Hybrid Solar Cell with TiO_2 Film: BBOT Polymer and Copper Phthalocyanine as Sensitizer

Saptadip SAHA, Priyanath DAS, Ajay Kumar CHAKRABORTY, Ruchira DEBBARMA, Sharmistha SARKAR

Department of Electrical Engineering, National Institute of Technology Agartala, Jirania, West Tripura 799046, India

saptadip.saha@gmail.com, priyanath70@gmail.com, akcall58@gmail.com, ruchira.debbarma85@gmail.com, sharmisthabsl@gmail.com

DOI: 10.15598/aeee.v14i3.1692

Abstract. *An organic-inorganic hybrid solar cell was fabricated using Titanium dioxide (TiO_2): 2,5-bis(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT) film and Copper Phthalocyanine (CuPc) as a sensitizer. BBOT was used in photodetector in other reported research works, but as per best of our knowledge, it was not implemented in solar cells till date. The blend of TiO_2: BBOT blend was used to fabricate the film on ITO-coated glass and further a thin layer of CuPc was coated on the film. This was acted as photoanode and another ITO coated glass with a platinum coating was used as a counter electrode (cathode). An optimal blend of acetonitrile (solvent) (50–100 %), 1,3-dimethylimidazolium iodide (10–25 %), iodine (2.5–10 %) and lithium iodide, pyridine derivative and thiocyanate was used as electrolytes in the hybrid solar cell. The different structural, optical and electrical characteristics were measured. The Hybrid solar cell showed a maximum conversion efficiency of 6.51 %.*

Keywords

BBOT, CuPc, electrolyte, organic, solar cell.

1. Introduction

Earth contains a finite amount of fossil fuels and continuous use of these fossil fuels in huge amount is resulting in the depletion and high cost of these resources. Fossil fuels are a non-renewable source of energy, which means that these resources once depleted cannot be replenished at a sufficient rate for sustainable economic extraction in meaningful human time-frames. In contrast, the many types of renewable energy resources, such as the wind and solar energy, are constantly replenished.

Solar energy in the direct or indirect form, is the source of most of the renewable energy, which can be used for heating homes, generating electricity and a variety of commercial and industrial uses. Therefore, to shift the dependency for energy from non-renewable to renewable resources, renewable energy has become an important topic for research [14]. Out of all the renewable energy sources, solar energy has the most advantages because it cuts down the need for a distribution network since it is possible to place the supply at or near the consumption area [11]. Photovoltaic effect was first observed by Becquerel [15]. The conventional solar cell or first generation based solar cell is made of crystalline silicon. With further research and modification of the first generation solar cell, the thin film solar cell came into picture. This was based on thin films of silicon and other materials which reduced the costs, normally associated with conventional semiconductor wafer production. Presently, the third generation solar is still a newly emerging field of research which is based on solar cell made of organic materials. This organic based solar cell has the advantage over the previous generation solar cell as far as the cost of materials and manufacturing is concerned [1] and [2]. The downside of the organic solar cell is the low efficiency. To overcome the major disadvantages of the pure organic solar cell, many significant changes have been made in the device structure, and also a new choice of materials consisting of both organic and inorganic materials was incorporated in the device. A solar cell based on organic and inorganic known as Hybrid solar cell has attracted attention due to its potential of reaching an efficiency of about 10 % [2], [3], [4], [5], [6] and [7].

In recent research investigation of polymer solar cell, a power conversion efficiency of ∼5 % was obtained [8] and [9]. Copper phthalocyanine is chosen as sensitizer and 2,5-bis(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT) for the organic blend of BBOT and TiO_2 in the active region of hybrid solar cell in this research because they have high optical stability, chemical stability and photovoltaic property [13].

2. Materials and Methods

The fabrication of hybrid solar cell involved following steps. Two pieces of ITO coated glass of the dimension of 2 cm × 1 cm were cleaned with Ethanol (C_2H_5OH) and de-ionized (DI) water (Fig. 1(a)). The resistance of the conducting side of the glass was measured with a multimeter to be 19–25 Ω on average. Then the glass slides were allowed for natural drying. A fine solution of nanoporous TiO2 powder (Global NanoTech), 2,5-Bis(5-tert-butyl-benzoxazo-2-yl) thiophene (BBOT) (Sigma Aldrich) (2:1) and acetic acid (CH_3COOH) (Nice chemicals) was prepared. A small portion of the conductive side of an ITO coated glass piece was covered with tape to avoid generation of TiO_2 film: BBOT blend during fabrication. A film of the blend was coated on the conductive side by using tape casting method, the colour of the film was light yellow (Fig. 1(b)). The dimension of the film was 2 cm × 1 cm. When the liquid part of the solution was evaporated naturally, it left a film of nanoporous TiO2 and BBOT (Fig. 1(c)). After the growth of the film the tape was removed. The sample was annealed for 25 minutes at 400 °C (Fig. 1(d)). After annealing the film colour changed to dark yellow (Fig. 1(e)). Now, a film of Copper Pthalocyanine (CuPc) was generated on the TiO_2 and BBOT film and was allowed for natural drying (Fig. 1(f)). For the fabrication of counter electrode, another glass slide was coated with platinum solution (Platisol, Solaronix) on the conductive

