Applied Biological Research 24(2): 184-190; (2022)
DOI: 10.5958/0974-4517.2022.00022.2

FABRICATION OF DYE-SENSITIZED SOLAR CELLS USING AQUEOUS AND ETHANOLIC EXTRACTS OF *Ixora macrothyrsa* FLOWERS

E. Selva Esakki*, L. Renuga Devi and S. Meenakshi Sundar

PG and Research Department of Physics, Sri Paramakalyani College, Alwarkurichi. Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli - 627 012 Tamilnadu (India)
*e-mail: *selvaesakki7270@gmail.com*

(Received 16 December, 2021; accepted 18 April, 2022)

ABSTRACT

Dye-sensitized solar cells (DSSCs) are promising types of photovoltaic cells which have the capability to generate electrical energy at low fabrication-cost in comparison to the silicon crystalline solar cells. Titanium dioxide (TiO_2) nanoparticles were synthesized by solvothermal method. DSSCs using *Ixora macrothyrsa* flowers as dye-sensitizer were fabricated using water and ethanol as solvents. The structural and surface properties of TiO_2 nanoparticles were characterized using X-ray diffraction and Field Emission Scanning Electron Microscopy. The synthesized TiO_2 material had tetragonal crystal structure which was highly stable and crystalline. The extracted natural dyes were characterized by UV-visible absorption spectroscopy and Fourier transform infrared (FTIR). The bandgap energy of TiO_2 photoanode was studied by using UV-visible spectra and the functional group by using FTIR spectra. The photo-electrochemical parameters and efficiency of DSSC were measured using J-V measurement system. The result of J-V characteristics showed that the efficiency of DSSC's based on TiO_2 nanoparticles extracted from *Ixora* flowers using ethanol solvent was better than water solvent.

Key words: FTO, photovoltaics, *Ixora*, solvothermal, TiO_2

INTRODUCTION

A dye-sensitized solar cell (DSSC) is a device that converts light energy into electrical energy using dye molecules, the sensitivity of semiconductor electrode materials and photovoltaic effect. DSSCs are considered as renewable energy sources and have intensively been studied as next-generation solar cells due to their relatively high efficiency and low production-cost as compared to the silicon solar cells (O'Regan *et al*., 1991). TiO_2- and ZnO-nanoparticles have mostly been used in DSSCs because both possess almost similar electron affinity and band gap energy (3.2 and 3. 3 eV, respectively). The band gap for DSSC should be in a wide range, and have much higher electron diffusivity and high electron mobility of 115-155 cm^2 (Trihutomo *et al.*, 2019), which favours efficient electron transport in a semiconductor and reduces recombination rate.

Sensitizing dye molecules react with photoanodes and electrolyte solutions; and these in solar cells convert light energy into electrical energy. In recent years, research is focused on natural dyes and pigments like chlorophyll, anthocyanin, flavonoid, betacyanin, etc. (Almahy *et al*., 2013; Shalini *et al*., 2015; Atli *et al*., 2019). Pigments like anthocyanin improve the efficiency of solar cells because they have light absorption ranges in visible zone and show good anchorage to photo-anodes, thereby enhance the efficiency of solar cells. Nanostructured metal oxides such as TiO_2, ZnO, Nb_2O_5, SnO_2, V_2O_5, Al_2O_3, CeO_2, Fe_2O_3, and ZrO_2 have been studied as photoanodes (Fukai *et al*., 2007; Caramori *et al*., 2010). In recent years, TiO_2 and ZnO have been used in DSSCs due to their corresponding band structure, high electronic mobility, and physical properties (Sowmya *et al*., 2020). ZnO photocatalysts are significantly influenced by their morphology, particle size, crystallinity, crystal orientation, and optical properties (Wang *et al*., 2018). In this paper, we report the synthesis of TiO_2 nanoparticles by a solvothermal method which was used as a photoanode in DSSC. The morphology, crystallite structure, and optical properties of synthesized TiO_2 nanoparticle were also characterized. The dyes were extracted from the flowers of *Ixora macrothyrsa* using water and ethanol as solvents. The extracts of natural dyes were analyzed by optical absorption spectrum and FTIR, and the efficiency of fabricated DSSC cells was accomplished via J-V characterization.

