

Analysis of Natural Sensitizers to Enhance the Efficiency in Dye Sensitized Solar Cell

S.Rajkumar^{1*}, K.Suguna²

¹M.Phil Research Scholar, Department of Physics, Thiruvalluvar Govt. Arts College , Rasipuram- 637401, Tamil Nadu, India.

²Associate Professor , Department of Physics, Thiruvalluvar Govt. Arts College , Rasipuram- 637401, Tamil Nadu, India.

ABSTRACT

Three vegetable dyes are used for the study: anthocyanin dye from pomegranate arils extract, betalain dye from beet root extract and chlorophyll dye from tridax procumbens leaf. The anthocyanin and betalain, anthocyanin and chlorophyll, betalain and chlorophyll dyes are blended in cocktail in equal proportions, by volume. This study determines the effect of different extraction concentrations and different vegetable dyes on energy gap using dye sensitized solar cells. The experimental results show that the cocktail dye blended using extracts of pomegranate arils, beet root and tridax procumbens leaf, in the volumetric proportion 1:1, using an extraction at room temperature the greatest energy gap (e_g) of up to 1.87eV.

Keywords: pomegranate, beet root, tridax procumbens, energy gap.

I. INTRODUCTION

Of the various renewable energy sources, wind power and solar energy have the greatest potential. Solar energy causes no public harm and can be used by anybody, without limits. Therefore, many countries are actively endeavoring to develop solar energy [1]. Dye-sensitized solar cells (DSSC) are increasingly used in conventional inorganic solid solar cells. TiO_2 is the most promising electrode material for DSSCs because of its wide band gaps, which are suitable for interfacial electron transport. In the early 1990s, Gratzel et al. developed a new type of solar cell that absorbs incident solar light in the visible light wavelength zone of the dye with a high surface area of titanium dioxide (TiO_2). The dye-sensitized TiO_2 solar cell can be prepared in an ordinary environment, which significantly reduces its cost [2]. Currently, the most efficient dye-sensitized solar cell (DSSC), which uses Ru compound absorbed onto nanoscale TiO_2 , has an efficiency of 11-12% [3,4]. Although this type of DSSC is more efficient, its use of expensive metals, such as N3 and N719, has several drawbacks.

Many inorganic, organic, and hybrid dyes have been employed as sensitizers [5-7]. Because ruthenium dyes, including N719 and N3, are very expensive and environmentally toxic, numerous metal-free organic dyes have been used in DSSCs [8, 9]. Recently, several natural organic dyes, such as anthocyanin, chlorophyll, tannin, and carotene, extracted from various plants, fruits, flowers, and leaves, have been successfully used as sensitizers in DSSCs [10-16]. Hao et al. extracted

photosensitizer from the plants of black rice, capsicum, Erythrina variegata flower, Rosa xanthina, and kelp to serve as natural dyes. Black rice achieves the greatest photoelectric conversion efficiency of 0.327% [17]. Wongcha-ree et al. extracted natural pigments from rosella and blue pea and blended these two pigment dyes in equal proportions to determine the performance of the blended dye, which achieved a maximum photoelectric conversion efficiency of 0.37% [14]. In 2008, Calogero used the extracted fluid from red Sicilian orange and purple eggplant as a photosensitizer. The cell using red Sicilian orange juice as the sensitizer achieved the highest photoelectric conversion efficiency, with a maximum efficiency of 0.66% [18]. Thambidurai et al., 2011, have fabricated Ixora coccinea, Mulberry, and beetroot extract sensitized ZnO nanorod-based solar cells and have reported that the efficiencies are 0.33, 0.41, and 0.28%, respectively [19]. Park et al., 2013, have fabricated yellow Gardenia as natural photosensitizer and reported maximum power conversion efficiency of 0.35% [20]. Senthil et al., 2014, have fabricated DSSCs using natural dyes extracted from strawberry, which showed a maximum conversion efficiency of 0.49% [21]. The dye-sensitized solar cells (DSSC) fabricated using the predye treated and pure TiO_2 nanoparticles sensitized by natural dye extract of Lawsonia inermis seed showed a promising solar light to electron conversion efficiency of 1.47% and 1%, respectively [22].