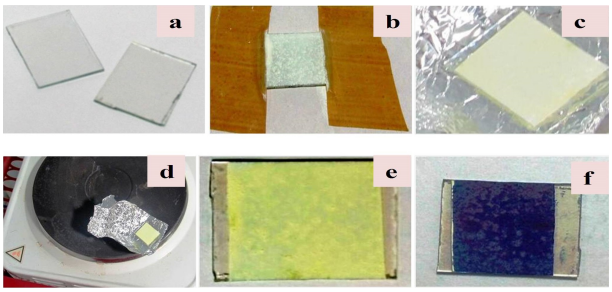


Fig. 1: (a) Cleaned ITO coated glass pieces, (b) fabricated film of TiO2 and BBOT blend on ITO coated glass by the tape casting method, (c) the film after drying (light yellow) (d) The sample is being annealed on a hot plate at 400?C, (e) The sample after annealing (color turned to bright yellow), (f) CuPc coated TiO2: BBOT film.

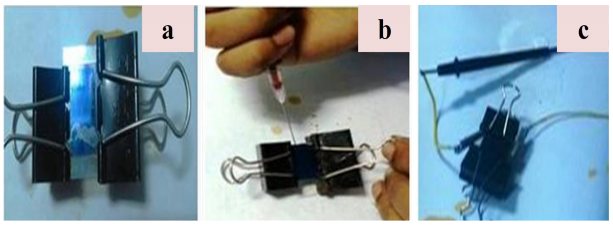


Fig. 2: (a) The solar cell is clamped between two binding clips, (b) electrolyte is being injected, (c) electrical characteristics are being measured.

side. Once both of the samples dried completely, they were clamped together facing two conductive sides using binder clips such that a conductive portion in both the slides was available to connect to the measurement probes (Fig. 2(a)). A small amount of electrolyte (HI-30, solaronix) was injected in the junction of the two slides (Fig. 2(b)). The electrolyte solution contained acetonitrile (50–100 %), 1,3-dimethylimidazolium iodide (10–25 %), iodine (2.5-10 %). Thus the device was ready to analyse different electrical characteristics. Finally the device was ready for electrical measurements (Fig. 2(c)). The schematic diagram is shown by Fig. 3.

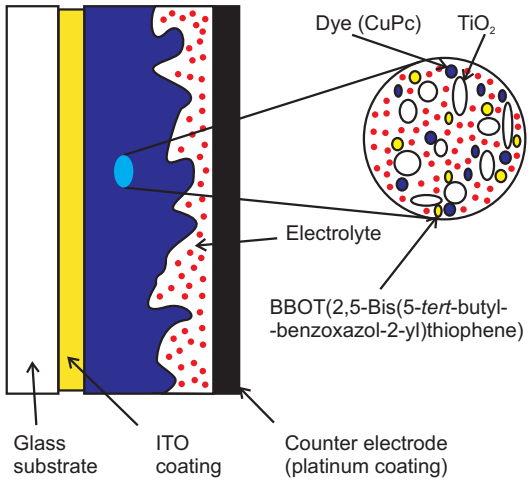


Fig. 3: Schematic diagram of the TiO_2 film, BBOT polymer and Copper Phthalocyanine based hybrid solar cell.

3. Working Principle

CuPc, which is a photo sensitizer, was fabricated on the top layer of the solar cell. CuPc absorbs photon from incident light. The BBOT particles, which were present next to the CuPc layer, are fluorescent in nature [17]. BBOT particles receive the photons donated by the CuPc layer and radiate the photons to the active material [18]. These radiated photons are absorbed and are trapped by the nanoporous TiO_2 particles, which are present in the blend. Some researchers have been

reported regarding fabrication of photodetector using BBOT [16]. The following mechanism was involved in conversion of electrical energy from the light energy [19], [20] and [21].