MATERIALS AND METHODS

Ixora macrothyrsa flowers were collected from Alwarkurici city in Tamilnadu (India). Iodolyte was purchased from Solaronix Egypt; acetic acid and HCl from Loba Chemical; isopropanol, titanium tetrachloride, ethylene, glycol and urea from Madras Scientific Tirunelveli, and fluorine-doped tin oxide (FTO) conductive glass (sheet resistance: 7Ω/sq) from Technistro, Nagpur, Maharashtra (India).

Preparation of TiO_2 nanoparticles

Analytical-grade precursor materials *viz*., titanium tetrachloride ($TiCl_4$) and urea were used in 1:3 ratio to synthesize nanoparticles by solvothermal method (Varadhasehan *et al*., 2012; Guruvammal *et al*., 2016; Esakki *et al*., 2021). These precursors were dissolved in ethylene glycol and mixed well for 1 h using a magnetic stirrer. The solution in a bowl was placed in a domestic microwave oven at 80°C. After the solution dried well, the bowl was taken out and powdered well. The deposits were washed four times with double distilled water and acetone to remove any unwanted water-soluble materials and organic compounds present in the samples. The synthesized nano-particles were filtered and dried in sunlight for one week.

Extraction of natural dye

The natural dye was extracted from the flowers of *Ixora macrothyrsa* and purified as per the method followed previously (Esakki *et al*., 2021). The extracts were washed in water and then placed in absolute ethanol at room temperature in a dark room for 1 day to extract the dye. The solids were filtered out, and the solution stored in a bottle.

Fabrication of dye-sensitized solar cells

For preparation of TiO_2 paste, 3.5 g titanium dioxide nanopowder (synthesized above), 1 mL acetic acid, and 4 mL ethanol, 5 mL distilled water and 2 drops of triton X-100 were mixed in a magnetic stirrer till the paste attained colloidal form. TiO_2 paste was coated on a fluorine-doped tin oxide-coated conductive glass substrate by doctor blade technique (Sowmiya *et al*., 2020; Esakki *et al*., 2021). The area of working electrode was approximately 0.5 cm^2. The working electrode of TiO_2 layer was annealed at 450°C for 30 min. The working electrode was immersed in natural dye for 24 h. The carbon was coated on FTO glass plate using a graphite pencil. After this, the solar cell was clipped (sandwich) together by a clip and an electrolyte solution was obtained by mixing 0.8 g KI, 10 mL acetonitrile, and 0.127 g I_2. The electrolyte solution was prepared as per Sanjay *et al*. (2019). The two drops of this electrolyte solution were added between the working and counter electrode. The efficiency of solar cell was also tested.

Characterization of nanoparticles

Structural properties were measured by X-ray diffractometer (XPERT-PRO). Surface morphology of prepared samples was studied by using a scanning electron microscope (FE-SEM; EVO 18 SEM) and the elemental composition of samples was analyzed by using an energy dispersive x-ray spectroscopy EDAX (QUANTA - FEG 250). The Fourier transmission infrared (FTIR) spectra were recorded by using NICOLET IS5–KBR windows with AR diamond crystal plate to analyze the functional groups of natural dyes. The UV visible absorption was recorded by using UV-visible spectrophotometer (HITACHI UH 5300). Impedance of solar cell performance were analyzed by electrochemical impedance spectra. The electrochemical parameters such as open-circuit voltage, current density, fill factor and J-V characterization were performed by using solar simulator (150W xenon lamp).

RESULTS AND DISCUSSION

Analysis of X-ray diffraction

The X-ray diffraction patterns of synthesized TiO_2 powder samples are shown in Fig. 1. The strong diffraction of all TiO_2 peaks at 27.52, 36.14, 41.32, 54.55, 56.68, 69.28 and 69.85 revealed that they were compatible with miller indices (hkl planes) as 110, 101, 111, 211, 220, 301 and 112, respectively. These planes were confirmed the tetragonal structure of nanoparticles.

