CHAPTRE VII

ROLE OF GRAPHENE OXIDE / YTTRIUM OXIDE NANOCOMPOSITES AS A CATHODE MATERIAL FOR NATURAL DYE (SOLANUM PROCUMENS (SP), SOLANUM TORVUM (ST), ARTABOTRYS HEXAPETALUS (AH), GALINSOGA PARVIFLORA (GP), AND JASMINUM GRANDIFLORUM L (JG) SENSITIZED SOLAR CELL

7.1. INTRODUCTION

Dye sensitized solar cell (DSSC), a green energy conversion device has made considerable power conversion efficiency enhancement during the last two decades. The counter electrode in DSSC system plays a vital role for the collection of electrons and reduction of I^-_3 ions. Hence an ideal Counter Electrode (CE) material must possess a good electrical conductivity and superior electrocatalytic activity for DSSC. In general, Platinum (Pt), a noble metal is the preferred counter electrode material however because of its high cost and limited availability, an intensive research has been directed towards the search for low cost counter electrode material. Among the carbon based materials, Graphene oxide has fascinated due to its large surface area, high electron conductivity, excellent electron mobility and electrochemical stability [1].

In recent times, rare earth nanomaterials are the most popular and commonly used material for its device application and are synthesized in the form of nanoparticles. Yttrium oxide, an inorganic nanoparticle which is one of the precious rare earth element, most stable metal, a silvery metallic transition metal and chemically alike to the lanthanides [2]. Yttrium oxide has a good electron conducting capacity and easy to mold into different shapes. These nanoparticles have a high absorption coefficient, a large band gap and a high dielectric constant, making them an attractive rare earth nanomaterial for energy storage applications.

The sensitizer plays an important role in the functioning of DSSCs and mainly defines its performance. Molar absorption coefficients are required for efficient light harvesting with TiO_2 (photoanode) films.

Hence natural dyes such as Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) dye extracts are used as a sensitizer for DSSCs. These natural extracts contain namely, chlorophyll, betanin, anthocyanins and carotenoids. These dyes exhibit wide ecological range and found extensively all over India. This chapter has reported a GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as a novel Pt free counter electrode for DSSC applications [3].

7.2 MATERIALS AND EXPERIMENTS

7.2.1 Natural Dye Preparation

Fresh Jasminum Grandiflorum L (JG) sleaves are used for the extraction of constituents.10 grams of Jasminum Grandiflorum L (JG) are mixed with 10 ml of distilled water and 10 ml of ethanol, kept under 45° C for 1 hour and left undisturbed for 24 hours at room temperature. The extract is filtered and used as a sensitizer in dye sensitized solar cell. Similar procedure is being used for Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH) and Galinsoga Parviflora (GP) [4].

7.2.2 Preparation of DSSCs

The fluorine-doped tin oxide (FTO) glass substrates are sequentially cleaned in distilled water, acetonitrile and ethanol for 10 min and dried. TiO_2 paste are coated on the cleaned FTO glass plate by doctor blade method and annealed at 450° C. The active area of the electrode is 0.2 cm. The prepared GO/Y_2O_3nanocomposites are coated on FTO glass plate by doctor blade method and annealed at 150° C, which act as a counter electrode. The ionic electrolytes (lithium iodide, iodine, acetonitrile and 2-dimelhyl-3propylimidazolium iodide) are injected between the sandwiches [5].

7.2.3 Characterization Techniques

A UV-Vis spectrometer is used to measure UV-Vis absorption at room temperature (Cary 60 UV-Vis). With the help of a simulated solar light source, photo current experiments are carried out in the SP 150 biologic instrument.

