Natural Grape dye used as a Sensitizer for Solar cells Applications

M. F. Hossain*(M, IEEE), M. Monirul Islam
Department of Electrical & Electronic Engineering
Rajshahi University of Engineering & Technology
Rajshahi-6204, Bangladesh
E-mail: professor.mdfaruk.hossain@ieee.org

T. Takahashi
Department of Electrical & Electronic Engineering
University of Toyama, 3190 Gofuku, Toyama,
930-8555, Japan

Abstract—**A natural grape juice has been extracted from grape fruits, purified and successfully applied as a dye on nanocrystalline TiO_2 photoelectrode for the fabrication of dye-sensitized solar cell (DSC). The KI/I_2 based electrolyte and carbon counter electrode were the other components in this DSC. The extracted grape-dye showed much similar photovoltaic performance to the previously studied natural dyes. The photoelectric conversion efficiency of 0.4 % (photocurrent density, J_{SC} = 1.71 mA/cm^2; open circuit voltage, *Voc* = 0.516 V, fill factor, FF = 46%) was achieved under irradiation with 100 mW/cm^2 white light.**
in price.

Keywords—Grape-dye, solar cells, TiO$_2$, and electrolyte.

I. INTRODUCTION

The conversion of sunlight to electricity using solar cells represents one of the most promising alternatives to energy production by fossil fuels. Consequently there has been enormous recent endeavor in a wide variety of solar cell technologies [1]. Silicon based solar cells were the most popular before the emerging of dye-sensitized solar cells. These solid -state junction devices have dominated photovoltaic industry. Since Grätzel et al. developed dye-sensitized solar cells (DSCs), a new type of solar cells, in 1991 [2], these have attracted considerable attention due to their environmental friendliness and low cost of production. A DSSC is composed of a nanocrystalline porous semiconductor (TiO_2) electrode-absorbed dye, an electrolyte (p-type semiconductor) and a counter electrode. In DSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electric energy [1-3]. So far, DSC based on the Ru-complex dyes can produce photoelectric conversion yield as high as 12.4% under standard AM1.5 sun-light irradiation [3, 4].

The large-scale application of ruthenium dyes is limited because of its costs and environmental issues. So more and more efforts have been dedicated to the development of organic dyes which have higher molar extinction coefficients, an important prerequisite for absorbed thin layer of the dye [5,6]. Usually the performance of these organic dyes is not as good as the Ru-based dye because of weak binding energy with TiO_2 film and low-charge transfer absorption in the whole visible range, but there are several other advantages in using these dyes due to their simple, inexpensive and environmental friendly processing steps. But organic dyes are not only cheaper but have also been reported to reach an efficiency as high as 9.8% [7]. In this connection, natural organic dye is the ideal choice which has also been tried as a photo-sensitizer in DSC [8-11]. To the best of our knowledge, so far, the maximum efficiency obtained in natural dye-sensitized solar cells is around 0.5% (as shown in Table-1) without any treatments.

In this paper, Grape-dye was extracted from grape fruits, and it has been successfully applied to sensitize nanocrystalline TiO_2 photoelectrode of DSC. The charatерizations of this grape-dye and TiO_2 have been investigated and discussed with their solar cells applications.

II. EXPERIMENTAL DETAILS

Dye-sensitized solar cell was prepared, using natural grape-dye as photosensitizers, sandwiched with nanocrystalline semiconductor oxide of TiO2 deposited and FTO coated glass as working electrode and carbon coated glass as counter electrodes respectively.

A. Extraction procedure of Grape-dye dye

The grape (anthocyanin) based natural dye was extracted from red Grapes using grape grains. Skin of the Grapes were taken off and grounded by grinder and the filter solution was an grape (anthocyanin) dye. Figure 1(a) and (b) shows the images of grape fruits grains and extracted grape-dye, respectively. The absorbance and transmittance of grape-dye

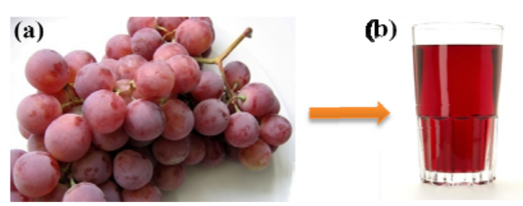

Fig. 1. Images of (a) Red Grape fruits, and (b) Extracted Grape dye.

