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Development of Low Cost- flexible Dye Sensitized Solar Cells using Polypyrrole Counter Electrodes

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Abstract—*Flexible dye sensitized solar cells (FDSSCs) have attracted scientific interests from researchers and companies worldwide. Flexibility of these solar cells allow roll-to-roll mass production, continuous manufacturing which reduces the overall cost. The major challenge of using these substrates is that they can only withstand temperatures up to 150°C. In the present study, a low temperature, binder-free TiO_2 paste was prepared to develop a porous photo-electrode. Polypyrrole (Ppy) nanoparticles were synthesized and deposited on ITO/PET substrates and used as counter electrodes. The surface morphology of the electrodes prepared on the substrates was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). FTIR spectrum of polypyrrole was analyzed to study the functional groups and confirm the presence of pure polypyrrole. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were done to evaluate the catalytic activity of the counter electrode and study its electrochemical behaviour. The FDSSC exhibited a photo-conversion efficiency of 1.03% at an illumination of 100mW/cm^2. Despite a modest efficiency, Ppy nanoparticles prove to be a good source of alternative in FDSSCs due to their low cost, photoelectric properties and simple techniques of preparation.*

1. INTRODUCTION

Over the last few years, there has been an increased demand for flexible electronics as they are light weight and can be manufactured in large scales with a reduced production cost.. Flexible DSSCs are usually based on plastic/polymer substrates such as transparent indium tin oxide (ITO) coated polyethylene terephthalate (PET) or polyethylene naphthalene (PEN) plastic substrates in place of glass. These are easily installed on buildings, flat, curved or any surface due to their flexible nature. Flexible DSSCs are adaptable to different shapes of surfaces and used in portable electronic devices. Transparent conducting oxide (TCO) glass accounts for more than half of the total cost of DSSCs [1]. So replacing these with polymer substrates like PET or PEN reduces the material cost of the device. The major challenge of using these substrates is that they can only withstand temperature up to 150°C. However, the working electrodes need to be sintered at 450-500 °C with any TiO_2 paste formulation containing organic binders. Absence of these binders could result in cracks in the films during sintering and thus reduces the electrical contact between the TiO_2 particles. This calls for some modifications in the preparation of TiO_2 pastes, which are coated over PET substrates and sintered at 150°C without producing cracks and thus giving a uniform layer [2]. In the present study, a flexible DSSC is constructed using a low-temperature, binder free paste of TiO_2 nanoparticles as the photo-electrode material, employing Ppy nanoparticles based counter electrode and injecting a liquid electrolyte containing I_3^-/I^- redox couple. Though the efficiency of the cell is far from the state of the art values (with platinum counter electrode), considering the fact that it employs a conducting polymer as the counter electrode material and this very application of polypyrrole in flexible DSSCs has not been reported anywhere, makes the work unique. However for commercial applications, further enhancement in conversion efficiency and stability of the FDSSCs is required.

2. EXPERIMENTAL

2.1 Fabrication of flexible porous TiO_2 photo-anode

A solution containing 4 ml of t-butyl alcohol and 2 ml of DI water is prepared, to which 1 gram of TiO_2 (21nm, Degussa) is added and mixed thoroughly by subjecting to magnetic stirring for 24 hours, to prepare the compact layer paste for the photo-electrode. No other additional binders were added. The paste was coated on ITO/PET substrates by screen printing method. This was followed by coating the electrode with a scattering layer paste,, consisting of the same composition of TiO_2 nanoparticles (250nm), over the dried compact layer. Prior to coating, ITO-PET (15 /sq , Sigma Aldrich) were cleaned in a detergent solution to get rid of the dirt and impurities . It was followed by sonicating it in acetone and later with deionised water. The active area of the photo anode was maintained as 0.25 cm^2 (Fig. 1(a)). The electrode after sintering (while hot) was immersed into a 0.3mM solution of N719 in an equimolar mixture of acetonitrile and t-butyl alcohol for 24 hours. Fig. 1(b) shows the image of the same.

