

DSSC Performance of Zinc - Tin - Vanadium Oxide Nanocomposite Using Beetroot (*Beta Vulgaris*) as Dye Sensitizer

K. Uthayarani

Sri Ramakrishna Engineering College

Chitra M (✉ mbchitramuthu@gmail.com)

Sri Ramakrishna Engineering College <https://orcid.org/0000-0002-0553-2239>

R. Vasanthapriya

Sri Ramakrishna Engineering College

N. Neelakandeswari

Nallamuthu Gounder Mahalingam College

E. K. Girija

Periyar University

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Abstract

In this present work, zinc - tin - vanadium oxide (ZTVO) nanocomposite was prepared using hydrothermal route and was subjected to calcination at 600 °C. The sample was systematically characterized by Powder X-ray Diffractometer (XRD), Attenuated Total Reflectance (ATR), Field Emission Scanning electron Microscope (FE-SEM), Transmission Electron Microscope (TEM) and Ultraviolet- Diffuse Reflectance Spectroscopic techniques. From the investigations, it is observed that this composite possess the combination of both individual and binary phases. The elongated nanostructures obtained due to the binary phases and spherical shaped nanostructures obtained due to the individual phase were observed from the FE-SEM image. The formation of the nanocomposite has further been confirmed from TEM and HRTEM images. ZTVO nanocomposite possess large surface area of 167.3 m²/g and pore size value around 11 nm. Also, the band gap of the material has been found to be 1.97 eV. Dye-sensitized solar cell (DSSC) has been fabricated using this ZTVO nanocomposite as the photoanode and betalain dye extracted from beetroot (*Beta vulgaris*) as the natural dye. This simple protocol was formulated at a low cost for the first time for DSSC fabrication and it has attained the efficiency of 3.41%. This better efficiency of ZTVO might be due to larger surface area, presence of pores in addition to smaller band gap.

1. Introduction

The low-cost, high-efficiency and non-pollution aspects of Dye-sensitized solar cells (DSSCs) has considered as one of the most promising alternatives to silicon based photovoltaic cells in the last two decades [1]. DSSCs became more interesting since after the phenomenal work carried out by O'Regan and Gratzel in 1991. In the present scenario, natural dyes are employed as light harvesting elements to provide the charge carriers. These natural dyes provide a feasible alternative to expensive organic based DSSCs (rare metal complexes) owing to its low cost, non-toxicity, ease of extraction using simple chemical procedures, environmental friendly, easily biodegradable, abundance and large absorption coefficient. Especially the pigments like anthocyanin, carotenoids, flavonoids, chlorophyll and betalain present in natural dyes have been emphasised nowadays as these pigments initiated different maximum absorption peak within the solar spectrum wavelength (λ_{max}) which support the electrical performance of DSSC. Also these pigmented dyes such as chlorophyll from fig leaves exhibited an efficiency of 0.64 %, anthocyanin extracted from eggplant and that of pomegranate records an efficiency of 0.64 % and 2.00 % respectively, betalain from red turnip gives out 1.7 % efficiency etc. Also, efforts on betalain extracted from purple wild sicilian prickly pear dye, Red Bougainvillea glabra flower, Opuntia dillenii have recorded the

energy conversion efficiency of 2.06 %, 0.98 % and 0.47 % respectively. Among them in this present work, betalain pigment extracted from beetroot has been chosen for its abundant availability and large absorption coefficient with an intention of achieving better efficiency.

The next critical component in such DSSCs is the photoanode with porous structured materials [2–4] over which dye molecules get adsorbed onto its surface. To achieve high performance, the photoanode needs

to possess large surface area and good electron transport capability [3]. It has been reported [5] by that the performance of DSSC could be improved by doping or sensitizing the material which in turn enhance the absorption of solar light. Also, nanocomposites made of metal oxides and multi-structured semiconductor metal oxides [5–7] provide efficient charge separation for effective path of electron transport and promotes larger surface area for dye adsorption. Amongst these various tools, composites using metal oxides have a remarkable impact due to the implementation of n-type metal oxide semiconductors in heterojunction formation.

