CHAPTER VIII

PLATINUM FREE GRAPHENE OXIDE/SnO_2 NANOCOMPOSITES AS A COUNTER ELECTRODE FOR NATURAL DYES (SOLANUM PROCUMENS (SP), SOLANUM TORVUM (ST), ARTABOTRYS HEXAPETALUS (AH), GALINSOGA PARVIFLORA (GP), AND JASMINUM GRANDIFLORUM L (JG) AS A SENSITIZER FOR SOLAR CELL APPLICATIONS

8.1. INTRODUCTION

Dye sensitized Solar cells (DSSCs) have drawn wide attention owing to their low cost, simple fabrication and high power conversion efficiency. The counter electrode in a conventional DSSC device is critical for transporting electrons to triiodide via an external circuit and catalyzing the redox pair. In DSSCs, Pt (platinum) is the most extensively researched counter electrodes, howeveris limited by its expensive cost and lack of stability.

Graphene oxide (GO) has emerged as one of the most promising counter electrode candidate materials. As SnO_2 nanoparticles have high electron transport compared to other metal oxides, these composite counter electrode improves the cell's stability and provides good conversion efficiency for DSSCs. SnO_2 can also bond to the graphene surface to increase the mechanical stability of the graphene sheet, thereby potentially improving the photovoltaic performance of graphehe-based DSSCs. The SnO_2nanoparticles can substantially increase the graphene catalytic activity for I_3^- reduction, reduce charge transfer resistance, and hence improve solar cell efficiency [1].

The sensitizer, which is used to capture electrons under the source of photon energy, is another crucial component of the DSSC. The two main types of sensitizers are metal complex dyes and organic dyes. Ruthenium dyes are based on metal complexes, but they are rare due to their hazardous nature, and they are also more expensive due to their synthetic origins. Organic dyes, on the other hand, have narrow absorption spectra, a high extinction coefficient, and a shorter exited state lifespan [2]. As compared to synthetic dyes, natural dyes are simple, inexpensive, and environmentally beneficial which may be easily extracted and utilized as sensitizers. Since there is such a wide variety of organic dyes available in nature and also they serve to reduce the overall cost of DSSC production while also being environmentally benign. Natural dye extracts from Solanum Procumbens (SP), Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) are employed as a sensitizer for DSSCs. Hence anode film is socked into the dye solutions and the dye forms the monomolecular layer due to its functional groups. This layer provides maximum feasibility of relaxation of the exited dye molecules and they are diffused into the anode conduction band by electron injection [3].

In this chapter, GO/ SnO_2 (51, 5:2, 5:3, 5:4 and 5:5) nanocomposites as a counter electrode is prepared with SP, ST, AH, GP and JG extracts as asensitizer in DSSCs.

8. 2. MATERIALS AND EXPERIMENTS

8.2.1 Natural Dye 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°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 Solanum Torvum (ST), Artabotrys Hexapetalus (AH), Galinsoga Parviflora (GP) and Jasminum Grandiflorum L (JG) leaves for the synthesis of natural dyes.

8.2.2 Preparation of DSSCs

The fluorine doped Tin oxide glass substrates are cleaned in distilled water, ethanol and acetone for approximately 10min each in an ultrasonic cleaner.0.5 of TiO_2,3ml of ethanol,1g of acetic acid,10CP ethyl cellulose and 1.4g of α-Terpineol stirred at 60º C for 48 hours to get a sticky paste. TiO_2 paste is coated on the cleaned FTO glass plate by doctor blade method and annealed at 450º C and the active area of the electrode is 0.2cm. The prepared photo anode is soaked in the dye extract (AH) for 24hours. The prepared nanocomposites GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) are coated on FTO glass plate by doctor blade method and annealed at 150º C, act as a CE. The ionic electrolytes (lithium iodine, iodine, acetonitrile and 2- dimelhyl –

3propyl imidazolium iodide) are injected between the sandwiches and are allowed to dry at room temperature [3].

8.2.3 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.