B. Preparation of nanocrystalline TiO_2 films

Opaque nanostructured TiO_2 film was deposited on fluorine-doped SnO_2 (FTO, 8 Ω/□, Solaronix, SA) coated glass substrate, which was appropriately cleaned prior to use. The TiO_2 electrode was prepared as mentioned previously in details [12]. The thickness of the TiO_2 film was ~5.4 µm, evaluated by ACCRETECH SURFCOM 1500 surface profiler. The crystal structures of the TiO_2 thin films were determined with grazing incident X-ray diffraction (GIXRD) analysis by X-ray diffractometer (SHIMADZU XRD-6000) with Cu-Kα line. The optical properties of the TiO_2 films were measured with UV/VIS spectrophotometer. The surface morphologies were studied using field-emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700F).

C. Fabrication of DSCs

The nanoporous TiO_2 film was sensitized by Grape-dye for 24 hours at room temperature. The DSC was fabricated by clamping the dye-sensitized TiO_2 electrode against carbon counter electrode [20, 21], and filling the inter-electrode space with the electrolytes of 0.5M KI/ 0.05M I_2/0.05M 4-tert butylpridine. The active cell area was 0.25 cm^2. The intensity of light was 100 mW/cm^2. The photovoltaic data of DSC, including current-voltage measurement in light and dark illumination were carried out with computer-controlled Keithley-2400 source meter.

III. Results and Discussion

The grape-dye shows the anthocyanin chemical structure of Grape-dye. The absorbance and transmittance spectrum of grape-dye is given in Figure 2 The grape-dye dye shows the broad absorbance peak over 450-650 nm. The absorbance spectrum is confirms the formation of a charge transfer (CT) complex between grape-dye molecules and TiO_2 nanoparticles. The average transmittance of this dye is around 35%.

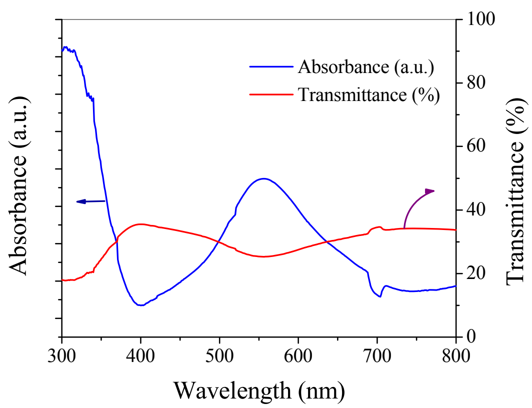

Fig. 2. Absorbance and Transmittance Spectrum for Grape dye.

Figure 3 shows the infrared (IR) spectrum of grape-dye dye. In the FT-IR spectrum, characteristic absorption bands are displayed at 3454 cm^{-1} relating to –OH groups. The characteristic absorption bands at 1642 cm^{-1} is assigned to the carbonyl carbon group (C=O); 1073 cm^{-1} stretching of C–O–C ester [3].

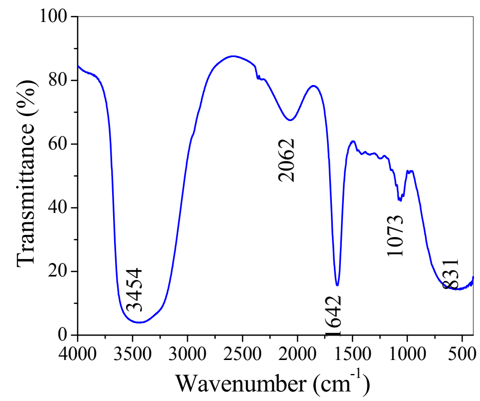

Fig. 3. Absorbance and Transmittance Spectrum for Grape dye.

