

CHAPTER II

PREPARATION AND CHARACTERIZATION OF GRAPHENE OXIDE NANOSHEETS

2.1 INTRODUCTION

Dye sensitized solar cells (DSSCs), the third generation solar cell technology, has been widely investigated in view of its easy of fabrication, low cost and eco-friendly nature providing promising photovoltaic efficiency. A DSSCs is typically composed of a dye coated crystalline semiconductor coated on a transparent conductive oxide, an electrolyte and a counter electrode. Recently researchers have adopted several approaches to enhance the performance of DSSC via introducing novel techniques for highly efficient photo anodes, counter electrode and electrolytes respectively. Counter electrode plays a key role in the overall power conversion efficiency of the devices as it serves as the main electron collecting repository from the external circuit as well as to reduce back the electrolyte that leads to the regeneration of the oxidized dye. Most commonly employed material on counter electrode in DSSC is platinum due to its excellent thermal and electrical properties with considerably low charge transfer resistance. However, the high cost associated with Pt is hardly towards commercialization for large scale production. Hence, an alternative electrode material with ample efficiency is inevitable to replace Pt based DSSC [1].

Graphene oxides have been explored in various fields of modern nanomaterial technology due to its properties differ from graphite which in turn has important applications in several fields such as sensors, photovoltaics, energy storage and electronics. Graphene is a high density two dimensional material that has strong transparency. There are many hydroxyl group with good hydrophilicity on its surface [2].

The main disadvantages of dye sensitized solar cell employing inorganic Ruthenium based sensitizer include purification difficulty, cost effectiveness and limitation on tailoring the absorption band of sensitizer in the solar spectrum. Therefore, introducing organic sensitizer has become a good competitor because of it

low cost purification process as well as the flexibility to tailor the absorption band in the solar spectrum [3]. Hence natural dyes such as Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) dyes extracts are used as a sensitizer for DSSCs, a natural dye never reported before and it is the novelty of the present work. This natural dye extract contains namely chlorophyll, betanins, anthocyanins and carotenoids. These dyes exhibit wide ecological range and found extensively all over India. The present work demonstrates the performance of GO (Pt free) based Counter electrode with SP/ST/AH/GP/JG extracts as a dye sensitizer for DSSCs [4].

2.2 MATERIALS AND METHODS

2.2.1 Materials

Graphite flakes, sulphuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) are purchased from Sigma Aldrich and are used without further purification.

2.2.2 Synthesis of Graphene Oxide Nanosheet

Graphene oxide is synthesized by a modified Hummers' method. Typically, 10 grams of graphite flakes are dispersed in pure H_2SO_4 by vigorous stirring for 1 hr. After complete dispersion, 25 grams of $KMnO_4$ is added slowly so that temperature must not increase above $10^\circ C$ in an ice bath. The temperature of the solution is raised to $35^\circ C$, to start the reaction and kept under the same condition for 8 hrs. This makes the complete oxidation of graphite, and solution colour is changed to dark brown. The deionized water is added to this solution dropwise, along with the addition of H_2O_2 (5 ml), which changes the colour of the solution to bright yellow. Finally the reaction suspension is centrifuged with concentrated HCL followed by distilled water and dried under vacuum for 12 hours at $60^\circ C$ [5].

2.2.3 Natural Dyes preparation

Fresh Solanum Procumbens (SP), leaves are used for the extraction of constituents. 10 g of Solanum Procumbens (SP) are mixed with 10 ml distilled water and 10 ml ethanol, then kept at $45^\circ C$ for 1 hour before being left at ambient

temperature for 24 hours. The extract is filtered and employed in dye-sensitized solar cells as a sensitizer. Similar procedures are being used for the synthesis of natural dyes from *Solanum Torvum* (ST), *Artabotrys Hexapetalus* (AH), *Galinsoga Parviflora* (GP) and *Jasminum Grandiflorum L* (JG) leaves [6].

