High Performance Dye Anchored Counter Electrodes with SPSQ2 Sensitizer for Dye Sensitized Solar Cell Applications

Journal:	*Materials Chemistry Frontiers*
Manuscript ID	QM-RES-06-2016-000101.R2
Article Type:	Research Article
Date Submitted by the Author:	01-Oct-2016
Complete List of Authors:	K, Susmitha; Yogi Vemana University, Physics M, Gurulakshmi; Yogi Vemana University, Physics M, Naresh Kumar; Osmania University College for Women, Physics Lingamallu, Giribabu; Indian Institute of Chemical Technology, Inorganic & Physical Chemistry Rao, G. Hanumantha; CSIR-Indian Institute of Chemical Technology, Inorganic and Physical Chemistry Division Singh, Surya; Indian Institute of Chemical Technology, Inorganic and Physical Chemistry Division Babu, S. Narendra; Osmania University College for Women, Physics M, Srinivas; Osmania University, Physics M, RAGHAVENDER; Yogi Vemana University, Physics

Materials Chemistry Frontiers

Full length article

High Performance Dye Anchored Counter Electrodes with SPSQ2 Sensitizer for Dye Sensitized Solar Cell Applications

Received 00th June 20xx,
Accepted 00th June 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

K. Susmitha[a], M. Gurulakshmi[a], M. Naresh Kumar[d], L. Giribabu[b, c, †], G. Hanumantha Rao[b, c], Surya Prakash Singh[b, c, †], S. Narendra Babu[d], M. Srinivas[e], M. Raghavender[a, †, *]

A high performance counter electrodes (CEs) based on dye anchoring has been developed via a low cost spray gun. Its performance was further optimized by PEDOT:PSS over the dye anchored counter electrode (DACE). Here we demonstrate the DACE based devices using of a near-infrared unsymmetrical squaraine sensitizer (SPSQ2) and commercially available N719 dye. The electrochemical impedance spectroscopy (EIS) revealed the charge transfer activity of DACE devices were shown optimal performance than that of without DACEs. A significant increase in photoconversion efficiency was observed for PEDOT: PSS sprayed DACE (5.75 %) as the counter electrodes associated with low series resistance, low electrolyte diffusion impedance, high open circuit voltage and fill factor when compared to the simple DACE and normal counter electrode DSSCs. The enhanced efficiency could be due to the charge carriers generated in the test cells associated SPSQ2 dye on counter electrode and additional PEDOT:PSS layer on DACE.

Introduction

Photovoltaic (PV) solar cells are well-designed and attractive devices for energy production. New concepts, such as the dye sensitized solar cell (DSSC) have progressed to a stage very close to a possible commercialization. DSSC was first invented by Grätzel and co-workers, [1] received much attention as a promising alternative to conventional solar energy conversion devices because of their low cost production, environmentally friendly components, better performance in diffuse light, less dependence of performance on the angle of light incidence, transparency, color, lower energy consumption during manufacture and relatively high energy conversion efficiency. A power conversion efficiency of 13 % [2] achieved for DSSC devices. The major components of the photo-related portion of the DSSCs are dye, redox shuttle, photo electrode and counter electrode have been investigated independently over the past 15 years, and the most efficient device architecture remains essentially unchanged from its conception.

The counter electrode was one of the major essential component of DSSC. The CE's stands to reduce the redox species, which are used as mediators in the regeneration of the sensitizer after electron injection. The reactions at the CE are dependent on the type of redox mediator used to transfer charge among the photo electrode and the counter electrode. Most of the DSSCs, the iodide tri-iodide couple has been employed as the redox mediator and the overall redox reaction in DSSCs can be described as: $I_3^- + 2e \leftrightarrow 3I^-$. The tri-iodides are generated near the dye sensitized TiO_2 electrode and reduced at the counter electrode. Platinum loaded conducting glass has been widely employed as the standard CE for DSSCs due to its high catalytic activity and excellent conductivity as well as its high corrosion stability against iodine in the electrolyte.[3-5]

DACE or counter electrode architect is modified [6] by Nam-Gyu Park, with structure of two different dyes in a solar cell at photo and counter electrodes. This method allows TiO_2 layers on photo and counter electrodes experience high temperature annealing without damage of dye molecules. Results of photocurrent transient measurement revealed photoexcited electrons at the TiO_2 layer on Pt CE are progressed initially to opposite direction at beginning stage of light illumination, immediately participated in conversion process towards enhance the performance.[6] Scientists were putting their efforts on to improve cell fabrication technology.