8.3 RESULTS AND DISCUSSION

8.3.1 UV- Vis analysis

The optical properties of the prepared nanocomposites GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) are examined by UV-Vis spectroscopy with the range of 200 nm to 600 nm and are shown in Figure 8.1. The pure graphene oxide nanoparticles exhibited an absorption peak at 278 nm as discussed in chapter II (Figure 2.3 (a)) and it is due to the $\pi - \pi *$ transition of aromatic ring. Figure 8.1 shows that the absorption peaks of GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites are found at 274 nm, 278 nm, 282 nm, 290 nm and 302 nm respectively. It is observed that the peaks are shifted to higher wavelengths, corresponding to the red shift indicates a gradual increase in the SnO_2 nanoparticles concentration on the surface of graphene oxide nanosheet as evident from EDX analysis as discussed in chapter V (Figure 5.1) and might also be due to the increase in the crystallite size of the nanocomposites as the concentration on SnO_2 increases as evident from XRD analysis discussed in chapter V (Figure 5.1) [4,5].

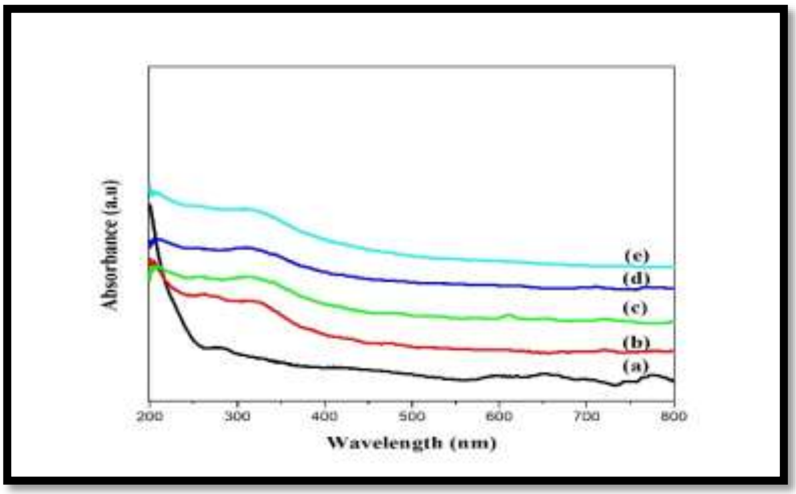


Figure 8.1 UV- Vis spectral analysis of GO/SnO_2 (a) 5:1 (b) 5:2 (c)5:3 (d) 5:4 and (e) 5:5 nanocomposite

The band gap GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites is calculated from the Tauc plot and is shown in the Figure 8.2. The band gap energy is determined by using the equation

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

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 [6, 7].

The band gap energy for GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposite is found to be 3.6 eV, 3.9 eV, 4.1 eV, 4.3 eV and 4.4 eV respectively. It is observed from the Figure 8.2 that the band gap increases due to increase in the SnO_2 nanoparticles concentration onto the surface of graphene oxide nanosheet. Since large bandgap materials can achieve more efficiency as it absorbs high frequency radiation. It is evident that SnO_2 nanoparticles of 5:5 nanocomposite yield best efficiency compared to other concentrations.

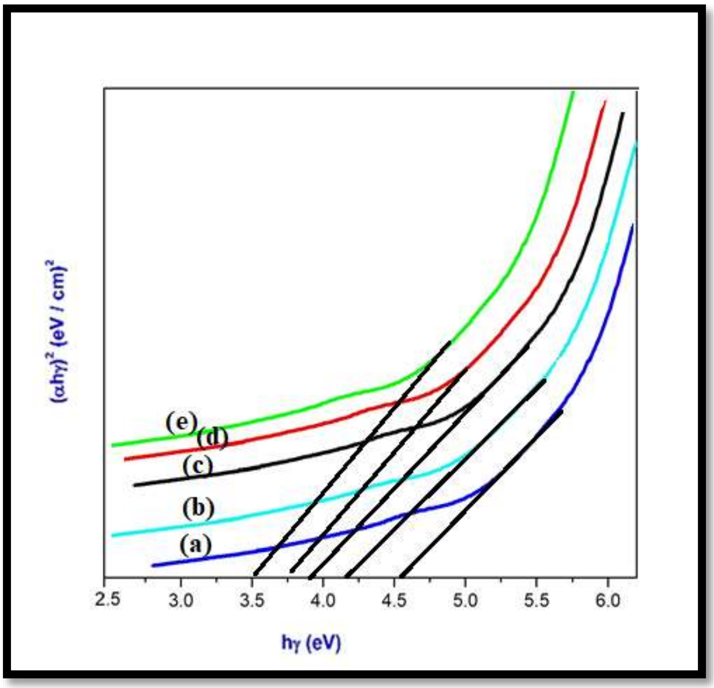


Figure 8.2 Band gap energy of GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) ananocomposites

