Fabrication and Characterization of Natural Dyes based ZnONPs Photoelectrode for Dye Sensitized Solar Cells (DSSCs)

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Abstract

This research focuses on the green synthesis of ZnONPs using Banana Peel Extract (BPE) from *Musa Balbisiana* Banana. ZnONPs powders were synthesized with three different ratios of Banana Peel:distilled water (2:10, 4:10, 6:10) and $Zn(NO_3)_2.6H_2O$. The structural and morphological properties of the synthesized ZnONPs powders were characterized by XRD and SEM. The crystal structure of ZnONPS (2:10, 4:10, 6:10) were found to be hexagonal wurtzite structure and their crystallite sizes were 43.06 nm, 29.40 nm and 22.23 nm respectively which form irregular grains having sizes of 2.77 μm, 2.39 μm, and 2.22 μm. ZnONPs (6:10) was deposited onto the fluorine doped tin oxide (FTO) substrates by using spin coating technique. Chlorophyll and Anthocyanin dyes solutions were extracted from Spinach Leaves and Grape Peel to use as sensitizer. ZnONPs substrates were dipped into two different natural dyes solutions, and natural dyes based ZnONPs photoelectrodes were prepared. The ZnONPs substrate, the natural dyes solutions and natural dyes based ZnONPs photoelectrodes were characterized by UV-Vis spectrophotometer. The energy band gap of ZnONPs substrate was found to be 2.48 eV. The optical band gap values were obtained 2.76 eV and 2.77 eV for Chlorophyll and Anthocyanin dyes solutions. Moreover, the optical band gap values of Chlorophyll and Anthocyanin based ZnONPs photoelectrodes were observed 2.63 eV and 2.49 eV respectively. According to obtained results, it can be reported that the two different natural dyes based ZnONPs photoelectrodes were suitable to use in DSSCs.

Keywords: Nanomaterials, ZnONPs, Photoelectrode, Natural Dyes, DSSCs

Introduction

Over the last years, various types of solar cells have been developed to convert sunlight to electricity. Crystalline, polycrystalline, and amorphous silicon solar cells have been widely used for different domestic and industrial application. Multi-junction semiconductor solar cells have shown the world record efficiency of 46%. However, their applications are mostly limited to space industry. There are other types of less efficient and low-cost cells, such as dyesensitized solar cells (DSSCs) and organic solar cells. DSSC was firstly reported by O'Regan and Gratzel in 1991. One of the main challenges of DSSCs is the long-term stability, electrolyte leakage, dyes desorption, and degradation of the dye itself are considered the most important parameters affecting the cell stability. Nanoparticles have packed interests in many researches in these recent years due to their advantageous application in various industries such as medicine, manufacturing electronics device, etc. A great example of nanoparticles with a wide array of uses is zinc oxide nanoparticles (ZnONPs). ZnONPs are used in a variety of applications including antibacterial agents, solar cell manufacturing materials, cosmetic ingredients, and so on.

One of environmental-friendly method for synthesis of ZnONPs nanoparticles is green method (Green synthesis of metal oxide nanoparticles is a fascinating issue of the nanoscience and nanobiotechnology fields). The nanoparticles prepared with plant extract are relatively cheap, efficient and ecological catalysts that help pollution. Green synthesis of ZnONPs has been carried out by many researchers including various kinds of fruits, leaves, petal of flowers, and so on. Bananas are used for various purpose in Myanmar and this subsequently lead to large amount

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of wastes in the form of banana peels which are often discared without furher thought to its potential. This research work, Banana Peel Extract used as a capping agents in ZnONPs synthesis. The use of Banana Peel Extract as a capping agent is possible because the banana peel extract contains secondary metabolite compounds such as flavonoids, polyphenois, alkaloids and saponins with various amounts.

In a solar application, improved photon absorption and load carriers' production are the essential requirements in the form of DSSCs. Therefore, because of their fundamental properties that can improve solar cells' converting power, nanomaterials are used in photovoltaic (PV) technology. They can found promising for visible spectral area light harvesting because of the improved electron mobility resulting from the generation of fast charging carrier. Due to their unique physical and chemical properties, ZnONPs nanoparticles have been used in solar cell applications.

In this research work, ZnONPs were synthesized from Banana Peel and distilled water with three different ratios of (2:10), (4:10), and (6:10) by a green synthesis method. Among the three different ratios, one of the ratios that have the smallest crystallite size using as an electron conducting medium (semiconducting materials) to fabricate the natural dyes based ZnONPs photo electrode. The natural dyes were extracted from Grape Peel and Spinach Leave used as sensitizer for photoelectrode.