7.3. RESULTS AND DISCUSSION

7.3.1 UV-Vis Spectral Analysis

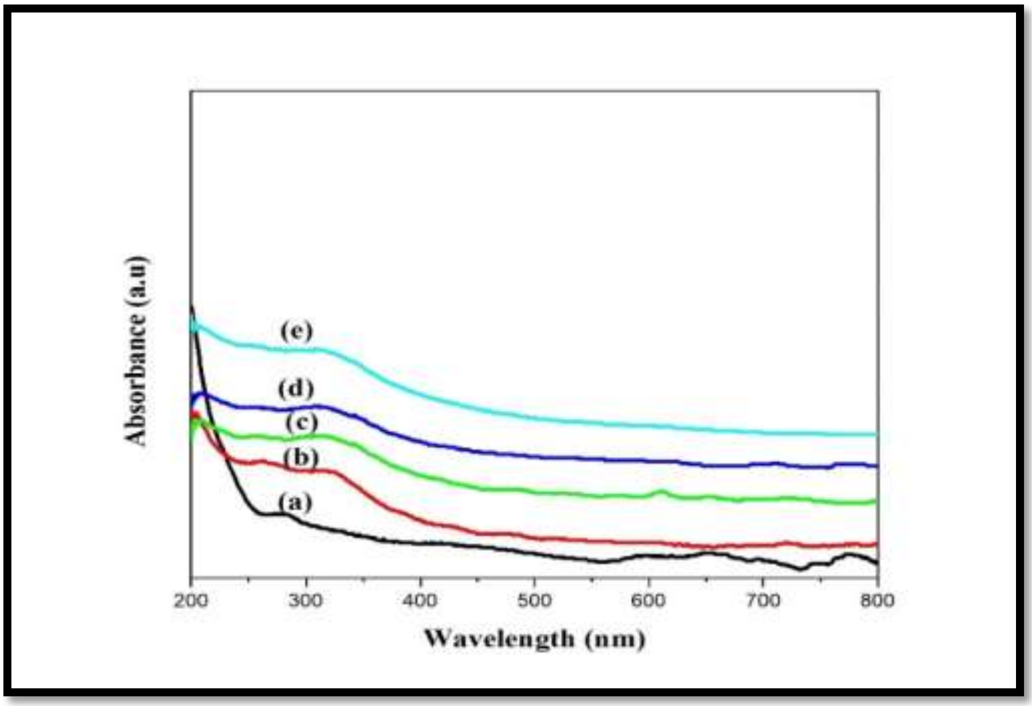


Figure 7.1 UV- Vis spectral analysis of GO/Y_2O_3 (a) 5:1 (b) 5:2 (c)5:3 (d) 5:4 and (e) 5:5 nanocomposites

The absorption spectra of the GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites are examined by UV-Vis spectrophotometer within the range of 200 nm to 800 nm and are shown in the Figure 7.1. It shows that the absorption peak of GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites at 250 nm and 408 nm, 257 nm and 411 nm, 260 nm and 416 nm, 262 nm and 419 nm, 268 nm and 421 nm respectively. It is observed that the peaks are shifted to higher wavelength and this red shift may be due to the increase in the concentration of Y_2O_3nanoparticles on the GO nanosheets as also evident from EDX analysis as discussed in chapter IV [6].

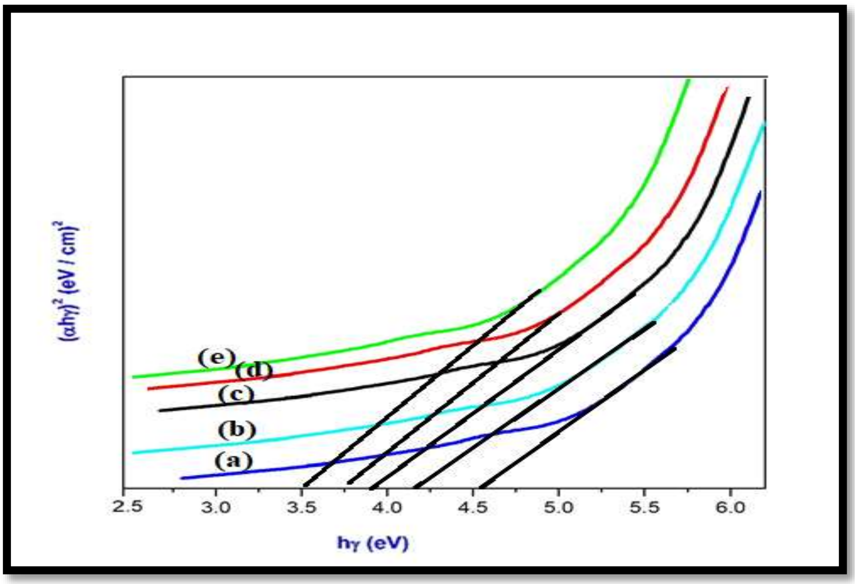


Figure 7.2 Band gap energy of GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) Nanocomposites

The band gap for GO/Y_2O_3 (5:1, 5:2, 5:3, 54 and 5:5) nanocomposites is calculated from the Tauc plot and is shown in the Figure 7.2 (a-e). The band gap energy is determined by using the equation [7].