- Absorption: The incident photon is absorbed by the CuPc on the TiO_2 surface. After absorbing photon, the photosensitizer is excited from the ground state (S) to the excited state (S^*).

$$S \xrightarrow{h\gamma} S^*. \quad (1)$$

- Electron injection: The excited electrons are injected into the conduction band of the TiO_2 and BBOT blend. This oxidizes the photosensitizer (S^+).

$$S^* \rightarrow S^+ + e^-(TiO_2). \quad (2)$$

- Regeneration: The I^- ion redox mediator, present in the electrolyte, donates electrons to the oxidized photosensitizer (S^+) and again regenerates the ground state (S), and the I^- is oxidized to I_3^-.

$$S^+ + \frac{3}{2}I^- \rightarrow S + \frac{1}{2}I_3^-. \quad (3)$$

- Collection: The oxidized redox mediator (I_3^-), diffuses toward the counter electrode and electron is collected by the counter electrode. Iodide (I^-) is regenerated by reduction of triiodide (I_3^-) on the counter electrode.

$$\frac{1}{2}I_3^- + e^- \rightarrow \frac{3}{2}I^-. \quad (4)$$

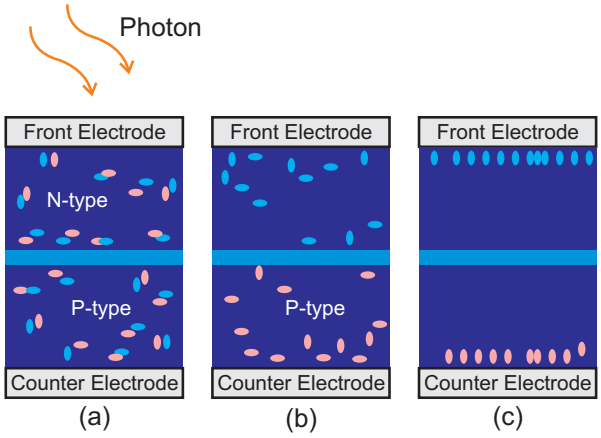


Fig. 4: Working mechanism of the fabricated solar cell: (a) light absorption and exciton formation, (b) charge separation and (c) charge collection.

4. Results and Discussion

4.1. Structural Characterizations

Atomic Force Microscopy (AFM) study was carried out to analyse the surface morphology of the TiO_2: BBOT. Figure 5(a) and Fig. 5(b) show the 2D and 3D AFM images of the film of TiO_2: BBOT blend. An average of 10 $\sim$ 15 nm TiO_2 and BBOT nanoparticles were observed in the images.

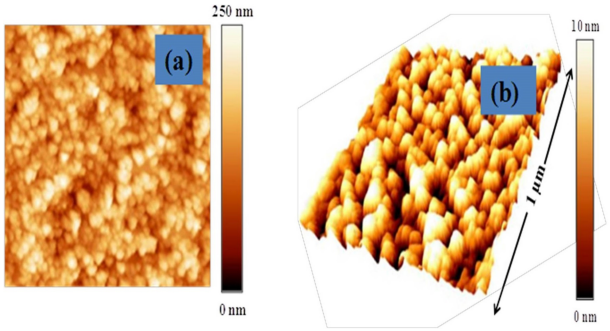
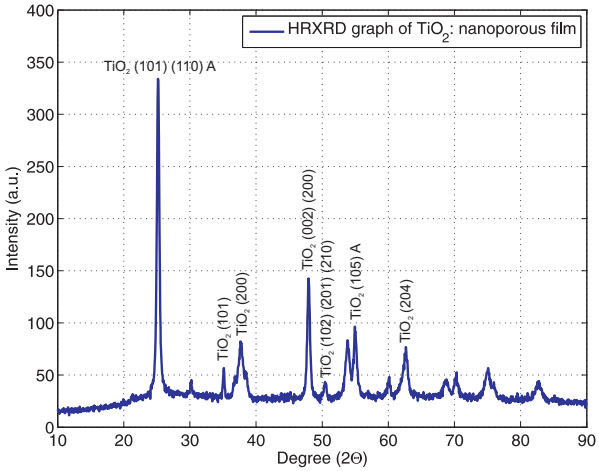
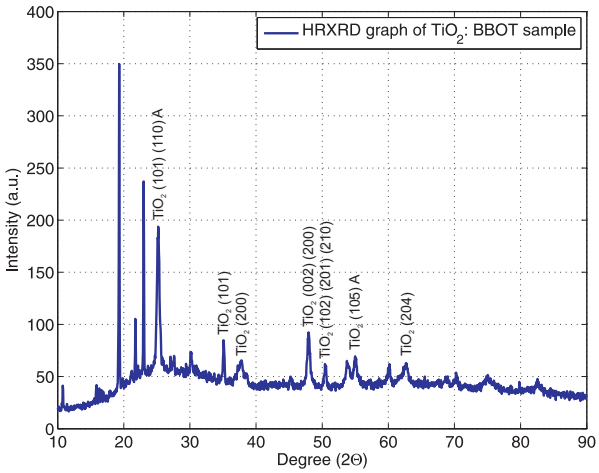


Fig. 5: (a) 2D and (b) 3D AFM images of the TiO_2: BBOT sample.