Experimental Procedure

Materials: Banana Peel *(Musa Balbisiana)*, Red-Brown Grape Peel *(Vitis Vinifera L.)* and Spinach Leaves *(Alternanthera Blitum L.)* used in this study were collected from Yenanchaung's Myoma Market, Yenanchaung Township, Magway. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Distilled water, Ethanol, citric acid, filter paper, and Fluorine doped Tin Oxide (FTO) glass substrates were purchased from Academy Chemical Shop, Yangon, Myanmar.

Synthesis of Zinc Oxide Nanoparticles

In this research work, the synthesis of ZnONPs has two major steps. The first step is the preparation of Banana Peel Extract (BPE) solution and the second one is the preparation of Zinc oxide nanoparticles with BPE solution. Firstly, Banana Peel Extract (BPE) solutions were prepared by using Banana Peel and Distilled water with three different ratios (2:10), (4:10) and (6:10). The Banana Peels were cleaned by not only tap water but also distilled water, and allowed to dry at room temperature overnight to remove excess moisture. Next, the peels were cut into small pieces and (20g, 40g, and 60 g) of the peels were dispersed to the 100 ml of the distilled water in 500 ml beaker for three different ratios. After that, each ratios of the solution were heated at 100˚C for 90 minutes and stirred using a magnetic stirrer. The mixing solutions were filtered through the filter paper to remove the Banana Peels. Then, the three different ratios of Banana Peel Extract (BPE) solutions [(2:10), (4:10) and (6:10)] had been prepared and these solutions were stored in the dark for the further use.

The second step is the preparation of ZnONPs. In this part, Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] precursor solution was prepared first. 0.5 M of $Zn(NO_3)_2.6H_2O$ and 0.2 M of citric acid were added to 50 ml of distilled water. The solution was stirred for 30 minutes to get homogeneous solution. Then, zinc nitrate precursor solution was obtained. After that, the zinc nitrate precursor solution was mixed into 40 ml of Banana Peel Extract (BPE) solutions with three different ratios of (2:10), (4:10) and (6:10). The mixed solutions (three different ratios) were heated at constant temperature and stirred on the hot plate (magnetic stirrer). Then, the mixed solutions were change into "gel" about 2 hours. These gel was continuously heated with constant temperature. After a few minutes, these gel changed into dust gray slices. These slices were calcined at 500˚C for 4 hours in the furnace. Moreover, the calcined slices were ground for 2 hours to get fine powder. After that, a dust gray powder of zinc oxide nanoparticles with three different ratios was obtained as shown in the following Figure 1.

Extraction of the Natural Dyes

Red-Brown Grape Peel and Spinach Leaves were used as the starting materials to extract the natural dyes in this work. Distilled water used as the extraction solvent for Red-Brown Grape Peel and Spinach Leaves. 10 g of Grape Peel (fresh) and 10g of Spinach leaves (fresh) were dispersed into 100 ml of distilled water. The dispersions were heated up at 90˚C for one and half hours on the hotplate. The dispersions were filtered through filter paper to extract the natural dyes for the use as sensitizers, after cooling down to room temperature. The Grape Peel extract solution was used as an Anthocyanin dye and the Spinach Leaves extract solution was used as Chlorophyll dye respectively. The flow-chart for the extraction of natural dyes are shown in Figure 2.

Fabrication of Natural Dyes based ZnONPs Photoelectrodes

At first, FTO conductive glass substrates (1" × 1" × 1.1 mm) were firstly cleaned tap water with soap for 15 minutes. Secondly, these FTO conductive glass substrates were washed with ethanol for 1 hour and distilled water for 30 minutes in an ultrasonic cleaner for impurity clearance and dry at room temperature. After that, a colloidal solution of ZnONPs (6:10) was prepared by mixing 50 mg of the zinc oxide nanopowders with 20 ml of ethanol. The mixed solution was stirred for 4 hours to get homogeneous solution. Then, the ZnONPs solutions were deposited onto the FTO glass substrates with the use of spin-coater (1000 rpm for 10s followed by 3000rpm for 60s) for three times and ZnONPs glass substrates were obtained. Those ZnONPs glass substrates were heated at 60˚C for 30 minutes. Then, the heated glass substrates were cooled down to room temperature for 30 minutes. After that, the ZnONPs glass substrates were dipped into natural dyes (Anthocyanin and Chlorophyll) solutions for 24 hours. The dipped ZnONPs glass substrates were dried at room temperature about 2 hours after taking the glass substrates from the natural dyes. Finally, natural dyes (Anthocyanin and Chlorophyll) based ZnONPs photoelectrodes were obtained as shown in Figure 3.