8.3.2 Electrochemical Impedance Spectroscopy Analysis

The electrochemical impedance spectroscopy (EIS) measurement are performed to understand the electron transport behaviour and internal resistance of DSSCs. EIS analysis is a powerful method to obtain additional information and deeper understanding on the interfacial reaction of photo excited electrons in DSSCs. It is well known that the impedance spectrum of DSSCs exhibit three semicircles. EIS of the prepared nanocomposites GO/SnO_2(5:1, 5:2, 5:3, 5:4 and 5:5) Pt free counter electrode is fabricated at open circuit condition under illumination at 100 W $cm^{-1}$with the simulated irradiation for an active area of 0.2 cm. The Nquist plots of GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites for the dyes SP, ST, AH, GP and JG is shown in the Figure 8.3 (a-e). It is observed from the Figure 8.3(a) that there is no semicircle in the frequency region and in the Figures 8.3(b, c & d) two semicircles have been observed for charge transfer resistance (R_1) and medium frequency resistance (R_2), which indicates huge electron transfer resistance and slow electron recombination occurs between counter electrode and dye. It is also observed in the Figure 8.3(d), in addition to two semicircles, there is an emergence of the third circle in the high frequency region and indicates better charge transfer compared to SP, ST and AH dyes. It is further observed from the Figure 8.3(e) that the GO/SnO_2 (5:5) nanocomposites with JG dye sensitizer achieves largest semicircle in the high frequency region. It is evident that a well-defined semicircle related to the charge transfer resistance between the counter electrode and the redox electrolyte (I^-/I^-_3) in the highest frequency region enhances the free electron mobility. Hence as compared to all other extracted sensitizers SP, ST, AH, and GP based DSSCs, the GO/SnO_2 (5:5) nanocomposites DSSC using JG dye sensitizer has a longer electron lifetime. Further JG possesses high percentage of anthocyanin that has the ability to absorb more light than the other dyes. It is evident that the JG-based DSSC reduces injected electron recombination with I_3^- in the electrolyte more effectively, which might lead to the enhanced photocurrent and device efficiency [8,9,10,11].