The crystalline structures of the nanoporous TiO_2 film (Fig. 6(a)) and TiO_2: BBOT (Fig. 6(b)) were con-



(a) TiO_2 nanoporous film.



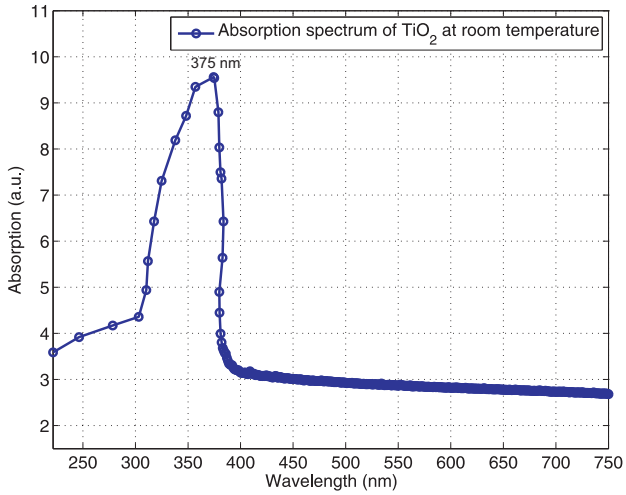
(b) TiO_2: BBOT film.

Fig. 6: HRXRD image.

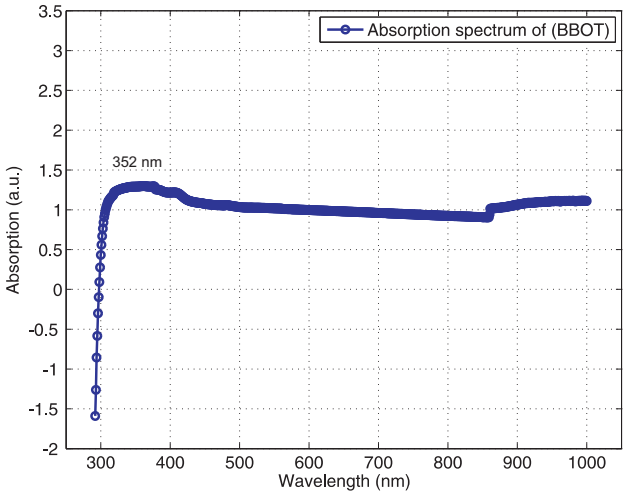
firmed by the High Resolution X-Ray Diffraction analysis (HRXRD) (Panalytical, X'Pert Pro X-ray diffractometer). The TiO_2: BBOT film showed new peaks due to the presence of the BBOT (Fig. 6(b)). These peaks were not present in the pattern of pure TiO_2 (Fig. 6(a)). All the diffraction peaks refer to anatase and rutile phases (JCPDS No. 84-1285 for anatase and 87-0920 for rutile) [7] and [12]. The pattern shows an average size for both the phases.