In this view, dye anchored counter electroded dye sensitized solar cell is developed [7] by our team using well studied N719 and PCH001 [8, 9] dyes, revealed a broad spectra of the incident photon to current conversion efficiency (IPCE). Its performance is optimized with carbon nanohorns (CNHs), an efficiency (η) of 7.14% is achieved.[7] Recently, our group is synthesized near-infrared unsymmetrical squaraine sensitizer SPSQ2[10] for DSSC applications.

---

[a] Department of Physics, Yogi Vemana University, Kadapa 516003, India.
[b] Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology (IICT), Hyderabad 500007, India.
[c] Academy of Scientific and Innovative Research, CSIR-IICT, Hyderabad 500007, India.
[d] Osmania University College for Women, Department of Physics and Electronics, Koti, Hyderabad 500095, India.
[e] Department of Physics, Osmania University, Hyderabad 500 007, India.
† Contributed equal work.
* Corresponding author Email: toraghavender@rediffmail.com (M. Raghavender).

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

The SPSQ2 revealed η = 3.08% in volatile liquid electrolyte.[10] Well studied N719 and near-infrared unsymmetrical squaraine SPSQ2 dye is used in the present study. Here, we optimized the DACE-DSSC performance with low cost PEDOT:PSS.

Experimental

Development of dye anchored mesoporous nanocrystalline TiO_2 electrodes

F-doped SnO_2 (FTO) coated glass substrates (TCO22-7Ω/cm, Solaronix) were carefully cleaned using mild detergent solution followed by deionized water, acetone and 2-proponol (Merck) in ultrasonic bath to remove organics or any other contaminants, and dried under N_2 purge. A compact TiO_2 blocking layer was deposited onto the surface of above cleaned FTO by treating with 40 mM $TiCl_4$ solution at 70 °C for 30 min for a good mechanical contact between the nanocrystalline TiO_2 and the FTO glass substrate. The $TiCl_4$ treated FTO glass plates were washed with deionized water and sinter at 500 °C for 30 min. The mesoporous TiO_2 films (~ 12 µm thickness) were developed with screen printing method using 18NR-T (Dyesol) TiO_2 paste and 43T mesh screen, and sinter at 500 °C for 30 min. The above TiO_2 coated substrates were again treated in 40 mM $TiCl_4$ solution for 30 min at 70 °C. After cooling to 100 °C, the resultant substrates were immersed under dark condition in two different dyes with variation of its dipping time. The details of the photo electrodes in SPSQ2, N719 dye and variation of dipping time was mentioned in the Table 1. The dye used here of SPSQ2 was dissolved in chloroform, 3×10^{-4} M and N719 dye (Solaronix) in a mixture of tert-butanol/acetonitrile (1/1 v/v) of 3×10^{-4} M concentration. The photo electrode was removed from the solution, rinsed with respective solvents for twice to remove the unanchored dye molecules on the surface of TiO_2 film to ensure that the film was covered with a monolayer of dye molecules, followed by dried under N_2 purge, the dye anchored active electrode area was 0.36 cm^2.

Development of counter electrodes (CEs)

Chloroplatinic acid hexahydrate (Sigma) was dissolved in 2-propanol and followed by ultrasonication for 50 min. To the resultant light yellow color solution, 10 mL of hydrochloric acid was added and ultrasonicated for 10 min. The resulted transparent platinum solution was used for the development of counter electrodes. In details, The FTO glass substrates were drilled by DREMEL 300 with a diamond tipped micro drill bit, and cleaned in 2-propanol, deionized water followed by absolute ethanol for 30 min. These substrates were placed over the hot plate (about 180 °C), which was adjusted during the spay, whereas resultant platinum solution was loaded into a simple spray air brush which was connected to N_2 gas cylinder and flow rate (1 mL min^{-1}) was controlled through 0.3 mm micro-tip needled and gas regulator (Messar, Germany). These substrates were sintered at 500 °C for 10 min and used as counter electrodes.