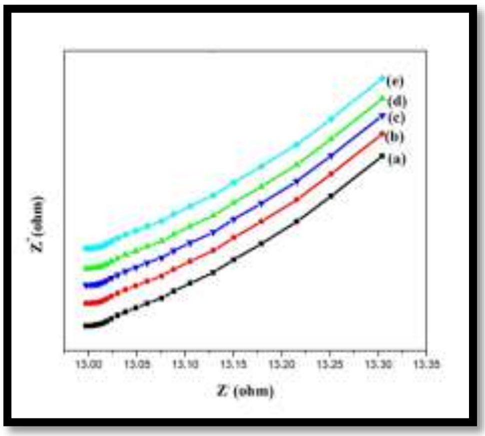
$$\alpha = \frac{\alpha_0(h\gamma - Eg)^n}{h\gamma}$$

where α_0 is a constant, Eg is the optical band gap and n is a constant, which depends on the probability of transition (i.e) n=1/2 for direct band gap.

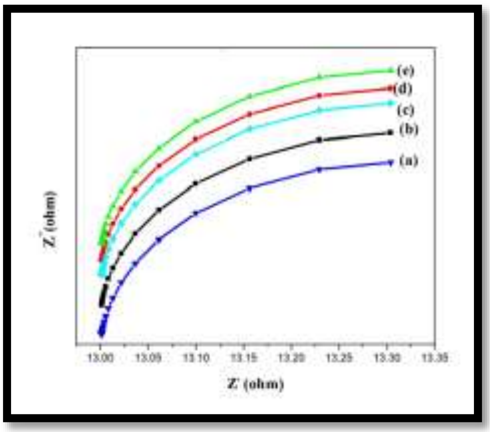
The band gap energies for GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites are found to be 3.5 eV, 3.7 eV, 3.9 eV, 4.3eV and 4.5eV respectively. It is observed from the Figure 7.2 that the band gap increases as the concentration of Y_2O_3 nanoparticles onto the surface of Graphene oxide nanosheets increases and may be attributed due to the increase in the crystallite size as evidenced from XRD analysis as discussed in chapter IV [8].

7.3.2 Electrochemical Impedance Spectroscopy

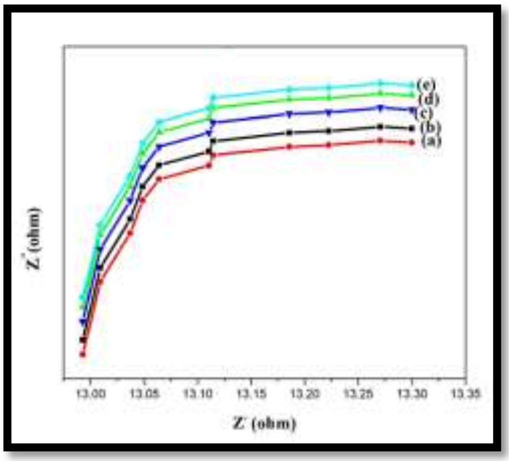
Electrochemical impedance Spectroscopy (EIS) analysis is regarded as a useful tool for investigating the charge transport on the counter electrode in DSSCs. The EIS Nyquist plots of Pt free GO/Y_2O_3 (5:1, 5:2. 5:3. 5:4 and 5:5) nanocomposites counter electrode with SP, ST, AH, GP and JG dyes as a sensitizer for DSSCs devices are shows in the Figure 7.3 (a-e). The EIS is performed by injecting small amplitude of alternating voltage to the solar cell to produce the current signals at a specific angular frequency. Based on the shape of impedance response over frequency, the electron transport in the mesoporous TiO_2 film, electron recombination at the TiO_2/ electrolyte, charge transfer at the counter electrode and diffusion of redox couple in the electrolyte can be evaluated [9]. The EIS results revealed that the GO/Y_2O_3 (5:4) concentration with JG dye sensitizer achieves the largest semicircle in the highest frequency region. The counter electrode made of GO/Y_2O_3 (5:4) with JG dye allows rapid electron transfer which is higher than the other concentrations [10].