Also, different morphologies such as nanoparticles, nanowires and nanoflowers in DSSCs afford improved light absorption and electron collecting efficiency in the devices [7, 8]. Thus, this made extensive research work to focuss on the metal oxide nanocomposite photoanodes using TiO_2 , ZnO , SnO_2 etc., than individual metal oxide semiconductors (MOS) [9]. Among these MOS, zinc oxide (ZnO), tin oxide (SnO_2) and vanadium oxide (V_2O_5) has been chosen in this present work to carry out studies on DSSC. ZnO , the MOS with different nanostructure morphologies, carrier mobility, direct band gap and high electron mobility has been considered as a promising candidate for DSSCs [10]. DSSCs based SnO_2 photoanode materials [11] are also reported owing to its larger band gap and their ability to create fewer oxidative holes in the valence band under UV illumination. This SnO_2 material minimizes dye degradation rate and improves the long term stability of DSSC. Vanadium oxide (V_2O_5) is a transition metal oxide which has important applications in various device fabrication and it shows metal–semiconductor transitions implying sudden change in electrical and optical properties [12]. All these individual MOS has been employed as DSSC materials by various researchers but as a single system, they possess low open circuit voltage (V_{oc}) due to high recombination kinetics with the electrolyte resulting in low conversion efficiency. To overcome these difficulties and to enhance the probability of photoconversion, band gap narrowing needs to be achieved. Therefore, to achieve this band gap modulation, synthesis of mixed oxides using these combinations has been identified. Hence, in this present work, zinc - tin - vanadium oxide nanocomposite (ZTVO) has been prepared via hydrothermal route. Powder X-ray Diffractometer (XRD), Attenuated Total Reflectance (ATR), Field Emission Scanning electron Microscope (FE-SEM), Transmission electron microscope (TEM), specific surface area analysis and Ultraviolet- Diffuse Reflectance Spectroscopic techniques have been carried out for this sample. DSSC studies has been carried by fabricating the cell using this nanocomposite aided by the betalain dye extracted from beetroot (*Beta vulgaris*) and the results are presented herein.

2. Experimental Details

2.1 Synthesis of zinc - tin - vanadium oxide nanocomposite using hydrothermal route

The reagents used for this present work were of analytical grade purchased from Rankem and were used as such. 0.1 M of 100 ml aqueous solutions of ZnCl_2 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and VCl_3 were taken as precursors and 0.3 M glyoxalic acid (surfactant) was added under constant stirring. The gel was obtained by adjusting

the pH to 9 by the addition of ammonia under stirring. It was then transferred into a Teflon – lined stainless – steel autoclave and maintained at 160°C for 3 h. Aerogel collected was washed several times, dried in air and calcined at 600 °C and was named as ZTVO. The protocol for the synthesis of this composite has been reported earlier [13] and it has been proved to be a better ethanol sensor at room temperature.

2.2. Fabrication of Dye Sensitized Solar Cell (DSSC) using the composite and the natural dye

Initially, Fluorinated tin oxide (FTO) glass substrates were subjected to cleaning using ethanol and double distilled water and were subjected to sonication. The nanopowders obtained were mixed with triton X and is grounded well and coated on FTO substrates. The film was calcined at 500° C for 15 min. 100 g of beetroot (purchased from local market) was taken, grinded well and it is treated with 50 ml of ethanol, kept in a hot plate at 100 C for 1h at room temperature. The crude solution was filtered using Whatman No. 41 filter paper to remove the solid residues. Finally, the concentrated dye solution was shielded from exposure to direct light and stored in a refrigerator and the extract has been used as the sensitizer. This concentrated dye solution extracted from beetroot was taken and the ZTVO film was soaked in the natural dye extract for 24 h, washed with distilled water and dried in air. The commercial graphite (99.99 % pure) which has 24–30 mm porosity was purchased from Ritu Industries and it serves as the counter electrode. I_3^- solution was used as the electrolyte and it has been prepared by mixing 0.05 M iodine and 0.5 M potassium iodide in 10 ml of ethylene glycol and the prepared solution was stored in a bottle covered with aluminium foil.

The DSSC was assembled using dye sensitized ZTVO as the working electrode and graphite as the counter electrode. These two electrodes were assembled using a semi-closed DSSC method and the electrolyte was filed into the cells and the photovoltaic measurements were carried out systematically.