Development of dye anchored counter electrodes (DACEs)

The above prepared CEs were used to develop dye anchored counter electrodes. In details, the 18NR-T titanium paste of area 6 mm x 6 mm (0.36 cm^2) was coated over the counter electrodes using screen printer and followed by sinter at 500 °C for 30 min. While cooling down to 100 °C, the substrates were immersed in SPSQ2 dye solution (in chloroform (3×10^{-4} M)) for 16 hours under dark condition. These electrodes were denoted as DACE. Further, the filtered PEDOT:PSS solution was sprayed over dye anchored area of DACE with a open mask of area 6 mm x 6 mm and its schematic representation was shown in Fig. 1(a). Its schematic set-up was shown in Fig. S1 (Electronic Supplementary Information) and slightly heated upto 120 °C for 5 min and resulted electrodes were named as PEDOT:PSS sprayed DACE. The photographs of the developed DACEs were shown in the inset of Fig. S1.

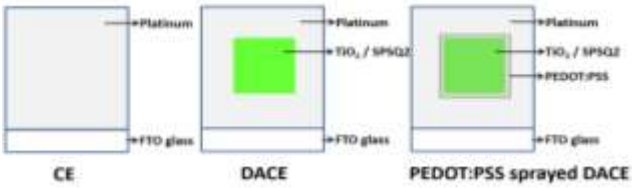

Fig. 1(a) Schematic representation of various counter electrodes.

Fabrication of dye sensitized solar cells with CE, DACE

The DSSC test cells were fabricated as similar reported in our earlier studies.[11] The photo electrodes were sandwiched with the respective counter electrodes and dye anchored counter electrodes using a thermal adhesive of 25 µm thick Surlyn film Meltonix 1170-25 (Solaronix) as a spacer. The assembly was then placed on a preheated hot plate (130 °C) and pressed gently to seal both the electrodes to produce a sandwich-type cells and labeled as DSSC, DACE-DSSC and PEDOT:PSS sprayed DACE DSSC and details of the test cells were given in Table 1 and the test cell architecture was shown in Fig. 2(a). The durable electrolyte Iodolyte Z-150 (Solaronix) was modified, injected through a pre drilled hole on the counter electrode side by using of back vacuum filling technique. The holes were sealed with Meltonix 1170-25 cover glass along with adhesive film.

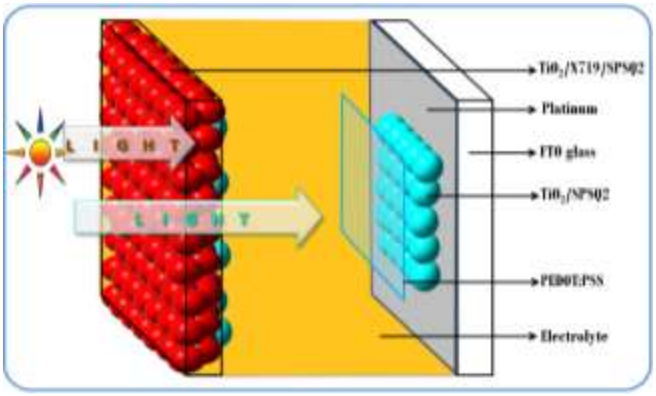

Fig. 2(a) Optimum performance DACE-DSSC architecture.

Characterization and measurements

Absorption spectra of photo electrodes were measured using UV-Vis-NIR Spectrophotometer (Agilent Technologies). Field

Emission Scanning Electron Microscopy (FE-SEM) was done using electron microscope (JEOL, model: 7610F, Oxford). The photocurrent density (J) - voltage (V) measurements of the test cells were conducted using a xenon arc solar simulator (PEC-L01, Peccell Inc., Japan) with an AM 1.5 spectral filter and sourcemeter (2401N Keithley Instruments Inc.), its light intensity was adjusted to 100 mW/cm^2 AM 1.5 using a calibrated mono-Si solar cell. The electrochemical impedance spectroscopy (EIS) measurements were performed under 100 mW/cm^2 using IVIUMSTAT electrochemical workstation at amplitude of 10 mV, and the frequency range from 1 Hz to 1 MHz.