2.2.4 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. 0.5 g of TiO_2 , 3 ml of ethanol, 1 g of acetic acid, 10 CP ethyl cellulose and 1.4 g α -Terpineol are stirred at 40°C for 48 hrs to get a sticky paste. The TiO_2 paste is coated on the cleaned FTO glass plate by doctor blade method and annealed at 450°C and the active area of the electrode is 0.2 cm. The prepared photoanode are soaked in the dyes extract (*Solanum Procumens* (SP), *Solanum Torvum* (ST), *Artabotrys Hexapetalus* (AH), *Galinsoga Parviflora* (GP) and *Jasminum Grandiflorum L* (JG)) for 24 hrs. The prepared nanosheets(GO) are coated on FTO glass plate by doctor blade method and annealed at 150°C , that act as a counter electrode for DSSCs. The ionic electrolytes (lithium iodide, iodine, acetonitrile, 2-dimethyl-3-propylimidazolium iodide) are injected between the sandwiches and are allowed to dry at room temperature respectively [7].

2.2.5 Characterisation Techniques

The crystalline structure of the prepared GO nanosheets is characterized using X'PERT³ Panalytical Diffractometer. The FT-IR spectrum is recorded for the presence of the nanosheet using Shimadzu IR affinity-1. Raman spectra are recorded at ambient temperature on a Nano Tech 1 (QEB0120) model. The morphology and microstructure of the sample are studied using field emission scanning electron microscopy (FESEM) using ZEISS-SIGMA and high resolution transmission electron microscopy (HR-TEM) using Jeol JEM 2100. The elemental composition is tested using Energy Dispersive X-ray Spectroscopy (EDX). A UV-Vis spectrometer is used to measure UV-Vis absorption at room temperature (Cary 60 UV-Vis).

2.3. RESULTS AND DISCUSSION

2.3.1 XRD, FTIR and Raman analysis of GO nanosheet

The structure and crystalline nature of the synthesized Graphene oxide nanosheet are characterized by using X-Ray diffraction (XRD). Figure 2.1 shows that the XRD pattern of synthesized GO nanosheets. The diffraction spectrum is recorded in the 2θ range of 5- 70 and Figure 2.1 confirms the formation of prepared GO nanosheet by the presence of a peak at 11.08° corresponds to the (022) and there is no peak observed at 23.83° , which indicates that there is no reduction of GO to rGO. The small additional peak at 43° corresponds to the (001) plane and is due to the incomplete oxidation of Graphite. The inter layer distance of GO is 7.60 (Å) for the corresponding peak at 11.08° that represents the plane (002) [8].

Fourier Transform Infrared (FTIR) analysis is performed to investigate the bonding interaction in GO nanosheets. FT-IR spectrum of the prepared nanosheets of GO is shown in the Figure 2.1 (b). It is observed from the Figure 2.1 (b), for the spectrum of GO that the bands appeared at 3670 cm^{-1} and 1740 cm^{-1} corresponds to O-H stretching and bending vibrations respectively [9]. The bands observed at 1421 cm^{-1} , 1220 cm^{-1} and 1012 cm^{-1} are due to O-H deformation, C-O of epoxy and C-O alkoxy vibration of Graphene oxide nanosheets respectively. The FTIR spectral analysis confirms the presence of Graphene oxide nanosheets.

Raman spectroscopy has widely been used to investigate the bonding properties of various carbon compounds. As shown in the Figure 2.1 c Raman analysis on the GO are used to further investigate the nature of sp^2 domains. Graphene oxide exhibit a characteristic D band at 1345 cm^{-1} and are assigned to the E_{2g} phonon mode of sp^2 hybridized carbon atom and a G band at 1574 cm^{-1} are assigned to the vibration of carbon atom with hanging bonds at the plane ends of disordered graphene, mostly at the edges which confirms the formation of Graphene oxide nanosheets. Therefore, these Raman spectroscopy measurements indicates that the in-plane sp^2 domain of graphene oxide nanosheets [10].