This study uses a cocktail of dyes, which are extracted from three different kinds of vegetable dyes, in DSSCs, in order to reduce the cost of fabrication.

II. EXPERIMENTAL

2. 1. Preparation of Natural Sensitizer

Pomegranate fruit arils were taken and the juice was extracted. Beet root was first cleaned using distilled water and its skin was peeled out. Then the vegetable was scrapped into small piece and crushed in a mortar to extract the required natural pigment. Matured leaves were collected from the *Tridax procumbens* plants. Leaves were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature for one hour. Then the leaves were crushed in a mortar to prepare the sensitizing dye. Each of these three samples were taken in three test tubes and dissolved in ethanol. The test tubes were covered with aluminium foil and kept in dark for one day at room temperature for adequate extraction without exposure to sunlight. Using a cocktail blending method, chlorophyll dye, betalain dye and anthocyanin dye were blended in the volumetric proportion 1: 1 to form three types of cocktail dyes. Anhydrous ethanol was used as the extraction solvent. Combinations of cocktail dyes shown in figure. The figure 2.1 shows the pomegranate and beetroot mixed dye, the figure 2.2 shows the pomegranate and tridax procumbens mixed dye, and the figure 2.3 shows the beetroot and tridax procumbens mixed dye.

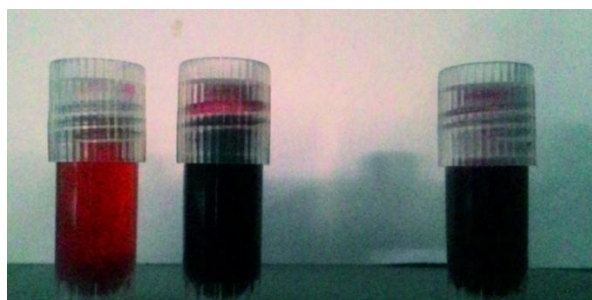


Fig.2.1. Pomegranate and Beetroot mixed dye

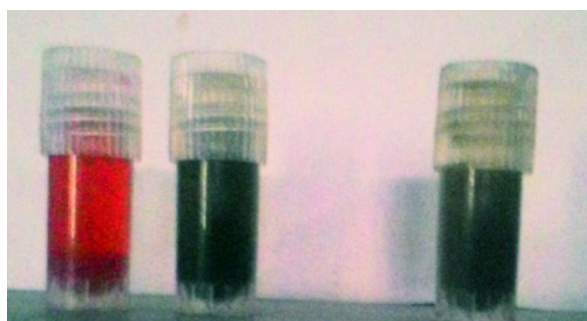


Fig.2.2. Pomegranate and Tridax procumbens mixed dye

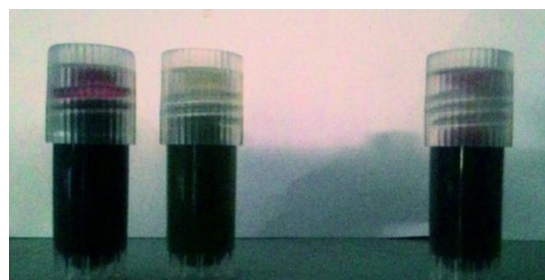


Fig.2.3. Beet root and *Tridax procumbens* mixed dye

2.2. Characterization methods

FT-IR spectroscopy measurements were carried out on a Bruker tensor 27 spectrophotometer using KBr pellets. UV-VIS absorption spectra of natural dyes were recorded using a spectrophotometer Lambda 35.