Table 1 Photo, counter electrode architecture details.

Test cell	Cell No.	Photo electrode	Counter electrode
SPSQ2	1	FTO/TiO_2/SPSQ2 (16 hrs)	FTO/Pt
N719/SPSQ2	2	FTO/TiO_2/N719 (2 hrs)/SPSQ2 (14 hrs)	FTO/Pt
DACE	3	FTO/TiO_2/N719 (2 hrs)/SPSQ2 (14 hrs)	FTO/Pt/TiO_2/ SPSQ2
PEDOT:PSS sprayed DACE	4	FTO/TiO_2/N719 dye (2 hrs)/ SPSQ2 (14 hrs)	FTO/Pt/TiO_2/SPSQ2 /PEDOT:PSS

Results and discussion

Fig. 2(b) represents the cross-sectional FE-SEM image of the developed PEDOT:PSS sprayed DACE. A thin PEDOT:PSS layer was deposited on the top of the SPSQ2 dye anchored counter electrodes and is clearly observed in Fig 2(b). Filtered PEDOT:PSS solution was sprayed using 0.3mm micro-tip needle spray gun, was controlled to 1mL/min by using N2 gas pure.[12] This dye anchored counter electrode total configuration was FTO/Pt/TiO_2/SPSQ2/PEDOT:PSS. A very thin white colored film represents the platinum on FTO glass substrate, over that TiO_2 with SPSQ2 film was clearly noticed.

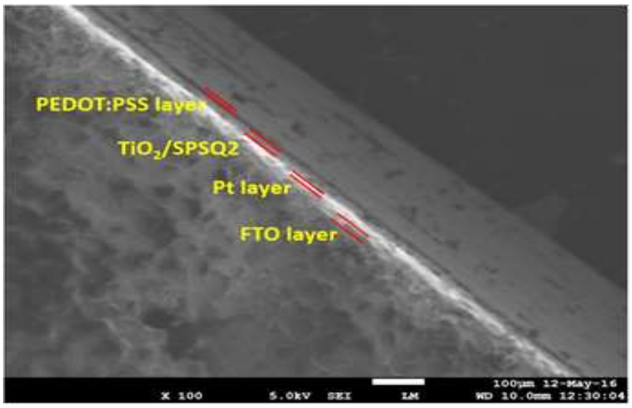

Fig. 2(b) Cross sectional FE-SEM image of PEDOT:PSS sprayed dye anchored counter electrode.

Fig. 3(a) shows the absorption spectra of dye solutions and dye anchored TiO_2 films of N719, SPSQ2, SPSQ2-N719. The absorption peaks of SPSQ2 at 690nm, 640 nm corresponds to the charge transfer and around at 385 nm transition was assigned to π-π* transition.[10] While the N719 dye anchored TiO_2 film exhibits peaks at 410 nm and 545 nm corresponds to metal-to-ligand charge transfer. In the case of SPSQ2-N719 sensitized TiO_2 electrode shown higher absorbance maxima, however, in the near IR region a small absorption was observed.

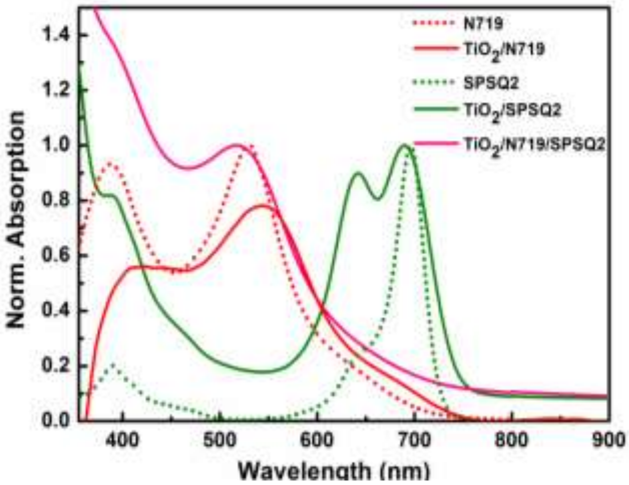

Fig. 3(a) Absorption spectra of the dye solutions, its sensitized TiO_2 film.