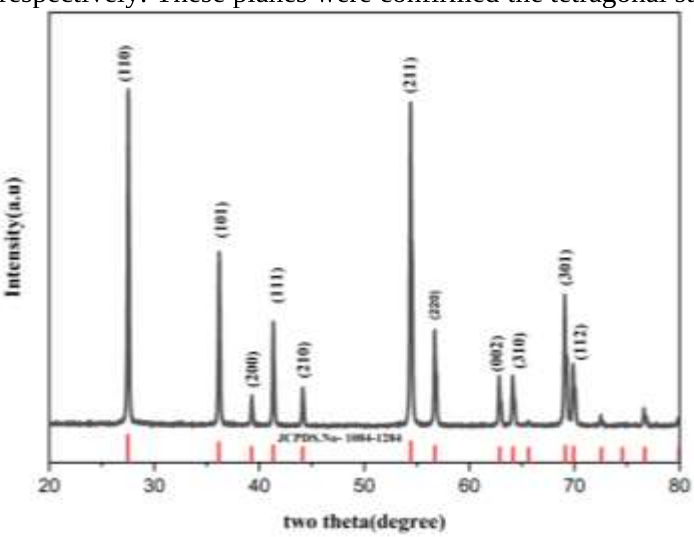

Fig. 2: XRD spectra of synthesized TiO_2 nanoparticle

All sharp and dominant peaks and positions were in good agreement with JCPDS File No. 1084-1284. The average particle size was measured by using the formula:

$$D = \frac{K\lambda}{\beta\cos\theta} \quad .... (1)$$

Where D is the crystallite size, K-0.89 is the Debye Scherer constant, β is the full width at half maximum (radians), λ is the wavelength of X-ray sources (0.154 nm) and θ is the angle of diffraction (radians).

From the calculations, the crystallite size of TiO_2 nanoparticle was of 22 nm. The structural parameters of TiO_2 nanoparticles were calculated using X-Pert high score software (Table 1).

Analysis of morphology

The surface morphology of the synthesized samples was studied by using field emission scanning electron microscope (FESEM) (Fig. 3). FESEM images confirmed that TiO_2 morphology was tetragonal by using Image J software. Some grains were spherical and others irregularly broad shaped. This kind of structure could play a significant role in improving the conducting property of a nanoparticle. The grain size of nanoparticle was 24 nm. The Fig. 3 displays the histograms of particle size distribution obtained by using particle size Analyzer Image J software. From the histogram, maximum particle size of 24 nm was obtained for synthesized sample. Our XRD results are in conformity with the FESEM images of Arora *et al.* (2014). It appears that this particle size might be due to the enhancement of efficiency in solar cell.

Table 1: The lattice parameters of TiO_2 nanoparticle

Sample	Structure	Lattice parameters		Volume	Density
		a = b (Å)	c (Å)	(10^6 Pm^3)	(g cm^{-3})
TiO_2	Tetragonal	4.5867	2.9541	62.15	4.27

