurrent enhanced by a significant factor increasing the photovoltage of the solar cell. The *tert*-butylpyridine in the electrolyte adsorb on the TiO_2 film is responsible for the improvement of the photovoltage. It passivate the trap sites on the TiO_2 film shifting the quasi Fermi level of the TiO_2 film. The other reason for the high photo current of the cell is due to the ultra thin layer of electrolyte that trapped inside the pores of the nano structured film which may facilitate to connect the two solid films of dye coated TiO_2 and P3HT layer together. We have tested a fabricated cell for several days, but we could not notice any decay in the photocurrent or photovoltage during that period. The P3HT polymer layer deposited on the mesoporous film might prevent the evaporation of ultra thin layer of electrolyte trapped in the pores of the film. On the other hand depositing P3HT alone by spin coating may not allow penetrating and occupying all the capillary space of the film as done by the electrolyte. Therefore this hybrid solar cell provides solutions to the problems that encountered in fabrication of solid state solar cells to make them more stable and efficient.

CONCLUSIONS

A dye sensitized quasi solid state solar cell has been fabricated using P3HT as a hole conducting material. Utilization of ultra thin layer of electrolyte in between the solid films of TiO_2 and P3HT found to enhance the efficient transfer of charge carriers between the donor

and acceptor materials. The electrical contact to the P3HT polymer was made by coating graphite to make the fabrication process simpler and cheaper. It is evident from this study that ultrathin layer of electrolyte is helpful to keep the contacts between the donor and acceptor materials for prolong operation of the solar cell that will be protected by the P3HT polymer from evaporation.

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