Fig. 3(b) represents the Incident Photon to Current Conversion Efficiency (IPCE) of the fabricated DSSCs. Higher IPCE of DACE-DSSCs were corresponds to improved photocurrent generation. The broader IPCE spectra observed for DACE-DSSCs and this effect is reflected in the enhanced photovoltaic performance.

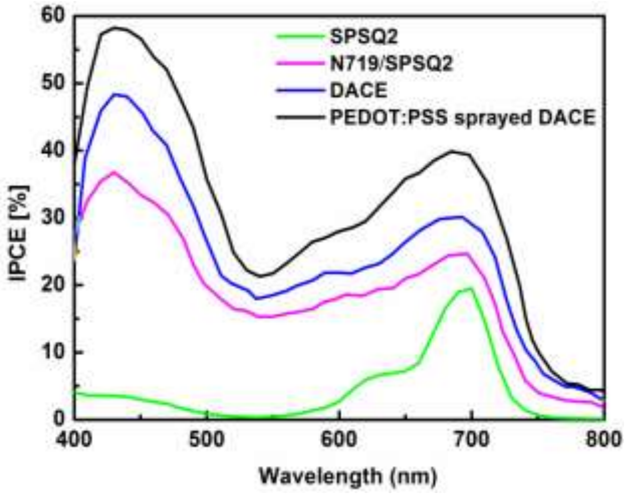

Fig. 3 (b) Incident photon to current conversion efficiency spectra of fabricated DSSCs.

To investigate the electrochemical impedance characterization of developed electrodes and fabricated solar cells, we performed electrochemical impedance spectroscopy studies (EIS). The IVIUMSTAT electrochemical impedance analyzer was used and presented the Nyquist plots of the test cells in Fig. 4(a) and Fig. S3 of Electronic Supplementary Information. All impedance parameters were extracted by fitting equivalent circuit using IVIUMSOFT software and summarized in Table 2. In typical EIS analysis, R_S is the series resistance normally determined by monitoring the real axis intercept at the high frequency side and R_{CT} and W as being derived from semicircles in the high and low frequency regimes respectively. R_{CT} represents interfacial charge transfer resistances at the counter electrode/electrolyte interface for I^-_3/I^- redox reaction, W provides the information of electrolyte diffusion impedance (Warburg impedance).

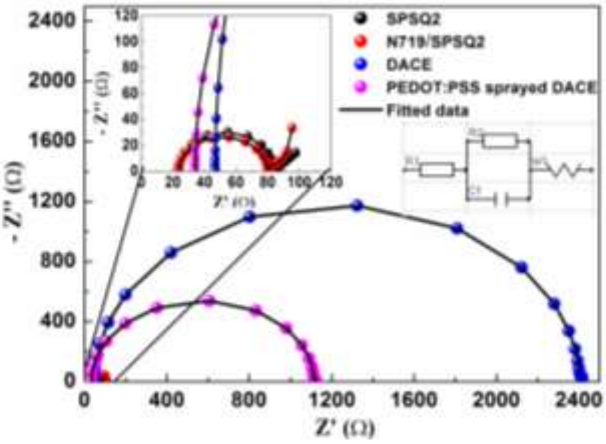

Fig. 4 (a) Nyquist plots of all the fabricated test cells measured in 1 Hz to 1MHz frequency range.

Table 2 EIS parameter of fabricated DSSCs measured under 100 mWcm^{-2}. (Details given in Electronic Supplementary Information, Fig. S2.)

	SPSQ2	N719/SPSQ2	DACE	PEDOT:PSS sprayed DACE
R1 (R_S) (Ω)	23.60	23.30	46.60	33.90
R2 (R_{CT}) (kΩ)	0.085	0.081	2.35	1.08
C1 (μF)	1.62	1.52	2.48	2.20
W (Ω)	11.30	16.10	16.64	8.95

