FABRICATION AND PERFORMANCE ANALYSIS OF NATURAL EXTRACT (SOLANUM PROCUMBENS, SOLANUM TORVUM, ARTABOTRYS HEXAPETALUS, GALINSOGA PARVIFLORA AND JASMINUM GRANDIFLORUM L) BASED DYE SENSITIZED SOLAR CELLS USING GRAPHENE OXIDE/ METAL OXIDE (NiO, Y_2O_3, SnO_2) NANOCOMPOSITES AS COUNTER ELECTRODES

THESIS

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CHAPTER IX

SUMMARY OF RESULTS AND CONCLUSION

A sustainable energy source is predicted to meet the energy crises in the near future. Solar energy is considered to be the most prevalent of the various natural energy sources. In this approach, solar cells attract the majority of researchers to work on the development of cost-effective and environmentally friendly devices. Dye-sensitized solar cells (DSSCs) are third-generation solar cells that have seen a significant advancement in research and development.

The counter electrode (CE) is one of the most important components in DSSC. Among DSSC, counter electrode plays a key role in the overall power conversion efficiency of the device as it serves as the main electron collecting repository from the external circuit.

The present work describes the influence of various concentrations of metal oxide nanoparticles on graphene oxide nanosheet for dye-sensitized solar cells. The structural, functional, morphological and composition of the prepared nanocomposites are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Field Emission Scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDX) and high resolution transmission electron microscopy (HRTEM). The photovoltaic behaviour of the prepared Pt-free Graphene oxide/metal oxide nanocomposites as counter electrode with natural dyes as sensitizer being studied.

9.1 FABRICATION OF GRAPHENE OXIDE NANOSHEETS AS A COUNTER ELECTRODE FOR Pt FREE NATURAL DYE SENSITIZED SOLAR CELL APPLICATION

The Graphene nanosheets are prepared by the modified Hummers' method in which graphite is treated with a mixture of very strong oxidizers such as sodium nitrate, sulfuric acid, and potassium permanganate. XRD, FE-SEM, and HR-TEM analysis revealed that the GO nanosheets are successfully prepared. The elemental analysis confirmed that 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 at 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 eVrespectively. This chapter confirms the preparation of GO nanosheet that can be used as a counter electrode in DSSC. The dyes such as SP, ST, AH, GP and JG are attractive for their use as a sensitizer in dye sensitized solar cell because of its low cost and environmental friendliness.

9.2 SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE / NICKEL OXIDE NANOCOMPOSITES FOR DYE SENSITIZED SOLAR CELL APPLICATION

The influence of the various concentrations (5:1, 5:2, 5:3, 5:4 and 5:5) of nickel oxide nanoparticles blended on the surface of the graphene oxide nanosheet is discussed. The crystalline nature of the prepared nanocomposites is confirmed by XRD analysis, and the crystallite size of the nanocomposites are 19 nm, 21.3 nm, 23 nm, 24 nm, and 24.3 nm, respectively. FESEM and HRTEM analysis confirmed that the NiO nanoparticles are equally spread on the surface of GO nanosheet. The three discrete bright rings which indicate the successful formation of Nickel oxide nanoparticles on the surface of graphene oxide nanosheet which could also be evidenced from XRD analysis. The prepared nanocomposites can serve as an excellent counter electrode for dye-sensitized solar cell applications.

9.3 PREPARATION AND CHARACTERIZATION OF GRAPHENE OXIDE / YTTRIUM OXIDE NANOCOMPOSITES FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

A novel graphene oxide / yttrium oxide nanocomposites of various concentrations (5:1, 5:2, 5:3, 5:4 and 5:5) are prepared by simple chemical precipitation method. The XRD analysis showed that the crystallite size of the GO / Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) is found to be around 23 nm, 25.2 nm, 26.92 nm, 27.1 mm and 27.8 nm. Field emission scanning electron microscopy (FESEM) revealed that the flakes like shaped yttrium oxide nanoparticles are uniformly dispersed on the surface of GO nanosheet. EDX analysis confirmed that with increase in the concentration of yttrium oxide from 5:1to 5:5, the number of Yttrium nanoparticles on the Graphene oxide surface increases. The prepared nanocomposites are suitable for dye sensitized solar cell applications.