2.2 Preparation of flexible counter electrode using polypyrrole nanoparticles

Polypyrrole nanoparticles are synthesized via micro emulsion polymerization of pyrrole in the presence of iron (III) chloride

as the oxidant. An aqueous solution (0.08 M) of p-toluene sulphonic acid, which is used as a dopant to increase the conductivity of polypyrrole was prepared, to which was added pyrrole and stirred for half an hour, followed by the addition of 10 ml of iron (III) chloride aqueous solution, as it has been studied as the best chemical oxidant [3,4]. The polymerization continued for 3 hours at 0^0 C. The black material obtained is filtered, washed and dried to obtain polypyrrole nanoparticles. These particles coated on the flexible PET substrates via drop casting (Fig. 1 (c)).

2.3 Assembly of the DSSC

Dye sensitized TiO_2 photo electrode and polypyrrole based counter electrode are sandwiched together with a hot melt gasket (25μm) inserted in between them as spacer, to seal the flexible cell and provide channels to inject the electrolyte. The electrolyte is a solution 0.60 M Butyl imilidazolium iodide, 0.03 M I_2 , 0.10 M guanidinium thiocyanate, and 0.50 M TBP in a mixed solvent of acetonitrile and valeonitrile. The filling of electrolyte was done via vacuum backfilling, which will aid in getting rid of the trapped air between the electrodes [5].

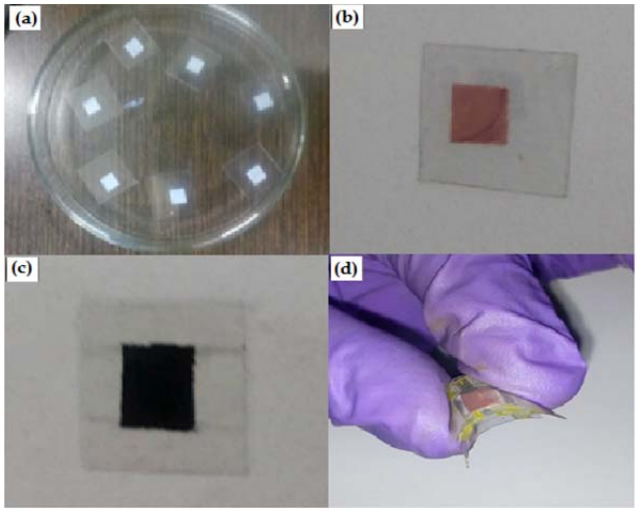

Fig. 1: The photoanode of DSSC (a) before and (b) after dipping in the dye (c) ITO/Ppy electrode as the counter electrode (d) Flexible DSSC after the assembly

3. CHARACTERIZATION AND MEASUREMENT

The morphology of the electrodes were examined by scanning electron microscopy (SEM). The catalytic activity of the electrode was measured using cyclic voltammetry (CV). It was carried out in a three-electrode system containing 10 mM LiI, 1 Mm I_2 and 0.1M $LiClO_4$. The scan rate was $50mVs^{-1}$. Electrochemical impedance spectra (EIS) measurements were obtained in order to determine the electrochemical behavior of the flexible cell, by a potentiostat/galvanostat under a frequency range of 10mHz to 65 kHz. J-V characteristics were obtained under AM 1.5 simulated illumination (100 mW cm^{-2}) illumination as shown in the figure. The performance parameters are evalutaed using the following equations [6]:

$$FF = \frac{Vmax\ Jmax}{Voc\ Jsc} \quad (1)$$

$$\eta\% = \frac{Voc\ Jsc\ FF}{Pin} \times 100 \quad (2)$$

where J_{sc} is the short-circuit current density ($mAcm^{-2}$), V_{oc} is the open-circuit voltage (V), J_{max} ($mAcm^{-2}$) and V_{max} (V) are the current density and voltage at the point of maximum power output on the plot, respectively and Pin is the incident light power.