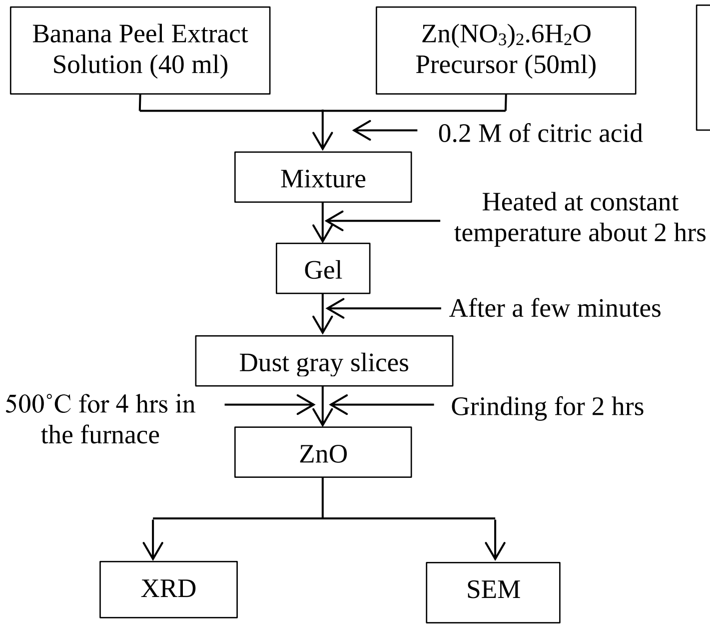


Figure 1 Flow-chart for green synthesis of Oxide Nanoparticles

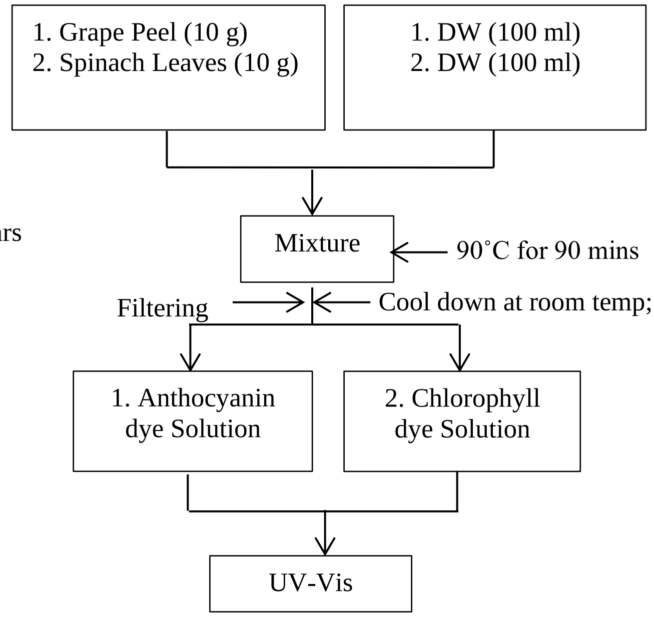


Figure 2 Flow-chart for the extraction of natural dyes

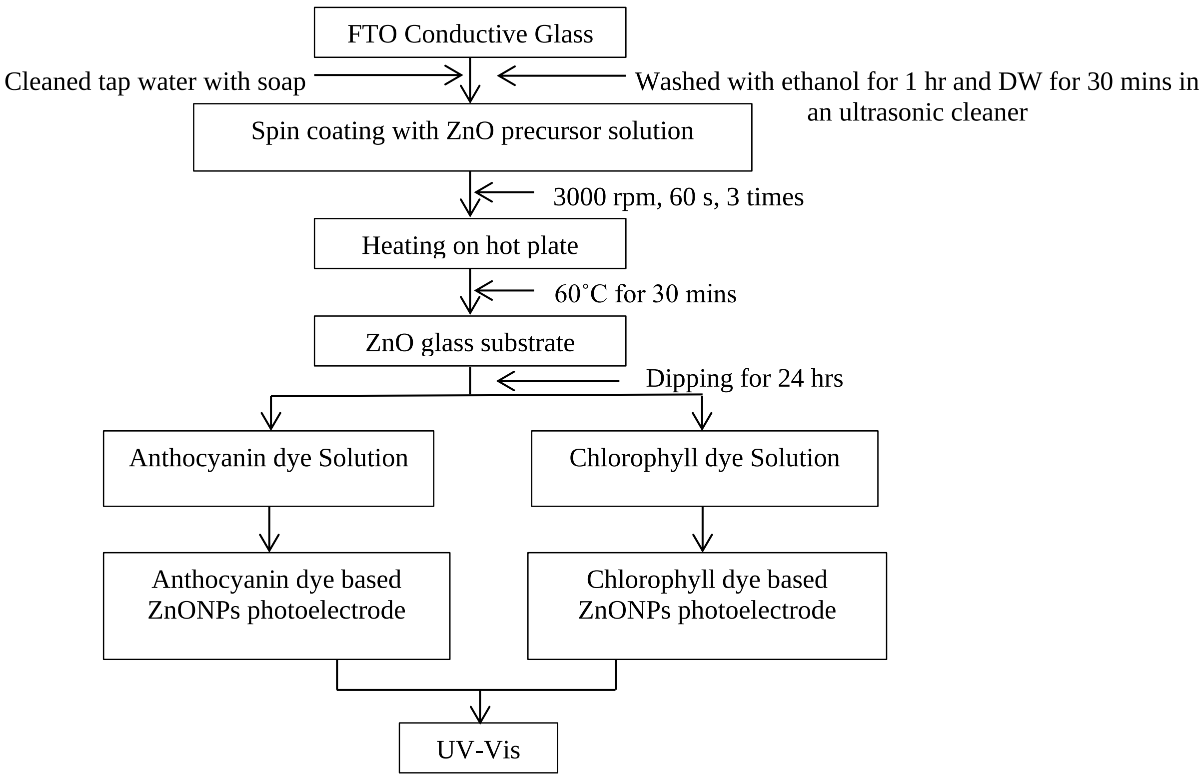


Figure 3 Flow-chart for the fabrication of natural dyes based ZnONPs photoelectrodes

Characterization

The structural properties of ZnONPs powders were examined by using X-ray diffractometer (Lab XRD-6100, University Research Centre, Magway) which oparates at 30 mA and 40 kV to generate radiation at a wavelength of 1.54050Å. The morphological properties of the ZnONPs powders were characterized by using Scanning Electron Microscopy (SEM Coxem – 610, University Research Centre, Pathein). The UV-Vis spectrophotometer (Shimadzu UV-Vis 2600, University Research Centre, Magway) was used to analyse the optical performance of ZnONPs glass substrates, natural dyes (Anthocyanin and Chlorophyll) solutions, and natural dyes (Anthocyanin and Chlorophyll) based ZnONPs photoelectrodes.

Results and Discussions

XRD Analysis

X-ray diffraction with Cuk$_\alpha$ (lambda = 1.54060 Å) was used to analyzed the crystal structure and crystallite size of prepared ZnONPs powders. The XRD patterns of ZnONPs with three different ratios of (2:10), (4:10), and (6:10) were shown in Figure 4. By referring to this figures, the Bragg's reflection