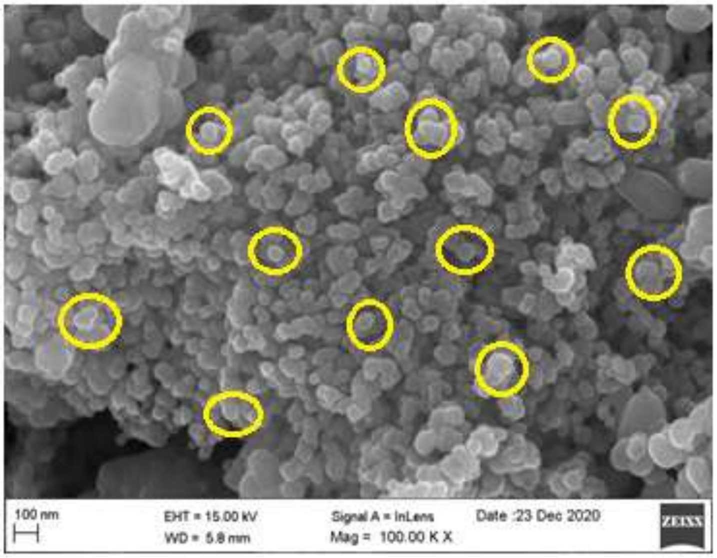

Fig. 3: FE-SEM image of a synthesized TiO_2 nanoparticle

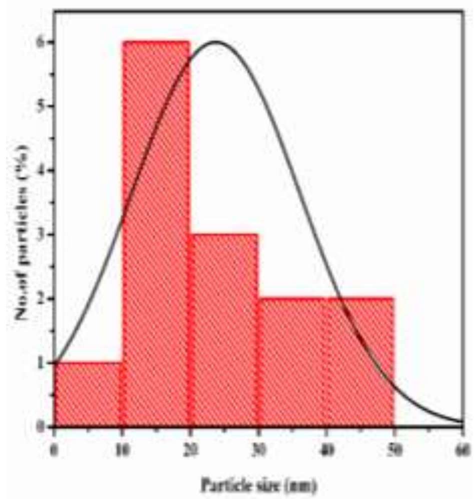

Fig. 4: Histogram of TiO_2 nanoparticle

Analysis of absorption spectra

Fig. 4. shows the UV-visible absorption spectra of red *Ixora* dyes of a) ethanolic- and b) water-TiO_2 nanoparticle. Fig. 5 i) and ii) represents the absorption spectra of *ixora* dye and pure TiO_2 nanoparticle. The maximum absorption for pure TiO_2 was at 248.49 nm. The UV-visible spectra were used to determine the band gap energy of these materials. The absorption spectra analysis was carried out in a wavelength range from 200 to 800 nm as shown in the figure, a sharp absorption peak in ultraviolet region was found at wavelengths of 304 and 306 nm for ethanolic- and water-extracts, respectively. The visible zone broadest absorption level ranges were 542 and 666 nm, which affirmed the presence of anthocyanin (Calogero *et al.*, 2012). The band gap values were 1.86 and 2.28 eV for ethanolic- and water-extracts, respectively.

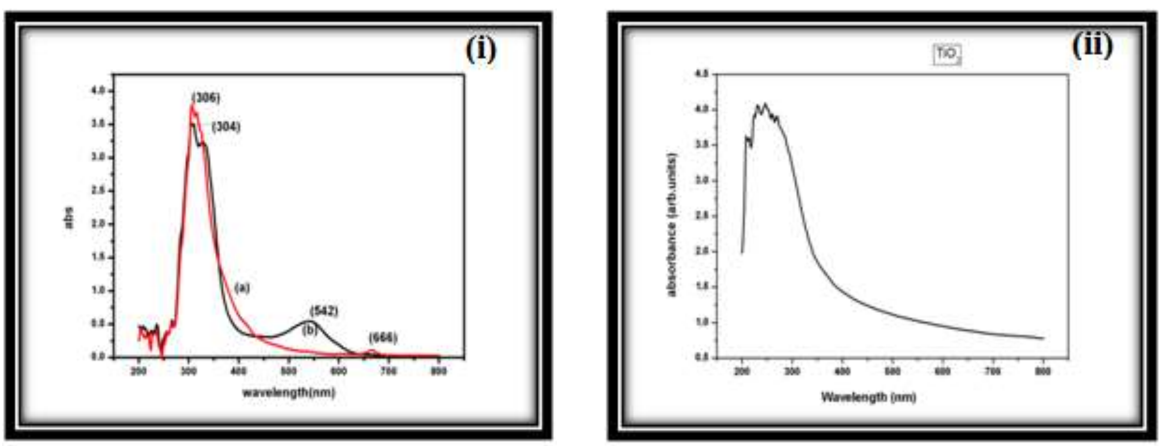

Fig. 5: i) UV visible absorption spectra of *Ixora* dyes in a) ethanol b) water; ii) TiO_2 nanoparticle