3. Characterisation Techniques

ATR spectrum of the sample was recorded in the 400–4000 cm^{-1} region using a Perkin Elmer RX1 FT-IR spectrophotometer by KBr pellet technique. The crystallinity of the sample was studied by X-ray powder diffraction (XRD) using PANALYTICAL X – Ray diffractometer (Cu- K α radiation, $\lambda = 1.54\text{\AA}$) in 2θ ranging from 20° – 80°. The morphology of the sample was studied using JEOL JSM Field emission scanning electron microscope (FE - SEM) and the elemental composition was obtained using JEOL Model JED – 2300 Energy Dispersive X-ray (EDAX) Spectrometer analysis. JOEL JEM 2100 Transmission microscope was used to record the Transmission electron microscopic (TEM) image and Selective area electron diffraction pattern (SAED) was also recorded using the same instrument. The optical property was studied using UV-visible diffuse reflectance spectrum (DRS) by JASCO - UV VIS spectrophotometer. The specific surface area was analysed using the Brunauer–Emmett–Teller (BET) equation based on the nitrogen adsorption isotherm. DSSC studies was carried out using LOT-LS0104 solar simulator under xenon lamp irradiance of 100 mW/cm^2 and AM 1.5. The radiation exposure area for the fabricated

DSSC was 1 cm^2 , which has been achieved by covering the cell with a thin black paper mask having an aperture of 1 cm^2 . The I - V measurements of the fabricated DSSC was recorded using electrochemical workstation (Metrohm, Autolab 302NFRA2).

4. Results And Discussion

4.1 Functional group analysis

From the ATR spectrum of ZTVO (not shown), it has been observed that the absorbance band around 3700 cm^{-1} occurs due to H-O-H stretching and the band around 1500 cm^{-1} is due to the bending vibration of O-H. It is attributed to the formation of terminal hydroxide. Either M-O-M or M-O bonding [14] in the composite material occurs in the bands around 900 cm^{-1} , 600 cm^{-1} and 500 cm^{-1} .

4.2 Structural analysis

XRD pattern of ZTVO is shown in Fig. 1 From the XRD pattern of ZTVO, phases such as SnO_2 [ICDD No:41-1445], Zn_2SnO_4 (ICDD No:24-1470), ZnV_2O_6 (ICDD No: 23-0757) and ZnV_3O_8 (ICDD No: 71-0731) were found to exist in sample in the proportion of 28%, 19%, 36% and 17% respectively. The formation of binary phases such as zinc stannate and zinc vanadate along with the individual SnO_2 is confirmed from the XRD pattern [13].

4.3 Morphological studies

FE-SEM image of the nanocomposite ZTVO is shown in Fig. 2 (a). It revealed flower like microstructures made up of nanoflakes and these microstructured flowers consist of enormous petals and minute pores. The nanoflakes which is clearly depicted as thin nanorods in TEM image (Fig. 2 (c)) has around 320 nm length and 13 nm width. These elongated structures are due to the formation of the binary phases ZnV_2O_6 and ZnV_3O_8 which has been further proved from the EDAX data. The EDAX recorded over the nanoflakes reveal the composition of vanadium to be 11.72 atomic% which is greater than tin and zinc. FE-SEM image also reveals the presence of nanoparticles of uniform grain size whose TEM image in Fig. 2 (b) also shows the same with grain size around 11 nm. The EDAX recorded over this area also supports the presence of higher composition of tin (9.09 atomic %) than vanadium and zinc.

High magnification HRTEM image of ZTVO is depicted in Fig. 3 (a) and the d-spacing for SnO_2 is found to be 0.332 nm and that of ZnV_2O_6 is found to be 0.312 nm and the values matches well with the corresponding standard values. From the SAED pattern shown in Fig. 3 (b), the polycrystalline nature is proved from the orientation of atoms in different planes and the presence of different phases has been indexed.

4.4 Optical studies

From the diffuse reflectance spectrum of ZTVO shown in the inset of Fig. 4, a broad absorption edge is noticed around 600 nm. This might be due to the synergistic effect of the composite material and the

band gap for ZTVO has been calculated to be 1.97 eV from the band gap determination plot in Fig. 4. Band gap (E_g) plays a crucial role in assisting the wavelength range for light absorption. It has reported [15–17] that all photons with energies larger than E_g are absorbed and contribute to photocurrent, those with smaller energies are transmitted and not used. So, smaller the band gap, larger will be the probability of photo conversion and hence ZTVO possessing the band gap of 1.97 eV could show better efficiency.

