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Preparation and characterization of zinc oxide nanosheets for dye-sensitized solar cell using vitis vinifera dye extraction

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Abstract

We have grown Zinc Oxide (ZnO) nanosheet layers on bare glass and conducting Fluorine doped tin oxide (FTO) glass substrates by hydrothermal route. Aluminum doped ZnO (AZO) layer was deposited using a spin coating method prior to growth of ZnO nanostructures which is then used as a seed layer in hydrothermal growth. As-grown zinc oxide films' structure, surface morphology and optical properties were studied by using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Ultraviolet Visible (UV-Vis) Spectrophotometer, respectively. XRD study confirmed hexagonal wurtzite structure of ZnO orienting along (002) planes. Scanning Electron Microscope image clearly shows the growth of nanosheet like structures of ZnO. The optical band gap of ZnO film deposited on glass substrate was found to be 3.25eV. We have also studied the influence of growth time on band gap of as grown ZnO film grown on FTO coated substrates. Out results showed that the band gap energy was decreased from 3.21eV to 3.16eV for the increase of growth time from 2 hours to 4 hours. We have used *Vitis vinifera dye* extraction as the natural dye sensitizer in the fabrication of dye-sensitized solar cell (DSSC). Our experimental results on I V measurement of assembled DSSC showed maximum short circuit current and open circuit voltage of about 30 microampers and 600 millivolts, respectively.

Key words: Dye-sensitized Solar Cell, Thin Film, Natural Dye, Anthocyanine, Band Gap Energy

Introduction

The sun being the ultimate source of all energy, solar energy is unquestionably the most abundant form of energy found on earth. The rising energy demand of our society could be sufficiently fulfilled through the development of solar cells which utilize this solar energy. Hence, solar photovoltaic technology has progressively received more and more attention as a potential source for the future [Grätzel, 2003; O'Regan & Grätzel, 1991]. A DSSC is a device which is used to convert solar energy into electrical energy via sensitization created on wide band gap energy semiconductors such as TiO_2 or ZnO [Grätzel, 2004]. The significant improvement in DSSC performance was observed by Brian O'Regan and Michael Grätzel [O'Regan & Grätzel, 1991] in 1991 when it was fabricated with a monolayer of Ruthenium dye adsorbed into the wide band mesoporous semiconducting layer of Titanium dioxide (TiO_2). Here, unlike the conventional system of p-n junction first generation silicon solar cells, in DSSC the light absorption and charge transport take place separately. The light absorption is performed by the adsorbed monolayer of dye molecules attached to the nanostructured layer of a wide band gap semiconductor such as TiO_2 or ZnO [Baxter, 2006]. The electron thus created at LUMO level of dye by absorption transfers to conduction band of wide band gap semiconductor and finally to the FTO electrode. Similarly, the dye is regenerated by taking electrons at HOMO level from redox couple and hence from FTO counter electrode. This creates photoelectric effect in DSSCs.

The DSSC has been widely investigated as a third generation solar cell because of its potential commercialization, low cost and simple construction. Recently, ZnO with various nanostructures such as nanorods, nanoflowers, or nanosheets have garnered attention due to excellent optical, electrical and structural properties. It has higher electron mobility than TiO_2 and lower recombination probability [Kanmani et al., 2012; Plank et al., 2009]. ZnO based solar cells can be fabricated at low cost using environmentally friendly materials: zinc oxide and natural dye extraction from locally available fruits and flowers [Pradhan et al., 2007]. One of the hindrances so far of ZnO based DSSCs with natural dyes is low efficiency. Hence, intensive studies have been conducted to lower the cost