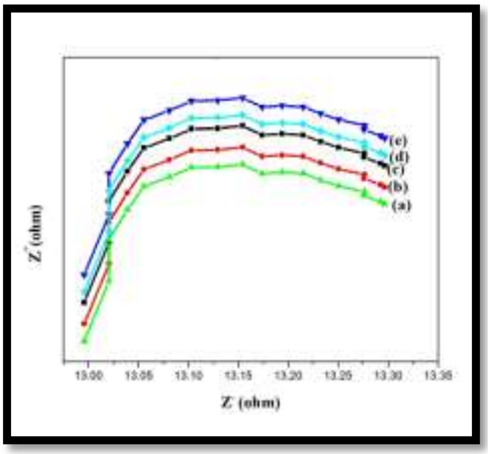
(a)



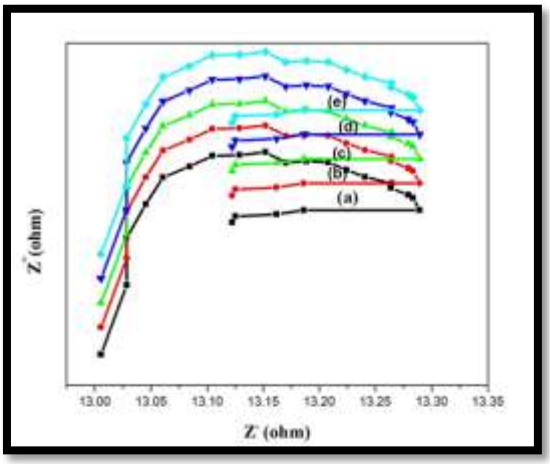
(b)



(c)



(d)



(e)

Figure 7.3Electrochemical impedance spectroscopy (EIS) of a (a)GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with SP as a sensitizer (b) GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with ST as a sensitizer (c) GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with AH as a sensitizer (d)GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with GP as a sensitizer (e) GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with JG as a sensitizer

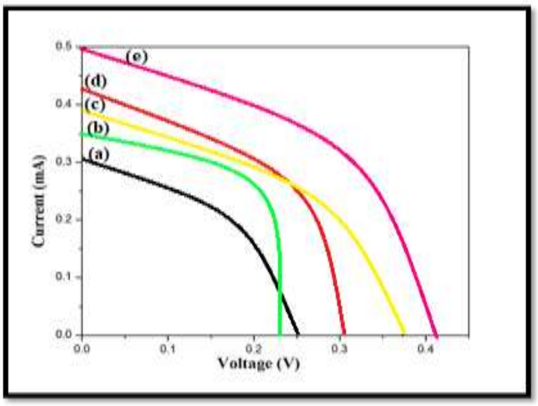
7.3.3 Efficiency Studies

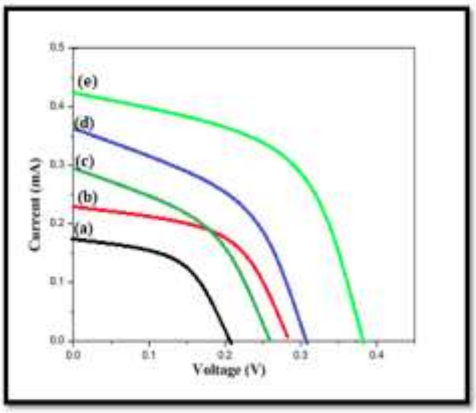
Photovoltaic characterization of the prepared GO/ Y_2O_3nanocomposites is investigated by I-V characterization. The prepared nanocomposites are used as a counter electrode and natural extract is used as a dye sensitizer. The effective area of the DSSC are measured to be 0.2 cm and the performance of DSSC are evaluated by short circuit current density(I_{sc}), open circuit current (v_{oc}) fill factor (FF) and the energy conversion efficiency (η) are calculated by using the equations (1) and (2).