4.2. Optical Characterizations

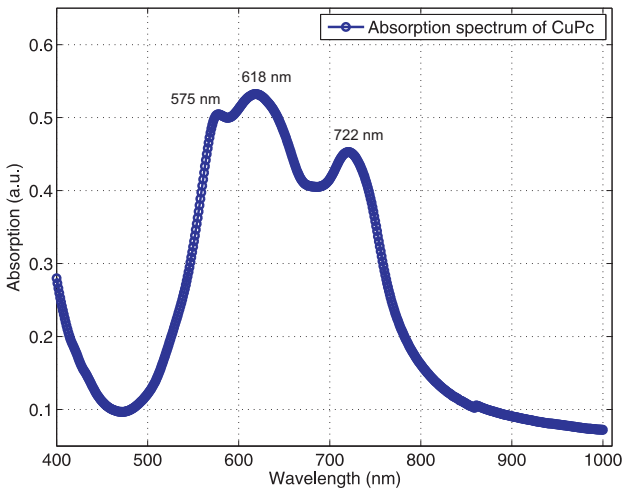
The UV-VIS optical absorption measurement (250 – 1000 nm) was done on the nanoporous TiO_2, BBOT, CuPc and CuPc: BBOT: TiO_2 sample at room temperature by a UV- visible near infrared spectrophotometer (Lambda 950, Perkin Elmer) (Fig. 7). The nanoporous TiO_2 film shows a peak in UV region (375 nm) (Fig. 7(a)). The BBOT showed large absorption spectra in the UV-visible region with a peak at 352 nm ((Fig. 7(b)). CuPc also had absorption spectra in visible region with main peaks at 618 nm and 722 nm and a small hump at 575 nm (Fig. 7(c)). CuPc: BBOT: TiO_2 sample had absorption peaks at 562 nm, 643 nm and 726 nm. The $(\alpha h\nu)^2$ versus eV curves of the nanoporous TiO_2 film and CuPc:BBOT:TiO_2 sample are shown by Fig. 8. In case of nanoporous TiO_2, the main band gap is shown for $\sim$ 3.29 eV, which was also reported by other authors [20]. However, TiO_2 film exhibits the band gap at $\sim$ 2.01 eV, which may correspond to the CuPc. Another major hump is obtained at $\sim$ 3.67 eV which may be due to sub band gap transition of the nanoporous TiO_2. The band gap shifting was reported in other journals as well [20].



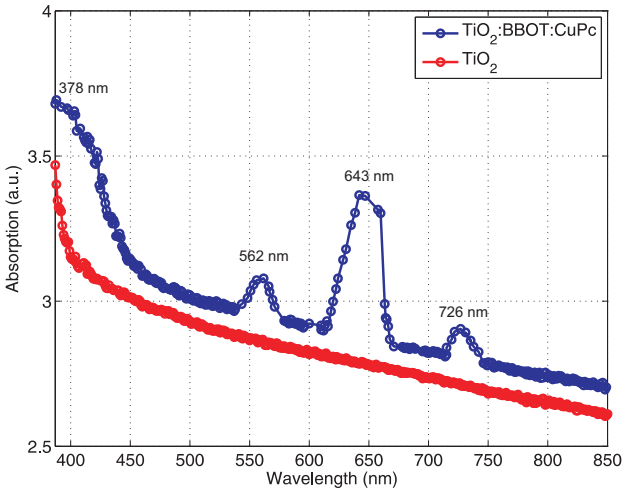
(a) nanoporous TiO_2 film.



(b) BBOT.



(c) CuPc.



(d) TiO_2: BBOT: CuPc.

Fig. 7: Absorption spectra.

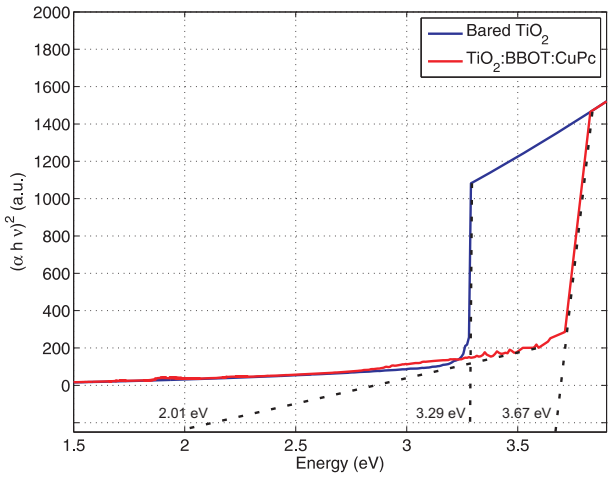


Fig. 8: $(\alpha h\nu)^2$ versus eV graph of nanoporous TiO_2 and TiO_2: BBOT: CuPc hybrid sample.

4.3. Electrical Characteristics

Figure 9 shows the Illuminance vs Voltage (L-V) characteristics of the solar cell at room temperature. The illuminance of incident light was measured by lux meter (HTC LX-101A) and a multimeter (FLUKE 289 TRUE RMS) was used to measure the voltage. The voltage was increasing with incident light and was saturated after a certain limit (0.645 V). The I-V characteristics study (Fig. 11(a)) was done using an I-V meter (Agilent technologies). The following parameters are measured as: open circuit voltage $V_{oc} = 0.6047$ V, short circuit current $I_{sc} = 16.9$ mA, maximum power point voltage $V_{mp} = 0.44$ V and maximum power point current $I_{mp} = 14.8$ mA. Figure 11(b) represents the current density vs voltage (J-V) characteristics graph, where device active-area was 2 cm^2 and short circuit current density J_{sc} was 8.45 $mA{\cdot}cm^{-2}$.