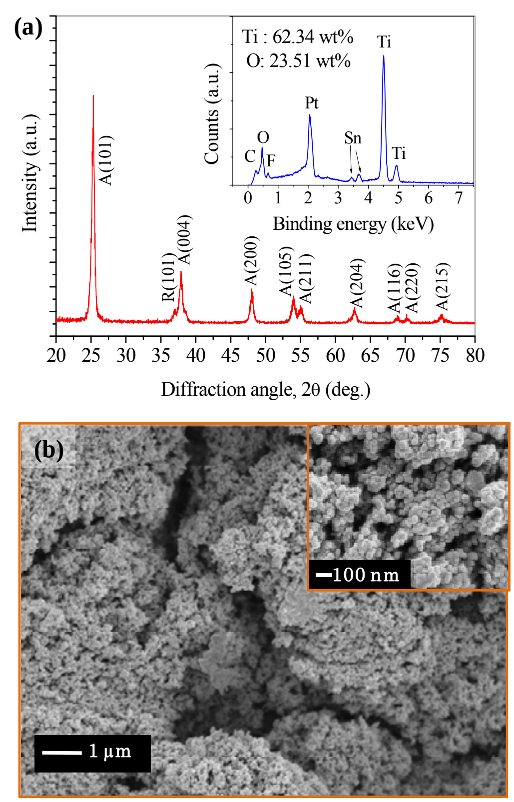

Fig. 4. Characterization of TiO_2 films: (a) X-ray analysis. (inset) EDS analysis, and (b) FE-SEM images with 1µm and 100nm scale.

Figure 4 (a) shows the GIXRD pattern (incidence angle $\alpha = 0.5°$) of TiO_2 electrode. It is observed that the films are of polycrystalline nature. Most of the peaks observed are of TiO_2 anatase phase. The dominant peak was observed at 2θ value, 25.3° for A(101) reflection. Only one rutile peak R(101) was observed at 2θ value, 36.08°. The crystallite sizes of the TiO_2 films were estimated by Debye-Scherrer's equation [23]: $D = 0.94\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength of the X-ray radiation (Cu K_α = 0.154 nm), θ is the diffraction angle and β is the full width at half maximum (FWHM).The crystallite size calculated using A(101) anatase peak was 14.9 nm. In the inset of Fig. 4(a), this GIXRD data has been agreed with the EDS spectra of TiO_2 films. The peaks of Ti, O, Sn and Pt have found. The peaks of Sn exhibits due to FTO glass substrate and Pt peak shows due to coat Pt for FESEM measurement. The peaks of Ti (62.34 wt%) and O (23.51 wt%) are found, which demonstrates that the composition of these products are high chemical purity. The general morphology of the TiO_2 structure is investigated by using FESEM image, shown in Fig. 4(b). The FE-SEM image of bare TiO_2 thin film shows highly porous structure with discrete grain clusters.

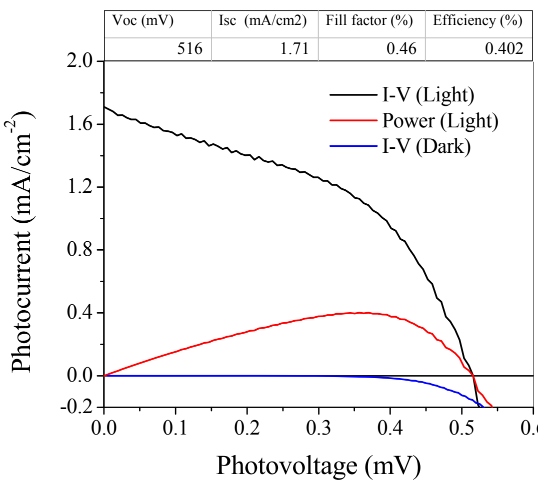

Fig. 5. I-V and P-V characteristics curves of DSC.