peaks are (100), (002), (101), (102), (110), (103), (200), (112), and (201) respectively. Among these peaks, (100), (002), and (101) are the strongest reflection peaks. The lattice parameters of ZnONPs with three different ratios of (2:10), (4:10) and (6:10) are a = b = 3.24962 Å and c = 5.20313 Å, a=b= 3.24910 Å and c = 5.20242 Å, and a=b= 3.24955 Å and c = 5.20401 Å. The $\frac{c}{a}$ ratio of three different ZnONPs powders was 1.6 as tabulated in Table 4. Therefore, this reveals that the resultant ZnONPs powders belong to a hexagonal wurtzite structure.

The diameter of the crystallite size of the ZnONPs powders were determined from the most prominent reflection peaks of (100), (002), and (101) by using Debye Scherrers' equation D =$\frac{k\lambda}{B\cos\theta}$. The crystallite sizes of ZnONPs powders with three different ratios were tabulated in Table 1, 2, and 3. The obtained mean crystallite sizes of three different samples were also tabulated in Table 4.

According to XRD result, when the peaks intensity of ZnONPs are decreased, increasing the peaks broadening from (2:10) to (6:10). Generally, the peaks in the XRD will broaden as crystallite size decrease. Therefore, the crystallite sizes are decreased from 40.06 nm (2:10) to 22.23 nm (6:10). Therefore, the smallest crystallite size of ZnONPs (6:10) was chosen to use as a semiconducting material.