9.4 PREPARATION AND CHARACTERIZATION OF GRAPHENE OXIDE/TIN OXIDE NANOCOMPOSITES AS COUNTER ELECTRODE IN DYE SENSITIZED SOLAR CELL

Graphene oxide/Tin oxide nanocomposites are prepared by chemical precipitation method. The various concentrations (5:1, 5:2, 5:3, 5:4 and 5:5) of Tin oxide nanoparticles are embellished on the GO surface, which is confirmed from FESEM and HRTEM analysis. XRD analysis showed that the prepared nanocomposites are crystalline in nature and the average crystallite size of GO/SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites is found to be 22.3 nm, 23.1nm, 24.5 nm, 25.2 and 25.9 nm respectively. Raman spectra showed that the GO and SnO_2 peaks have slight shift due to increase in the concentration (5:1, 5:2, 5:3, 5:4 and 5:5) of SnO_2 nanoparticles on the surface of Graphene oxide nanosheet. It is evident that the Raman results are consistent with XRD results, confirming the formation of GO/SnO_2 nanocomposites. This prepared GO/SnO_2 nanocomposite is suitable material to act as a counter electrode in a Pt-free dye-sensitized solar cell.

9.5 EFFICIENCY STUDIES OF SOLANUM PROCUMBENS (SP) AS A SENSITIZER IN Pt-FREE GRAPHENE OXIDE /METAL OXIDES (NiO, Y_2O_3 AND SnO_2) COUNTER ELECTRODE FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

Natural dye sensitized solar cells (DSSCs) are becoming favourable candidates for replacing synthetic dyes. Solanum Procumbens (SP) is comprised of compounds like polyphenol, terpenoids, steroids and anthocyanin. Anthocyanins are the major colouring component in this dye, which plays a vital role in photosynthesis. The chemical absorption of hydroxyl and methoxy electrons with the hydroxyl groups on the surface of nanostructured TiO_2 enhances the DSSC efficiency.

Pt is commonly used as a counter electrode in DSSC but due to its high cost, an alternative to Pt, graphene has attracted much attention due to its large surface, high electron conductivity, and excellent mobility. The UV- Vis studies showed that the absorption and band gap of Solanum Procumbens (SP) dye is 260 nm and 4.6 eV respectively as discussed in chapter II.

Efficiency of Pt free GO and GO / NiO (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as a counter electrode with SP sensitizer achieves 0.3 %, 0.42%, 0.51%, 0.57%, 0.61% and 0.65% respectively. GO / NiO (5:5) nanocomposites counter electrode achieves the best efficiency than the other concentration and may be due to the increase in the concentration of nickel oxide nanoparticles on the surface of graphene oxide nanosheet. Hence the prepared Pt-free GO/NiO (5:5) nanocomposites counter electrode with SP achieves high efficiency of 0.65%

The counter electrode of GO/Y_2O_3 (5:1, 5:2, 5:3, 5:4, and 5:5) nanocomposites with SP sensitised DSSC achieves 1.23%, 1.26%, 1.28%, 1.3%, and 1.2%, respectively. Compared to other concentrations, GO/Y_2O_3(5:4) nanocomposites achieve the highest efficiency. This may be due to the electron transport of GO/Y_2O_3 (5:4) nanocomposites being more than the other concentrations, which is also evident from EIS analysis as discussed in chapter VII.

Pt free GO / SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with SP sensitized DSSC achieves 0.64%, 0.74%, 0.87%, 0.9% and 0.8% respectively. Hence the prepared GO / SnO_2 (5:4) nanocomposites achieve the highest efficiency and this may be due to the increase in the concentration of SnO_2 nanoparticles.

Hence by comparing the three metal oxides NiO, Y_2O_3 and SnO_2 embellished on the surface of GO, nanocomposites of GO/Y_2O_3 (5:4) concentration as counter electrode with SP as sensitizer achieves the highest efficiency than other counter electrode.

9.6. EFFICIENCY STUDIES OF SOLANUM TORVUM (ST) AS A SENSITIZER IN Pt-FREE GRAPHENE OXIDE / METAL OXIDES (NiO, Y_2O_3 AND SnO_2) AS COUNTER ELECTRODE FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

Ever-increasing global energy demand promotes most intensive research in the area of harvesting energy from sunlight using photovoltaic technology. Dye sensitized solar cells have gained considerable interest as alternatives to the semiconductor based thin film solar cell. Solanum Torvum (ST) belonging to the family of solanaceae and these leaves has been reported to contain compounds like steroidal gluco-alkaloid and solasoine. This SP leaves absorption and bandgap are 270 nm and 4.4 eV respectively, which is evident fromUV-Vis analysis as discussed in chapter II.