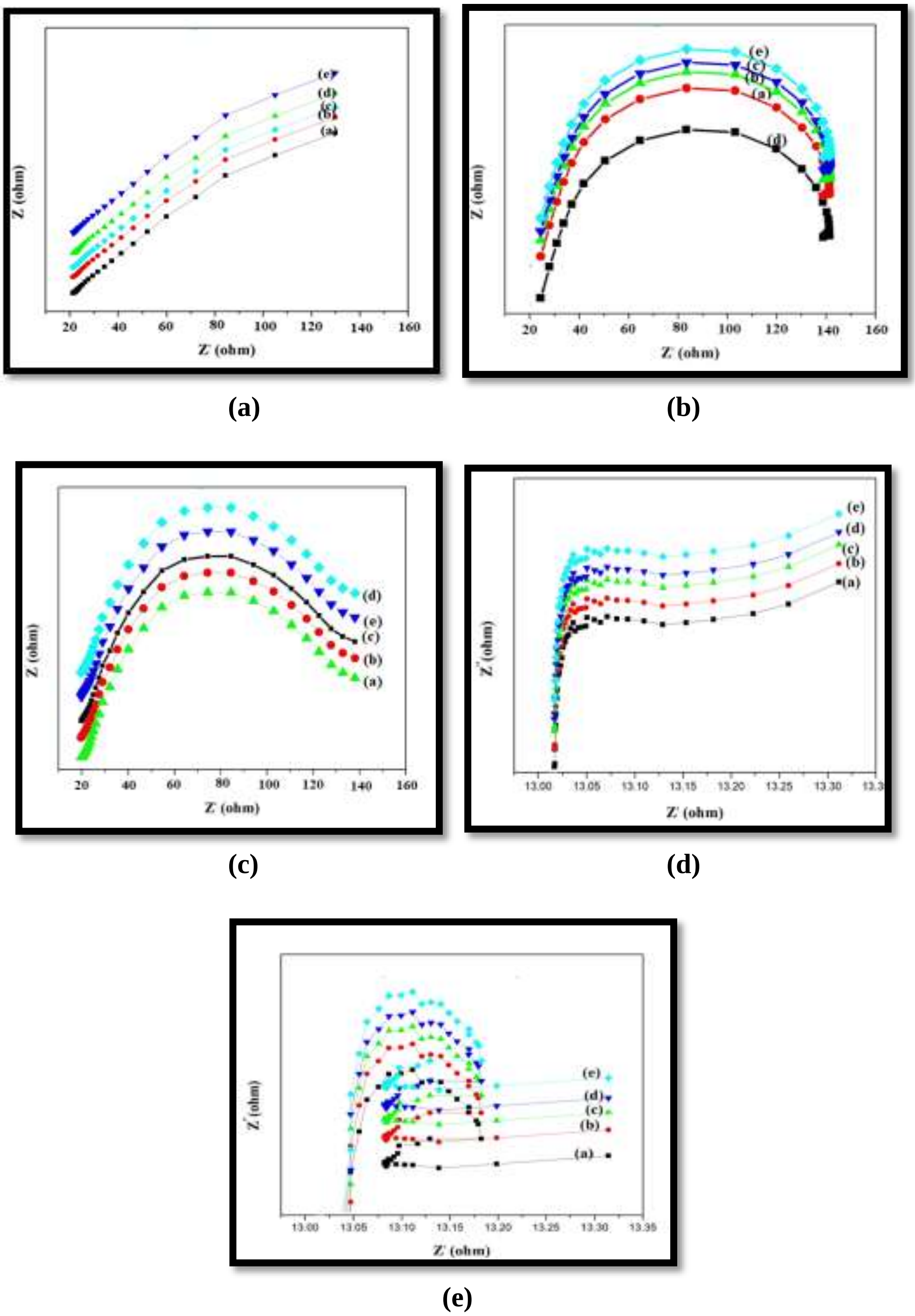


Figure 8.3Electrochemical impedance spectroscopy (EIS) of a (a)GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with SP as a sensitizer (b) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with ST as a sensitizer (c) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with AH as a sensitizer (d)GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with GP as a sensitizer (e) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with JG as a sensitizer

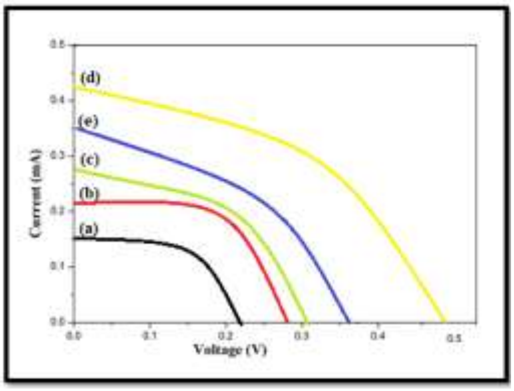
8.3.3 Efficiency Studies

Photovoltaic characterization of the prepared nanocomposites 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 (ɳ) are calculated by using the equations (1) and (2) [12,13].

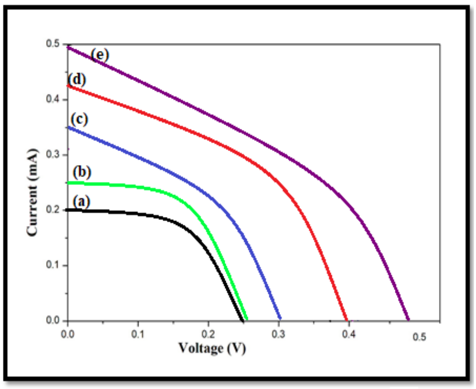
$$FF = (I_{max} \, x V_{max}) / (I_{sc} \text{ x } V_{oc}) \quad (1)$$

