

SYNTHESIS AND CHARACTERIZATION OF DYE-SENSITIZED SOLAR CELL BASED ON SILVER OXIDE NANOWIRES

Zin Min Myat¹, Zin Min Tun², Than Than Win³ and Yin Maung Maung¹

Abstract

In this paper, silver oxide (Ag_2O) nanowires grown onto ITO glass substrate from aqueous solution of silver nitrate (AgNO_3) and sodium hydroxide (NaOH) were used in dye-sensitized solar cells. Ag_2O nanowires were fabricated by using chemical bath deposition method at 300 °C and 400 °C for 1 h. Ag_2O nanowires were fabricated by using chemical bath deposition method (CBD). Phase formation and crystal structure of silver oxide were characterized by XRD analysis. The surface morphology of silver oxide nanowires were examined by SEM. The prepared nanowires structures were dye-sensitized with dragon fruit and assembled into a dye-sensitizer. Absorption and transmission properties of extracted dyes and silver oxide nanowires were carried out with UV-Vis spectroscopy. The DSSCs were converted the energy in light absorbed by dyes or pigments into other form of energy. Conversion efficiency (η_{con}) and fill factor (FF) were measured and determined by using I-V characteristics. Silver oxide (Ag_2O) nanowires photo-electrodes with dragon fruit dye sensitizers for DSSCs exhibited the optimum values of conversion efficiency 0.67 % at 300 °C and 0.63 % at 400 °C at two temperatures and it might be dye to good performance of anthocyanin molecules. Photovoltaic properties of silver oxide (Ag_2O) nanowires cells were measured and it was expected to utilize the dye sensitized solar cells applications.

Keywords: *Ag₂O nanowires, CBD method, XRD, SEM, UV-Vis, I-V characteristics*

Introduction

Dye sensitized solar cells (DSSCs) can be defined as photo-electrochemical solar cells. The cell is composed of sandwich electrodes, which are photoelectrode, counter electrode, and a redox electrolyte system. Both electrodes are mainly made from a transparent conductive oxide (TCO) coated glass. Fluorine doped tin oxide (ITO) on glass substrate are well

¹. Dr. Assistant Lecturer, Department of Physics, University of Yangon

². Department of Physics, West Yangon University

³. Department of Physics, Mandalay University of Distance Education

known materials as TCO applications due to having few surface electrical resistivity (Ωm^{-2}) and good optical transmission on the whole solar spectrum.

A typical DSSC consists of a transparent conductive oxide (TCO), semiconductor oxide, dye sensitizer, electrolyte and counter electrode. The working electrode is a nanoporous semiconductor oxide that is placed on conducting glass and is separated from the counter electrode by only a thin layer of electrolyte solution. The extension of the photoelectrode dye enables the collection of lower-energy photons. The dye is chemisorbed onto the semiconductor oxide surface. An ideal sensitizer should absorb a wide range of wavelengths and possess high thermal stability due to its strong binding to the semiconductor oxide. The photoanode of DSSCs is typically constructed using a thick film ($\sim 10\mu\text{m}$) of TiO_2 or, less often, ZnO or Ag_2O nanoparticles [Matudnmura M et al 1980].

Dye sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity, based on the sensitization of wide band gap semiconductor. The performance of the cell mainly depends on a dye used as sensitizer. Dye-sensitized solar cells (DSSCs) based on semiconductor electrodes have been investigated since 1960. DSSCs are unique compared with almost all other kinds of solar cells in that electron transport, light absorption and hole transport are each handled by different materials in the cells. The sensitizing dye in a DSSC is anchored to a wide-band gap semiconductor such as TiO_2 , Ag_2O or ZnO [Regan B O et al 1991].

Materials and Methods

Preparation of Silver Oxide (Ag_2O) seed layer films

The precursor solution of silver oxide nanoparticles were coated onto the indium doped tin oxide (ITO) /glass substrates by spin coating method. Firstly, the ITO /glass substrates were cleaned in a mixture solution of hydrochloric acid (HCl) and nitric acid (HNO_3) for 5 min. And then the substrates were also cleaned in a solution of acetone. These substrates were rinsed with distilled water and dried at room temperature. The prepared silver oxide nanoparticles were dissolved with 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) as solvent to form viscous paste at 120°C for 3 h. This viscous paste was then coated onto indium doped tin oxide (ITO) /glass substrates at 3000 rpm for

30 s by spin coating technique. Silver oxide colloidal solution was deposited onto chemically cleaned ITO conductive glass substrates. The seed layer coated films were annealed at 300 °C and 400 °C for 1h for diffusion films. The crystal structure and morphology of silver oxide (Ag₂O) films were confirmed by XRD and SEM analysis. Optical transmission spectra of the silver oxide films were recorded using a UV- vis spectrometer. The block diagram of preparation of silver oxide (Ag₂O) seed layer films was shown in Figure 1.

