Development of quasi solid state dye sensitized solar cells

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Abstract

Dye Sensitized Solar Cells (DSSCs) present a significant renewable energy source in terms of control of different parameters governing flexibility, efficiency, lifetime and cost. The liquid electrolytes used inside the cells are generally responsible for the leakage and inefficient encapsulation related issues. These are critical for practical applications of DSSCs. The choice of electrolyte medium used in the cell should take into account the fast regeneration of electrolyte and redox potential of the dye. Organic dyes in general, exhibit better extinction coefficients and variant color ranges. The present work is focused on quasi solid state DSSCs based on an organic dye. For the fabrication of devices, nanocrystalline titanium-di-oxide (TiO_2) films were used as the photoanode and well known organic dye Eosin B as the sensitizer. The photovoltaic performance of the cells was measured at different light intensities. The results exhibited the quantum efficiency of organic dye Eosin B which can be used as a potential sensitizer in conjugation with quasi solid state electrolytes. Copyright © 2017 VBRI Press.

Keywords: Quasi solid state dye sensitized solar cells, gel electrolyte, efficiency, lifetime, eosin B.

Introduction

Since the first demonstration of dye sensitized solar cells (DSSCs) by B. O'Regan and M. Gratzel in 1991**[1]**, these devices have gained significant research interest due to their simplified fabrication procedures, low cost, low environmental impact and relatively good power conversion efficiency values **[2]**. Rapid technological advancements in the field has resulted in solar-to-electric power conversion efficiency of 11.9% and up to 15% using perovskite materials under full sun illumination (AM 1.5G, 100 mW/cm^2) **[3, 4]**. Recently, many attempts are also being made to improve design, structure and performance of the dye based solar cells **[5, 6]**. In spite of lower efficiency of these cells as compared to classical silicon based solar cells, DSSCs hold a great potential for performance improvements **[7]**.

A typical DSSC consists of a fluorine doped tin oxide glass coated with a mesoporous nanocrystalline semiconductor oxide (usually TiO_2) film as a photoanode, photosensitive dye, redox electrolyte medium and a platinized cathode. As shown in **Fig. 1**, the photovoltaic process in a DSSC is primarily based upon excitation of dye in response to illuminated light. The chemical reactions occurring inside the DSSC can be fundamentally expressed in terms of following equations (1-4) explaining the processes of (1) dye excitation, (2) Electron injection with generation of electrical energy, (3) Dye regeneration and (4) electron recapture by the electrolyte from the counter electrode.

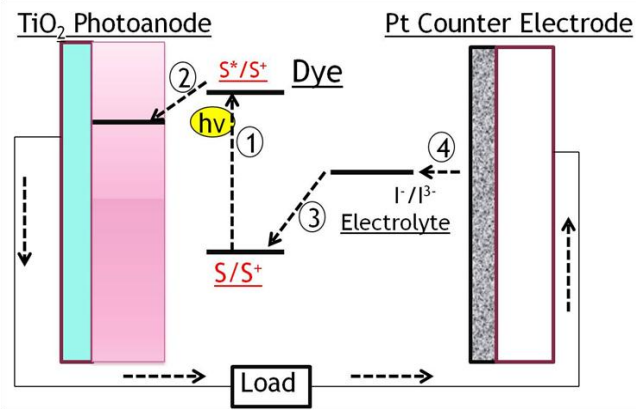

Fig. 1. A schematic diagram representing working principle of DSSCs.

As a first step of cell operation, the light sensitive dye gets photoexcited when illuminated and gets an electron into its excited state called as LUMO- Lowest unoccupied molecular orbital (in case of organic dyes). As a second step, the electron from the photoexcited state of the dye is injected to conduction band of TiO_2. This electron transfer from dye to semiconductor oxide is energetically favorable if and only if the excited state of the dye is at higher energy level as compared to the conduction band of the semiconductor oxide. Furthermore, this charge transfer kinetics has to be fast enough to take place as compared to the other recombination processes inside the

cell. After the successful injection or electron transfer, the electrons are now present in the conduction band of nanocrystalline TiO_2 (nc-TiO_2) film where they percolate through the mesoporous network to the working electrode and travel in the outer circuit doing some work.