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

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. Figure 8.4 (a-e) shows that the photo-current characteristics of DSSCs employing TiO_2 as an anode and GO/SnO_2 (5:1, 5:2, 4:3, 5:4 and 5:5) Pt free counter electrode and SP, ST, AH, GP and JG extract as a dye sensitizer under 100 mW cm^{-1} illumination with active area of 0.2 cm.The conversion efficiency of the prepared Pt free GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with SP, ST, AH, GP and JG dyes sensitized DSSCs are tabulated in (8.1-8.5) [14,15]



(a)



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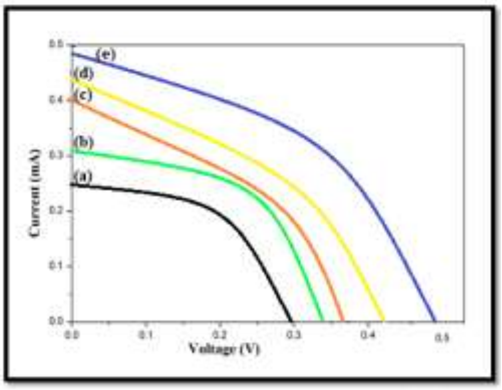

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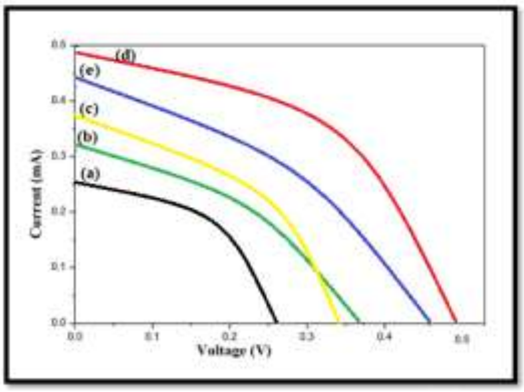
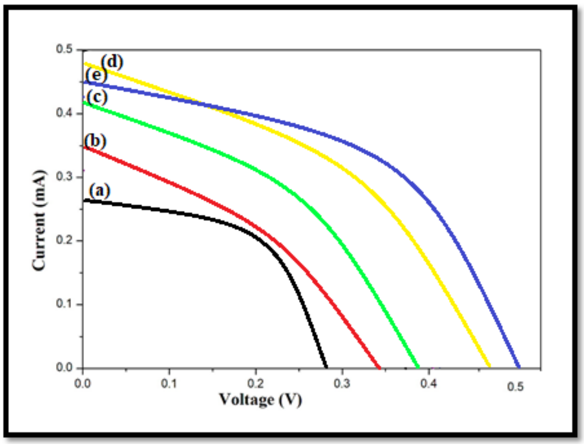


(d)



(e)

Figure 8.4 Current density Voltage (I-V) curves of (a) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with SP as a sensitizer (b) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with ST as a sensitizer (c) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with AH as a sensitizer (d) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with GP as a sensitizer (e) GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) counter electrode with JG as a sensitize

Table 8.1 photovoltaic parameters of the GO/SnO_2 (5:1 to 5:5) nanocomposites counter electrode and SP as a sensitizer for DSSCs

Dye	Counter Electrode (concentration) GO/SnO_2	V_{oc}(mV)	I_{sc}(mA)	Fill Factor (%)	Efficiency (%)
SP	5:1	0.3	0.2	27%	0.64%
SP	5:2	0.3	0.2	29%	0.74%
SP	5:3	0.3	0.3	30%	0.87%
SP	**5:4**	**0.35**	**0.3**	**32.5%**	**0.9%**
SP	5:5	0.3	0.3	31%	0.8%

Table 8.2 photovoltaic parameters of the GO/SnO_2 (5:1 to 5:5) nanocomposites counter electrode and ST as a sensitizer for DSSCs

Dye	Counter Electrode (concentration) GO/SnO_2	V_{oc}(mV)	I_{sc}(mA)	Fill Factor (%)	Efficiency (%)
ST	5:1	0.2	0.2	35%	1.29%
ST	5:2	0.3	0.3	36%	1.3%
ST	5:3	0.3	0.3	38%	1.35%
ST	**5:4**	**0.3**	**0.31**	**39.1%**	**1.4%**
ST	5:5	0.2	0.3	37%	1.37%

