

## **Quasi-solid State Dye Sensitized Solar Cells Constructed using PEDOT:PSS as the Hole Conductor**

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### **ABSTRACT**

Many solid hole conductors have been studied to replace the electrolyte of photoelectrochemical DSSCs. In this study PEDOT:PSS is used as the hole conductor in the heterostructure of TiO<sub>2</sub>/Ru-N3 Dye/PEDOT:PSS solid state DSSC. The photocurrent and photovoltage of this solid state DSSC is relatively low. The photocurrent of the DSSC enhanced significantly when the dye coated TiO<sub>2</sub> film was immersed in an electrolyte containing iodine tri-iodide redox couple prior to the deposition of PEDOT:PSS layer. But the photovoltage remained the same even after introducing the thin electrolyte layer. The low photovoltage of this configuration is explained considering the energy level at HOMO of PEDOT:PSS polymer film. The charge carriers are supposed to transfer from the excited dye to the PEDOT:PSS film in the quasi solid state DSSC so that the redox potential of thin electrolyte layer is dominated by the HOMO of PEDOT:PSS.

### **1. INTRODUCTION**

It was realized that the dye sensitized solar cells could efficiently convert solar energy into electricity by using mesoscopic nanostructured titanium dioxide films after being reported by Gratzel and coworkers in 1991 [1]. Since then dye sensitized photoelectrochemical solar cells have been a subject of intensive research in the last few decades. The presence of a liquid electrolyte makes the manufacturing process of dye sensitized solar cells (DSSC) difficult. Therefore, recent efforts in dye sensitized solar cell research are more focusing on the replacement of the liquid electrolyte with a solid or quasi-solid material to eliminate practical problems encountered with evaporation of electrolyte and sealing problems. A solid state cell exhibits a structure similar to the dye sensitized photoelectrochemical cells except for the substitution of electrolyte with a p-type semiconductor material. However, the efficiencies of such solar cells are still lower than that of photoelectrochemical solar cells.

In this report performance of quasi-solid state dye sensitized solar cell constructed based on Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the hole conductor is presented. In this study it is evident that quasi solid cells are more efficient than fully solid state cell when PEDOT:PSS is used as the hole conductor.

## 2. MATERIAL AND METHODS

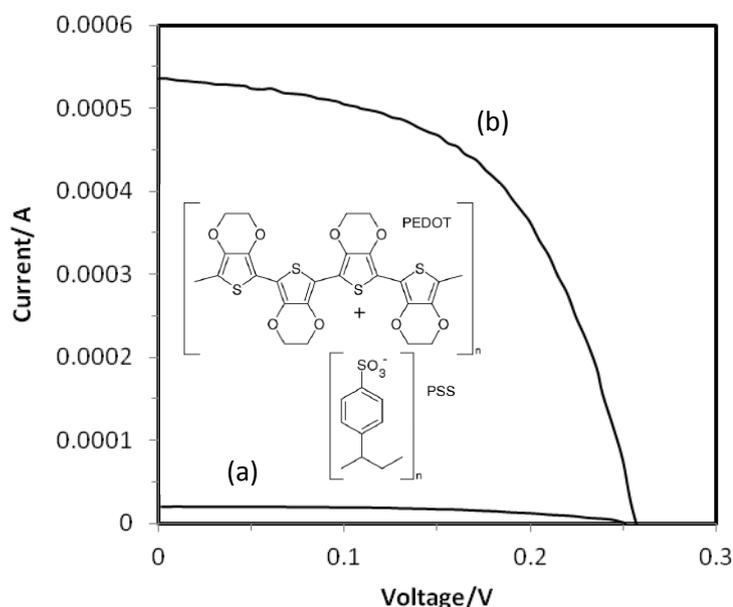
TiO<sub>2</sub> film of 10 μm thick was deposited on conducting tin oxide (CTO) glass (12 Ω cm<sup>-2</sup>) by the following method. Titanium isopropoxide 5 ml was mixed with 5.5 ml of acetic acid. The mixture was diluted with 10 ml of propan-2-ol and 5 ml of water was added drop-wise keeping the solution vigorously stirred. Hydrolyzed titanium isopropoxide was mixed with 0.6 g of Degussa P-25 TiO<sub>2</sub> powder. A cleaned CTO glass plate cut into the size of 1 x 1.5 cm<sup>2</sup> was placed on a hot plate at 120 °C and the viscous TiO<sub>2</sub> suspension was spread on the conducting surface and sintered at 450 °C for 10 min. Coating and sintering process were repeated several times until a film of 10 μm thick was formed. TiO<sub>2</sub> film was dyed with Ru-N3 dye. Dye coated film was put again in a solution containing 0.05 M I<sub>2</sub>, 0.5 M tert-butylpyridine, and 0.6 M dimethylpropylimidazolium iodide in acetonitrile for 10 minutes. It was allowed to dry and PEDOT:PSS (0.8 % PEDOT and 0.5 % PSS dispersion in water, Aldrich) was gently spread on the dye coated surface with a teat pipette and allowed to dry again on a hot plate at 80 °C. Also PEDOT:PSS was printed on dye coated TiO<sub>2</sub> film without treating in acetonitrile solution containing I<sub>2</sub>/I<sub>3</sub><sup>-</sup> redox couple. Finally CTO glass was pressed on the PEDOT:PSS layer to make the back contact. Photocurrent-photovoltage measurements of the cells were recorded with a galvanostat/potentiostat coupled to a computer at 1000 Wm<sup>-2</sup> light illumination.