As a third step of the cell operation, regeneration of the photo sensitive dye is achieved using redox couple in the electrolyte medium (usually iodide-triiodide) close to the dye. Finally, the reduction of triiodide ions in the electrolyte restores the presence of iodide ions at the cathode, thereby, completing the circuit by electronic charge being migrated through the external load **[1, 2]**. In the whole process of dye cell operation, it generates electric power from the incident light with no enduring chemical conversion. In addition to these favorable reactions during the process of light to electricity conversion inside the cell, there are some unfavorable recombination processes also. For example, recapture of the electrons by oxidized electrolyte ions or recombination of oxidized dye by electrons from conduction band of TiO_2. Assuming the photosensitive dye to be sufficient enough to absorb all the incoming light and to transfer the electrons to semiconductor oxide, competent conduction of electrons in the entire cell, long lasting multiple regeneration of the dye, the whole process works well producing a reasonable efficiency of 10-11% [**8, 9**].

The selection of all the components inside the cell is crucial for efficient performance. Ideally, the photosensitive dye is responsible for the efficient incident light capture and electron transfer to semiconductor oxide. They can be categorized as metal based complexes or metal free organic dyes. Out of these, organic dyes exhibit better extinction coefficients and allow more variation in color with faster electron injection rate in general. In the present work organic dye Eosin B is used as a sensitizer to fabricate DSSCs. Moreover, the choice of electrolyte medium used in the cell should take into account the fast regeneration of itself and redox potential of the dye. The electrolyte medium should be able to exhibit long term stability to ensure maximum lifetime of the cell which can be efficiently achieved in quasi solid state DSSCs **[10]**. In the present work, quasi solid state electrolyte based on poly- ethylene glycol, potassium iodide/iodine (KI/I_2) and TiO_2 is used. A detailed analysis of quasi solid state electrolyte based DSSCs using Eosin B as sensitizing dye has been performed.

Experimental

Materials/ chemicals details

Eosin B with molecular formula $C_{20}H_8Br_2N_2O_9$ and molecular weight 580.09 g/mol, purchased from Sigma Aldrich (with 95% purity), USA was used as the sensitizing material. TiO_2 nanopowder, polyethylene glycol, iodine, succinonitrile (SCN), titanium isopropoxide (TTIP) and acetonitrile were purchased from Sigma Aldrich, USA (with 99% purity). Potassium iodide (Excela R), thiourea (TU) (Merck), and acetic acid (Merck) were also used as such without further purification. Optically transparent fluorine doped tin oxide (FTO) coated films (7Ω/sq) were also purchased from Sigma Aldrich.

Fabrication of photoanode

The conducting glass substrates, FTO were cleaned sequentially with soap solution, deionized water, acetone and isopropanol in ultrasonic bath and dried. A white TiO_2 paste was prepared by grinding the TiO_2 powder with acetic acid in mortar pestle for 20 minutes. Polyethylene glycol (PEG) was added with continuous mixing. The as prepared paste was then coated over the conductive side of the cleaned FTO coated glass plates using doctor blading technique. These plates were then dried in air first then sintered at 450^0C for one and a half hour in a muffle furnace. A 1.12M solution of Eosin B dye was prepared in ethanol. The TiO_2 coated plates were then dipped in this solution for 48 hours at room temperature and then dried at 70^0C.

Preparation of electrolyte

The electrolyte composition was prepared using a mixture of PEG, KI and I_2 in acetonitrile as a solvent. Then nc-TiO_2 was blended together to make a fine paste. This composition consisted of PEG: TiO_2: KI: I_2 in the ratio 36:16:40:8. Further, a 1:1 mixture of SCN: TU was prepared in acetonitrile and added to the above composition to improve its electrolytic activity.

Assembling of DSSC

The gel electrolyte was then applied over the prepared photoanode impregnated with dye solution. These glass plates were first kept for 5 minutes to get stabilized. The assembling of DSSC was finally accomplished by clamping this electrolyte containing dye sensitized photoanode with platinum as a counter electrode to make a sandwich type structure as shown in **Fig. 2.** The active cell area was 0.49 cm^2.