of DSSCs to maintain the same efficiency of silicon-based solar cells. The overall effectiveness of DSSCs depends on several factors such as adsorption of dye into the ZnO nanostructures and absorption spectrum of dye, the grafting behavior of the sensitizer with ZnO nanostructure. Two of the most commonly used synthetic dyes for DSSC assembly are N719 and N_3 dye [Grätzel, 2003; Gratzel, 2004]. These dyes have intense absorption in the visible range and highly efficient metal-to-ligand charge transfer. The high production cost as well as environmentally-detrimental by-products limits the possibility for future use. One of the alternatives to overcome these problems is to use natural dyes from locally available fruits and flowers. Natural dye extractions from different parts of plants such as fruits, flowers and barks etc., have been used in fabricating dye-sensitized solar cells. The sensitization of wide band gap semiconductors using natural pigments is usually ascribed to anthocyanins [Hao et al., 2006]. In this report, we present a way to prepare zinc oxide nanosheets on glass and FTO substrates. The ZnO seed layer was deposited at first on FTO substrate using a spin coating technique [Shrestha et al., 2010]. The ZnO nanostructured films were grown on it using a hydrothermal route [Zhang et al., 2012]. The effects of the concentration of the growth solution and growth time on the band gap of ZnO were also studied. The annealed zinc oxide films were immersed into the natural dye solution at 60^oC for 6 hours for the dye loading process. A thin layer of platinum was deposited using a spin coater on conducting fluorine doped tin oxide glass substrates followed by annealing at 400^oC for 30 minutes to prepare the counter electrode of the DSSCs [Kanmani et al.,2012]. The two electrodes were separated by a thin layer of Mylar sheet to fabricate DSSC. The cells were filled with liquid electrolyte consisting of potassium iodide and iodine solution by capillary action. Finally, a current voltage (I-V) characteristic curve of the DSSCs assembled with *Vitis vinifera* dye extraction was reported.

Experimental

Firstly, transparent conducting substrates of fluorine doped tin oxide were made using homemade spray pyrolysis unit. The required spray solution was prepared by dissolving 10gm of stannous chloride ($SnCl_2 \bullet 2H_2O$) in 5ml of

concentrated hydrochloride acid (HCl) and 25ml of distilled water at 90^{o}C with continuous stirring for 2 hours. Few drops of HCl were added again into the solution to break down the polymer molecules that were formed when diluting with water [Thangaraju, 2002]. For fluorine doping, ammonium fluoride (NH_4Cl) was used. The glass substrates were cleaned using chromic acid and distilled water several times. The prepared solution was sprayed into the hot glass substrate kept at 400 ±5 ^{o}C. After spraying, the samples were allowed to cool down to room temperature. All the chemicals used in this work were of analytical grade. We prepared the seed layers of Aluminum doped Zinc Oxide (AZO) from this solution using a spin coating technique. For this, we prepared the precursor solutions of 0.1M zinc acetate in ethanol with diethanolamine [DEA,

$(CH_2OHCH_2)_2NH$] and 0.1M aqueous solution of Aluminum Chloride hexahydrated ($AlCl_3$•$6H_2O$) separately [Shrestha et al., 2010]. Then the two solutions were mixed with appropriate amount to prepare 2 at% Al-doped precursor solution to deposit AZO seed layer. In our experiment the spin time and spin rate were fixed as 30 seconds and 3000 rpm respectively. As-prepared seed layers were heated at first to 130^{o}C for 10 minutes for soft bake and then high baked at 400^{o}C for 15 minutes to convert zinc acetate into ZnO. For hydrothermal growth, 20mM aqueous solutions of zinc nitrate hexahydrated (Zn $(NO_3)_2.6H_2O$) and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were prepared and the solutions were mixed and kept at 75 ±5^{o}C. This is used as a growth solution for hydrothermal growth of ZnO nanosheets. We have also prepared the solutions of 25mM zinc nitrate and 25mM of HMTA in another beaker at constant temperature of 90±5^{o}C for different set of experiment [Zhang et al., 2012]. The AZO coated substrates were then immersed vertically into the growth solutions for 2 to 4 hours. Subsequently, the substrates were rinsed with distilled water and annealed in air at 400^{o}C for 30 minutes to remove any residue. The details of prepared samples were tabulated in Table 1 below. The structural study of as-grown ZnO film was performed using X-ray diffraction technique. Optical properties of deposited ZnO materials were studied using an ultraviolet-visible spectrophotometer USB 2000, Ocean Optics, Singapore. To study its morphology a scanning electron microscope experiment was performed.