Pt free GO and GO / NiO (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with ST as a sensitizer achieves 0.7%, 1.0%, 1.2%, 1.23%, 1.25% and 1.2% respectively. GO counter electrode DSSC achieves 0.7% efficiency, which is less than the GO / NiO nanocomposites (counter electrode) DSSC and this may be due to the doped nickel oxide nanoparticles on the graphene oxide nanosheet.

GO / Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with ST as dye sensitized DSSC achieves 0.79%, 0.83%, 0.86%, 0.9% and 0.81% efficiency. The GO / Y_2O_3 (5:5) concentration nanocomposite efficiency is decreased and this may be due to non-electron injection to the counter electrode.

Pt free GO / SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with ST dye sensitized solar cell efficiency are 1.29%, 1.3%, 1.35%, 1.4% and 1.37% respectively. The electron transition occurs at much faster rate as the concentration is increased from 5:1 to 5:4 but decreased for 5:5 concentrations, this may be due to the concentration of SnO_2 nanoparticles on the surface of GO nanosheet. Hence GO / SnO_2 (5:4) nanocomposites counter electrode with ST sensitizer achieves the highest efficiency in DSSC.

9.7. EFFICIENCY STUDIES OF ARTABOTRYS HEXAPETALUS (AH)AS A SENSITIZER IN Pt-FREE GRAPHENE OXIDE /METAL OXIDES (NiO, Y_2O_3 AND SnO_2) COUNTER ELECTRODE FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

Artabotrys Hexapetalus (AH) is distributed throughout the southern part of India. As an Indian traditional folk medicine, its roots and fruits are used for treating malaria and scrofula respectively. AH extract are belonging to the Annonaceae family and this chlorophyll extract are not degrading for long time which act as a efficient sensitizer in DSSC. AH extract contains rich polyphenols that helps for the photosynthesis process and hence this can be a more efficient absorber of DSSC. This leaf extract has high absorption at 220 nm and band gap are found to be 4.3 eV respectively.

The prepared Pt free GO and GO / NiO (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with AH extract sensitized DSSC efficiency are 0.65%, 0.6%, 0.65%, 0.7%, 0.89% and 0.9% respectively. The prepared GO / NiO nanocomposites counter electrode efficiency is gradually increased by increasing the concentration of NiO on the surface of graphene oxide nanosheet.

Pt free GO / Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with AH as sensitizer in DSSC achieves 1.7%, 1.73%, 1.75%, 1.7% and 1.65% respectively. In GO / Y_2O_3 nanocomposites, the maximum efficiency is found for 5:3 concentration. This indicates that the charge transport electron resistance is increased for GO/Y_2O_3 (5:4 and 5:5) nanocomposites hence the efficiency is decreased.

GO / SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with AH as sensitizer in DSSC achieves the efficiency of 1.89 %, 2.0 %, 2.1 %, 1.9 % and 1.8 % respectively. The highest efficiency in a GO/SnO_2 counter electrode is 2.1% and is achieved for 5:3 concentrations. Comparing these three metal oxides, AH dyes with SnO_2 (5:3) concentration achieves the highest efficiency.

9.8. EFFICIENCY STUDIES OF GALINSOGA PARVIFLORA (GP) AS A SENSITIZER IN Pt-FREE GRAPHENE OXIDE /METAL OXIDES (NiO, Y_2O_3 AND SnO_2) COUNTER ELECTRODE FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

A dye sensitized solar cell is low cost solar cell and it works even in low light condition. The sensitizer plays a vital role in the functioning of DSSC. Galinsoga Parviflora (GP) is an easily available plant and these extract contain electron rich polyphenols, amino acids and anthocyanin. The chlorogenic acid is a good chemical sensitizer and is found to be the main constituent of GP dye and thereby this extracts act as a good sensitizer in DSSC. The leaf extract has high absorption at 288 nm and the band gap are found to be 4.1 eV. GP contain the anthocyanin molecules which can be easily bond with the surface of anode electrode.

Pt free GO and GO / NiO (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with GP as sensitizer in DSSC achieves the efficiency of 0.8%, 1.81%, 1.9%, 1.95%, 1.97% and 1.8% respectively. GO/ NiO (5:4) nanocomposites counter electrode efficiency is remarkably higher than other concentrations. Hence GO/NiO (5:4) nanocomposite counter electrode achieves the highest efficiency in DSSC.