(inset : Diffuse reflectance spectrum)

4.5 Surface area analysis

The performance of DSSC greatly depends on the surface area and also on the nature of pores. The nitrogen adsorption-desorption isotherm obtained for ZTVO exhibited type IV with type H3 hysteresis loop for the relative pressure P/P_0 in the range of 0.1–1 [13, 18]. Which indicates the mesoporous nature of the material. The specific surface area of ZTVO calculated using BET analysis was found to be 167.3 m^2/g and pore size of 11 nm is obtained from the PSD plot. The synergistic effect [19–21] of the hierarchical nanostructured ZTVO offers large surface area which could favour better performance of the photoanode and henceforth DSSC performance.

4.6 DSSC measurements

The fabricated DSSC was subjected to V- I characteristics from which power was calculated using the equation $P_{max} = V_{max} \times I_{max}$. Current - Voltage characteristics of DSSCs fabricated using ZTVO photoanodes is presented in Fig. 5. The solar to electrical energy conversion efficiency η , is calculated from the photo current density, open circuit photovoltage, fill factor of the cell and the power input using the formula in Eq. 1 [22],

$$\eta (\%) = (J_{SC} \cdot Voc \cdot FF / P_{in}) \cdot 100 \text{ ————— (Eq. 1)}$$

The fill factor (FF) is the ratio between the maximum output power density available ($J_m \cdot V_m$) and the maximum power combining short – circuit and open – circuit situations [19–21]. This nanocomposite serving the role of photoanode has been reported for the first time in which ZTVO executes an conversion efficiency of 3.41% with a fill factor of 0.15.

The schematic representation of the contribution of the dye molecules over the ZTVO nanocomposite in DSSC fabrication is depicted in Fig. 6.

A very strong parameter which favours the conversion efficiency is the smaller band gap [23–25] and in which the band gap of ZTVO (1.97 eV) proves to be the better photon converter. Since, porosity of the nanocomposite is also an important factor to be taken into account in which adsorption of dye molecules could be favoured so that better performance of DSSC could be achieved.

The efficiency of DSSC using the beetroot as a natural dye with ZTVO as photoanode seems to be better than reported by M. Mazhar et al (0.30 %) and S. Sathyajothi et al (1.3 %) but further investigations are in

progress, to optimise the proportion of the individual precursors to achieve uniform porous morphology and also to monitor the thickness of the film.

5. Conclusion

Zinc-tin-vanadium oxide nanocomposite prepared via hydrothermal method was implemented as a photoanode and extract from beetroot was used as the natural dye in fabricating a low cost DSSC for the first time. The photoanode material was systematically characterised by various state-of-the art facilities. It is observed that the nanocomposite material possess both elongated microstructures contributed by the presence of binary phases and the spherical nanostructures corresponding to the individual phase. These structures possessing larger surface area of $167.3 \text{ m}^2/\text{g}$ and smaller band gap of 1.97 eV are the strongest factors which gives a wide scope of ZTVO in fabricating DSSC to the commercial scale. These fabricated DSSC using beetroot extract as the dye reported for the first time exhibits considerable efficiency but yet achieving high porous morphology is still a challenge.

Declarations

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Conflicts of interest/Competing interests