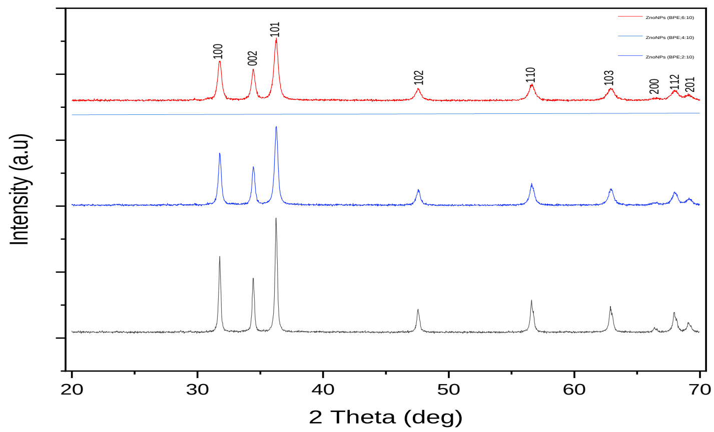


Figure 4 XRD pattrens of ZnONPs (2:10, 4:10, 6:10)

Table (1) XRD parameters and crystallite sizes of Zinc Oxide Nanoparticles (2:10)

Types of sample	(hkl)	2Ө (deg)	FWHM (deg)	CrystalliteSizes (nm)
ZnONPs	100	31.7918	0.19560	42.23
	002	34.4564	0.18800	44.25
	101	36.2761	0.19570	42.72
Average Crystallite Size				43.06

Table (2) XRD parameters and crystallite sizes of Zinc Oxide Nanoparticles (4:10)

Types of sample	(hkl)	2Ө (deg)	FWHM (deg)	CrystalliteSizes (nm)
ZnONPs	100	31.7973	0.27990	29.51
	002	34.4656	0.26810	31.03
	101	36.2812	0.30210	27.67
Average Crystallite Size				29.40

Table (3) XRD parameters and crystallite sizes of Zinc Oxide Nanoparticles (6:10)

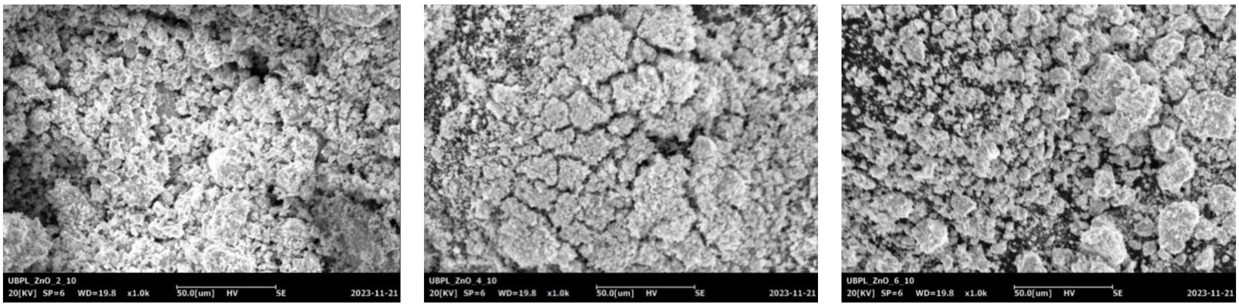
Types of sample	(hkl)	2Ө (deg)	FWHM (deg)	CrystalliteSizes (nm)
ZnONPs	100	31.7344	0.37630	21.95
	002	34.4581	0.34810	23.89
	101	36.2669	0.40110	20.84
Average Crystallite Size				22.23

Table (4) Lattice parameters, lattice distortion and mean crystallite sizes for zinc oxide nanoparticles

Types of Sample	a (Å)	c (Å)	$\frac{c}{a}$	Mean Crystallite Sizes (nm)
ZnONPs (2:10)	3.24962	5.20313	1.60	43.06
ZnONPs (4:10)	3.24910	5.20242	1.60	29.4
ZnONPs (6:10)	3.24955	5.20401	1.60	22.23

SEM Analysis

The surface morphological features of synthesized ZnO nanoparticles with three different ratios were examined by Scanning Electron Miscrope (SEM) as shown in Figure 5**.** These micrographs indicate that a good microsttucture with no discontinuities in terms of microcracks, some pores are found among the grains, and a few number of large grain size are also found. Grain sizes are little difference and they were measured by using well known bar code system with Image J software. The grain sizes were estimated to be 2.77 μm, 2.39 μm, and 2.22 μm for three different ratios (2:10, 4:10, and 6:10) respectively. From the result, it is found that the grain size is smallest for the ratio (6:10) among the three ratios.