III. RESULTS AND DISCUSSIONS

3. 1. Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) Spectra of Cocktail dyes of Pomegranate and Beetroot mixed dye, Pomegranate and *Tridaxprocumbens* mixed dye and Beetroot and *Tridaxprocumbens* dye are extracted were recorded on Perkin Elmer spectrometer using KBr pellet technique in the range of 4000 – 400 cm^{-1} . FTIR spectra of cocktail dyes extracted from ethanol as shown in Figure 3.1. From the Pomegranate and Beetroot mixed cocktail dye the peak absorbed at 3435 cm^{-1} is due to presence of O-H stretching in the compound type of alcohols, phenols. The peak absorbed at 1639 cm^{-1} is due to presence of N-H bend in the compound type of 1^o amines. The peak absorbed at 1407 cm^{-1} is due to presence of C-C stretching in the aromatics. The peak absorbed at 1245 cm^{-1} is due to presence of C-O stretching in alcohols. The peak absorbed at 1069 cm^{-1} is due to presence of C-N stretching in aliphatic amines. The peak absorbed at 642 cm^{-1} is due to presence of $\text{-C}\equiv\text{C-H:C-H}$ in alkynes. From the Pomegranate and *Tridaxprocumbens* mixed cocktail dye the peak absorbed at 3434 cm^{-1} is due to presence of O-H stretching in the compound type of alcohols, phenols. The peak absorbed at 1638 cm^{-1} is due to presence of N-H bend in the compound type of 1^o amines. The peak absorbed at 1383 cm^{-1} is due to presence of C-H rock in the alkanes. The peak absorbed at 1071 cm^{-1} is due to presence of C-N stretching in aliphatic amines. The peak absorbed at 685 cm^{-1} is due to presence of $\text{-C}\equiv\text{C-H:C-H}$ in alkynes. From the Beetroot and *Tridaxprocumbens* mixed cocktail dye the peak absorbed at 3430 cm^{-1} is due to presence of O-H stretching in the compound type of alcohols, phenols. The peak absorbed at 1638 cm^{-1} is due to presence of N-H bend in the compound type of 1^o amines. The peak

absorbed at 1408 cm^{-1} is due to presence of C-C stretching in the aromatics. The peak absorbed at 1077 cm^{-1} is due to presence of C-N stretching in aliphatic amines. The peak absorbed at 693 cm^{-1} is due to presence of $\text{-C}\equiv\text{C-H}:\text{C-H}$ in alkynes.

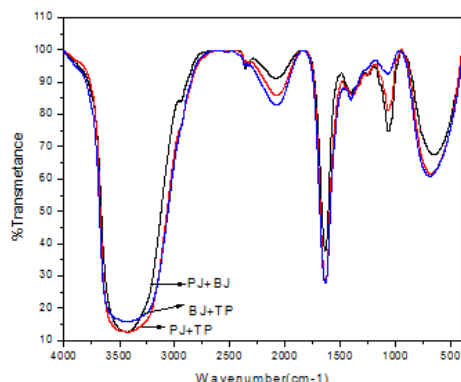


Fig.3.1.FT-IR spectra

3.2. UV-VIS Analysis for Natural Sensitizer

Figure 3.2 shows the absorption spectra for three natural dyes. The figure shows the maximum absorption peaks for pomegranate juice is at 529.22nm and absorbance is at 1.2489, the maximum absorption peaks for beetroot juice are at 479 and 534.98nm and absorbance are at 1.7848 and 1.4532, and the maximum absorption peaks for tridaxprocumbens extract are at 663.84 and 985.70 nm and absorbance are at 1.4035 and 0.85181.

Figure 3.3 shows the absorption spectra for the cocktail dye of pomegranate and beetroot juice. The cocktail dye shows an increase in the range of the wave length of absorption. The absorption representing the red shift may increase the number of electrons in the excited state of the dye which in turn increase the photoelectric conversion efficiency of a DSSC. Figure 3.4 shows the absorption spectra for pomegranate and tridaxprocumbens of cocktail dye. Figure shows that the cocktail dye decreases the range of the absorption wave length and allows further absorption of lower visible light, which decrease the photoelectric conversion efficiency of a DSSC. Figure 3.5 shows the absorption spectra for beetroot juice and tridaxprocumbens of cocktail dye. It was observed that the cocktail dye shows a blue shift in the absorption spectrum.