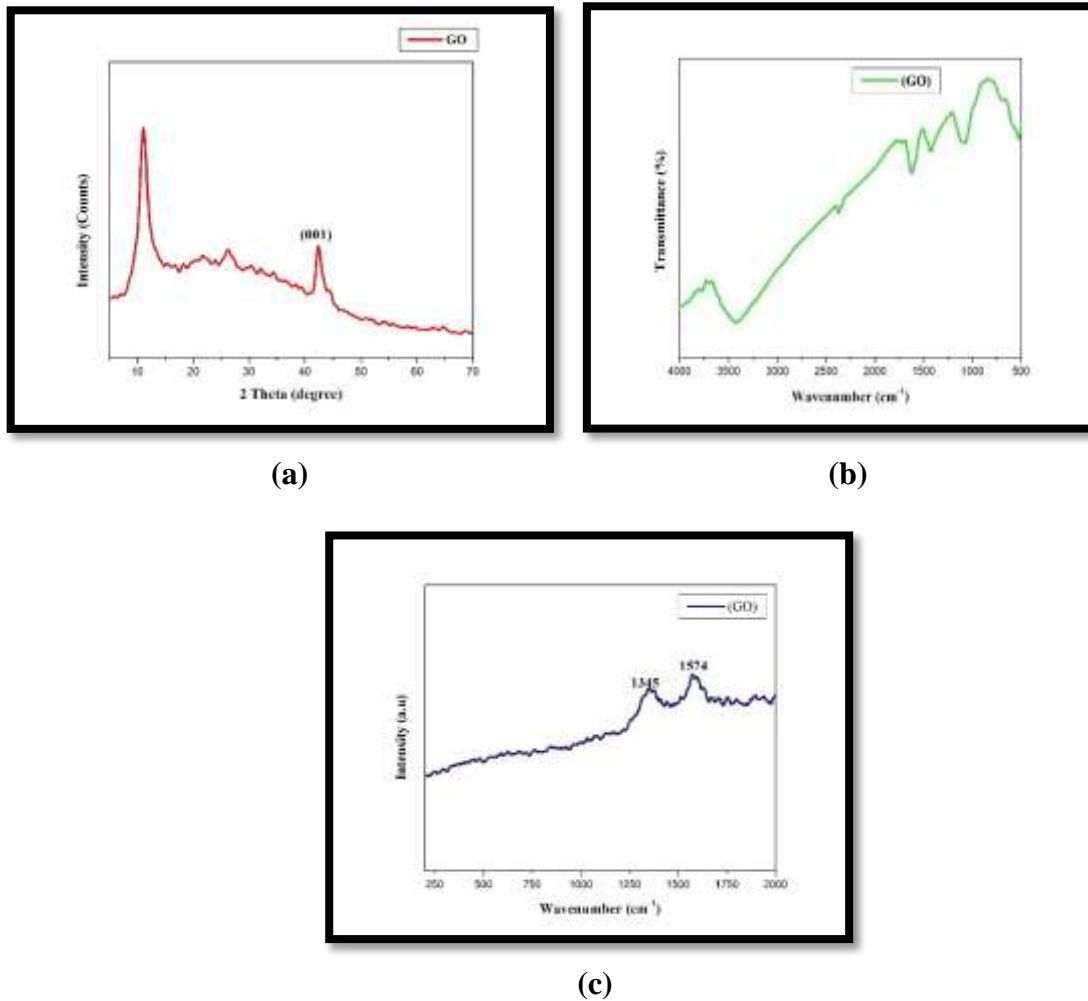


Figure 2.1 (a) XRD (b) FTIR and (c) Raman analysis of GO nanosheet

2.3.2 FESEM, HRTEM and EDX analysis of GO Nanosheet

Field Emission Scanning Electron Microscope (FESEM) analysis is performed to study the surface morphology and the shape of prepared Graphene oxide. Figure 2.2(a) shows the FESEM images of the prepared GO. It is observed from the Figure 2.2(a) that the prepared graphene oxide appeared as a sheet like structure. Due to its unique sheet-like structure, graphene oxide is the ultimate material for composites with metal oxides. This nanosheet will improve charge transfer and enhance the photovoltaic activity [11].

High Resolution Transmission Electron microscopy (HR-TEM) is a microscopic technique used for morphological analysis. The morphology and structure of the prepared GO nanosheet were confirmed by HR-TEM analysis. Figure 2.2 (b) clearly shows that the prepared Graphene oxide has sheet-like

structure and this GO nanosheet are very thin and transparent and it is easily noticed that the folding of GO nanosheet occurred at the edges. This HR-TEM analysis confirmed the formation of GO nanosheet which is also evident from FESEM analysis. The Selected area electron diffraction (SAED) analysis further confirmed that the nature of prepared GO nanosheet [12]. The SAED pattern of the prepared GO is shown in the Figure 2.2 (c). It is observed from the Figure 2.2 (c) that there are two bright rings that indicate the successful formation of graphene oxide nanosheet and each ring corresponds to the (002) and (001) planes, which could also be evident from XRD analysis.