There is no conflict of interest

Availability of data and material

There is no availability of data and material

Code availability

There is no code availability

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Figures

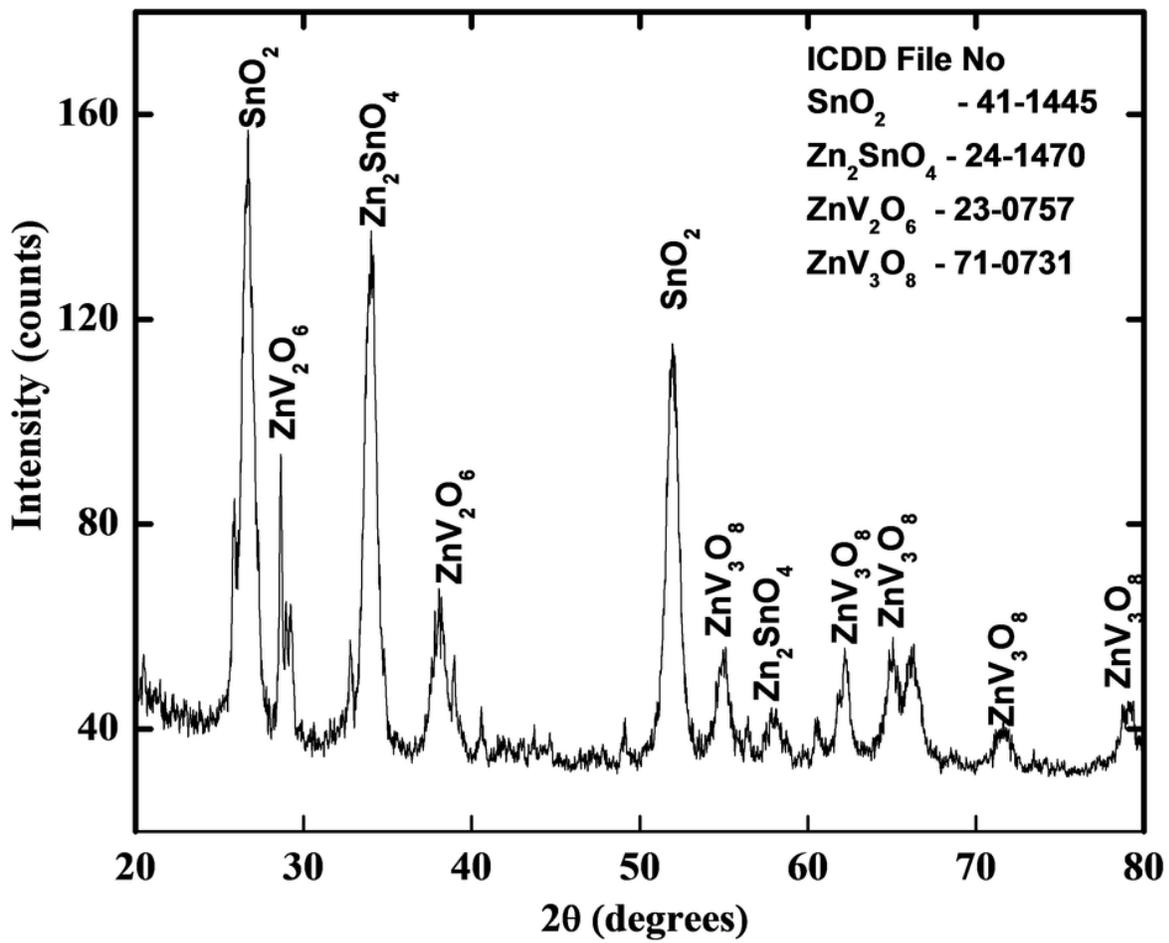


Figure 1

XRD pattern of ZTVO

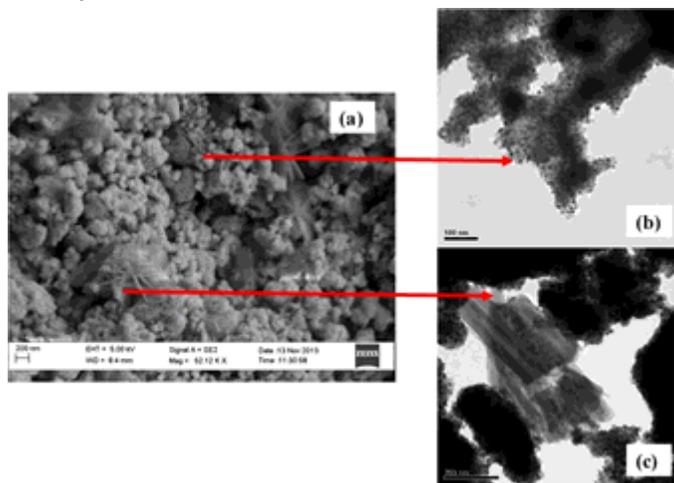


Figure 2

(a) FE-SEM image, (b) TEM image depicting nanoparticles and (c) TEM image depicting elongated nanostructures of ZTVO