(a) **(b)** **(c)**

Figure 5 SEM photographs of ZnONPs (a) (2:10), (b) (4:10), and (c) (6:10)

UV-Vis measurement for ZnONPs films

The absorption spectrum of zinc oxide nanopowder films (colloidal nanoparticles) is shown in Figure 6. This figure shows that the UV absorption of the ZnONPs film is in the visible region with maximum wavelength at 542 nm (absorption intensity is 0.0025) indicating that band to band excitation of ZnONPs, which is used for calculation of optical band gap of nanoparticle by using equation**,** $\lambda\ (nm) = \frac{1240}{E_g\ (eV)}$

The optical absorption provides the dependence of the absorption coefficient (α) on the photon energy (hv) for direct allowed.

$(\alpha hv)^2 = K(hv - E_g)$, Tauc Plot equation was applied to find the optical band gap by plotting $(\alpha hv)^2$ vs photon energy (hv) using the data obtained from the optical absorption spectrum of ZnONPs film. The optical band gap of ZnONPs film determined from this curve (absorption spectrum) is 2.48 eV as shown in Figure 7.

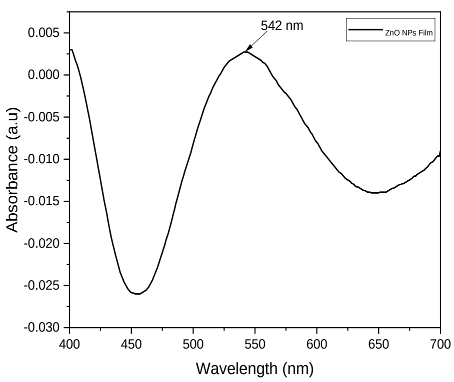


Figure 6 Absorption spectrum of ZnONPs film

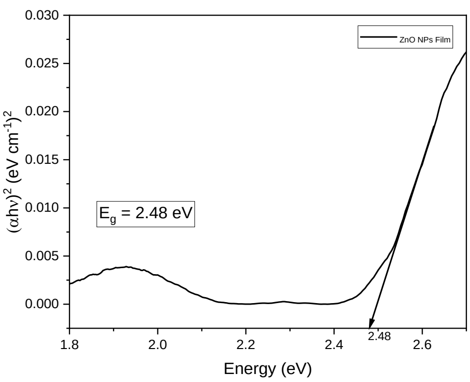


Figure 7 Energy band gap of ZnONPs film

UV-Visible Spectroscopy for the Natural Dyes

The absorption spectra of Chlorophyll and Anthocyanin dyes solutions were shown in Figure 8 and 9. Figure 8 showed that the presence of distinct absorption peak in the visible region at about 665 nm and the absorption intensity is 0.24 for the extract solution from the Spinach Leaves (Chlorophyll dyes). Figure 9 showed that the presence of absorption peak at about 512 nm and the absorption intensity is 1.07 for the Anthocyanin pigment dye solution (extracted from Grape Peel). The optical band gap value of Anthocyanin dye solution and Chlorophyll dye solution are 2.77 eV and 2.76 eV respectively as shown in Figure 10 and 11. From the result, the optical band gap values of two different dyes solutions were nearly equal while the absorption intensity of Anthocyanin dye solution is higher than that of Chlorophyll dye solution. It can be seen that the absorption peaks of two different dyes are in the visible region (approximately 500 – 670 nm). Therefore, these two natural dyes (Anthocyanin & Chlorophyll) were possibility used as sensitizers in DSSCs.