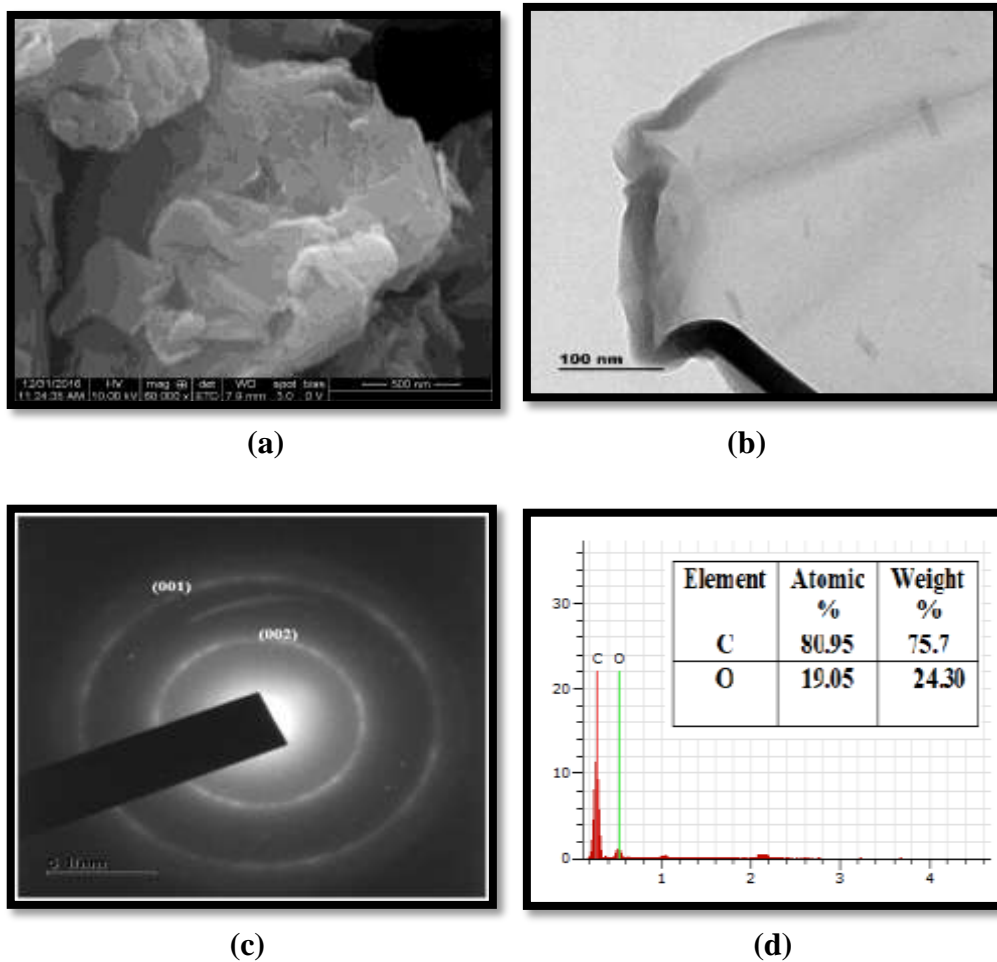
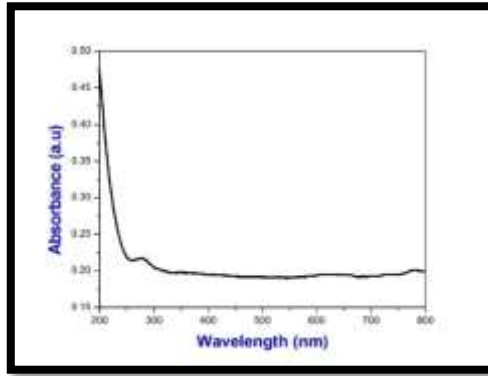