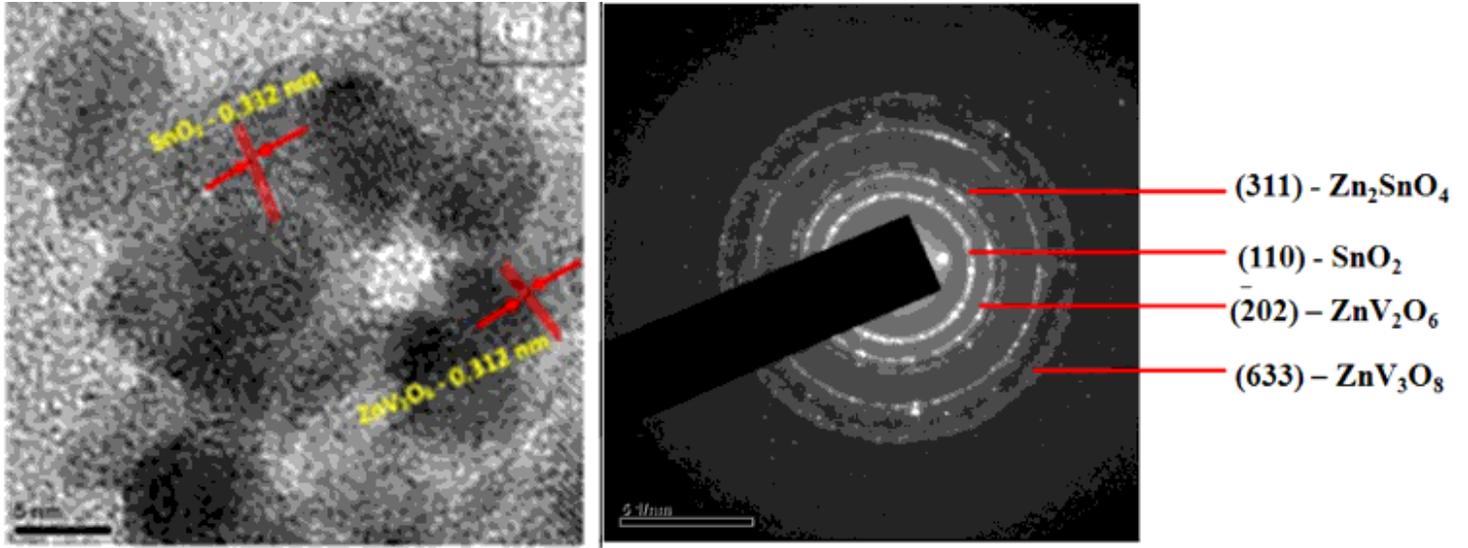


Figure 3

(a) HRTEM image and (b) SAED pattern of ZTVO