4. RESULTS AND DISCUSSION

The morphology of the electrodes was examined by scanning electron microscopy. In a binder free- low temperature TiO_2 electrode, it is very important to ensure good electron transfer within the TiO_2 film and from the layer to the substrate. This is ensured by looking into the bonding between the particles and ITO/PET and the inter-connectivity between themselves [2]. The morphology of TiO_2 photo electrode subjected to thermal treatment at 150^0C for 24 hours is shown in the Fig. 2 (a) using SEM. The particle to particle connectivity is good enough resulting in a compact structure. It also shows that the layer is quite porous in nature [7]. The surface morphology of Ppy/ITO-PET electrode is shown in Fig. 2(b). It shows that polypyrrole nanoparticles (150-200 nm) are deposited on the surface of ITO-PET substrate. The surface is porous that facilitates better performance of the electrode and hence the cell as it promotes good contact between the electrode and the electrolyte [8].

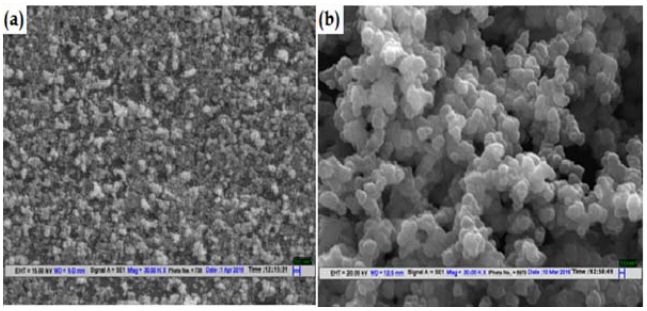

Fig. 2: SEM image of (a) porous TiO_2 layer on ITO /PET substrate (b) Ppy layer on PET/ITO substrate

The surface roughness was evaluated by atomic force microscopy (Fig. 3). Root mean square (RMS) roughness of bare ITO/PET substrate was found to be 20.8nm, which increased after it was coated with polypyrrole nanoparticles, to 215 nm. Greater the roughness, higher is the electro catalytic activity of the CE for the I^-/I_3^- redox reaction which in turn enhances the conversion efficiency of the cell [9].

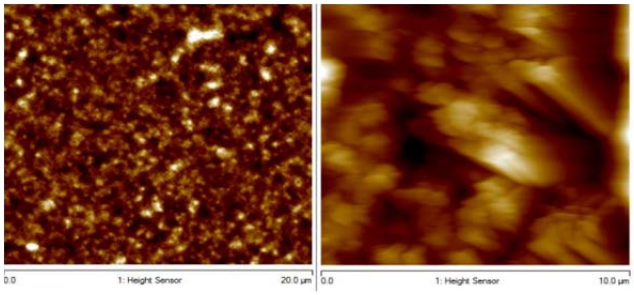

Fig. 3: AFM images of (a) ITO/PET substrate (b) Ppy coated substrate

The FTIR spectrum of Ppy particles is given in Fig. 4, which exhibits all characteristic vibrations of Ppy [3,4]. The band at 1510 $cm^{-1}$is attributed to C=C stretching vibrations), 1480 $cm^{-1}$to C-N stretching vibration, and 1291 cm^{-1} to C-H deformation and the band at 1155 cm^{-1}corresponding to C-H in-plane deformation vibration.

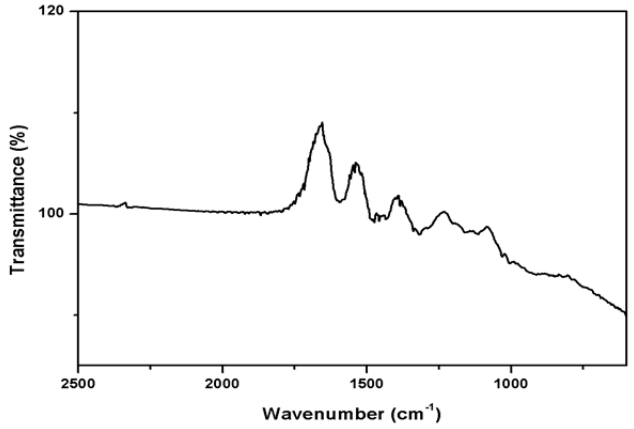

Fig. 4: FTIR spectrum of polypyrrole nanoparticles

Fig. 5 shows the cyclic voltammogram of I_3^-/I^- systems. It has oxidation and reduction peaks. The peak at 0.2 V describes the reduction of $I_3^-$to I^-, that estimates the performance of the counter electrode in the DSSC. However, the peak current density is very low for ITO/PET- Ppy, which is apparently due to the poor conductivity of the substrate resulting in lower catalytic activity [10].