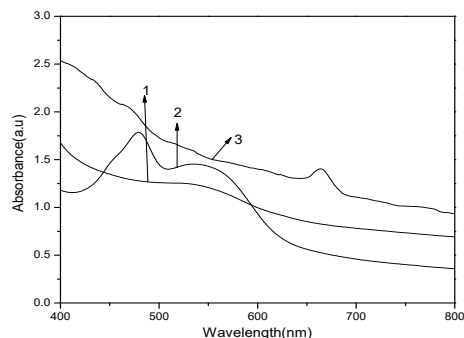


Fig.3.2: The absorption spectra for extracts of (1) pomegranate juice, (2) beetroot juice, (3) tridaxprocumbens, in ethanol solution.

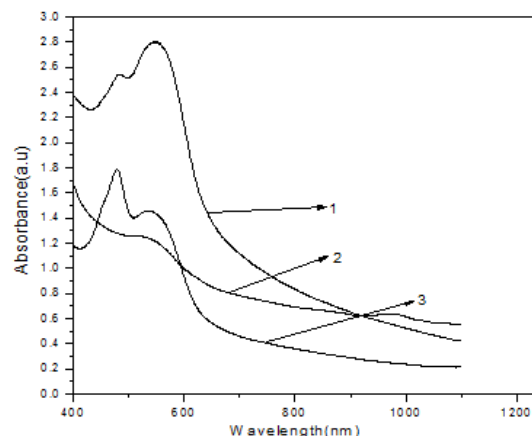


Fig.3.3: The absorption spectra for extracts of (1) Pomegranate and Beetroot mixed cocktail dye, (2) Pomegranate juice, (3) Beetroot juice, in ethanol solution.

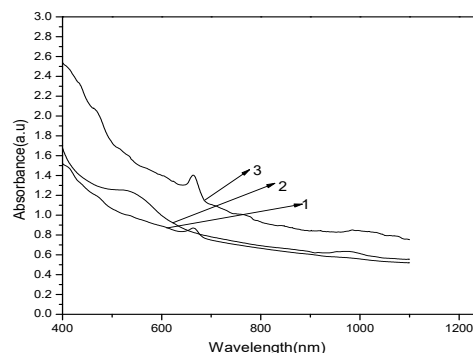


Fig.3.4: The absorption spectra for extracts of (1) Pomegranate and TridaxProcumbens mixed cocktail dye, (2) Pomegranate juice, (3) TridaxProcumbens, in ethanol solution.

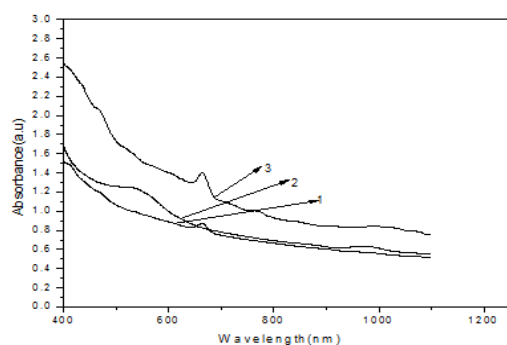


Fig.3.5: The absorption spectra for extracts of (1) Beetroot and TridaxProcumbens mixed cocktail dye, (2) Beetroot juice, (3) TridaxProcumbens, in ethanol solution.

3.3. Energy gap determination

The UV-visible spectral studies of the pomegranate, beetroot, tridaxprocumbens and cocktail dye extracts were carried out by UV-visible spectrometer in the range of 400 to 1100 nm. The pomegranate and beetroot mixed dye is extracted from ethanol corresponding to pomegranate and tridaxprocumbens mixed beetroot and tridaxprocumbens mixed, and pomegranate, beetroot, and tridaxprocumbens respectively as shown in figure 3.6. The optical band gap of the Pomegranate, Beetroot, Tritaxprocumbens was determined from the absorption spectra using the relation $E_g = hc/\lambda$, where h is Planck's constant, c is speed of velocity of light and λ is the cut-off wavelength. The table 1 shows wave length and its corresponding band gap value of dyes. The broad absorption and sharp intense peak is obtained in between 350 to 650 nm. In the pomegranate and tridaxprocumbens mixed cocktail dye obtained at longer wavelength compare to other samples. The peak at 485 nm and 550 nm observed at a beetroot and tridaxprocumbens mixed cocktail dye corresponding to band gap value of 2.56 eV and 2.258864eV respectively. In the pomegranate and tridaxprocumbens mixed cocktail dye the sharp intense absorption peak is observed at the wavelength of 663 nm and its corresponding band gap value is 1.873869 eV. In the beet root and tridaxprocumbens the sharp intense peak observed at 384 nm and 663 nm and its corresponding band gap value is 3.235 eV and 1.873869 eV respectively. The peak at 529 nm observed at pomegranate dye corresponding to band gap value of 2.348 eV. In the beetroot dye the sharp intense peak observed at 479 and 534 nm and its corresponding band gap value is 2.593685 eV and 2.326545eV respectively. In the tridaxprocumbens the sharp intense absorption peak is observed at 663 of 985 nm and its corresponding band gap value is 1.873869eV and 1.261294 eV respectively. These results concluded that the pomegranate and