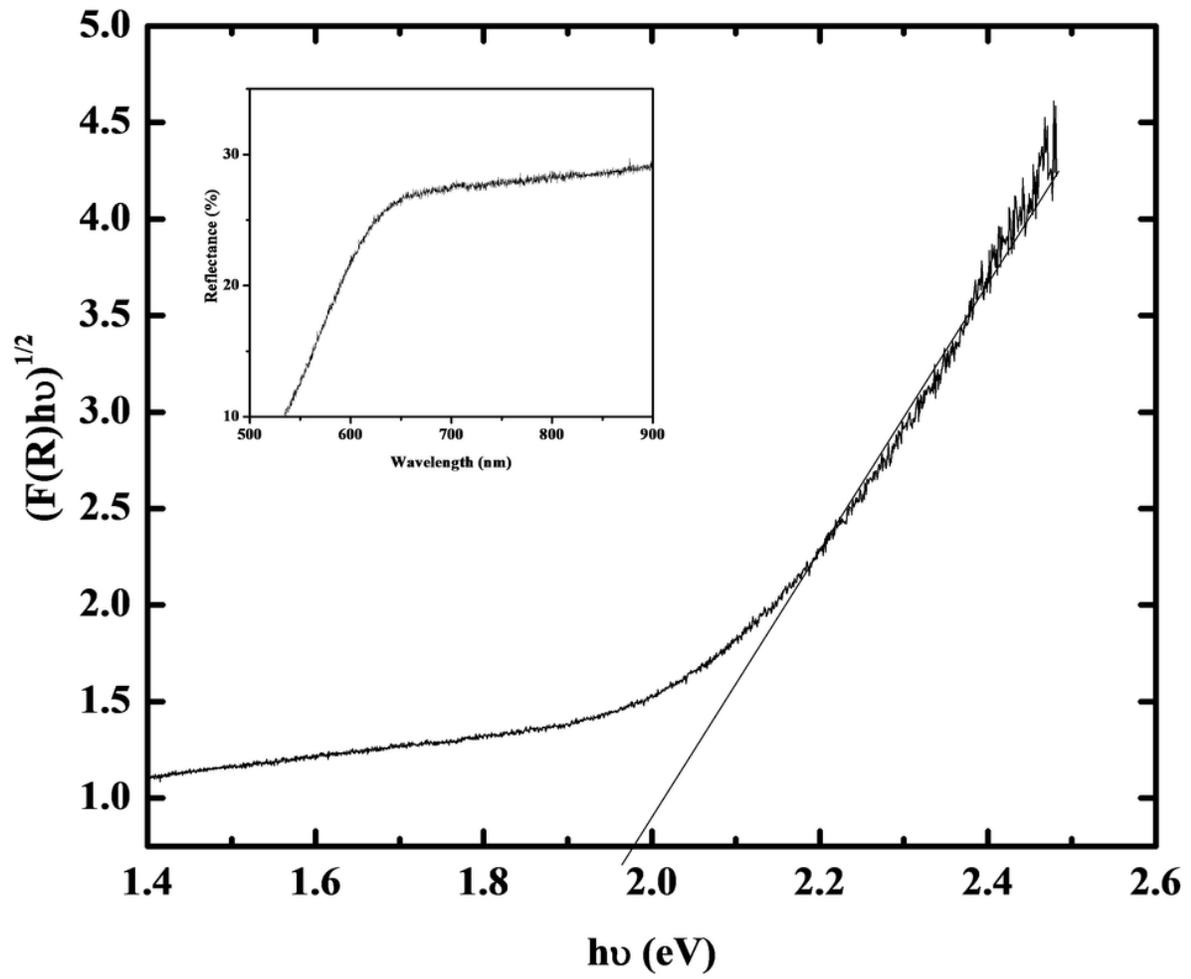


Figure 4

Band gap determination plot of ZTVO (inset : Diffuse reflectance spectrum)