$$FF=(I_{max}\ x V_{max}) / (I_{sc}\ x\ V_{oc}) \qquad (1)$$

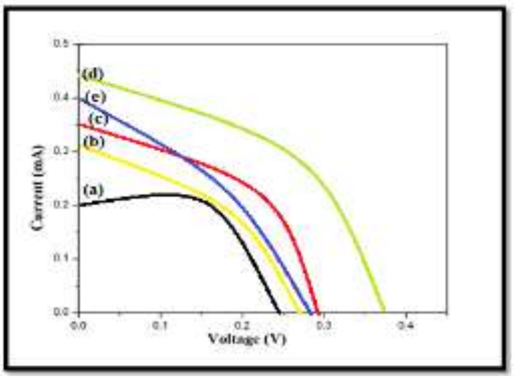
$$\eta = J_{sc}V_{oc}FF / P_{in}\ x\ 100 \qquad (2)$$

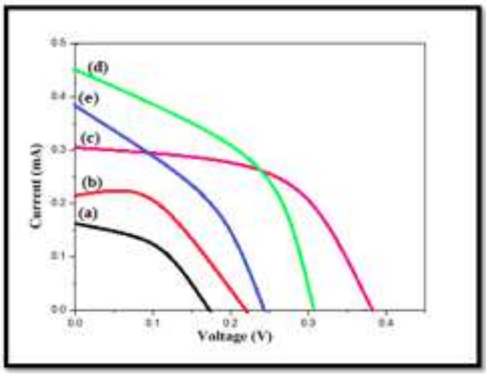
where I_{max} and V_{max} denotes the maximum output value of current and voltage respectively and $I_{sc}$is the short circuit current density. The performance of JG extract as dye sensitizer are evaluated by determining the open circuit current, short circuit current, Fill Factor and conversion efficiency under the irradiance of 100 W/cm^2 [11].



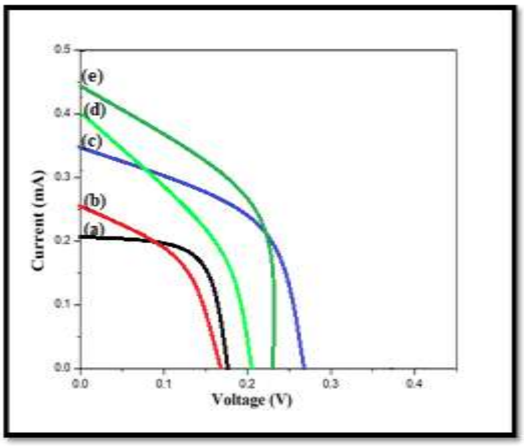


(a) **(b)**





(c) **(d)**



(e)

Figure 7.4 Current density Voltage (I-V) curves of (a) GO/Y_2O_3 (5:1) with JG (b) GO/Y_2O_3 (5:2) With JG (c) GO/Y_2O_3 (5:3) with JG (d) GO/Y_2O_3 (5:4) with JG and (e) GO/Y_2O_3 (5:5) with JG

Figure 7.4 (a-e) shows that the GO/ Y_2O_3 (5:4) nanocomposites counter electrode with JG sensitizer archive the better efficiency than the other concentrations, it may due to the concentrations of Yttrium oxide nanoparticles on the Graphene oxide nanosheets. The prepared GO/Y_2O_3 nanocomposites as a counter electrode, with platinum free DSSCs and with sensitizer as a natural dye achieve high efficiency of 2.8%.