FTIR analysis

The FTIR spectrum of TiO_2 nanoparticles and *Ixora* flowers of different solvents of extraction are shown in Fig. 6 i & ii. The transmittance spectra were measured in the range of 4000-400 cm^{-1}. The strong peaks at 352.2 cm^{-1} corresponded to Ti-O bond. The strong and broad peaks at 3361.3 and 3340.1 cm^{-1} corresponded to O–H stretching vibration mode. The bands observed in the range of 1040-1090 cm^{-1} were due to C-O stretching of vibrations. The band ranges of 1085 and 1043 cm^{-1} represented C–O bond stretch. The band at 877.9 cm^{-1} was attributed to C=C bonding. The appearance of hydroxyl (O–H) and carbonyl (C-O), and other functional groups confirmed that the extracted natural pigment from *Ixora macrothyrsa* be related to anthocyanin (Sanjay *et al*., 2019). These functional groups were useful to enhancement of solar cell efficiency.

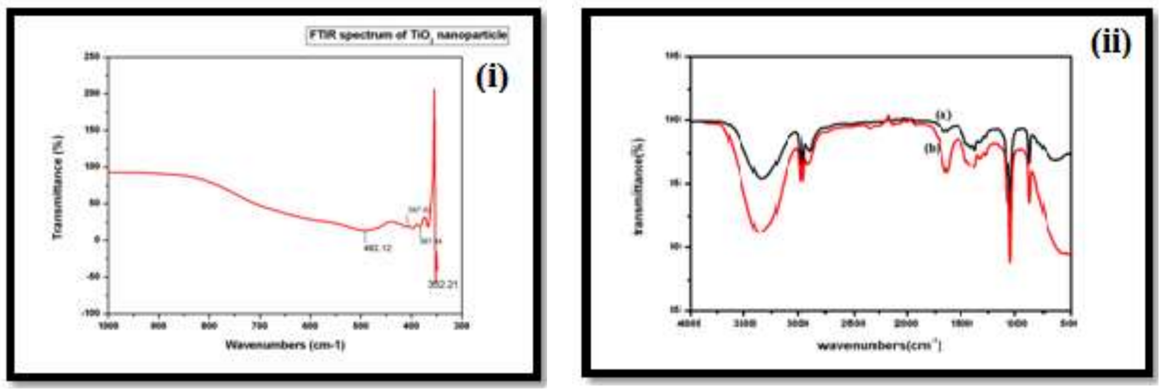

Fig. 6: i) FTIR spectra for TiO_2 nanoparticle and extracted natural dyes of *Ixora* ii) a) ethanol b) water

Open-circuit voltage (V_{OC})

The open-circuit voltage is the measured cell voltage when there is no current flow within the cell. It is the maximum voltage available from a solar cell when the resistance between the working and counter electrodes is infinite. This represents the difference between the redox potential of the electrolyte and the Fermi level of the semiconducting oxide.

Short-circuit current density (J_{SC})

The short-circuit current is the output current of the cell when the voltage difference between the electrodes is zero. In other words, it is the current obtained from the cell when the load resistance is zero. Usually, it is presented in terms of the short-circuit current density (J_{SC}), which is the ratio between the measured short-circuit current and the active area of the cell.

Fill factor (FF)

Fill factor is another important parameter for solar cells characterization. It indicates the quality of the cell and is closely related to the series and shunt resistances. Increasing the shunt resistance and decreasing the series resistance increases the fill factor, because V_{MPP} and I_{MPP} come closer to the theoretical maximum. This parameter is calculated using the formula:

$$FF = Pm\ (I_{SC} \times V_{OC}) = \frac{Im \times Vm}{(ISC \times VOC)}$$

The ratio of the maximum power output (Pm) to the product of the short-circuit photocurrent (I_{SC}) and the open-circuit photovoltage (V_{OC}) is known as the FF. Maximum power (Pm) is obtained by the multiplication of Im and Vm that respectively represents the photocurrent and photovoltage corresponding to the maximal power point. It represents the extent of electrical and electrochemical losses within DSSC.