Preparation of Silver Oxide (Ag₂O) Nanowires Photoelectrode

Silver oxide (Ag₂O) nanowires were fabricated by chemical bath deposition method. Firstly, in order to grow Ag₂O nanowires, the seed layer films were used in this experiment. The prepared Ag₂O solution was synthesized by mixing of 50 ml silver nitrate and 20 ml of hexamethylenetetramine (C₆H₁₂N₄) solution with deionized water (DIW) by using chemical bath deposition method (CBD). For Ag₂O nanowire preparation, the seed layer films were subsequently dipped in a mixture solution and annealed at 80 °C for 10 h. During this period, the reaction heterogeneous growth of nanowires was limited by homogeneous nucleation of Ag₂O nanoparticles. Finally, the substrates were taken out from the growth solution and rinsed with deionized water and annealed at 300 °C and 400 °C for 1 h. The morphological characterization of Ag₂O nanowires were examined by Scanning Electron Microscopy (SEM).

Preparation of Natural Dye Sensitizers from Dragon Fruit

Dragon fruit was used dye extract in this work. Firstly, the oxide layer of dragon fruit skins was peeled off and washed with water and cut to get small pieces. The dragon fruit skins were cured in boil water at 100 °C for 30 min to be softer and enhanced colour. Fresh dragon fruit skins weight (50 g) were mixed into 50 ml of ethanol and equal weight of other skins were also mixed into 50 ml of distilled water at room temperature. The mixtures were annealed at 120 °C for 1 h until the mixture show homogeneous in colour. After cooling, the pH level of dragon fruit skins was measured with a pH meter and found to be 5 for ethanol and 6 for distilled water. The optical properties of natural dye-sensitizer were examined by UV-vis spectroscopy.

The block diagram of extract dye from dragon fruit skin was shown in Figure 2.