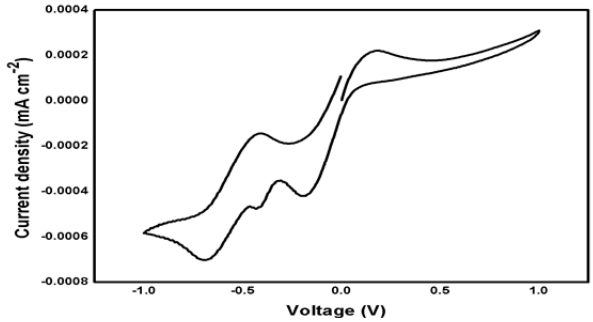

Fig. 5. Cyclic voltammogram of PET-ITO/Ppy electrode at a scan rate of 50 mVs^{-1}

The catalytic performance of the cell is further investigated by performing EIS. The value of R_{ct} was found to be 44 Ωcm^2 after fitting the Nyquist plot using an equivalent circuit, as shown in Fig. 6, which is quite high when compared with what has been obtained for Pt or FTO/Ppy electrodes, as per literature. High charge transfer resistance indicates poor catalytic ability of this flexible electrode to facilitate the reduction of tri-iodide, which in turn will lead to poor performance of the cell [11]. This observation is substantiated by the results from J-V plot. The series resistance was also higher than FTO based DSSCs, around 10 Ωcm^2. While the value increased to 30 Ωcm^2, which adversely affects the power conversion efficiency of the cell, as is seen later.

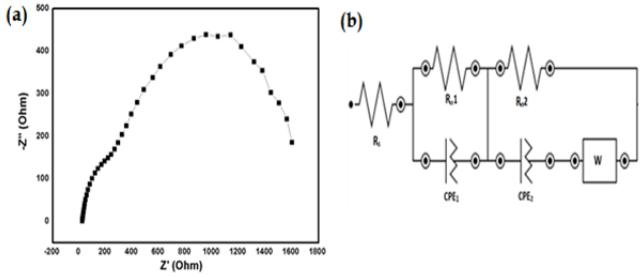

Fig. 6: (a) Nyquist plot of the flexible DSSC (b) the corresponding equivalent circuit

The photovoltaic characteristics of the flexible DSSC employing the Ppy counter electrode are shown in figure. 7. The squareness of the plot increases with the fill factor, which in turn is dependent on the series resistance of the cell. When irradiated, the cell exhibits a J_{sc} of 7.86 mA cm^{-2}, V_{oc} of 630 mV, and a FF of 0.2, which could be attributed to larger value of R_s, thus giving an efficiency of 1.032%. The current of this device is very small, which could be because of relatively weak inter particle connectivity of TiO_2 nanoparticles due to the lack of high-temperature sintering. Low fill factor of 0.2. This could possibly be the reason for the lower efficiency of the cell based on Ppy electrode.