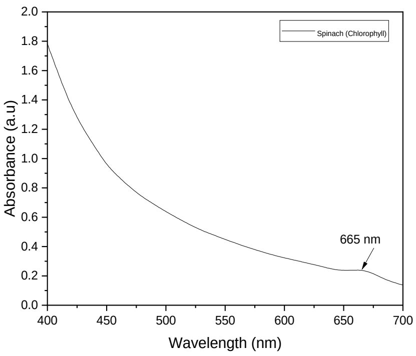


Figure 8 Absorption Spectrum of Chlorophyll dye solution

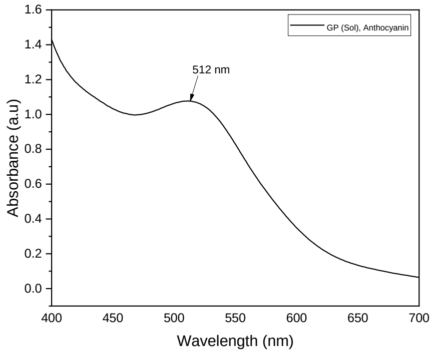


Figure 9 Absorption Spectrum of Anthocyanin dye solution

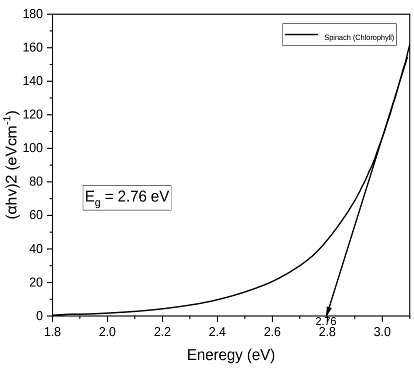


Figure 10 Energy band gap of Chlorophyll dye solution

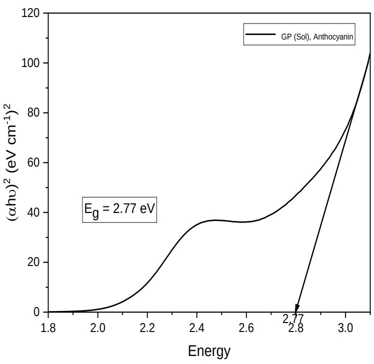


Figure 11 Energy band gap of Anthocyanin dye solution

Optical Energy Gap (E_g) of Natural Dyes based ZnONPs Photoelectrodes

The two different natural dyes (Chlorophyll & Anthocyanin) solutions, ZnONPs glass substrates and natural dyes (Chlorophyll & Anthocyanin) based ZnONPs Photoelectrodes had been prepared. In this section, the optical performance of prepared natural dyes based ZnONPs photoelectrodes were characterized by UV-Vis spectrophotometer. The absorption spectrum of Chlorophyll dyes based ZnONPs photoelectrode and Anthocyanin dyes based ZnONPs photoelectrode are shown in Figure 12 and 13. The absorption intensity of Chlorophyll dyes based ZnONPs photoelectrode are 0.147 and 0.0840 at 400 nm and 541 nm. The absorption peaks of Anthocyanin dyes based ZnONPs photoelectrode are presenced at 420 nm and 578 nm with absorption intensity of 0.069 and 0.059. The absorption peaks of both photoelectrodes were in visible region and the optical band gap values of both photoelectrodes were 2.63 eV and 2.49 eV as shown in Figure 14 and 15. From the above result, the optical band gap value of two different natural dyes based ZnONPs photoelectrodes are lower than the suitable value used in DSSCs. Because of the optical band gap value of the ZnONPs glass substrate was low. The reason why the optical band gap of ZnONPs glass substrates is low due to the temperature of these substrates was low. It is mentioned in the paper "Amal Bouich, Muhammad Aamir Shafi, et.al, Effect of deposition cycles on the properties of ZnO thin films deposited by spin coating method for CZT based solar cells, Vol-258, May 22", there is a relatioinship between the E_g of the film and the temperature. However, the optical band gap values of the two different natural dyes based ZnONPs photoelectrodes are above 2 eV. Therefore, they were suitable for use as a photoelectrode in DSSCs.