Semi-circles with higher R_{CT} values were observed for DACE and PEDOT: PSS sprayed DACE cells, however a lower R_{CT} value with a small tail peak were present in the lower frequency regime for without DACE cells. TiO_2 with dye loading on the counter electrodes resultant DACE based DSSCs exhibits higher charge transfer resistances will contribute to the electron transfer kinetics at the electrolyte/electrode interface which associates of its inferior electron transfer. The PEDOT:PSS sprayed DACE showed smallest electrolyte diffusion impedance W (8.95 Ω) value among the four counter electrodes that may favourably influence the solar cell performance. The diffusion impedance in these counter electrodes was attributed to their compact surface morphologies, which significantly hamper the diffusion behaviour of the electrolyte throughout the CEs. In addition, the higher impedance values of counter electrodes will affect the cell performance in the succeeding facets, the electrical performance or sheet resistance and electrochemical nature or catalysis effectiveness, which was typically determined by the inverse of charge transfer resistance and optical property or reflection of light.[13-15] The inverse of charge transfer resistance value for PEDOT:PSS sprayed DACE was higher (0.92 x10^{-3}) compared to DACE (0.42x10^{-3}) gave the higher rate of catalysis redox reduction at counter electrode side will represent more number of negatively charged ions were accumulated, and reflects in higher values of Voc. The area of PEDOT:PSS sprayed DACE was higher compared to bare DACE (Fig.1).

Tafel polarization measurements were performed using symmetrical dummy cells [16] (two similar counter electrodes are sandwiched followed by filled the same electrolyte into the cell to get the symmetrical dummy cells) to confirm the interfacial charge-transfer properties of redox couple on the DACEs surface. The corresponding Tafel polarization plots are shown in Fig. 4(b). The anodic and cathodic branches of the Tafel curve for the PEDOT:PSS sprayed DACEs showed a larger slop which indicating the higher exchange current density. Thus the Tafel polarization results suggest the superior electrocatalytic activity of the PEDOT:PSS sprayed DACEs. From this electrochemical studies, PEDOT:PSS sprayed DACEs is expected to show the reasonable higher power conversion efficiency.

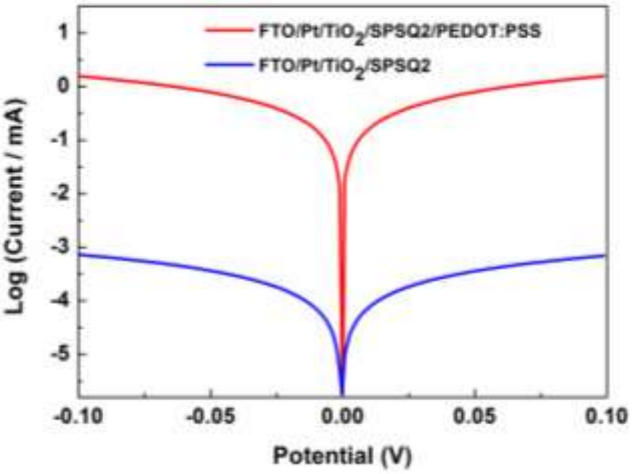

Fig. 4 (b) Tafel polarization plots of the fabricated symmetrical cells using different CEs.

The EIS, Tofel results indicates the DACE, PEDOT:PSS sprayed DACE electrodes developed through spray coat approach can be a potential counter electrodes for high performance DSSCs. Subsequently, the developed DACE were sandwiched with N719 sensitized TiO_2 electrodes to fabricate DSSC devices. For comparison, the Platinum, TiO_2/SPSQ2 dye loaded counter electrodes were also exploited as the CEs. The photocurrent density (J) – Voltage (V) characteristic curves of DSSCs fabricated with various CEs measured under illumination of 100 mW/cm^2 AM 1.5 were shown in Fig. 5 and the corresponding photovoltaic parameters include open circuit voltage (Voc), short circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (η) were summarized in Table 3 (09 cells fabricated for each type, reported high performance test cell value). These are connected by the equations FF = (P_{max}) / (J_{SC} Voc) and η = (P_{max} * 100) / (P_{in}), where P_{in} the input illumination light power and P_{max} the maximum power output from the cells. As expected, the devices of without DACE cells showed a low power conversion efficiency of 1.60, 3.60 %.