GO / Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with GP as sensitizer achieves the solar cell efficiency of 2%, 2.7%, 2.75%, 2.76% and 2.7% respectively. The highest efficiency of GO / Y_2O_3 nanocomposites is 2.76 % and it could be due to the fast dye regeneration process in DSSC.

Pt free GO / SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites counter electrode with GP as sensitizer in DSSC achieves the efficiency of 1.7%, 1.8%, 1.9%, 2.1% and 2.3% respectively. Hence GO / SnO_2 (5:5) concentration nanocomposites counter electrode achieves the best efficiency of 2.3%.

Comparing all the metal oxides, it is found that GO / Y_2O_3 (5:4) nanocomposites as counter electrode with GP as dye achieves the highest efficiency in DSSC.

9.9. EFFICIENCY STUDIES OF JASMINUM GRANDIFLORUM L (JG) AS A SENSITIZER IN Pt-FREE GRAPHENE OXIDE /METAL OXIDES (NiO, Y_2O_3 AND SnO_2) AS COUNTER ELECTRODE FOR DYE SENSITIZED SOLAR CELL APPLICATIONS

Dye sensitized solar cell have paved the way for the development of a photovoltaic technology because of its low-cost, light-weight, and environmental friendly. Natural dye sensitized solar cells are environmental friendly, low cost and pollution free that have great attention as an alternative for synthetic dye solar cells. Jasminum Grandiflorum L (JG) dye extract is used as a sensitizer for DSSC and this natural dye has never been reported, hence a novel sensitizer has been employed. This natural dye extract contains namely, chlorophyll, betanins, anthocyanins and carotenoids. JG exhibits wide ecological range and found extensively all over India. The extract from JG contains high level of chlorophyll, which are useful for DSSC.

Pt free GO and GO / NiO (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with JG extract as sensitizer in DSSC achieves 0.96%, 1.81%, 1.9%, 1.95%, 1.97% and 1.8% efficiency respectively. GO/NiO (5:4) concentration nanocomposites achieves the highest photo current efficiency, when compared to GO and other concentrations of GO / NiO nanocomposites.

GO / Y_2O_3 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with JG as a sensitizer in DSSC achieves 2.3%, 2.5%, 2.6%, 2.8 % and 2.7% efficiency respectively. GO / Y_2O_3 (5:4) nanocomposites counter electrode achieves the highest efficiency. The photo current efficiency of DSSC is decreased for the concentration of Y_2O_3 (5:5) and this may be due to increase in the charge transfer resistance, which is also evident from EIS analysis as discussed in chapter VII.

Pt free GO / SnO_2 (5:1, 5:2, 5:3, 5:4 and 5:5) nanocomposites as counter electrode with JG as dye sensitizer in DSSC achieves the efficiency of 2.1%, 2.3%, 2.5%, 2.7% and 2.9% respectively. GO/SnO_2 (5:5) nanocomposites achieve the highest efficiency of 2.9%. This may be due to the increase in the concentration of SnO_2 nanoparticles on the surface of graphene oxide nanosheet. Comparing all three metal oxides, SnO_2 achieves the highest efficiency of 2.9% for JG as sensitizer in DSSC.

9.10. CONCLUSION

Five natural dye extracts are used as sensitizers for Pt free GO/ metal oxide (NiO, Y_2O_3 and SnO_2) nanocomposites and their photo current performance are studied. The extract dye contains betanins, anthocyanins, gluco-alkaloid, polyphenol and terpenoids. Chlorophyll is the common component present in all these five dyes. In most cases, natural dye extracts are a combination of multiple compounds. As a result, there is a variation in dye sensitization actions and this may be due to their different ability to adsorb onto the anode (TiO_2) surface. Hence the electron transfers from dye molecule to the conduction band of the anode enhances, the DSSC efficiency. By comparing the three metal oxides with graphene oxide nanocomposites, SnO_2 with Graphene oxide as counter electrode with JG dye, achieve the highest efficiency. As the concentration of doped metal oxide on the graphene oxide nanosheet increases, the amount of electron movements on the graphene oxide nanosheet increases this can improve the efficiency of DSSC. The photovoltaic performance of SP, ST, AH, GP and JG dyes with Pt free GO / metal oxide (NiO, Y_2O_3 and SnO_2) nanocomposites as counter electrode is cheaper, durable and an alternative for Pt counter electrode.