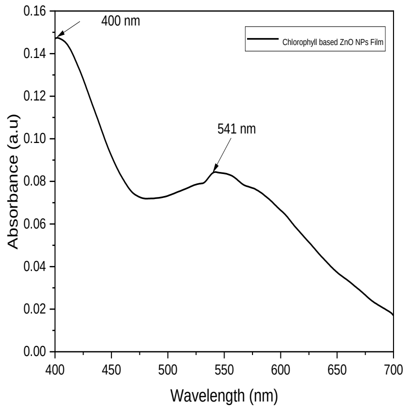


Figure 12 Absorption spectrum of Chlorophyll dye based ZnONPs Photoelectrode

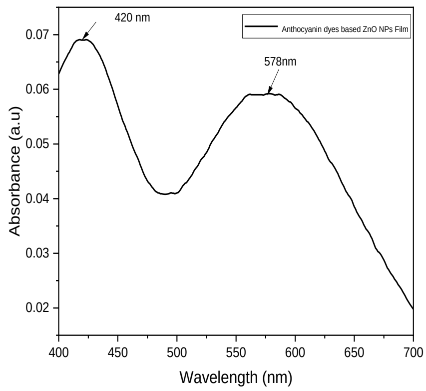


Figure 13 Absorption spectrum of Anthocyanin dye based ZnONPs

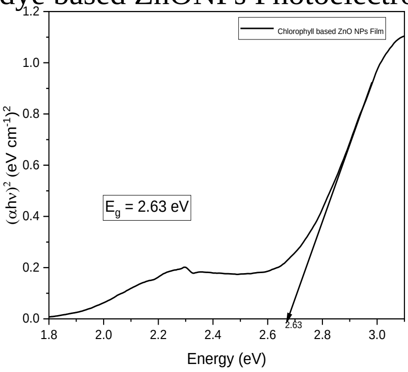


Figure 14 Energy band gap of Chlorophyll dye based ZnONPs Photoelectrode

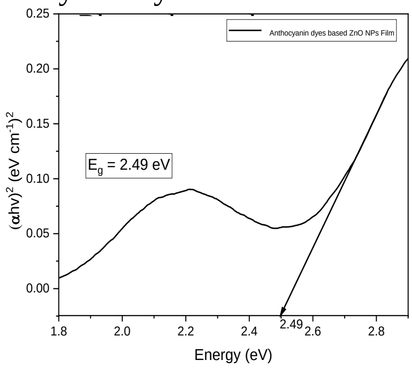


Figure 15 Energy band gap of Anthocyanin dye based ZnONPs Photoelectrode

Conclusion

In this research work, Chlorophyll and Anthocyanin dyes based zinc oxide nanoparticles (ZnONPs) photoelectrodes were fabricated for DSSCs. The crystal structure of ZnONPS (2:10, 4:10, 6:10) were found to be hexagonal wurtzite structure and their crystallite sizes were 43.06 nm, 29.40 nm and 22.23 nm respectively. The micrographs of three different ZnONPs have no cracking and some pores were formed among the grains and also found irregular particles structure. The grain sizes of ZnONPs with three different ratios (2:10, 4:10, 6:10) were 2.77 µm, 2.39 µm, and 2.22 µm respectively. Among them, ZnONPS of (6:10) will be chosen to construct natural dye based ZnONPs photoelectrodes because it has smallest crystallite size of 22.23 nm and smallest grain size of 2.22 µm. Then, ZnONPs (6:10) was deposited onto FTO substrates and the band gap value of this substrates was found to be 2.48 eV. The optical band gap values of Chlorophyll and Anthocyanin dyes were found to be 2.76 eV and 2.77 eV respectively. Natural dyes based ZnONPs photoelectrodes were successfully fabricated by using ZnONPs coated glass substrates and Chlorophyll and Anthocyanin natural dyes. The band gap values of Chlorophyll and Anthocyanin dyes based ZnONPs photoelectrodes were obtained 2.63 eV and 2.49 eV and they were slightly increased compare to the band gap value of ZnONPs coated glass substrate. The band gap value has changed slightly because of the dye molecules which attached to ZnONPs weakly. According to the above results, the optical band gap values of the two different natural dyes based ZnONPs photoelectrodes are lower than suitable values of the optical energy gap (3-3.2eV) in DSSCs. As the optical band gap values of the two different natural dyes based ZnONPs photoelectrodes are above 2 eV (wide band gap semiconductor materials have band gaps in the range above 2eV), they were suitable photoelectrode to be used in DSSCs.

Acknowledgements

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References

Andualem, A., Demiss, S. (2018) "Review on Dye-Sensitized Solar Cells (DSSCs)". Edelweiss Appli Sci Tech 2:145–150.

O'Regan, B. and Grätzel, M., (1991) "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," Nature, vol. 353, no. 6346, pp. 737–740.

Schindler, F., Fell, A., Müller, R., et al., (2018) "Towards the efficiency limits of multicrystalline silicon solar cells," Solar Energy Materials and Solar Cells, vol. 185, pp. 198–204.

Wong, H.L. (2016). Green Synthesis, "Characterization of Zinc Oxide Nanoparticles and Their Photocatalytic Activity", Department of Chemical Science, Faculty of Science, Universiti Tunku Abdul Rahman, pp.1-108.