Table7.1 Photovoltaic parameters of the GO/Y_2O_3 (5:1 to 5:5) nanocomposites counter electrode and SP as a sensitizer for DSSCs

Dye	**Counter Electrode (concentration) GO/Y_2O_3**	**V_{oc}(mV)**	**I_{sc} (mA)**	**Fill Factor (%)**	**Efficiency (%)**
SP	5:1	0.2	0.3	28 %	1.23 %
SP	5:2	0.2	0.3	30 %	126 %
SP	5:3	0.31	0.31	31 %	1.28 %
SP	**5:4**	**0.3**	**032**	**32 %**	**1.3 %**
SP	5:5	0.3	0.32	31 %	1.2 %

Table 7.2 Photovoltaic parameters of the GO/Y_2O_3 (5:1 to 5:5) nanocomposites counter electrode and ST as a sensitizer for DSSCs

Dye	**Counter Electrode (concentration) GO/Y_2O_3**	**V_{oc}(mV)**	**I_{sc} (mA)**	**Fill Factor (%)**	**Efficiency (%)**
ST	5:1	0.2	0.26	32%	0.79%
ST	5:2	0.3	0.28	35%	0.83%
ST	5:3	0.3	0.3	37%	0.86%
ST	**5:4**	**0.3**	**0.3**	**39%**	**0.9%**
ST	5:5	0.2	0.3	36%	0.81%

Table 7.3 Photovoltaic parameters of the GO/Y_2O_3 (5:1 to 5:5) nanocomposites counter electrode and AH as a sensitizer for DSSCs

Dye	Counter Electrode (concentration) GO/Y_2O_3	V_{oc}(mV)	I_{sc} (mA)	Fill Factor (%)	Efficiency (%)
AH	5:1	0.39	0.33	39%	1.7%
AH	5:2	0.4	0.34	40%	1.73%
AH	**5:3**	**0.4**	**0.36**	**41%**	**1.75%**
AH	5:4	0.4	0.35	40%	1.7%
AH	5:5	0.36	0.35	38%	1.65%

Table 7.4 Photovoltaic parameters of the GO/Y_2O_3 (5:1 to 5:5) nanocomposites counter electrode and GP as a sensitizer for DSSCs

Dye	Counter Electrode (concentration) GO/Y_2O_3	V_{oc}(mV)	I_{sc} (mA)	Fill Factor (%)	Efficiency (%)
GP	5:1	0.35	0.37	42%	2%
GP	5:2	0.36	0.38	43%	2.7%
GP	5:3	0.38	0.4	45%	2.75%
GP	**5:4**	**0.4**	**0.4**	**46%**	**2.76%**
GP	5:5	0.36	0.4	45%	2.7%

Table 7.5 Photovoltaic parameters of the GO/Y_2O_3 (5:1 to 5:5) nanocomposites counter electrode and JG as a sensitizer for DSSCs

Dye	Counter Electrode (concentration) GO/Y_2O_3	V_{oc}(mV)	I_{sc} (mA)	Fill Factor (%)	Efficiency (%)
JG	5:1	0.4	0.4	36%	2.3%
JG	5:2	0.4	0.43	38%	2.5%
JG	5:3	0.45	0.45	41%	2.6%
JG	**5:4**	**0.45**	**0.46**	**43%**	**2.8%**
JG	5:5	0.44	0.44	42%	2.7%

Table (7.1-7.2) shows that the GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites works as a counter electrode with SP, ST, AH, GP and JG dye extracts act as a sensitizer for DSSCs. From Table (7.1), the GO/Y_2O_3 (5:4) nanocomposites with SP sensitizer achieve 1.3% efficiency than the other concentration. From Table 7.2, the GO/Y_2O_3 (5:4) concentration nanocomposites with ST sensitizer achieve 0.9% and from Table 7.3 the nanocomposites GO/Y_2O_3 (5:3) concentration achieve 1.75% efficiency. From Table (7.4 and 7.5), GO/Y_2O_3 (5:4) concentration nanocomposites achieve 2.76% and 2.8% efficiency respectively. It is evident from the Table (7.1 – 7.5) that the GO/Y_2O_3 (5:4) nanocomposites as a counter electrode with JG sensitizer achieve better efficiency than other dyes. JG dye extract achieve the best absorption range and band gap [12,13]. The results showed that the JG dye have higher intensities and wide range of light absorption with GO/Y_2O_3 (5:4) concentration as evident from optical studies and better charge transfer of GO/Y_2O_3 (5:4) with JG dye. Hence JG sensitizer shows higher efficiency compared with SP, ST, AH and GP dyes [14].