## 3. RESULTS AND DISCUSSION

Figure 1 (a) shows the I-V characteristics curve of the solid state dye sensitized solar cell with the hetero structure, TiO<sub>2</sub>/Ru-N3 Dye/PEDOT:PSS. The cell has a short circuit photocurrent of 20 μAcm<sup>-2</sup> and open circuit photovoltage of 250 mV. Insertion of figure 1 the molecular structure of the conducting polymer PEDOT:PSS that used in this study as the hole conducting material is shown. The fill factor of this cell is around 0.53% which is at an agreeable limit for a solid state DSSC. But surprisingly, after treating the TiO<sub>2</sub> film coated with dye in acetonitrile solution containing 0.05 M I<sub>2</sub>, 0.5 M tert-butylpyridine, and 0.6 M dimethylpropylimidazolium iodide for 10 minutes, the photocurrent of the cell increased to 0.6 mAcm<sup>-2</sup>. Although the photocurrent increased, photovoltage of the cell still remained at a low value which was around 260 mV. Fill factor of iodine treated cell was 54% and the efficiency of the cell calculated to be around 0.1%. The high photocurrent may be attributed to the collection of majority of photo generated charge carriers by the I<sub>2</sub>/I<sub>3</sub><sup>-</sup> redox couple in the thin electrolyte layer trapped in the pores of the TiO<sub>2</sub> film and their efficient delivery to the PEDOT:PSS film where the PEDOT:PSS alone was unable to do so because the polymer molecules could not or do not penetrate throughout all the pores of the TiO<sub>2</sub> film.

The intercalation of iodine in the pores of the dye coated TiO<sub>2</sub> film enhances only the photocurrent of the cell increasing the efficiency. PEDOT:PSS, a transport material, has been reported to be used in the counter electrodes of DSSCs instead of Pt, since it is a cheaper and also could be coated at low temperatures on plastics for flexible DSSCs [2]. But the photovoltage of those dye sensitized photoelectrochemical solar cells with the iodine tri-iodide redox couple is not such low comparable to already reported values, which are higher than 650 mV very often [3]. Therefore no much different observed in the DSSCs that has Pt counter electrodes or PEDOT:PSS counter electrodes. Thus in

this study it is important to investigate the reason for the low photovoltage of iodine embedded quasi solid state DSSCs with the structure of TiO<sub>2</sub>/Ru-N3 Dye/PEDOT:PSS. The previous work on a solid state DSSCs of similar structures also reported to have low photovoltages, but the reason is not clearly explained [4].

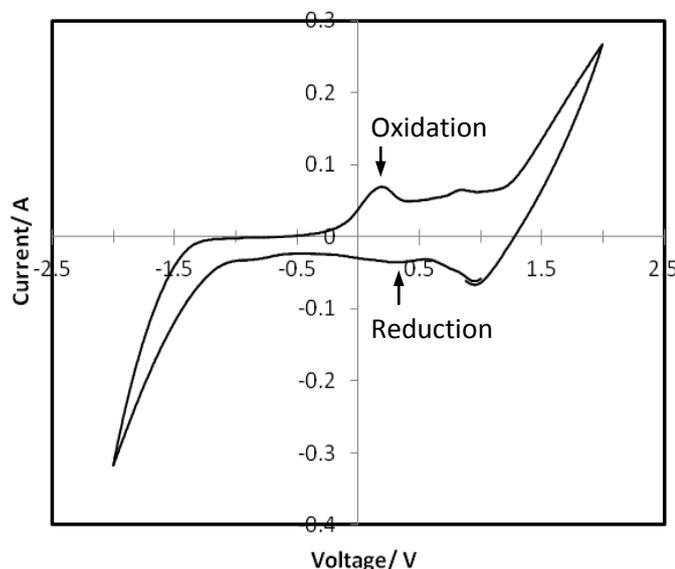


**Figure 1:** I-V characteristic curves of DSSCs with the hetero structure TiO<sub>2</sub>/Ru-N3 Dye/PEDOT:PSS (a) fully solid state cell (b) quasi-solid state cell. Insertion is the molecular structure of the PEDOT:PSS.