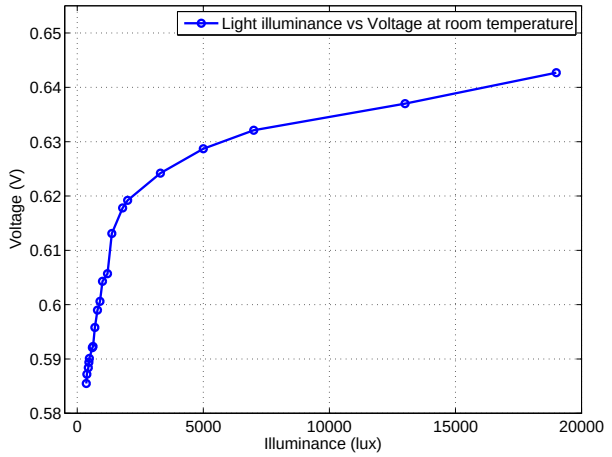


Fig. 9: Illuminance vs. output voltage characteristics of hybrid solar cell.

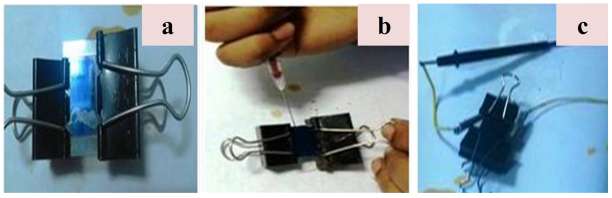
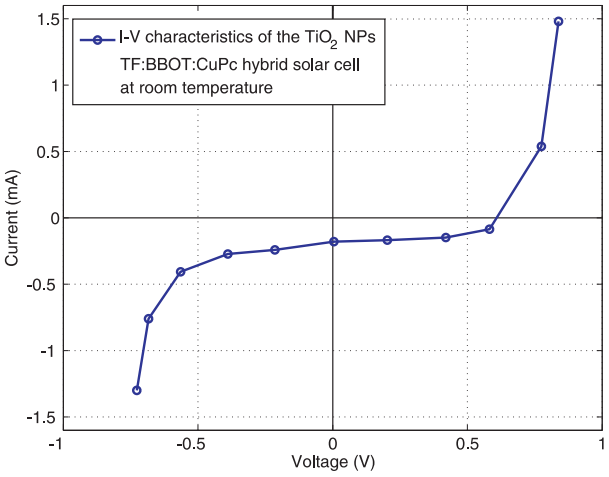
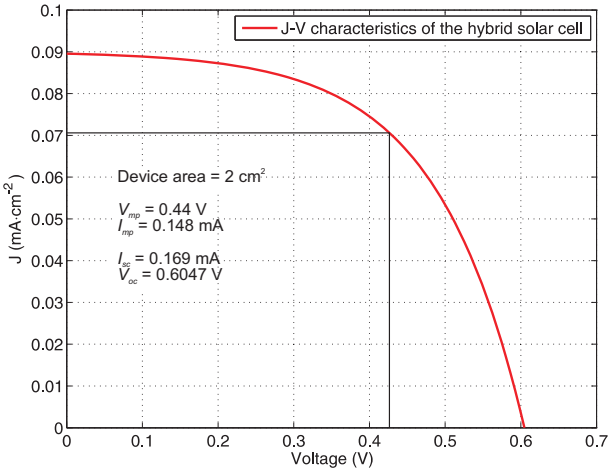


Fig. 10: (a) the solar cell is clamped between two binding clips, (b) electrolyte is being injected, (c) electrical characteristics are being measured.



(a) Current I to voltage V.



(b) Current density J to voltage V.

Fig. 11: Characteristics of the cell.

5. Calculation

During the calculation of maximum conversion efficiency at room temperature, the irradiation G, which was served as input power, was measured as 1000 $W{\cdot}m^{-2}$ i.e. 0.1 $W{\cdot}cm^{-2}$ and Air Mass (AM) of 1.5.

$$\text{Fill Factor: } FF = \frac{V_{mp} \cdot I_{mp}}{V_{oc} \cdot I_{sc}} = \frac{0.44 \cdot 14.8}{0.6047 \cdot 16.9} = 0.6372.$$

$$\text{Efficency: } \eta = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} \cdot 100 = \\ = \frac{0.6047 \cdot 16.9 \cdot 0.6372}{0.1 \cdot 1000} \cdot 100 = 6.51\ \%.$$