The outcome of the I-V and P-V measurement in light also follows this trend. From the Figure 5, Grape-dye DSC with $TiCl_4$ treatment shows efficiency, 1.03 %, open circuit voltage, V_{OC}=0.516 V, photocurrent density, I_{SC}=1.71 mA/cm^2 and FF= 0.4%. Rather, it may be due to the increase of total effective-binding sites on TiO_2 for dye absorption, which may prefer the particular orientation of moieties that leads to compact and packed arrangement of dye molecules [5]. Better dark current, characteristics, observed grape-dye-DSC, indicates better effective dye absorption on TiO_2 surface that reduces back-electron transfer from TiO_2 to electrolyte.

IV. CONCLUSION

In summary, a natural dye has been synthesized. from grape fruits grains and successfully applied as an sensitizer to nanocrystalline TiO_2 electrode. Subsequently an efficient dye-sensitized solar cell has been fabricated with this grape dye sensitized TiO_2 electrode, which sows solar energy to photoelectric conversion efficiency of 0.4% (J_{SC}=1.21 mA/cm^2, V_{OC}=0.516 V, FF=46%) under 100 mW/cm^2 of solar simulator. Further improvement of the photoelectric conversion efficiency in dye based TiO_2 cell will be possible by modification of the TiO_2 structure, and these works are now in progress.

REFERENCES

[1] W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. S. Mende, M. K. Nazeeruddin, Q. Wang, M. Grätzel, and D. L. Officer, Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells, *J. Phys. Chem. C Letts.* Vol. 111, pp. 11760-11762, 2007.

[2] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO_2 films, *Nature*, Vol.353, pp. 737–740, 1991.

[3] D.P. Hagberg, J.H. Yum, H. Lee, L.C. Sun, M. Grätzel. Molecular Engineering of Organic Sensitizers for Dye-Sensitized Solar Cell Applications, *J. Am. Chem. Soc.* Vol. 130, No. 19, pp. 6259-6266, 2008.

[4] J.E. Kroeze, N. Hirata, S. Koops, M.K. Nazeeruddin, L. S. Mende, M. Grätzel, Alkyl Chain Barriers for Kinetic Optimization in Dye-Sensitized Solar Cells, *J. Am. Chem. Soc.* Vol. 128, No. 50, pp. 16376-16383, 2006.

[5] Z.J. Ning, Q. Zhang, H. Tian, Starburst Triarylamine Based Dyes for Efficient Dye-Sensitized Solar Cells, *J. Org. Chem.* Vol. 73, No. 10, pp. 3791-3797, 2008.

[6] [6]. Z.G. Chen, F.Y. Li, C.H. Huang, Organic D-π-A Dyes for Dye-Sensitized Solar Cell, *Curr. Org. Chem.* Vol. 11, No. 14, pp. 1241-1258, 2007.

[7] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary n-conjugated spacer, *Chem. Commun.*, pp. 2198–2200, 2009.

[8] N.M. Gomez-Ortız, I.A.V. Maldonado, A.R.P. Espadas, G.J.M. Rejon, J.A.A. Barrios, G. Oskama, Dye-sensitized solar cells with natural dyes extracted from achiote seeds, *Sol. Energy Mater. Sol. Cells*, Vol. 94, No. 1, pp. 40-44, 2010.

[9]] K. Wongcharee, V. Meeyoo, S. Chavadej, Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flower, *Sol. Energy Mater. Sol. Cells*, Vol. 91, No. 7, pp. 566-571, 2007.

[10] S. Furukawa, H. Iino, T. Iwamoto, K. Kukita, S. Yamauchi, Characteristics of dye-sensitized solar cells using natural dye, *Thin Solid Films*, Vol. 518, No.2, pp. 526-529, 2009.

[11] M. Grätzel, Dye-sensitzed solar cells, *J. Photochem. Photobiology C: Photochem. Rev.* Vol. 4, No. 2, pp. 145-153, 2003.

[12] M.F. Hossain, S. Biswas, T. Takahashi, Study of CdS-sensitized solar cells, prepared by ammonia-free chemical bath technique, *Thin Solid Films*, Vol. 518, No.5, pp. 1599-1602, 2009.