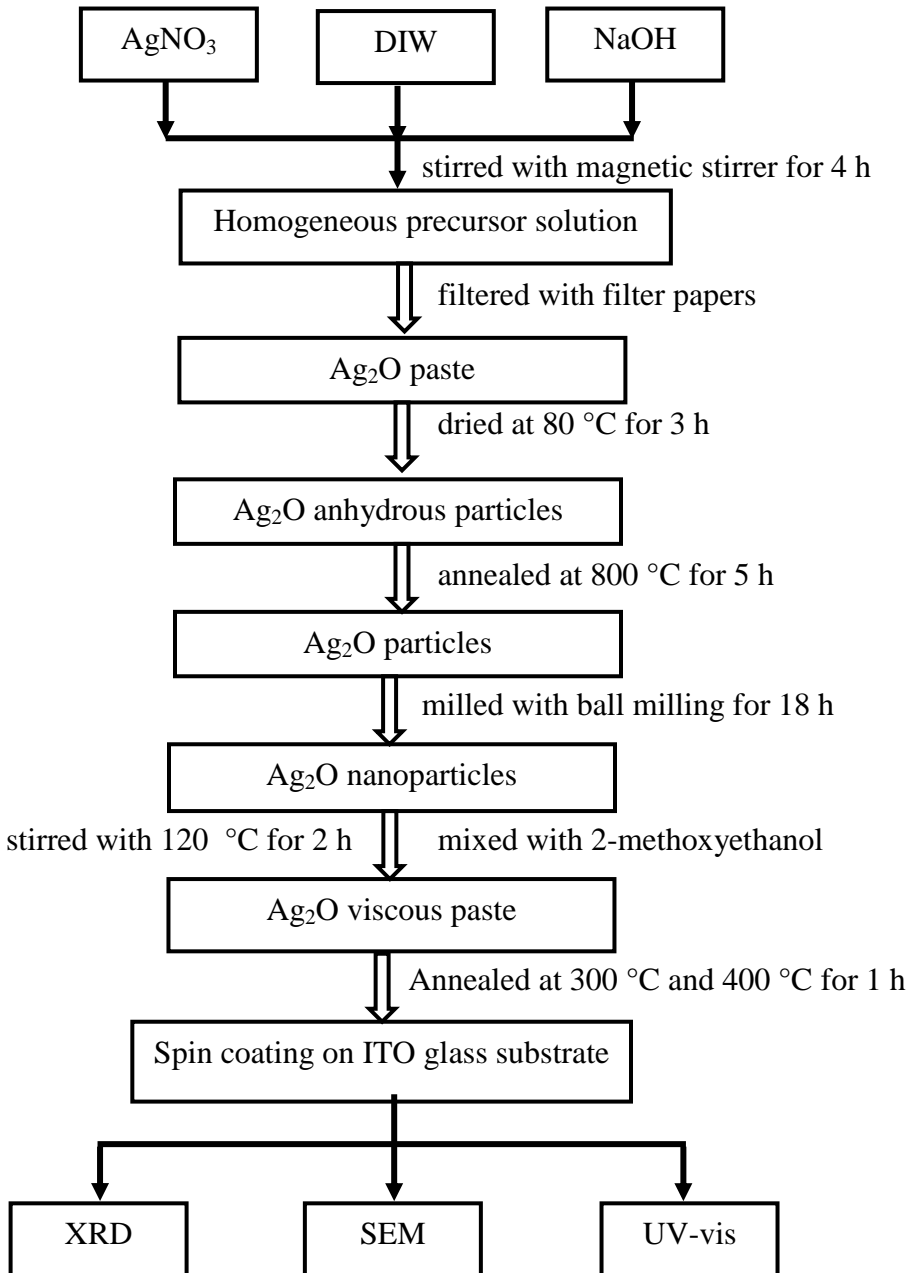


Figure 1: Block diagram of Ag₂O nanostructure of seed layer films

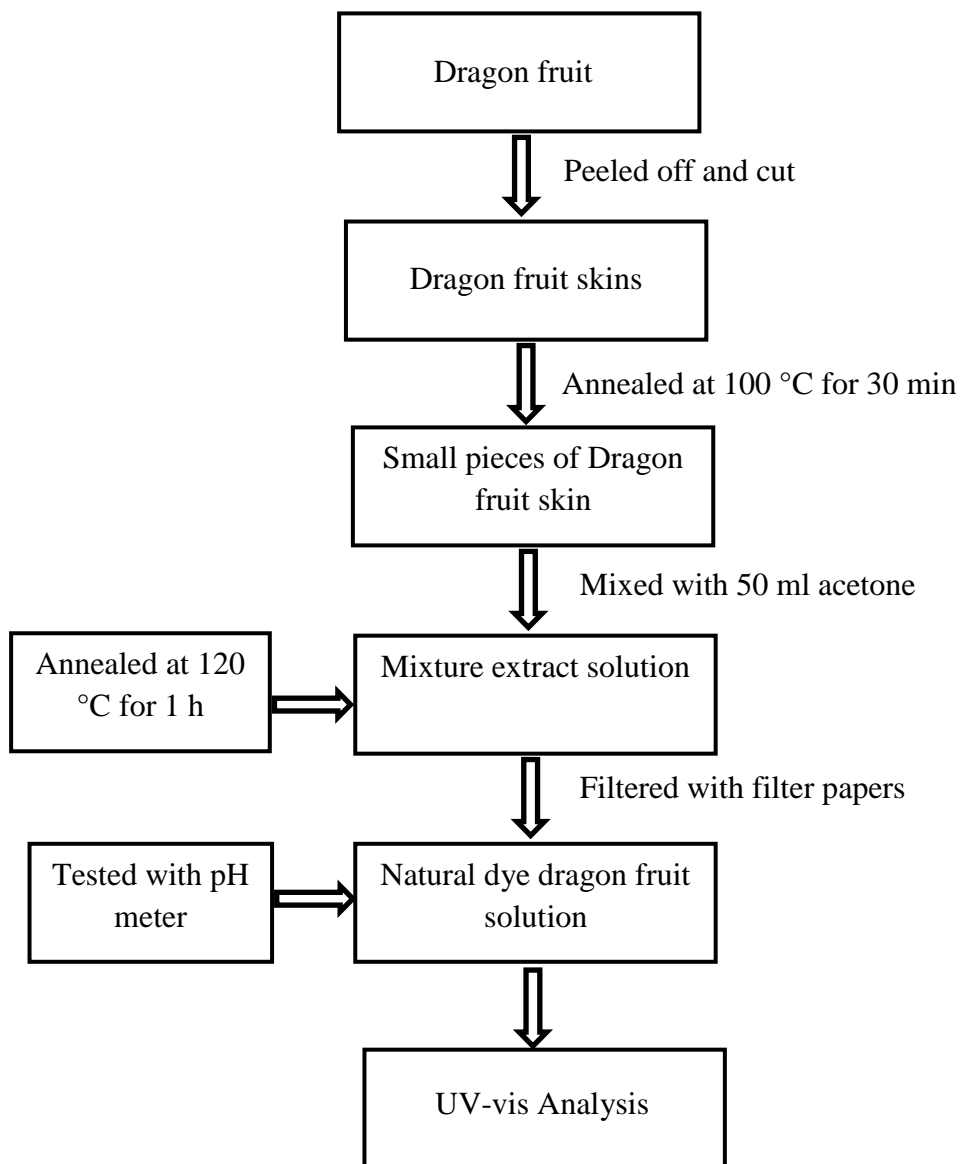


Figure 2: The block diagram of extract dye from dragon fruit skin

Results and Discussion

XRD analysis of Silver Oxide Seed Layer Films

X-ray diffraction is a powerful technique for investigating the structure of crystalline materials. The upper side of XRD profile was represented the observed profile while the lower side indicated the standard JCPDF (Joint Committee on Powder Diffraction Standards) library file. The dominant peaks were compared the data from the library (or) standard file. They were well matched with standard library profile. Figure 3 (a-b) showed the XRD spectrum of Silver Oxide (Ag_2O) seed layer films. The dominant peaks were well matched with the library (or) standard file. The most dominant peak was also occur at (111) peak. X-ray diffraction (XRD) demonstrated the cubic structure of the Ag_2O films. The crystallite size of silver oxide silver oxide seed layer films were calculated 23.16 nm at 300 °C and 20.44 nm at 400 °C.