In this work, we have used the natural fruit dye extraction of *Vitis vinifera* locally called as black grapes to sensitize the ZnO photo anode. Clean 50gms of fresh *Vitis vinifera* were boiled after peeled off its skin in a beaker containing 100ml of distilled water at 60^{o}C for 2 hours. The warm fuits in solution begin to spawn its color. The colored solution was then filtered using a clean strainer [Kim et al., 2013; Chang, & Lo, 2010; Gomez-Ortiz et al. 2010; Taya et al., 2013]. As-grown ZnO nanosheets were dipped into this dye solution at 60^{o}C for 6 hours for dye loading to take place. The absorbance of *Vitis vinifera* dye extraction was recorded using the Ocean Optics USB 2000 Spectrophotometer, Singapore. To prepare a counter electrode of DSSC we have used a spin coating technique. A 5mM dispersion solution was prepared by dissolving H_2PtCl_6 into the 2propanol [Kanmani et al., 2012]. A single coat of platinum chloride solution was deposited into the conducting FTO substrate using a spin coater. The coated substrate was soft baked at 100^{o}C for 5 minutes and hard baked at 350^{o}C for 30 minutes to remove any residues. The two electrodes, working electrode of ZnO and platinum coated counter electrode were finally brought together to fabricate dye-sensitized solar cell. The two electrodes were separated by a thin strip of Mylar sheet using a hot press method. Another major component of dyesensitized solar cell is the filling of liquid electrolyte between two electrodes. The photovoltaic performances of liquid electrolyte-based DSSCs depend strongly on the choice of electrolyte solvent used. Liquid electrolyte typically consists of a redox couple solution. The electrolyte is used for dye regeneration and charge transport between working electrode of ZnO with dye and counter electrodes of DSSC [Hemmatzadeh & Mohammadi, 2013]. In this work, the solution of potassium iodide, iodine in acetonitrile electrolyte is used as electrolyte for hole transport. An assembled dye-sensitized solar cell was characterized by drawing current voltage (I-V) characteristic curve in the presence of halogen light sources of 500W and 1000W. The current and voltage measurements were taken using Fluke 179 digital multimeters.

Table 1: Concentration of zinc acetate, thickness of AZO, concentration of growth solution, and growth time to deposit ZnO films on glass and FTO substrates.

S.N.	Sample Name	Substrate	Seed Layer Concentration (M)	No. of Coats	Growth Solution Concentration (mM)	Growth Time (hrs)	Growth Temp (T±5°C)
1	C3	Glass	0.1	5	25	4	75
2	C4	Glass	0.1	5	20	4	75
3	K1	FTO	0.1	2	20	2	90
4	K4	FTO	0.1	2	20	3	90
5	K5	FTO	0.1	2	20	4	90

Results and Discussion

The crystal structure of ZnO film grown on glass substrates was investigated using X-ray diffraction. Figure 1 shows the X-ray diffraction pattern of as-grown ZnO film on glass substrate. The figure shows sharp peak at $2\theta = 35.47^{o}$ with d = 2.56 Å orienting along (002) planes. The indexing of (hkl) plane was made with reference to JCPDS PDF# 36-1451 [Ilican et al., 2007; Dedova et al., 2007]. Inset shows the other smaller peaks at $2\theta = 32.77^{o}$ (d = 2.75Å), and 37.19^{o} (d = 2.41Å) corresponding to (100) and (101) planes respectively. These peaks demonstrate the formation of polycrystallline ZnO film. The observed d-spacing values were slightly shifted from d-spacing on JCPDS, PDF # 36-1451 for ZnO which might be because of Al doping and strain in the film. No impurity peaks of Zn and $Zn(OH)_2$ have been significantly observed. In the X-ray diffraction pattern, the sharp peak can be related to the preferential c-axis growth of ZnO. The crystallite size was estimated using Debye Scherrer's equation $D=\frac{0.9\lambda}{\beta\cos\theta}$, where D is the crystallite size, λ is the wavelength of the X-ray used, β is the broadening of peak at

half the maximum intensity and θ is the bragg's angle[Shakti, 2010]. Using above equation the average crystallite size was found to be 358Å shown in the Table 2.