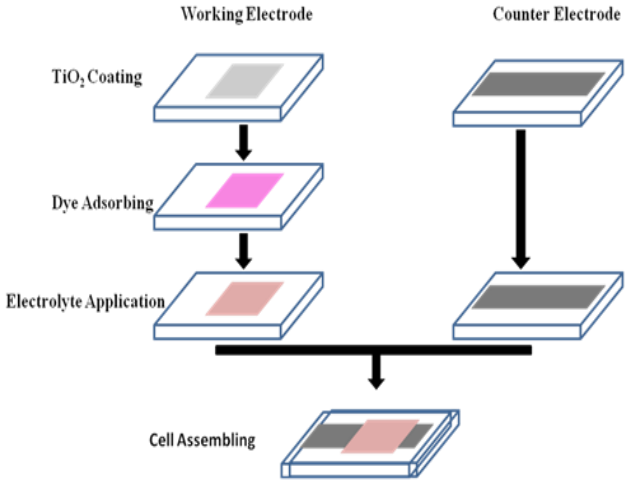

Fig.2: Preparation of cell components and assembling of final DSSC

Characterizations Measurements

Scanning electron microscopy (Carl Zeiss) was used analyze the surface morphology of nanocrystalline TiO_2 films used in DSSCs. The optical absorption of the photosensitive dye was recorded by a spectrophotometer (Shimadzu). Photo response measurements of the DSSCs fabricated were performed by recording the J–V characteristics with a solar simulator (Sciencetech) in the dark as well as under illumination.

Results and discussion

Scanning electron microscopy (SEM) is generally regarded as an effective tool to characterize the surface morphology of nanostructured surfaces. **Fig. 3** shows the top view of nc-TiO_2-coated and sintered glass surface as recorded by SEM. The surface exhibited uniform morphology with some aggregations. The structure was found to be porous as required for efficient dye adsorption. Such uniform layers are generally expected to provide convenient electron pathways for the electrons percolating through porous TiO_2 films to FTO and improve the electron transfer efficiency.

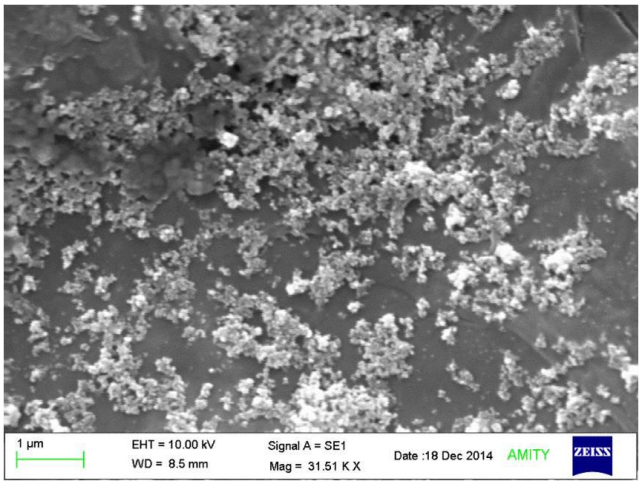

Fig. 3: SEM image of sintered nc-TiO2 coated glass surface.

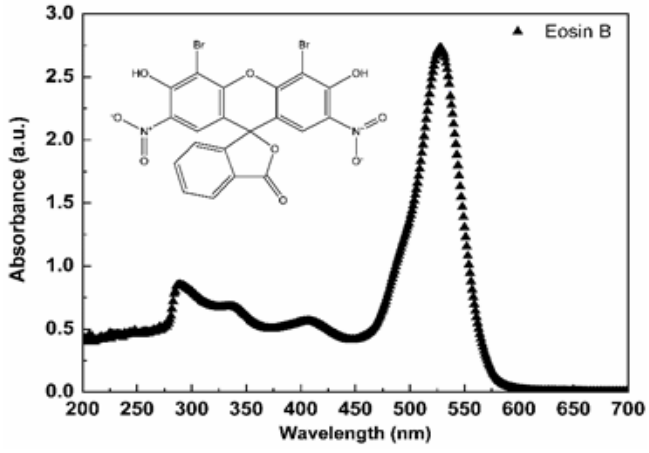

Fig. 4: UV-Vis absorption spectra of the sensitizer Eosin B in ethanol as a solvent.