Figure 2.2 (a) FESEM, (b) HRTEM (c) SAED and (d) EDX analysis of GO nanosheet

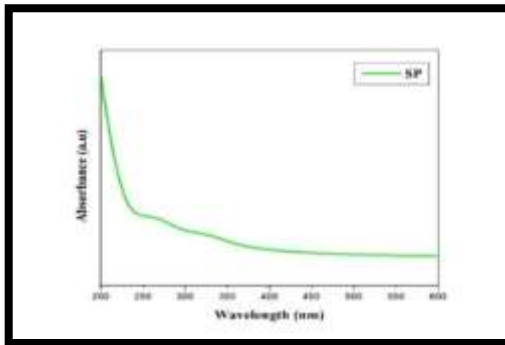
EDX analysis is used to identify the elemental presence in the prepared nanocomposites. Figure 2.2 (d) represents the EDX spectrum of GO nanosheet. Figure 2.2 (d) shows the presence of C and O that confirms the formation of graphene oxide and its atomic and weight percentage are given as inset table. From EDX analysis, the atomic % of GO is found to be 80.98 % and 19.05 % for C and O respectively. EDX analysis further confirms that the prepared GO nanosheet is formed without any impurities [13].

2.3.3 UV- Vis Spectral Analysis

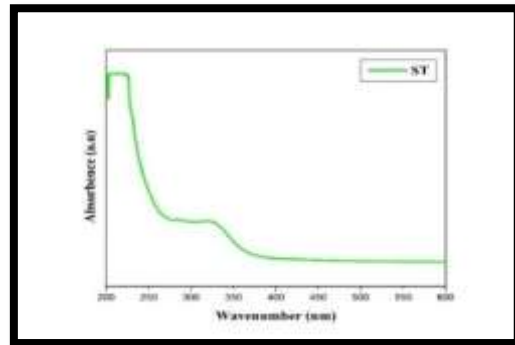
The optical properties of the pure GO nanosheet, Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) dyes are examined by UV-Vis Spectrophotometer within the range of 200 nm - 600 nm and are as shown in the Figure 2.3 (a-f). Figure 2.3 (a) shows the pure Graphene oxide nanoparticles exhibits an absorption peak at 278 nm and is due to the π - π^* transitions of aromatic ring. Figure 2.3 (b-f) shows the UV-Vis absorption spectrum of Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) dyes are at 260 nm, 270 nm, 220 nm, 288 nm and 339 nm respectively [14]. The large absorption of natural dyes makes the electron transport from dyes to the conduction band of the anode material possible, enhancing the efficiency of the solar cell.



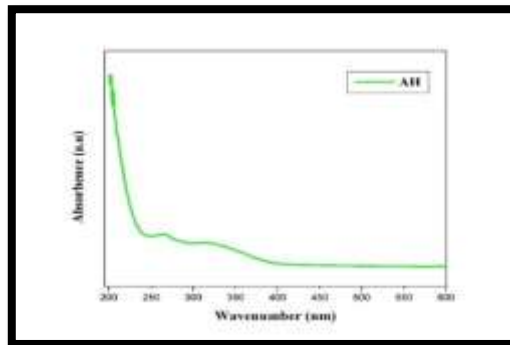
(a)



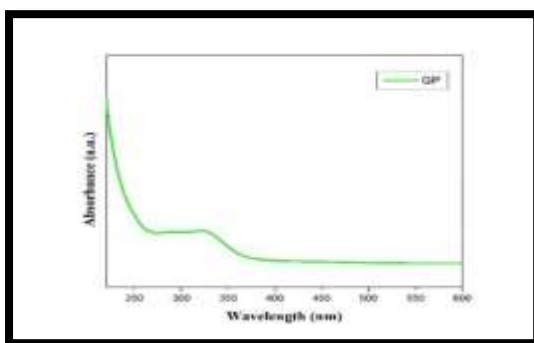
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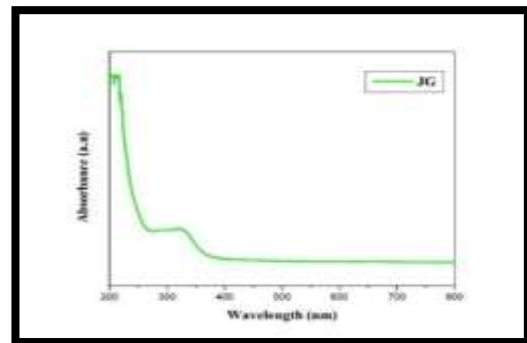
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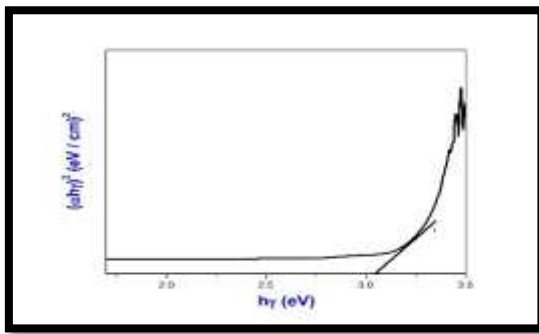