Photo conversion efficiency (PCE)

The overall power-conversion efficiency (η) measures the efficiency of the conversion of incident light into electrical energy. PCE efficiency is calculated according to equation using the parameters obtained from I–V.

$$\boldsymbol{\eta = \frac{JSC \times VOC \times FF}{P_{in}}}$$

where J_{SC}, V_{OC}, FF, and P_{in} are the short-circuit current density, the open-circuit voltage, the fill factor, and the incident power, respectively.

Performance of DSSC

The current density-voltage (J-V) characteristics curves of dye sensitized solar cellsare given in Fig. 7. The photo electrochemical parameters like open circuit voltage, short circuit current density, fill

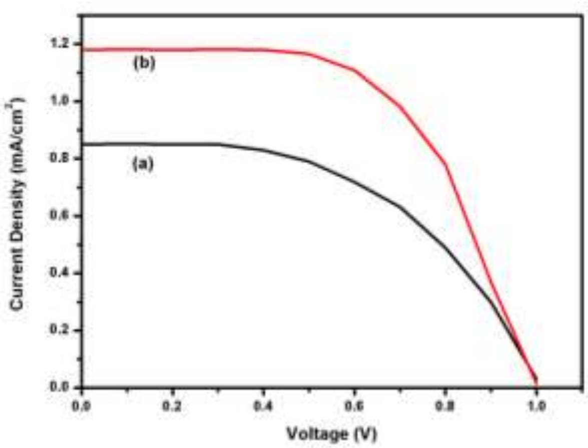

Fig. 7: J-V characteristics of dye sensitized solar cells

Table 2: Photoelectrochemical parameter of DSSC

Solvents	Voc (V)	Jsc (mA cm^{-2})	FF	Efficiency (%)
Water	1	0.87	0.46	0.43
Ethanol	1	1.18	0.49	0.70

factor and photo-current conversion efficiency were determined. The efficiency of ethanolic extract (of *Ixora macrothyrsa*) dye was 0.70% and that of water extract dye 0.43%. The improved performance of ethanol extract could mainly be attributed to the increase in Jsc values. Increase in the efficiency of DSSC depends on the area (thickness) of cell, electrolyte, and the colour of sensitizer (Vasanthapriya *et al*., 2018).

Conclusion: TiO_2 nanoparticles were successfully synthesized using solvo-thermal method and characterized by XRD, FESEM analysis, etc. Natural dyes extracted from *Ixora* flowers using water and ethanol as solvents were characterized by UV-vis spectroscopy and analysis. Natural dyes extracted from *Ixora* flowers using water and ethanol as solvents were characterized by UV-vis spectroscopy and FTIR analysis. The performance of fabricated DSSC with *Ixora* showed the efficiency of 0.70% for ethanolic extract and 0.43% for water extract. The performance of fabricated DSSC showed the power conversion efficiency of *ixora* which in case of ethanolic flower extract was better than that of water extract.

Declaration of complicit interest: The authors declare that they have no conflict of interest.

Acknowledgement: The authors thankful to the DST-FIST sponsored centralized instrumentation facility of Sri Paramakalyani College, Alwarkurichi for providing all the necessary facilities to carry out this work.

Funding: The research was conducted without any financial grant from any funding agency.

REFERENCES

Almahy, H.A., Ali, M.A. and Band, A. 2013. Extraction of carotenoids as natural dyes from *Daucus carota* Linn (carrot) using ulturasound in Kingdom of Saudi Arabia. *Research Journal of Chemical Sciences*, **3**(1): 63-66.

Arora, A.K., Devi, S., Jaswal, V.S., Singh, J., Kinger, M. and Gupta, V.D. 2014. Synthesis and characterization of ZnO nanoparticles. *Oriental Journal of Chemistry*, **30**(4): 1671-1679.

Atli, A., Atilgan, A., Altinkaya, C., Ozel, K. and Yildiz, A. 2019. St. Lucie cherry, yellow jasmine, and madder berries as novel natural sensitizers for dye-sensitized solar cells. *International Journal of Energy Research*, **43**(8): 3914-3922.

Calogero, G., Yum, J.H., Sinopoli, A., Di Marco, G., Grätzel, M. and Nazeeruddin, M.K. 2012. Anthocyanins and betalains as light-harvesting pigments for dye-sensitized solar cells. *Solar Energy*, **86**(5): 1563-1575.