6. Conclusion

In this paper, we have demonstrated the fabrication of nanoporous TiO_2: BBOT: CuPc film based hybrid solar cell. A layer of Copper Pthalocyanine (CuPc) was used as sensitizer and optimal blend of electrolytes was used to maximize the cell efficiency. ITO coated glass was used for both - the front and counter electrodes and a platinum solution coating was used on the counter electrode to maximize the collection of electrons and to reduce the current loss. The AFM and HRXRD studies confirmed the nanoporous morphology of the cell and the crystalline structure of the TiO_2 film respectively. The optical absorption study revealed the absorption properties of the TiO_2, CuPc and BBOT individually and their absorption contributions in the blend. The I-V characteristics graph defined the values $V_{oc} = 0.6047$ V, $I_{sc} = 16.9$ mA, $V_{mp} = 0.44$ V and $I_{mp} = 14.8$ mA. The maximum conversion efficiency of the cell was measured to be 6.51 %, which is much higher than in other research works reported earlier for this type of solar cell.

Acknowledgment

The authors thankfully acknowledge the financial support provided by The Institution of Engineers (India) for carrying out Research & Development work in this subject.

References

[1] CHAMBERLAIN, G. A. Organic solar cells: a review. *Solar Cells*. 1982, vol. 8, iss. 1, pp. 47–83. ISSN 1878-2655. DOI: 10.1016/0379-6787(83)90039-X.

[2] SPANGGAARD, H. and F. C. KREBS. A brief history of the development of organic and polymeric photovoltaics. *Solar Energy Materials and Solar Cells*. 2004, vol. 83, iss. 2–3, pp. 125–146. ISSN 0927-0248. DOI: 10.1016/j.solmat.2004.02.021.

[3] PEUMANS, P., A. YAKIMOV and S. R. FORREST. Small molecularweight organic thin-film photodetectors and solar cells. *Journal of Applied Physics*. 2003, vol. 425, iss. 7, pp. 158–162. ISSN 0021-8979. DOI: 10.1063/1.1534621.

[4] WINDER, C. and N. S. SARICIFTCI. Low Bandgap polymers for photonharvesting in bulk heterojunction solar cells. *Journal of Materials Chemistry*. 2004, vol. 14, iss. 1, pp. 1077–1086. ISSN 0959-9428. DOI: 10.1039/b306630d.

[5] SERVAITES, D. J., S. YEGANEH, T. J. MARKS and M. A. RATNER. Efficiency Enhancement in Organic Photovoltaic Cells: Consequences of Optimizing Series Resistance. *Advanced Functional Materials*. 2010, vol. 20, iss. 1, pp. 97–104. ISSN 1616-3028. DOI: 10.1002/adfm.200901107.

[6] ARICI, E., D. MEISSNER, F. SCHAEFFLER and N. S. SARICIFTCI. Core/shell nanomaterials in photovoltaics. *International Journal of Photoenergy*. 2003, vol. 5, iss. 1, pp. 199–208. ISSN 1687-529X. DOI: 10.1155/S1110662X03000333.

[7] BRABEC, C. J., V. DYAKONOV, J. PARISI and N. S. SARICIFTCI. *Organic Photovoltaics: Concepts and Realization*. New York: Springer, 2003. ISBN 978-3-642-05580-5.

[8] PADINGER, F., R. S. RITTBERGER and N. S. SARUCIFTCI. Effect of Postproduction Treatment on Plastic Solar Cells. *Advanced Functional Materials*. 2003, vol. 13, iss. 1, pp. 85–88. ISSN 1616-3028. DOI: 10.1002/adfm.200390011.

[9] WRIGHT, M., C. YANG, X. GONG, K. LEE and A. J. HEEGER. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Advanced Functional Materials*. 2005, vol. 15, iss. 10, pp. 1617–1622. ISSN 1616-3028. DOI: 10.1002/adfm.200500211.

[10] HAUCH, J. A., P. SCHILINSKY, S. A. CHOULIS, R. CHILDERS, M. BIELE and C. J. BRABEC. Flexible Organic P3HT:PCBM Bulk-Heterojunction Modules with More than 1 Year Outdoor Lifetime. *Solar Energy Materials and Solar Cells*. 2008, vol. 92, iss. 1, pp. 727–731. ISSN 0927-0248. DOI: 10.1016/j.solmat.2008.01.004.