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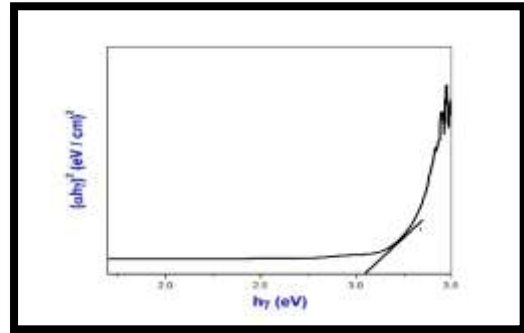


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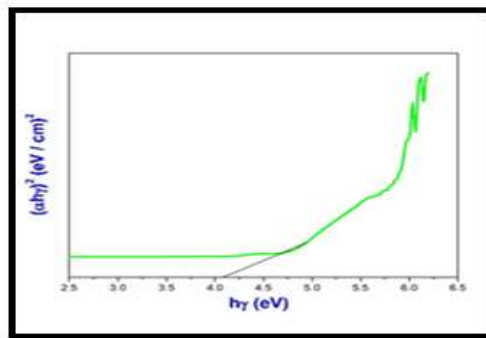
Figure 2.3 (a-f) UV-Vis spectral analysis of (a) GO dye (b) Solanum Procumbens (SP), (c) Solanum Torvum (ST) (d) Artabotrys Hexapetalus (AH) (e) Galinsoga Parviflora (GP) (f) Jasminum Grandiflorum L (JG)



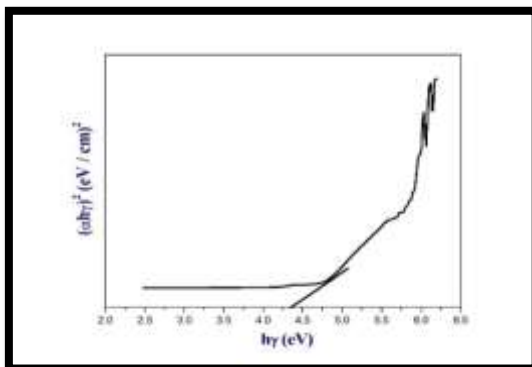
(a)



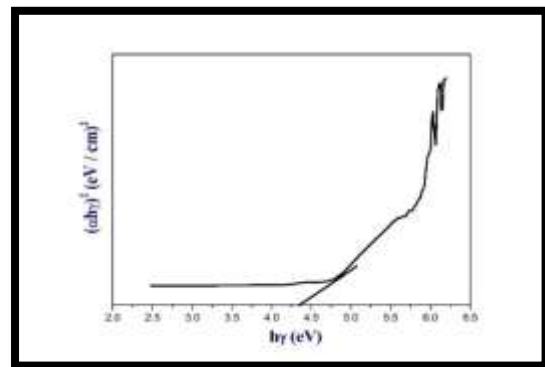
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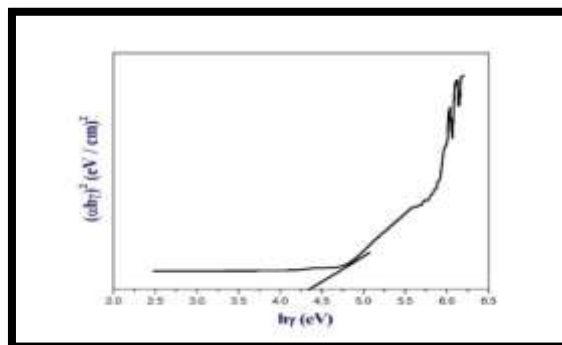
(c)



(d)



(e)



(f)