tridaxprocumbens mixed cocktail dye shows the small band gap value when compared with the other dyes. The absorption spectrum of pomegranate and beetroot mixed cocktail dye in ethanol cover almost the visible region.

Dye	λ_{max} (nm)	$E_g = hc/\lambda$ (eV)
Pomegranate and Beetroot	485 550	2.56 2.258864
Pomegranate and Tridaxprocumbens	663	1.873869
Beetroot and Tridaxprocumbens	384 663	3.235 1.873869
Pomegranate	529	2.348
Beetroot	479 534	2.593685 2.326545
Tridaxprocumbens	663 985	1.873869 1.261294

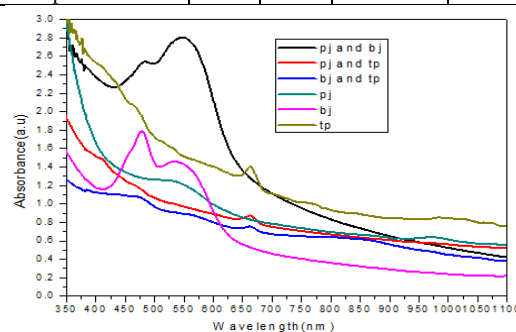


Fig.3.6: The absorption spectra for natural dyes

IV. CONCLUSION

Dyes extracted from Pomegranate, Beetroot and Tridaxprocumbens and all the possible cocktail dyes prepared were analysed as light harvesters in DSSC's. FT-IR spectral measurements were used to analyse the functional groups present in the dye. UV-Visible absorption spectra of the various dyes were measured to observe the range of absorption by the active components. Among them Tridaxprocumbens and mixed dye prepared using Pomegranate and Tridaxprocumbens shows significant absorption in the visible region. Smaller energy gap of these dyes when compared with other types of dyes also support the conclusion

REFERENCES

- [1]. D. M. Chapin, C. S. Fuller, and G. L. Pearson, "A new silicon p-n junction photocell for converting solar radiation into electrical power," *Journal of Applied Physics*, vol. 25, no. 5, pp. 676-677, 1954.
- [2]. B. O'Regan and M. Graetzel, "Low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol. 353, no. 6346, pp. 737-740, 1991.
- [3]. Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, "Dye-sensitized solar cells with conversion efficiency of 11.1%," *Japanese Journal*