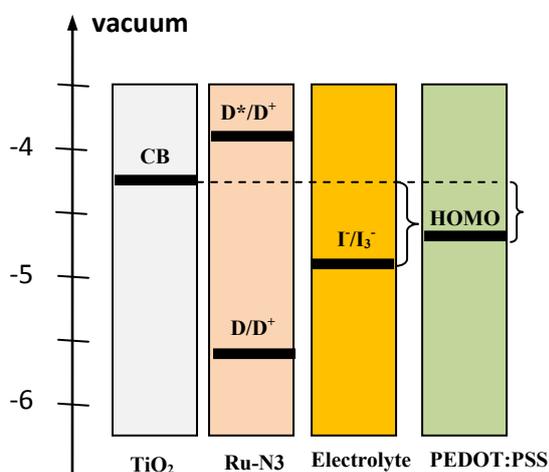
Generally the open circuit photovoltage of photoelectrochemical solar cell is defined as the difference between the conduction band edge of TiO<sub>2</sub> and the redox potential of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple which is about 0.4 V with respect to Ag/AgCl reference electrode [3]. But for a solid state cell, open circuit photovoltage is the difference between the conduction band edge and the valance band edge of n-type and p-type semiconductor materials respectively. When a conducting polymer is introduced instead of a p-type semiconductor, highest occupied molecular orbital (HOMO) level is taken in the place of the valance band position.

Figure 2 shows the cyclic voltogram of the PEDOT:PSS coated CTO glass taken in 0.5M aqueous solution of Na<sub>2</sub>SO<sub>4</sub> with reference to Ag/AgCl reference electrode. The oxidation and reduction peaks appear at 0.18 V and 0.30 V respectively related to the energy state at HOMO of PEDOT:PSS. Therefore, taking the average of oxidation and reduction peaks, HOMO level of PEDOT:PSS is calculated to be at 0.24 V with respect to the reference electrode. Figure 3 shows the schematic diagram of band positions of TiO<sub>2</sub>, Ru-N3 dye, PEDOT:PSS and the redox potential of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> couple. Reason for the low photovoltage of the solid state DSSC with the TiO<sub>2</sub>/Ru-N3 Dye/PEDOT:PSS heterostructure could be easily elucidated referring to this diagram. But it is not clear as to why the photovoltage is still low after insertion of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple to the dye coated TiO<sub>2</sub> matrix that expected to enhance the photovoltage. Since the electrolyte

layer containing the pores of the film is very thin, the redox potential of the electrolyte may be dominated by the energy level of the HOMO of the PEDOT:PSS. That is germinated electrons or holes might directly be transferred from dye to the PEDOT:PSS in most the part.



**Figure 2:** Cyclic voltogram of the PEDOT:PSS coated CTO glass taken in 0.5M aqueous solution of  $\text{Na}_2\text{SO}_4$  with reference to Ag/AgCl reference electrode.



**Figure 3:** Schematic diagram of band positions of  $\text{TiO}_2$ , Ru-N3 dye, PEDOT:PSS and the redox potential of  $\text{I}^-/\text{I}_3^-$  electrolyte.

Photoelectropolymerization of PEDOT on the dye coated  $\text{TiO}_2$  films doped with different anions other than poly(styrenesulfonate) (PSS) in situ polymerization yields to produce high photocurrents and photovoltages from fully solid state heterostructures of similar cells. Doping with anionic groups such as  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{TSFI}^-$  and  $\text{CF}_3\text{SO}_3^-$  seems

to improve the photovoltage of these types of cells significantly [5]. Therefore PEDOT is a promising hole conductor for solid state DSSCs to meet the future energy demands.

#### 4. CONCLUSION

DSSC is constructed with the heterostructure of  $\text{TiO}_2/\text{Ru-N3 Dye}/\text{PEDOT:PSS}$ . The quasi-solid state DSSC by the made insertion of thin layer of electrolyte containing  $\text{I}^-/\text{I}_3^-$  redox couple seems to be efficient more than the fully solid state configuration. In addition PEDOT:PSS polymer layer is capable of protecting the electrolyte thin layer embedded in the pores of the dye coated  $\text{TiO}_2$  film from evaporation for several weeks that under investigation without the proper sealing of the cell, which is an advantage. Polymerization of PEDOT layer on a dye coated  $\text{TiO}_2$  film from the monomer reported to function better because it fills the pores of the  $\text{TiO}_2$  film completely than applying the solution on top of the dye coated  $\text{TiO}_2$  film. Therefore practicing a strategy to fill the pores of the films with PEDOT:PSS by suck back technique will definitely improve the cell performance even without the insertion of thin electrolyte layer.

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