[11] PATHAK, D., T. WAGNER, T. ADHIKARI and J. M. NUNZI. Photovoltaic performance of $AgInSe_2$-conjugated polymer hybrid system bulk heterojunction solar cell. *Synthetic Metals*. 2015, vol. 199, iss. 1, pp. 87–92. ISSN 0379-6779. DOI: 10.1016/j.synthmet.2014.11.015.

[12] CHEN, H. Y., J. HOU, S. ZHANG, Y. LIANG, G. YANG, Y. YANG, L. YU, Y. WU and G. LI. Polymer solar cells with enhanced open-circuit voltage and efficiency. *Nature Photonics*. 2009, vol. 3, iss. 1, pp. 649–653. ISSN 1749-4893. DOI: 10.1038/nphoton.2009.192.

[13] YANG, J., K. C. GORDON, A. J. MCQUILLAN, Y. ZIDON and Y. SHAPIRA. Photoexcited carriers in organic light emitting materials and blended films observed by surface photovoltage spectroscopy. *Physical Review B*. 2005, vol. 71, iss. 1, pp. 155–209. ISSN 0556-2805. DOI: 10.1103/PhysRevB.71.155209.

[14] WRIGHT, M. and A. UDDIN. Organic-inorganic Hybrid solar cells: A comparative review. *Solar Energy Materials and Solar Cells*. 2012, vol. 107, iss. 1, pp. 87–111. ISSN 0927-0248. DOI: 10.1016/j.solmat.2012.07.006.

[15] BECQUEREL, A. E. Memoire sur les effets electriques produits sous l'influence des rayons solaires. *Comptes Rendus des Seances Hebdomadaires*. 1839, vol. 9, iss. 1, pp. 561–567. ISSN 0001-4036.

[16] KUROSAWA, K., W. WATANABE, A. TANAKA, Y. KOJIMA, K. FUJII and M. YAMADA. *Light detecting device*. US Patent. US5585915 A, 1996.

[17] FOURATI, M. A., T. MARIS, W. G. SKENE, C. G. BAZUIN and R. E. PRUD'HOMME. Photophysical, electrochemical and crystallographic investigations of the fluorophore 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene. *Journal Physical Chemistry B*. 2011, vol. 115, iss. 43, pp. 12362–12369. ISSN 1520-6106. DOI: 10.1021/jp207136k.

[18] LEWINSKA, G., A. PUSZYNSKI and J. SANETRA. BBOT for applications in photovoltaic cells devices and organic diodes. *Synthetic Metal*. 2015, vol. 199, iss. 1, pp. 335–338. ISSN 0379-6779. DOI: 10.1016/j.synthmet.2014.11.013.

[19] NARAYAN, M. R. Review: Dye sensitized solar cells based on natural photosensitizers. *Renewable and Sustainable Energy Reviews*. 2011, vol. 16, iss. 1, pp. 208–215. ISSN 1879-0690. DOI: 10.1016/j.rser.2011.07.148.

[20] HUG, H., M. BADER, P. MAIR and T. GLATZEL. Biophotovoltaics: Natural pigments in dye-sensitized solar cells. *Applied Energy*. 2013, vol. 115, iss. 1, pp. 216–225. ISSN 0306-2619. DOI: 10.1016/j.apenergy.2013.10.055.

[21] LUDIN, N. A., A. M. A. A. MAHMOUD, A. B. MOHAMAD, A. A. H. KADHUM, K. SOPIAN and N. S. A. KARIM. Review on the development of natural dye photosensitizer for dye-sensitized solar cells. *Renewable Sustainable Energy Reviews*. 2013, vol. 31, iss. 1, pp. 386–396. ISSN 1879-0690. DOI: 10.1016/j.rser.2013.12.001.

About Authors

Saptadip SAHA was born in Agartala, India. He received his M.Tech. from National Institute of Technology Agartala in 2014. His research interests include fabrication of photodector, organic and inorganic solar cells, DSSC, different studies of PV system.

Priyanath DAS was born in Agartala, India. He received his Ph.D. from Jadavpur University in 2012. His research interests include PV systems, PV faults and grid connected PV systems.

Ajoy Kumar CHAKRABORTY was born in Jhargram, India. He received his Ph.D. from Jadavpur University in 2007. His research interests include PV systems, Smart Metering and grid connected PV systems.

Ruchira DEBBARMA was born in Agartala, India. She received her B.E. from Hindustan Institute of Technology And Science in 2013. Her research interest includes Hybrid Solar Cell, Organic Solar Cell.

Sharmistha SARKAR was born in Bishalgarh, India. She received her B.E. from Tripura Institute of Technology in 2014. Her research interest includes Dye Sensitized Solar Cell, Organic Solar Cell.