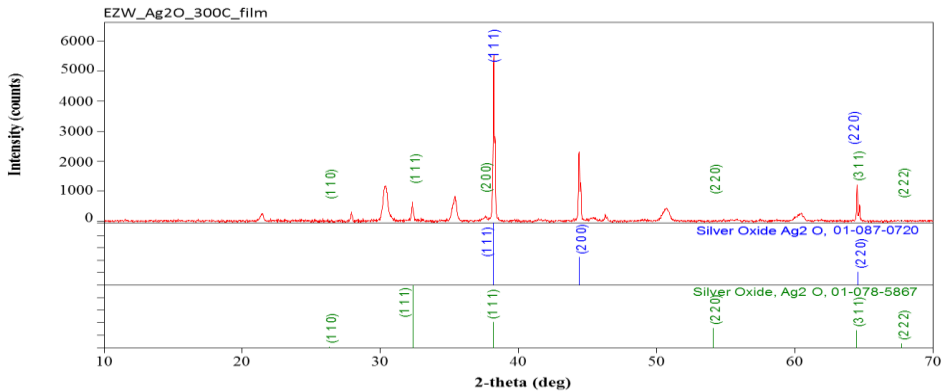


Figure 3: (a) XRD spectrum of Ag_2O seed layer film at 300 °C

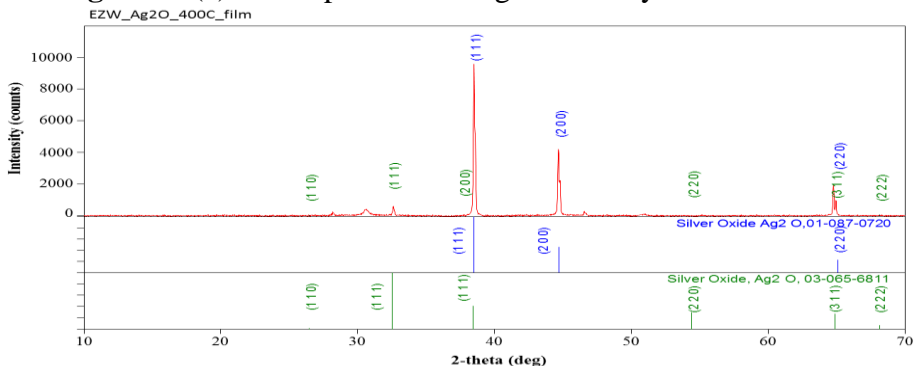


Figure 3: (b) XRD spectrum of Ag_2O seed layer film at 400 °C

SEM Analysis of Ag₂O Nanowire

Ag₂O nanowires onto indium doped tin oxide (ITO/glass) were carried out to examine by SEM analysis. Figure 4 (a-b) indicated the SEM micrograph of Ag₂O nanowires. From SEM image, it was observed that the diffusion wire was smooth, irregular shaped cylindrical grains. In order to study the morphology and nano structural properties of fabricated Ag₂O nanowires arrays grown at 300 °C and 400 °C for the same growing time. These figures showed the SEM micrographs with the respective diameter and the lengths of Ag₂O nanowire photoelectrode. The Ag₂O nanowires were disorderly, and had a wide size distribution. The growth temperature is the key parameter to dominate the diameter Ag₂O nanowires. It could be seen that the Ag₂O nanowires grown oriented on the substrates. It can be seen from these figures, different structural and morphological changes were observed. The diameter and the length distributions between the Ag₂O nanowires for different growth temperature exhibited a significant difference which shows growth dense nanowires with diameters between (365 nm- 450 1nm) at 300 °C and (175 nm- 236 nm) at 400 °C respectively. According these results, the morphologies of the nanowires were varied strongly and sharp with different growing temperature. As a result, it was obvious that Ag₂O nanowire was significantly formed onto Ag₂O seed layer films at different deposition temperature.

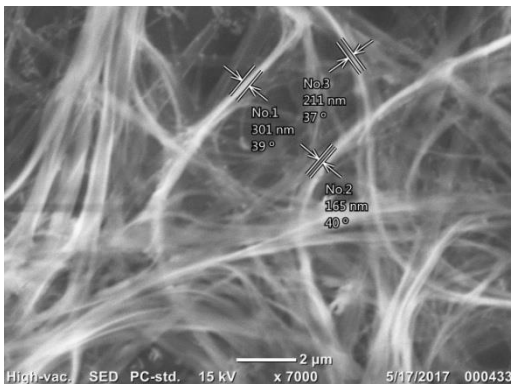


Figure 4: (a) SEM image of as-prepared silver oxide nanowires at 300 °C

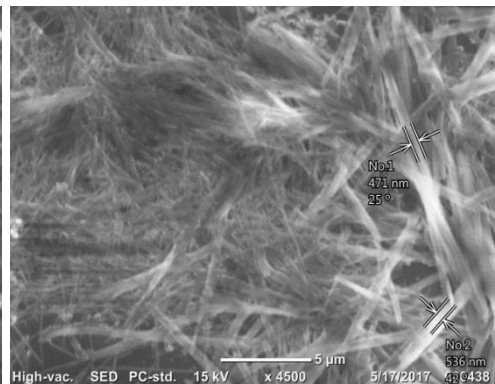


Figure 4: (b) SEM image of as-prepared silver oxide nanowires at 400 °C

UV-vis Analysis of dye solutions from dragon fruit skins

The absorption spectrum and the energy band gap of dragon fruit dyes were performed using UV-vis spectrometer (SMIMADZU). Figure 5 (a-b) shows the absorption spectra of distilled water and ethanol and the dye's ability to absorb photons from visible light spectrum. It was found that the maximum absorption of wavelength obtained by distilled water is about 533 nm and slightly red shifted compared to ethanol with the peak wavelength of 535 nm. Dragon fruits dye which is extracted using ethanol is resulted in deep coloured solutions. The wavelength range of spectrum laid between 400 nm to 700 nm. The dragon fruit showed good absorption level between 500 nm and 600 nm wavelength. Basically, the absorption was due to anthocyanin obtained in the dragon fruit. The measured and calculated values of UV-vis spectrum were described in Table 2.

Table 2: Optical band gap energy and absorption coefficient of dragon fruit skin dye

Dyes	Extract solvent	Structural class	Peak absorbance (nm)	Absorption range (nm)	Energy band gap (eV)	Absorption coefficient, α (m^{-1})
Dragon fruit skin	Ethanol	Betalain pigment	535	400-600	2.32	2.16
	Distilled water		533		2.33	2.03