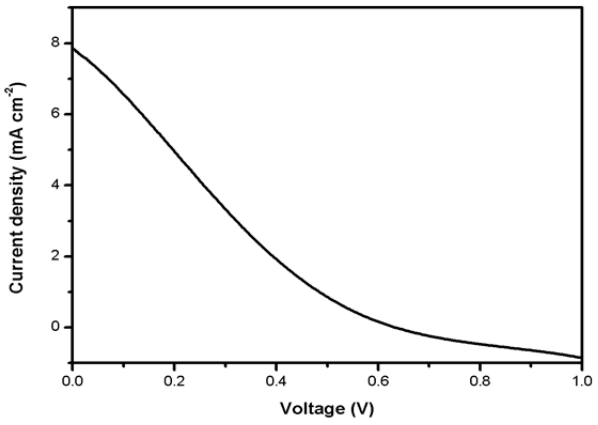

Fig. 7: J-V curve of Ppy based flexible DSSC

5. CONCLUSION

Flexible DSSCs are light weight and have a wide application. They are fabricated on polymer substrates (ITO/PET), which are limited by low temperature tolerance (maximum 150^0C for PET sheets).A flexible DSSC was assembled using a low temperature TiO_2 paste and a polypyrrole based counter electrode employing ITO/PET flexible substrates, which has not been reported anywhere till date, to the best of our knowledge. The nanoparticles are 150-200nm in size, exhibit good porosity and surface roughness to carry out the reduction reaction. Though the conversion efficiency of the cell is not very high, this involves a very effective, low cost strategy to fabricate platinum free flexible dye sensitized solar cells.

6. ACKNOWLEDGEMENTS

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REFERENCES

[1] Veerender, P., Saxena. V., Jha, P., Koiry.,S.P., Gusain, A., Samanta,S. (2012). Free-standing polypyrrole films as substrate-free and Pt –free counter electrodes for quasi-solid state dye-sensitized soalr cells. Organic Electronics,13(12), 3032–3039.

[2] Yune, J. H., Karatchevtseva, I., Triani, G., Wagner, K., & Officer, D. (2013). A study of TiO_2 binder-free paste prepared for low temperature dye-sensitized solar cells. Journal of Materials Research, 28(03), 488-496.

[3] Reung-U-Rai, A., Prom-Jun, A., Prissanaroon-Ouajai, W., &Ouajai, S. (2008). Synthesis of highly conductive polypyrrole nanoparticles via microemulsion polymerization. Journal of Metals, Materials and Minerals,18(2), 27-31.

[4] Machida, S., Miyata, S., Techagumpuch, A. (1989). Chemical synthesis of highly electrically conductive polypyrrole. Synthetic metals, 31(3), 311-318.

[5] Mathew, A., Rao, G. M., &Munichandraiah, N. (2014). Towards fabrication of stable dye sensitized solar cells based on acetonitrile as solvent for the redox couple. Adv. Mater. Lett., 5, 180-183.

[6] Wu, J., Li, Q., Fan, L., Lan, Z., Li, P., Lin, J., Hao, S. (2008). High-performance polypyrrole nanoparticles counter electrode for dye-sensitized solar cells. Journal of Power Sources, 181(1), 172-176.

[7] Yune, J. H., Karatchevtseva, I., Evans, P. J., Wagner, K., Griffith, M. J., Officer, D., &Triani, G. (2015). A versatile binder-free TiO 2 paste for dye-sensitized solar cells. RSC Advances, 5(37), 29513-29523.Any paper- highperformance

[8] Gao, Y., Chu, L., Wu, M., Wang, L., Guo, W., Ma, T. (2012). Improvement of adhesion of Pt-free counter electrodes for low-cost dye-sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry, 245, 66-71. doi:10.1016/j.jphotochem.2012.07.005.

[9] Chang, L. Y., Li, C. T., Li, Y. Y., Lee, C. P., Yeh, M. H., Ho, K. C., Lin, J. J. (2015). Morphological Influence of Polypyrrole Nanoparticles on the Performance of Dye–Sensitized Solar Cells. ElectrochimicaActa, 155, 263-271.doi:10.1016/j.electacta.2014.12.127.

[10] Tathavadekar, M., Biswal, M., Agarkar, S., Giribabu, L., Ogale, S. (2014). Electronically and catalytically functional carbon cloth as a permeable and flexible counter electrode for dye sensitized solar cell. Electrochimica Acta,123, 248-253.248–253. doi:10.1016/j.electacta.2013.12.175.

[11] Murakami, T. N., Ito, S., Wang, Q., Nazeeruddin, M. K., Bessho, T., Cesar, I., Grätzel, M. (2006). Highly efficient dye-sensitized solar cells based on carbon black counter electrodes. Journal of the Electrochemical Society,153(12), A2255-A2261.