Table 8.3 photovoltaic parameters of the GO/SnO_2 (5:1 to 5:5) nanocomposites counter electrode and AH as a sensitizer for DSSCs

Dye	**Counter Electrode (concentration) GO/SnO_2**	**V_{oc}(mV)**	**I_{sc}(mA)**	**Fill Factor (%)**	**Efficiency (%)**
AH	5:1	0.2	0.3	37	1.89
AH	5:2	0.3	0.35	38	2.0
AH	**5:3**	**0.3**	**0.26**	**40**	**2.1**
AH	5:4	0.3	0.35	39	1.9
AH	5:5	0.3	0.3	36	1.8

Table 8.4 photovoltaic parameters of the GO/SnO_2 (5:1 to 5:5) nanocomposites counter electrode and GP as a sensitizer for DSSCs

Dye	**Counter Electrode (concentration) GO/SnO_2**	**V_{oc}(mV)**	**I_{sc}(mA)**	**Fill Factor (%)**	**Efficiency (%)**
GP	5:1	0.2	0.43	35%	1.7%
GP	5:2	0.2	0.36	36%	1.8%
GP	5:3	0.3	0.38	38%	1.9%
GP	5:4	0.3	0.4	40%	2.1%
GP	**5:5**	**0.3**	**0.4**	**41%**	**2.3%**

Table 8.5 photovoltaic parameters of the GO/SnO_2 (5:1 to 5:5) nanocomposites counter electrode and JG as a sensitizer for DSSCs

Dye	**Counter Electrode (concentration) GO/SnO_2**	**V_{oc}(mV)**	**I_{sc}(mA)**	**Fill Factor (%)**	**Efficiency (%)**
JG	5:1	0.35	0.4	38%	2.1%
JG	5:2	0.36	0.43	41%	2.3%
JG	5:3	0.37	0.44	43%	2.5%
JG	5:4	0.37	0.46	44%	2.7%
JG	**5:5**	**0.4**	**0.46**	**46**%	**2.95**%

Table (8.1-8.5) shows that the prepared Pt free GO/SnO_2 (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 sensitized DSSCs. It is observed from Table 8.1 and 8.2 that the prepared counter electrode GO/ SnO_2 (5:4) nanocomposites with SP and ST as a sensitizer achieve 0.9% and 1.4 % efficiency than the other concentration respectively and from Table 8.3 GO/SnO_2 (5:3) concentration nanocomposites achieves 2.1 % efficiency. It is evident from the Table 8.4 and 8.5 that the GO/SnO_2 (5.5) nanocomposites achieve 2.3 % and 2.9 % efficiency respectively. In DSSCs the short circuit current I_{sc} depends on the quantity of dye molecule absorbed on the anode surface, dye structure, light harvesting efficiency and the electron injection ability of the dye. More absorption of dye molecule on the anode surface generates large number of photons from sunlight, which in turn leads to faster electron injection [16,17]. It is further evident that JGdye extract has a high absorption range, as reported in Chapter II of UV-Vis Spectral analysis. Hence, these results confirm that JG dye with GO/SnO_2(5:5) nanocomposites have higher efficiency compared to all other dyes.

8.4. CONCLUSION

This chapter describes the preparation of Pt free GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as a counter electrode with SP, ST, AH, GP and JG dyes as a sensitized DSSCs. The UV-Vis studies showed that the prepared GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites absorption peak at 274 nm, 278 nm, 282 nm, 290 nm and 302 nm respectively. The EIS results revealed that the GO/SnO_2 (5:5) nanocomposites with JG sensitizer achieve the largest semicircle in the highest frequency region. The I-V characteristic showed that the best efficiency for Pt free counter electrode GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites with SP, ST, AH, GP and JG sensitized DSSC as 0.9 %, 1.4%, 2.1 %, 12.3 % and 2.9 % respectively. It is confirmed that Pt free counter electrode with GO/SnO_2 (5:5) nanocomposites has highest efficiency. Hence, an alternative, eco-friendly material with low cost has been successfully fabricated.

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