7.4 CONCLUSION

This chapter describes the preparation of natural dyes and fabrication of DSSCs. The UV-Vis studies showed that the prepared GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites absorption peak about 250 nm and 408 nm, 257 nm and 411 nm, 260 nm and 416 nm, 262 nm and 419 nm, 268 nm and 421 nm respectively. The energy gap of GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites are around 4.5 eV, 4.3 eV, 3.9 eV, 3.7eV, 3.5eV respectively. The EIS results revealed that the GO/Y_2O_3 (5:4) with JG dye sensitizer achieves the largest semicircle in the highest region. I-V characteristics showed that the photovoltaic efficiency of GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites Pt free counter electrode with SP, ST, AH, GP and JG as a sensitizer for DSSCs and the best efficiency is found to be 1.3%, 0.9%, 1.75%, 2.76% and 2.8% respectively. GO/Y_2O_3 (5:4) nanocomposites as a counter electrode with JG extract as a sensitizer for DSSCs achieve better efficiency than the other sensitizers and it may be due to the JG dye have large absorption range when compared to other dyes.

REFERENCES

1. S. Ebrahim, M. Soliman, M. Anas, M. Hafez, and T. M. Abdel-Fattah, International Journal of Photoenergy , 1 (2013).

2. B.-X. Lei, W.-J. Fang, Y.-F. Hou, J.-Y. Liao, D.-B. Kuang, and C.-Y. Su, Journal of Photochemistry and Photobiology A: Chemistry 216, 8 (2010).

3. W. Wei and Y. H. Hu, International Journal of Energy Research 39, 842 (2015). [126] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, and M. Gratzel, Nature 395, 583 (1998). [127]

4. E. Chatzivasiloglou, T. Stergiopoulos, N. Spyrellis, and P. Falaras, Journal of Materials Processing Technology 161, 234 (2005), 3rd Japenese-Mediterranean Workshop on Applied Electromagnetic Engineering for Magnetic and Superconducting Materials and 3rd Workshop on Superconducting Flywheels.

5. B. Li, L. Wang, B. Kang, P. Wang, and Y. Qiu, Solar Energy Materials and Solar Cells 90, 549 (2006).

6. Y. Duan, Q. Tang, Y. Chen, Z. Zhao, Y. Lv, M. Hou, P. Yang, B. He, and L. Yu, J. Mater. Chem. A 3, 5368 (2015).

7. J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Huang, P. Li, S. Yin, and T. Sato, Journal of the American Chemical Society 130, 11568 (2008), pMID: 18693733, https://doi.org/10.1021/ja802158q .

8. A. Magomedov, S. Paek, P. Gratia, E. Kasparavicius, M. Daskeviciene, E. Kamarauskas, A. Gruodis, V. Jankauskas, K. Kantminiene, K. T. Cho, K. Rakstys, T. Malinauskas, V. Getautis, and M. K. Nazeeruddin, Advanced Functional Materials 28, 1704351 (2018), https://onlinelibrary.wiley.com/doi/pdf/10.1002/adfm.201704351 .

9. G. Wang, S. Zhuo, and Y. Lin, Journal of Applied Polymer Science 127, 2574 (2013), https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.37933 . 209 210

10. H. Wang, J. Li, F. Gong, G. Zhou, and Z.-S. Wang, Journal of the American Chemical Society 135, 12627 (2013), pMID: 23909762, https://doi.org/10.1021/ja401827w .

11. X. Xu, H. Wang, F. Gong, G. Zhou, and Z.-S. Wang, ACS Applied Materials & Interfaces 5, 3219 (2013), pMID: 23506533, https://doi.org/10.1021 /am4002293 .

12. K. Ha Kim, J. Hoon Moon, E. Yi Kim, H. Jin Kim, S. Hee Jang, and W. Lee, Journal of Materials Chemistry 22, 11179 (2012).

13. Y.-C. Shih, C.-W. Yeh, and K.-F. Lin, Materials Chemistry and Physics 171, 352 (2016).

14. J.-A. He, R. Mosurkal, L. A. Samuelson, L. Li, and J. Kumar, Langmuir 19, 2169 (2002).