Caramori, S., Cristino, V., Boaretto, R., Argazzi, R., Bignozzi, C.A. and Di Carlo, A. 2010. New components for dye-sensitized solar cells. *International Journal of Photoenergy*, **2010**: Article ID 458614 [*doi:10.1155/2010/458614*].

Esakki, E.S., Sarathi, R., Sundar, S.M. and Devi, L.R. 2021. Fabrication of dye sensitized solar cells using *Ixora macrothyrsa*. *Materials Today: Proceedings*, **9**: 2182-2187.

Fukai, Y., Kondo, Y., Mori, S. and Suzuki, E. 2007. Highly efficient dye-sensitized SnO_2 solar cells having sufficient electron diffusion length. *Electrochemistry Communications*, **9**: 1439-1443.

Guruvammal, D., Selvaraj, S. and Sundar, S.M. 2016. Effect of Ni-doping on the structural, optical and magnetic properties of ZnO nanoparticles by solvothermal method. *Journal of Alloys and Compounds*, **682**: 850-855.

Harborne, J.B. and Williams, C.A. 2000. Advances in flavonoid research since 1992. *Phytochemistry*, **55**(6): 481-504.

O'Regan, B. and Grätzel, B. 1991. A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO_2 films. *Nature*, **353**: 737-739.

Sanjay, P., Isaivani, I., Deepa, K., Madhavan, J. and Senthil, S. 2019. The preparation of dye sensitized solar cells using natural dyes extracted from *Phytolacca icosandra* and *Phyllanthus reticulatus* with ZnO as photoanode. *Materials Letters*, **244**: 142-146.

Sayama, K., Sugihara, H. and Arakawa, H. 1998. Photoelectrochemical properties of a porous Nb_2O_5 electrode sensitized by a ruthenium dye. *Chemical Materials*, **10**: 3825-3832.

Shalini, S., Prasanna, S., Mallick, T.K. and Senthilarasu, S. 2015. Review on natural dye sensitized solar cells: Operation, materials and methods. *Renewable and Sustainable Energy Reviews*, **51**: 1306-1325.

Sowmya, S., Prakash, P., Ruba, N., Janarthanan, B., Nagamani Prabu, A. and Chandrasekaran, J. 2020. A study on the fabrication and characterization of dye-sensitized solar cells with Amaranthus red and *Lawsonia inermis* as sensitizers with maximum absorption of visible light. *Journal of Materials Science: Materials in Electronics*, **31**(8): 6027-6035.

Trihutomo, P., Soeparman, S., Widhiyanuriyawan, D. and Yuliati, L. 2019. Performance improvement of dye-sensitized solar cell-(DSSC-)-based natural dyes by clathrin protein. *International Journal of Photoenergy*, **2019:** Article ID 4384728 [*https://doi.org/10.1155/2019/4384728*].

Varadhaseshan, R. and Sundar, S.M. 2012. Existence of ferromagnetism and structural characterization of nickel doped ZnO nanocrystals. *Applied Surface Science*, **258**(18): 7161-7165.

Vasanthapriya, R., Neelakandeswari, N., Rajasekaran, N., Uthayarani, K. and Chitra, M. 2018. Synthesis and characterization of SnO_2 nanostructures for dye-sensitized solar cells. *Materials Letters*, **220**: 218-221.

Wang, X.F., Matsuda, A., Koyama, Y., Nagae, H., Sasaki, S.I., Tamiaki, H. and Wada, Y. 2006. Effects of plant carotenoid spacers on the performance of a dye-sensitized solar cell using a chlorophyll derivative: Enhancement of photocurrent determined by one electron-oxidation potential of each carotenoid. *Chemical Physics Letters*, **423**(4-6): 470-475.

Wang, Y.X., Shen, Z.C., Huang, D.D. and Yang, Z.S. 2018. High-performance ZnO nanosheets/ nanocrystalline aggregates composite photoanode film in dye-sensitized solar cells. *Materials Letters*, **214**: 90-99.