Concept of dye anchoring over CEs as a result, the conversion efficiency of the cells based on DACE increased to 4.74 %. The corresponding open circuit voltage (Voc), short circuit photocurrent density (J_{SC}), fill factor (FF) in the solar cell were 0.59V, 13.76 mA/cm^2 and 0.57 respectively. A further better power conversion efficiency was gained when the PEDOT:PSS sprayed on the DACEs based cell. The DSSC based on the PEDOT:PSS sprayed DACE presented the highest conversion efficiency of 5.75% with Voc of 0.65 V, J_{SC} of 13.25 mA/cm^2, and FF of 0.63. Photocurrent density (J_{SC}) of DACE cell of 13.76 mA/cm^2 was close to that of PEDOT:PSS sprayed DACE cells of 13.25 mA/cm^2 which ascribed to their series resistance values. Compared with TiO_2/ SPSQ2/N719 and DACE cells, the PEDOT:PSS sprayed DACE cells achieved an improvement of 59.7 and 21.3 % respectively.

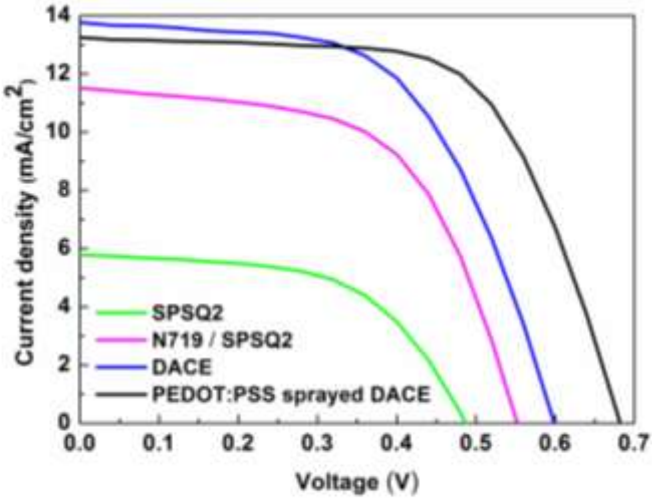

Fig. 5 Current density-Voltage characteristics of with and without DACE DSSCs.

Table 3 Photovoltaic parameters of fabricated DSSCs with non-volatile electrolyte, measured under 100 mWcm^{-2}.

DSSC	SPSQ2	Published work*, [10]	N719/ SPSQ2	DACE	PEDOT:PSS sprayed DACE
V_{OC} (V) #	0.49	0.67	0.55	0.59	0.65
J_{SC} (mA/cm^2) #	5.81	6.24	11.51	13.76	13.25
Fill factor (FF) #	0.56	0.72	0.58	0.57	0.63
Efficiency (η) (%) #	1.60	3.08	3.60	4.74	5.75

* Volatile acetonitrile based electrolyte.

J_{SC} = ± 0.20 mA/cm^2, V_{OC} = ± 30 mV, FF = ± 0.03, η = ± 0.10

Among these devices, the device with a PEDOT:PSS sprayed DACE presented the high fill factor (0.64), while the device with platinum associated with SPSQ2 showed lowest fill factor value (0.56). Moreover, the open circuit voltage (Voc) and fill factor (FF), reflecting the photovoltaic performance of the fabricated devices. For PEDOT:PSS sprayed DACE, the decrease of R_S was beneficial to enhance the electron transportation ability and thereby to increase the fill factor of DSSCs.[17]

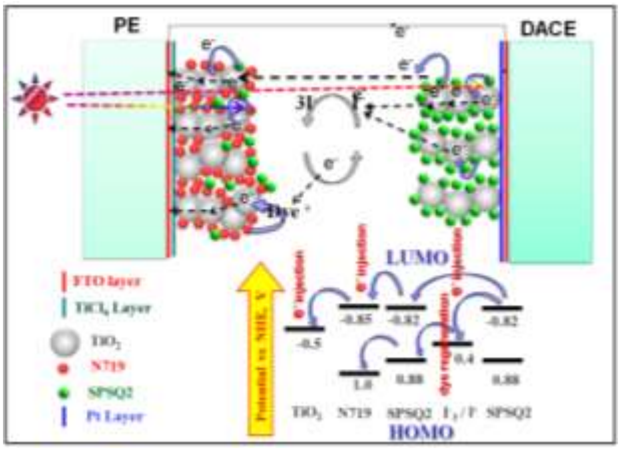

Fig. 6 Schematic representation of energy level diagram of proposed DACE-DSSC.