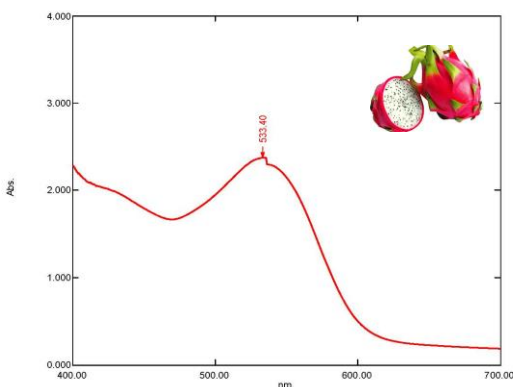


Figure 5: (a) Absorption spectra of dragon fruit skin with distilled water

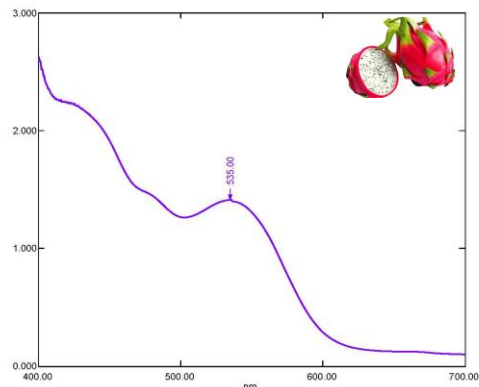


Figure 5: (b) Absorption spectra of dragon fruit skin with ethanol

UV-vis Analysis of Silver Oxide Nanowires Films

The absorbance spectrum of silver oxide nanowires films on ITO glass substrates by using UV-vis Spectrometer. The wavelength range of spectrum lied between 190 nm and 1100 nm. The observed absorption peaks of silver oxide nanowires films were 314 nm at 300 °C and 416 nm at 400 °C. It was observed that the UV-vis absorption spectrum of silver oxide nanowires at 300 °C and 400 °C were shown in Figure 6 (a-b). The measured and calculated values of energy band-gap in UV-vis spectra of silver oxide nanowires were described in Table 3. The alternative method to observe the band gap is Beer-Lambert law. The $(\alpha h\nu)^2$ and $h\nu$ characteristic curve of Ag_2O nanowires films at 300 °C and 400 °C were shown in Figure 7 (a-b). On the characteristic curve, the extrapolating the straight line onto horizontal axis ($(\alpha h\nu)^2 = 0$), give the value of band gap and the obtained nanowires films had a direct band gap 1.79 eV for the absorbance spectrum at 300 °C and 2.06 eV for the absorbance spectrum at 400 °C.

Table 3: Optical band –gap energy of Ag_2O nanowires films at 300 °C and 400 °C

Temperature (°C)	Optical band gap (eV)		Standard band gap (eV)
	Direct method	Beer-Lambert law	
300	1.95	1.79	1.3 – 2.4
400	2.16	2.06	