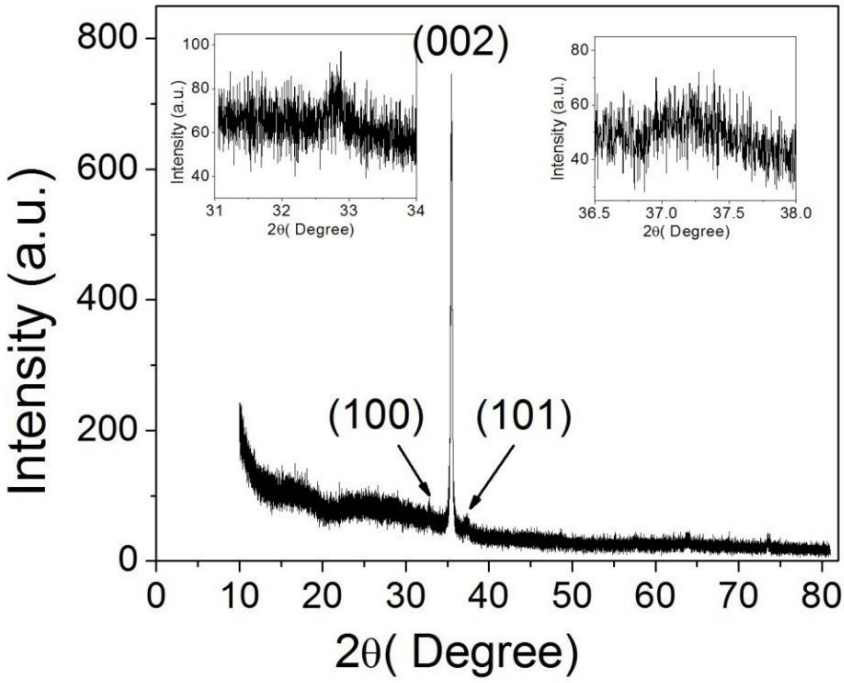


Figure 1: X-ray diffraction pattern of ZnO film prepared on glass substrate.

Table 2: Two theta, calculated and JCPDS d- spacing, (hkl) values and crystallite size of ZnO film (sampleC4).

S. N.	Angle 2θ / Deg	Calculated d-spacing / Å	JCPDS (36-1451) d- spacing / Å	(hkl)	Estimated Grain Size D/ Å
1.	32.77	2.75	2.81	(100)	
2.	35.47	2.56	2.60	(002)	358 Å
3.	37.19	2.41	2.47	(101)	

Figure 2 below shows the scanning electron microscope image of as-grown ZnO film. The SEM image very clearly shows the nanosheet structures of ZnO film. The average thickness and breadth of nanoplates were of 92nm and 360nm respectively. Figure 3a shows the transmittance of the ZnO nanostructured film grown on glass substrates using the two different concentrations of precursor solutions. The transmittance curves were captured in the wavelength of range of 350-900nm. Figure 3a shows the transmittance curves of samples C3(25mM) and C4(20mM) respectively. The result shows the ZnO film prepared with 20mM growth solution was more transparent in the visible region than film prepared with 25mM solution. Corresponding $(\alpha h\nu)^2$ versus $h\nu$ plot was shown in the Figure 3b. By extrapolating the linear portion of this plot we determined the direct band gap energy of ZnO [Shankar et al., 2010]. The calculated band gaps of sample c3 and c4 were of found to be 3.23eV and 3.25eV, respectively.

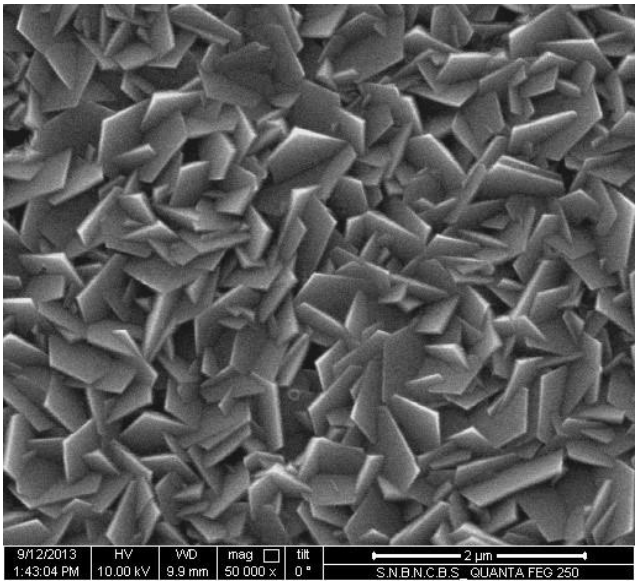
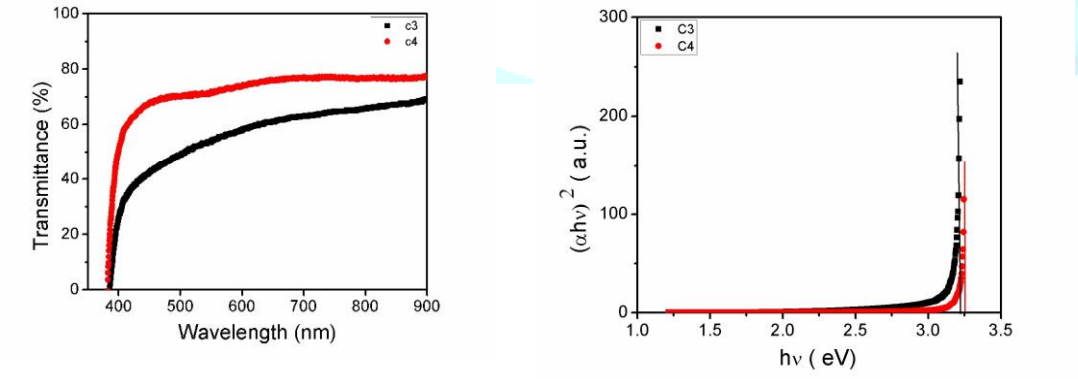