Dye loading is a significant step in governing photosensitive properties of dye based solar cells. The process requires dyes with efficient spectral response to enhance absorption efficiency of DSSCs. The inset of **Fig. 4** shows the chemical structure of the sensitizer used. Eosin B, also known as Eosin bluish binds to TiO_2 surface due to the actions of bromine. The optical absorption analysis of this photosensitive dye Eosin B solution in ethanol was performed. The spectra exhibited maximum peak at 528 nm with some low intensity absorption peaks at lower wavelengths. These values were found close to the reported values. As the dye concentration was increased, the absorption peaks in blue region of the absorption curve were found to become prominent. The intensity of absorption at 1.12 M concentration was found to be quite significant with good spectral coverage from 300 to 580 nm. This concentration was used for further application as sensitizer in DSSCs.

Current density versus voltage characteristics of the DSSCs made with Eosin B dye were recorded at different light intensities as shown in **Fig. 5(a).** The curves clearly represent the fourth quadrant region of the J-V curves recorded.

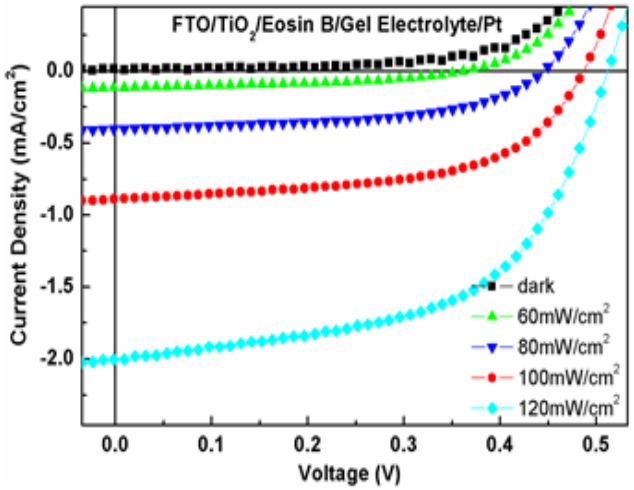

Fig. 4. (a) Current density versus voltage characteristics.

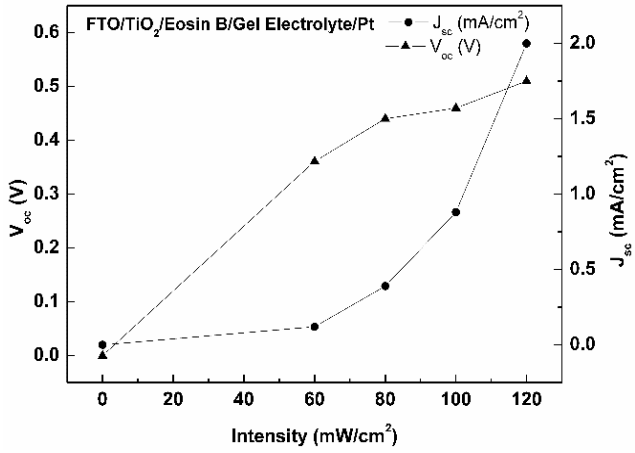

Fig. 5. (b) J_{sc} and V_{oc} values as a function of illumination intensity.

Dye sensitized semiconductor materials are known to generate high photo voltages with low photocurrents. This is generally attributed to aggregation or self-quenching of particles as manifested in SEM images (**Fig. 3**) also. It is clear from the analysis that Eosin B dye based DSSC was able to produce a short circuit current density of 2 mA/cm^2, open circuit potential of 0.5 V and a fill factor of 0.55 at 120 mw/cm^2 light intensity. The observed values of the short-circuit current density and the open circuit voltage (from **Fig. 5(a)**) are plotted as a function of the illumination intensity values as shown in **Fig. 5(b).** It can be observed from the figure that both the short circuit current J_{sc} and the open circuit voltage V_{oc} increased with the increasing illumination intensities. The observed parameters for the DSSC fabricated have also been summarized in **Table 1.**

Table 1. Photovoltaic performance of DSSCs at 120mW/cm^2.