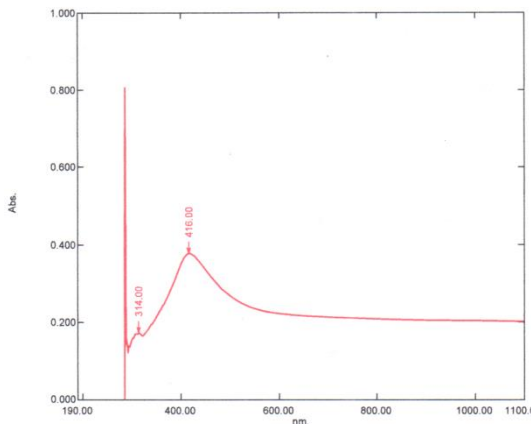


Figure 6: (a) Absorption spectra of silver oxide nanowires film at 300 °C

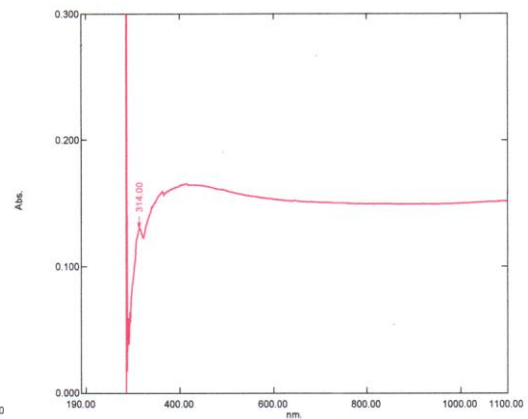


Figure 6: (b) Absorption spectra of silver oxide nanowires film at 400 °C

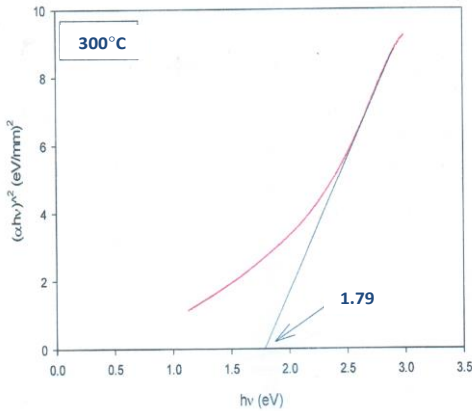


Figure 7: (a) Photon energy for silver oxide nanowires film at 300 °C

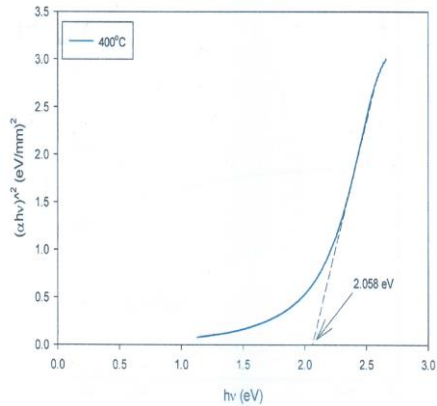


Figure 7:(b) Photon energy for silver oxide nanowires film at 400 °C

Photovoltaic Performance Analysis of Silver Oxide Nanowires

The photovoltaic performance analysis of fabricated DSSCs was carried out under the illumination of 5083 lux. The performance of Ag₂O nanowires at 300 °C and at 400 °C were defined by several parameters such as short-circuit current I_{sc} and open-circuit voltage V_{oc} obtained under illumination conditions. The current-voltage characteristics at different temperatures with natural dyes were represented in Figure 8 (a-b). These figures showed the solar cells behavior of natural dye sensitized solar cells. The maximum power point P_{max} was obtained by tangential point on I-V characteristic curve. By drawing the maximum power point onto X-axis, the maximum voltage (V_m) was obtained. By drawing the maximum power point onto Y-axis, the maximum current (I_m) was obtained. Based on the natural dye sensitizers, silver oxide nanowires coated counter electrodes were observed to be 0.67 % at 300 °C and 0.89 % at 400 °C. The detail analysis of short circuit current (I_{sc}), short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill-factor (FF) and conversion efficiency (η_{con}) of dye sensitized solar cells were shown in Table 4.

Table 4: Solar cell parameters of the cell with dragon fruit dye

Specimen	lux	I _{sc} (μA)	V _{oc} (mV)	FF	η (%)
Ag ₂ O (300°C)	5086	330.36	115.89	0.78	0.67
Ag ₂ O (400°C)	5086	348.36	119.80	0.89	0.63

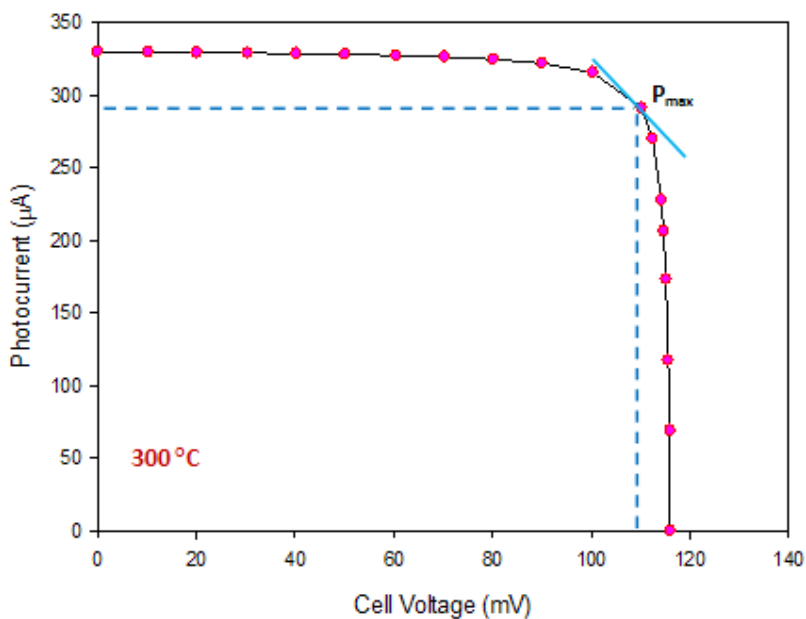


Figure 8: (a) I-V characteristics curve of silver oxide nanowires DSSCs at 300 °C