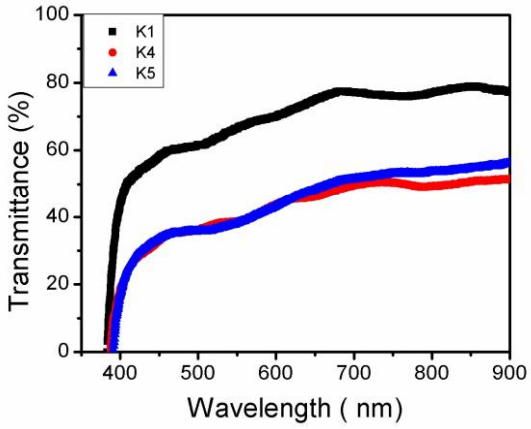
Figure 2: Scanning Electron Microscope image of ZnO film grown on glass substrate.



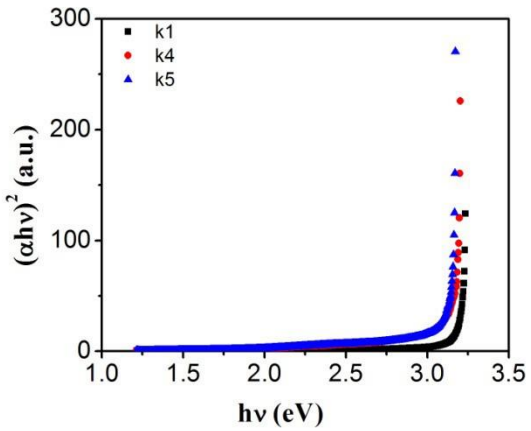
(a) (b)

Figure 3:(a) Transmittance curves (b) corresponding plot of $(\alpha h\nu)^2$ versus hν of ZnO film grown on glass substrate. The black filled square and and red filled circle symbols represent the C3 (25mM) and C4 (20mM) growth solution respectively.

Figure 4a shows the transmittance curves of ZnO films grown on FTO substrates. We prepared samples, k1, k4, k5 with three different growth times as 2 hours, 3 hours and 4 hours respectively. The figure shows that as the growth time increased from 2 to 3 hours the transmittance is found to be decreased. However no significant increase in transmittance was observed for the increase of growth time from 3 hours to 4 hours. Corresponding $(\alpha h\nu)^2$ versus $h\nu$ plot is shown in figure 4b. The band gap measurement shows that as the growth time increased the band gap energy is found to be decreased from 3.21eV to 3.16eV. This decrease in band gap with increase in growth time as well as decrease in band gap with increase in molar concentration of growth solution shown figure 3b is possibly due to increase in particle size with respect to increase in growth time and concentration.



(a)



(b)

Figure 4:(a) Transmittance curves (b) $(\alpha h\nu)^2$ versus hv plot of ZnO films grown on FTO substrates with various growth times. The black filled square, red filled circle, and blue filled triangle symbols represent the corresponding graphs with growth time of 2 hours, 3 hours and 4 hours respectively.