Fig 6 depicted energy level diagram of DACE-DSSC After excitation of dye (here SPSQ2) followed by release of electrons at DACE by light illumination, few electrons may transport to photo electrode towards energy conversions, and few were to electrolyte. Nevertheless, the exact mechanism of DACE working was not yet clear, which realizes more work to be done for this type of architecture devices [6] invented by Nam-Gyu Park.

Conclusions

In conclusion, a dye anchored counter electrodes developed using a low cost spray gun for dye sensitized solar cell applications. The optimal PEDOT:PSS sprayed DACE cell presents a power conversion efficiency of 5.75%, which was higher than the platinum based DSSC in the present study. The superior performance, low series resistance, and higher open circuit voltage and fill factor were the major consensus of these electrodes. The enhanced efficiency could be due to the number of electrons generated in the test cells associated SPSQ2 dye on counter electrode and additional PEDOT:PSS layer on DACE. The DACE architect DSSC could become potential for higher power conversion efficiency.

Acknowledgements

Author MR thank DST-SERB (Department of Science and Technology-Science and Engineering Research Board), India for financial support through the award of DST young scientist (SR/FTP/PS-111/2010). Authors thank to S. V. Manorama, IICT, Hyderabad, India for FE-SEM characterization. MR thank to

Dr. K. Venkateswarlu, Dept. of Chemistry, YVU for provide lab facilities.

Notes and references

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737−740.
2 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, Md. K. Nazeerruddin, M. Grätzel, *Nature Chemistry*, 2014, ***6***, 242–247.
3 X. Fang, T. Ma, G. Guan, M. Akiyama, T. Kida, E. Abe, *J. Electroanal. Chem*., 2004, **570**, 257–263.
4 N. Papageorgiou, W. F. Maiera, M. Grätzel, *J. Electrochem. Soc.,*1997, **144**, 876-884.
5 S. S. Kim, Y. C. Nah, Y. Y. Noh, J. Jo, D. Y. Kim, *Electrochim. Acta*, 2006, **51**, 3814–3819.
6 H-J Koo, K. Kim, Nam-Gyu Park, S. Hwang,C. Park, C. Kim, *Appl Phys Lett.,* 2008, **92,** 142103.
7 K. Susmitha, M. Raghavender, M. Naresh Kumar, L. Giribabu, *RSC Adv*., 2016, **6**, 22620.
8 P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikanta, J. Hum, K. Kalyanasundaram, M. Gratzel, M. Nazeeruddin, *Angew. Chem., Int. Ed*., 2007, **46**, 373.
9 L. Giribabu, C. Vijay Kumar, M. Raghavender, K. Somaiah, P. Yella Reddy, P. Venkateswara Rao, *J. Nano Res*., 2008, **2**, 39.
10. G. Hanumantha Rao, A. Venkateswararao, L. Giribabu, Surya Prakash Singh, *Photochem. Photobiol. Sci.,* 2016, **15**, 287–296.
11. K. Susmitha, M. Naresh Kumar, G. Rajkumar, L. Giribabu, M. Raghavender, *Solar Energy,* 2015, **118**, 126–133.
12. N. Charanadhar, K. Susmitha, M. Raghavender, L. Giribabu, K. Bhanu Sankara Rao, C.T.G. Smith, C.A. Mills, S.R.P. Silva, V.V.S.S. Srikanth, *Solar Energy*, 2016, **137**, 143–147.
13. A. Hauch and A.Georg, *Electrochim Acta,* 2001,**46(22)**, 3457–66.
14. L. Han, N. Koide, Y. Chiba, T. Mitate, *Appl Phys Lett.,* 2004, **84**, 2433–5.
15. N. Koide, A. Islam, Y. Chiba, L. Han, *J Photochem Photobiol A: Chem,* 2006, **182**, 296–305.
16. J. Theerthagiri, R.A.Senthil, M.H.Buraidah, M.Raghavender, J.Madhavan, A.K.Arof, *J Solid State Chem, 2016,* **238**, 113–120.
17. M.Ikegami, K. Miyoshi, T. Miyasaka, K. Teshima, T. C, C. C. Wan, *Appl Phys Lett.,* 2007, **90(15)**, 153122.