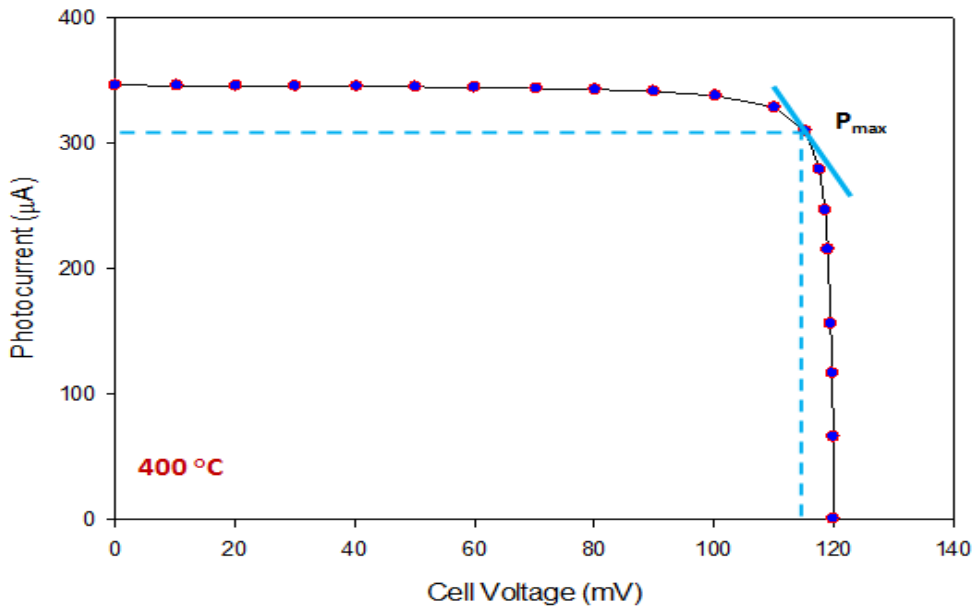


Figure 8: (a) I-V characteristics curve of silver oxide nanowires DSSCs at 400 °C

Conclusion

Silver oxide nanowires were deposited onto ITO glass substrates by chemical bath deposition technique. Silver oxide nanoparticles with different sizes were synthesized using co-precipitation method. XRD analysis showed that nanoparticles in the fabricated films at 300 °C and 400 °C were crystallized in the cubic structure and their average crystallite sizes were observed to be 23.16 nm and 20.44 nm. According to SEM images, it can be said that the average diameter of silver oxide nanowires at 400°C (175 nm - 236 nm) is smaller than that of at 300 °C (365 nm- 450nm). The results showed that the silver oxide nanowires were successfully fabricated by chemical bath deposition technique. Natural dye was extracted from dragon fruit skins as organic dye materials. The optical absorption analysis indicated that dragon fruit dye has a wide transparency window in the entire visible and near IR region. The result showed that the dye extracted from absorption wavelengths at 500 nm to 600 nm. It was revealed that anthocyanin dye from dragon fruit quite worked well as natural dye sensitizers for silver oxide

nanowires DSSCs. It was revealed that anthocyanin dye from dragon fruit quite worked well as natural dye sensitizers for silver oxide nanowires DSSCs. From the experimental photovoltaic parameters results, it was found that the efficiencies of Ag₂O nanowires photoelectrodes were 0.67 % at 300 °C and 0.63 % at 400 °C. The results have been pointed out the photovoltaic properties by measuring the I-V characteristics curve and calculating the fill factors and conversion efficiencies. It was proved that the extract dye from dragon fruit quite worked well as a natural dye sensitizers for DSSCs and they are promising to use in light energy harvesting application because of their environmental friendliness and low cost production.

Acknowledgements

I would like to thank Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon, for her kind permission.

I would like to thank Professor Dr Aye Aye Thant, Department of Physics, University of Yangon, for her valuable advice in the preparation of this paper.

References

- Azulai D, Belenkova T, et al, Transparent Metal Nanowires Thin Films Prepared in Mesostructured Templates. *Nano let*, (2009) **9** 4246-4249.
- Andre R, Natalio F, et al., *Adv. Funct. Matet.* (2011) 21: 501-509.
- Boyle DS, Bayer A, et al, Characterization of ZnO thin films grown by chemical bath deposition. *Thin Solid Films*, (2000) 150:361.
- Chang H, Lo Y-J. Pomegranate leaves and mulberry fruits as natural sensitizers for dye sensitized solar cells. *Solar Energy*, (2010) 84:1833-1837.
- Greene LE, Yuhas BD, Law M, et al, Solution-grown zinc oxide nanowires. *Inorg Chem*, (2006) 45: 7535-7543.
- Hochabaum AI, Yang P, Semiconductor nanowires for energy conversion. *Chem Rev*, (2010) 110:527-546.
- Kalaiarasan E, Palvannan Tj, *Taiwan Inst. Chem. Eng.* (2014) 45: 625-634.
- Liu Y, Zhu G, Bao C, Yuan A, Shen X, *Chin. J. Chem.* (2014) 32: 151-156.
- Nakade, S. et al. Dependence of TiO₂ nanoparticle preparation methods and annealing temperature on the efficiency of dye-sensitized solar cells. *J. Phys. Chem.* (2002) B 106, 10004-10010.
- Perkampus H. *UV-vis Spectroscopy and Its Applications*, Springer, (1992).