We have used *Vitis Vinifera* which possesses the anthocyanine pigment as a sensitizer to prepare ZnO working electrode. The absorbance of *Vitis vinifera* dye extraction is shown in figure 5a. The figure shows the absorption peak at 535nm which is an indication of light absorption in the visible region [Zhou et al., 2011]. We assembled DSSC using this dye extraction. The current voltage measurements of assembled DSSC were performed with halogen light source of two different powers, 500W and 1000W shown in the figure 5b. This measurement was completed using the two Fluke 179 digital multimeters. From the figure we clearly see that with light input the current-voltage of the device lies in the 4th quadrant which signifies the power generation from the device [Heo et al., 2013]. With increasing power level from 500W to 1000W the open circuit voltage and short circuit current was observed to increase from 370 to 600 millivolts and 15 to 30 microampere respectively. As expected output power of device increases with increasing input power of incident light. The observation shows the maximum voltage and current of assembled ZnO DSSC were 600 millivolts and 30 microamperes.

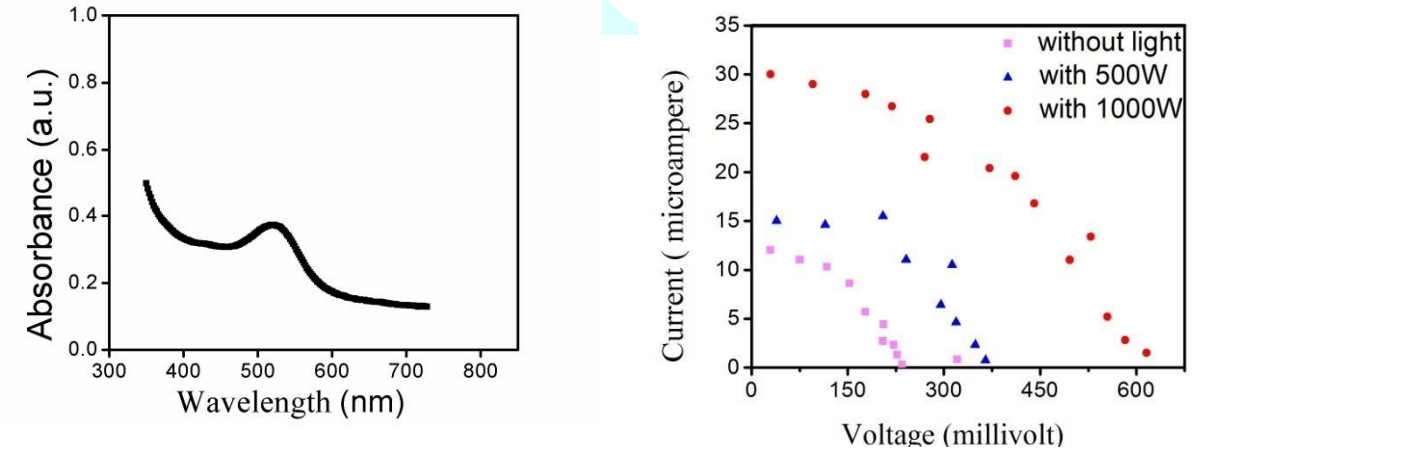


Figure 5: An optical absorption spectrum of Vitis v inifera as a function of wavelength (b) the current voltage measurement of assembled ZnO based DSSC with halogen light sources. The red filled square, blue filled triangle, and purple filled square symbols in figure b represent current voltage measurement with halogen light source of 1000W, 500W and without light source condition respectively.

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Competing Interests

The authors declare that no competing interests exist.

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Conclusions

ZnO nanosheets were deposited on AZO coated substrates using a hydrothermal route. Seed layers of AZO were deposited on glass and FTO substrates using a spin coating technique. The XRD analysis shows ZnO film deposited on glass substrate was of wurtzite structure with c-axis (002) oriented planes. The average crystallite size was found to be of 358Å. Scanning electron microscope textures study shows the formation of ZnO nanosheets of about 70nm thicknesses. The band gap of ZnO film was found to be 3.25eV. The band gap of ZnO grown on glass substrate was found to be slightly decreased as the concentration of growth solution increased from 20mM to 25mM. Similarly, as the growth time increased the band gap of ZnO grown on FTO substrate was found to be slightly decreased from 3.21eV to 3.16eV. The results of I-V characteristic curves confirmed that the power generation from DSSC fabricated from ZnO nanostructured loaded with *Vitis vinifera* dye extraction.

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