Photovoltaic Performance of DSSC @ 120mW/cm^2	
J_{sc} (mA/cm^2)	2.00
V_{oc} (V)	0.51
V_{max} (V)	0.372
J_{max} (mA/cm^2)	1.52
P_{max} (mW)	0.2
FF	0.55
η	0.47%

These cells exhibited low power conversion efficiency values which may be attributed to the large internal resistance of the DSSCs fabricated. High internal resistance values are responsible for reducing the continuous flow of the actual charge carriers inside the device. Furthermore, in an attempt to enhance the overall efficiency of the DSSCs, the concept of blocking layer was tried to be used. Blocking layer in DSSCs provide a compact and uniform surface for growth of porous TiO_2 and good adhesion properties between the FTO layer and TiO_2 porous layer. In general, compact blocking layer also reduces the probability of recombination losses inside DSSCs. In the present work, blocking layer was grown using titanium isopropoxide onto cleaned FTO substrate and was found to exhibit a uniform surface without any cracks. The applicability of this compact layer was further explored to be used in DSSCs in the configuration FTO/ TTIP/ TiO_2/Dye/ Electrolyte/ Pt.

Fig. 6 shows the current density-voltage characteristics of the devices with and without blocking layer at 120 mW/cm^2 light intensity. However, the short circuit density and open circuit voltage values decreased from 2 mA/cm^2 and 0.5 V to 1.22 mA/cm^2 and 0.47 V, respectively. Accordingly, approx. 39% decrease in Jsc and approx. 6% decrease in V_{oc} were clearly observed which was absolutely opposite to the expected increment in these values.

In an ideal DSSC, zero series resistance and infinite shunt resistance are highly desirable to maximize the overall efficiency and unity fill factor. High values of shunt resistance are generally expected to introduce hindrance to electron back transfer and charge recombination inside the device. On the contrary, low series resistance is expected to reduce resistance of transparent electrode, resistance of ionic diffusion and interfacial resistance at electrolyte/counter electrode interface **[11]**. In the present case, it can be clearly seen from Fig. 6 that the introduction of blocking layer has more negative impact on J_{sc} as compared to its negative impact on V_{oc} values. It was observed that in the DSSCs fabricated with Eosin B as the sensitizer and gel electrolyte having SCN and TU as the additive, blocking layer is not required. The introduction of blocking layer was observed to introduce more negative effect on series resistance values as compared to shunt resistance. One of the significant factors in this decrement may be thickness of the blocking layer also. Further investigations on the effect of blocking layer on DSSCs with Eosin B as the sensitizer and quasi solid state electrolytes is in progress. It can be inferred from the above analysis; Eosin B can be used as a potential sensitizer in conjugation with quasi solid-state electrolyte based on poly ethylene glycol and potassium iodide/ iodine in presence of TiO_2.

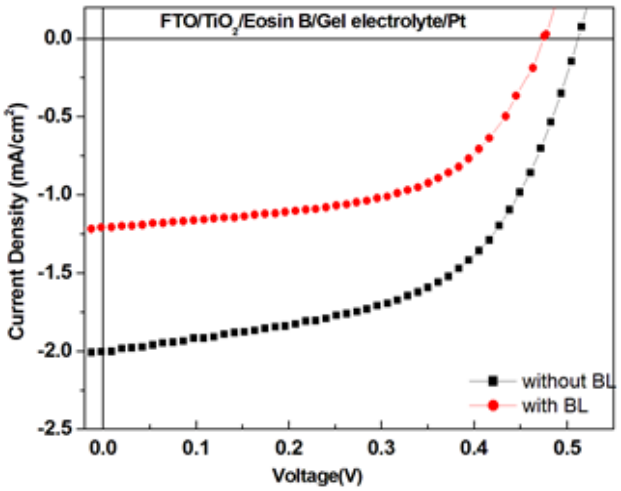

Fig. 5. Current density-voltage characteristics of the devices with and without blocking layer at 120mW/cm^2.

Conclusion

Dye sensitized solar cells built upon nanocrystalline semiconductor oxide based photoanodes sensitized by a light sensitive dye have attracted substantial consideration due to their environmental friendliness and cost-effective advantages. Organic sensitizers are generally known to exhibit better extinction coefficients and allow more variation in color with faster electron injection rate. The DSSCs with configuration FTO/nc-TiO_2/ Eosin B/ gel electrolyte/ Pt was fabricated and characterized to analyze their photo response. Eosin B was used as the organic dye or the light sensitive element. The DSSCs exhibited a short circuit current density of 2 mA/cm^2, open circuit potential of 0.5 V and a fill factor of 0.55 at 120 mw/cm^2 light intensity. These efficiency values can be further

improved by using the principle of co sensitization of energy relay dyes to enhance the dye absorption as well as electron transfer properties.

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