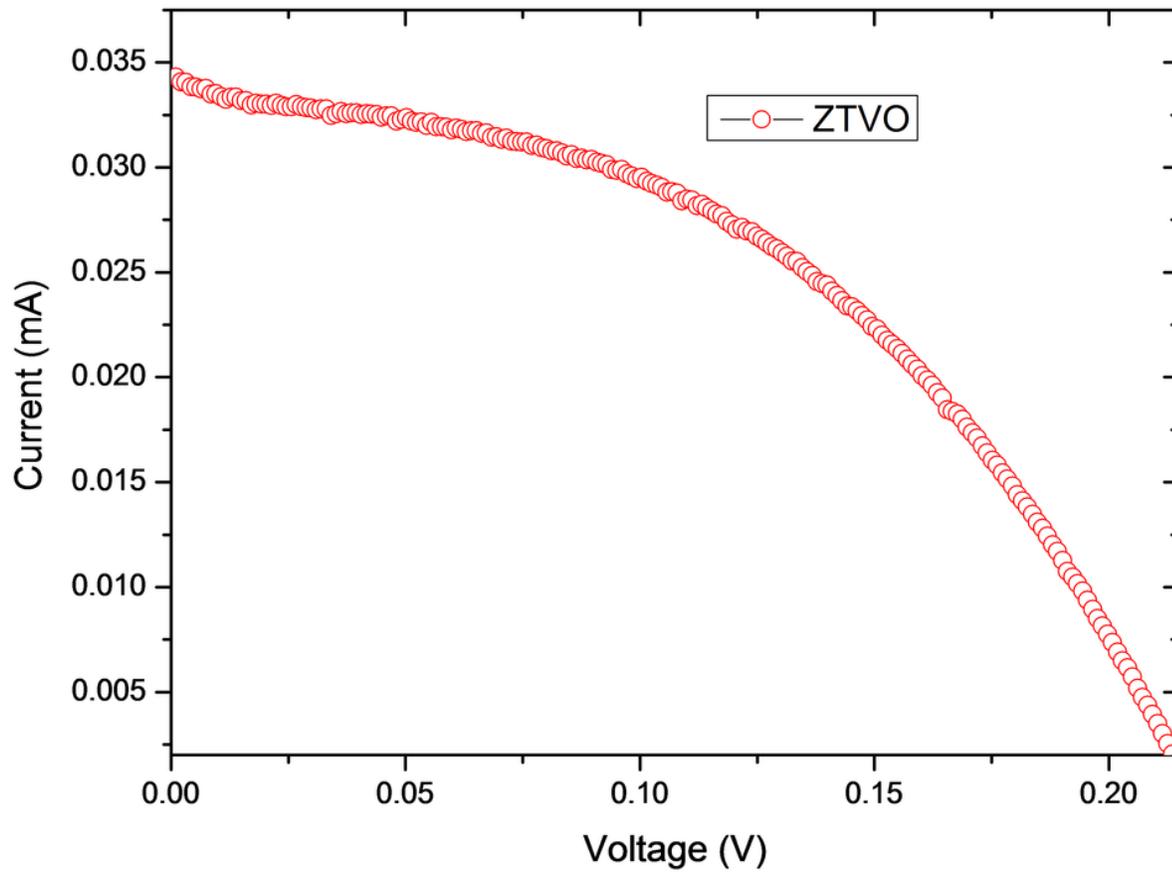


Figure 5

Current- Power characteristics of the fabricated DSSC

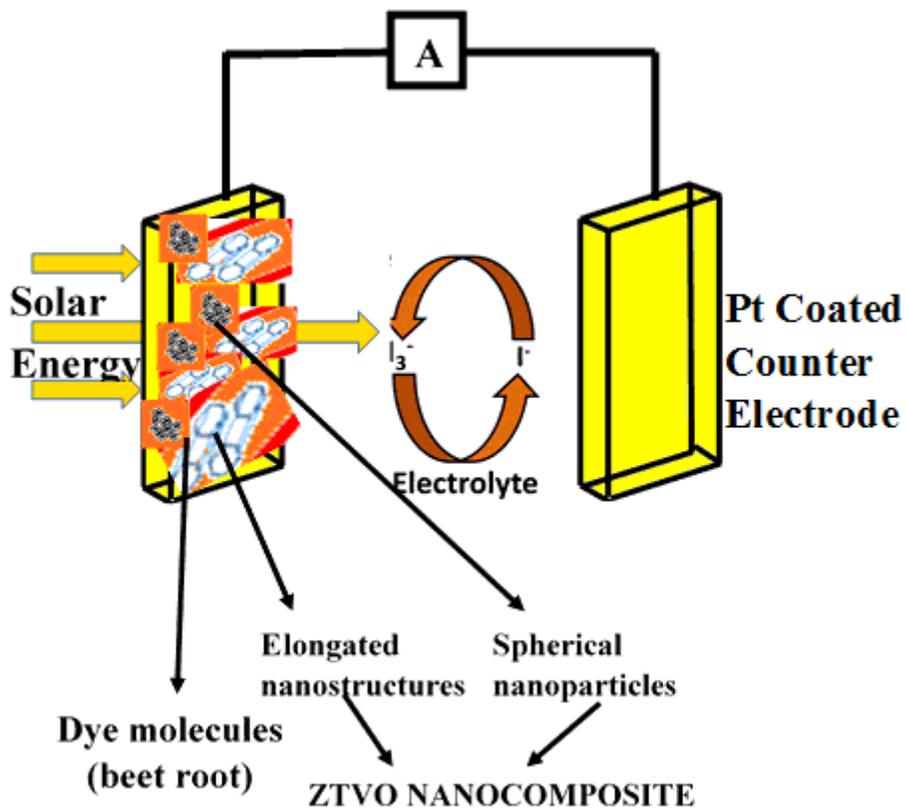


Figure 6

Schematic Diagram of the fabricated DSSC using ZTVO and dye from Beetroot extract