- of Applied Physics, vol.45, no.24-28, part 2, article L638, 2006.
- [4]. R. Buscaino, C. Baiocchi, C. Barolo et al., "A mass spectrometric analysis of sensitizer solution used for dye-sensitized solar cell," *Inorganica Chimica Acta*, vol.361, no.3, pp.798-805, 2008.
- [5]. K. H. Park, T. Y. Kim, S. Han et al., "Light harvesting over a wide range of wavelength using natural dyes of gardenia and cochineal for dye-sensitized solar cells," *Spectrochimica Acta A*, vol. 128, pp. 868-873, 2014.
- [6]. F. G. Gao, A. J. Bard, and L. D. Kispert, "Photocurrent generated on a carotenoid-sensitized TiO₂ nanocrystalline mesoporous electrode," *Journal of Photochemistry and Photobiology A Chemistry*, vol.130, no.1, pp.49-56, 2000.
- [7]. H. Zhou, L. Wu, Y. Gao, and T. Ma, "Dye-sensitized solar cells using 20 natural dyes as sensitizers," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 219, no. 2-3, pp. 188-194, 2011.
- [8]. J. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin, and M. Gratzel, "Panchromatic engineering for dye-sensitized solar cells," *Energy and Environmental Science*, vol.4, no.3, pp.842-857, 2011.
- [9]. G. Calogero, J. H. Yum, A. Sinopoli, G. Di Marco, M. Graetzel, and M. K. Nazeeruddin, "Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells," *Solar Energy*, vol. 86, no. 5, pp. 1563-1575, 2012.
- [10]. E. M. Abdou, H. S. Hafez, E. Bakir, and M. S. A. Abdel-Mottaleb, "Photostability of low cost dye-sensitized solar cells based on natural and synthetic dyes," *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy*, vol. 115, pp. 202-207, 2013.
- [11]. C. Sandquist and J. L. McHale, "Improved efficiency of betanin-based dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A*, vol. 221, no. 1, pp. 90-97, 2011.
- [12]. V. Shanmugam, S. Manoharan, S. Anandan, and R. Murugan, "Performance of dye-sensitized solar cells fabricated with extracts from fruits of ivy gourd and flowers of red frangipani as sensitizers," *Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy*, vol.104, pp.35-40, 2013.
- [13]. D. Zhang, N. Yamamoto, T. Yoshida, and H. Minoura, "Natural dye sensitized solar cells," *Transactions of the Materials Research Society of Japan*, vol. 27, pp. 811-814, 2002.
- [14]. K. Wongcharee, V. Meeyoo, and S. Chavadej, "Dye-sensitized solar cell using natural dyes extracted from rosella and blue pea flowers," *Solar Energy Materials and Solar Cells*, vol. 91, no. 7, pp. 566-571, 2007.
- [15]. A. S. Polo and N. Y. M. Iha, "Blue sensitizers for solar cells: natural dyes from Calafate and Jaboticaba," *Solar Energy Materials & Solar Cells*, vol.90, no.13, pp.1936-1944, 2006.
- [16]. H. Chang, M. Kao, T. Chen, C. Chen, K. Cho, and X. Lai, "Characterization of natural dye extracted from wormwood and purple cabbage for dye-sensitized solar cells," *International Journal of Photoenergy*, vol. 2013, Article ID 159502, 8 pages, 2013.
- [17]. S. Hao, J. Wu, Y. Huang, and J. Lin, "Natural dyes as photosensitizers for dye-sensitized solar cell," *Solar Energy*, vol.80, no.2, pp.209-214, 2006.
- [18]. G. Calogero and G. D. Marco, "Red Sicilian orange and purple eggplant fruits as natural sensitizers for dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 92, no. 11, pp. 1341-1346, 2008.
- [19]. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai, N. Sabari Arul, S. Agilan, and R. Balasundaraprabhu, "Dye-sensitized ZnO nanorod based photoelectrochemical solar cells with natural dyes extracted from *Ixora coccinea*, *Mulberry* and *Beetroot*," *Journal of Materials Science: Materials in Electronics*, vol.22, no.11, pp.1662-1666, 2011.
- [20]. K. Park, T. Kim, J. Park et al., "Adsorption characteristics of gardenia yellow as natural photosensitizer for dye-sensitized solar cells," *Dyes and Pigments*, vol.96, no.2, pp.595-601, 2013.
- [21]. T. S. Senthil, N. Muthukumarasamy, and M. Kang, "ZnO nanorods based dye sensitized solar cells sensitized using natural dyes extracted from beetroot, rose and strawberry," *Bulletin of the Korean Chemical Society*, vol.35, pp.1050-1056, 2014.
- [22]. S. Ananth, P. Vivek, T. Arumanayagam, and P. Murugakoothan, "Natural dye extract of lawsonia inermis seed as photosensitizer for titanium dioxide based dye sensitized solar cells," *Spectrochimica Acta A*, vol.128, pp.420-426, 2014.