Figure 2.4 Band gap energy of (a) GO (b) Solanum Procumbens (SP), (c) Solanum Torvum (ST) (d) Artabotrys Hexapetalus (AH) (e) Galinsoga Parviflora (GP) (f) Jasminum Grandiflorum L (JG)

The band gap energies for GO, Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG)dyes are found to be 3.2eV, 4.6 eV, 4.4 eV, 4.3 eV, 4.1 eV and 4.2 eV respectively. These SP, ST, AH, GP and JG dyes contains the anthocyanin molecules which can be easily bound with the surface of GO nanosheet due to the presence of carbonyl and polyphenols groups and this might be a reason for enhancing the efficiency of GO based Pt free counter electrode DSSCs [15].

2.4. Conclusion

In this chapter, Graphene nanosheet are prepared by the modified Hummers' method. XRD, FE-SEM and HR-TEM analysis revealed that the GO nanosheet are successfully prepared. The elemental analysis confirmed the Graphene oxide is prepared without any impurities. The UV-Vis studies showed that the prepared dyes Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) belong to chlorophyll group with absorption peak 272 nm, 260 nm, 270 nm, 220 nm, 288 nm and 339 nm respectively. The energy band gap of GO, SP, ST, AH, GP and JG is 3.2 eV, 4.6 eV, 4.4 eV, 4.3 eV, 4.1 eV and 4.2 eV respectively. This chapter confirms the preparation of GO nanosheet as counter electrode and the low cost and environmental friendliness of these dyes make them attractive for their use as a sensitizer in Dye sensitized solar cells. Hence environmental friendly DSSCs can be fabricated using natural dyes which is a cheaper and more durable alternative for the platinum counter electrode.

REFERENCES

1. G. Boschloo and A. Hagfeldt, *Accounts of Chemical Research* 42, 1819 (2009), pMID: 19845388, <https://doi.org/10.1021/ar900138m> .
2. K. Zhu, N. Kopidakis, N. R. Neale, J. van de Lagemaat, , and A. J. Frank, *The Journal of Physical Chemistry B* 110, 25174 (2006).
3. R. M. M., S. A. E., L.-C. Mónica, and A.-M. M. S. A., *Applied Nanoscience* 3, 167 (2013).
4. A. Subramanian, C.-Y. Ho, and H. Wang, *Journal of Alloys and Compounds* 572, 11 (2013).
5. S. M. Sawanta, J. V. Patil, P. M. Kadam, H. P. Deshamukh, S. C. Su, S. P. Pramod, and H. C. Kook, *Journal of Nanoparticle Research* 16, 2406 (2014).
6. H. Wenchao, Z. X. Li, H. Fuzhi, Z. Zhipan, H. Jiangjing, and C. Yi-Bing, *Journal of Nanoparticle Research* 14, 838 (2012).
7. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, and M. Gratzel, *Nature materials* 2, 402 (2003).
8. B. O'Regan and D. T. Schwartz, *Chemistry of Materials* 7, 1349 (1995), <https://doi.org/10.1021/cm00055a012> .
9. J. KIM, M. J. Chu, and J. M. Kim, "Electrolyte for dye-sensitized solar cell and dye-sensitized solar cell including the same," (2015).
10. J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, and G. Luo, *Chemical Reviews* 115, 2136 (2015). [36] C. Lie-Hang, X. Bo-Fei, L. Xi-Zhe, L. Ke-Xin, L. Yan-Hong, M. Qing-Bo, W. Rui-Lin, and C. LiQuan, *Chinese Physics Letters* 24, 555 (2007). 204 205
11. Z. Yu, N. Vlachopoulos, M. Gorlov, and L. Kloo, *Dalton Trans.* 40, 10289 (2011)
12. M. Gorlov and L. Kloo, *Dalton Trans.* , 2655 (2008).

13. V. Gondane and P. Bhargava, *RSC Advances* 6, 37167 (2016).
14. Z. Fei, V. M. Manzanares, and P. J. Dyson, *CHIMIA International Journal for Chemistry* 71, 762 (2017).
15. N. Arora, M. I. Dar, A. Hinderhofer, N. Pellet, F. Schreiber, S. M. Zakeeruddin, and M. Grätzel, *Science* 358, 768 (2017), <http://science.sciencemag.org/content/358/6364/768.full.pdf> .