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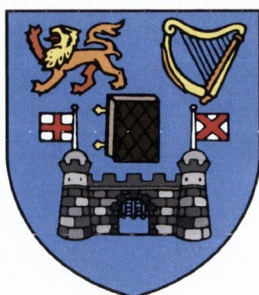
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Carbon based Nanomaterials Application in Dye Sensitized Solar Cell

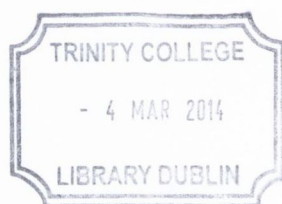
by

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A thesis submitted for the degree of
Doctor of Philosophy
in the University of Dublin

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Thesis 10239

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Iftikhar Ahmad

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Summary

Sunlight is the largest of all available carbon-neutral energy sources. Therefore, currently solar cell or photovoltaic cell based technologies, which can convert solar energy into electricity, are of extreme importance. Over 20 years ago, Gratzel et al. developed a new type of photovoltaic cell which is known as dye-sensitized solar cell (DSSC.) DSSCs are relatively easy to produce and they can work in very varied weather conditions (e.g. under diffused light, cloudy day, indoor, etc.) without a real drop of their efficiency, but these cells still have a very limited applications due the low efficiency and the presence of unstable, volatile and expensive components. The main aim of this work was to improve the power conversion efficiencies and long term stabilities of DSSCs by using low cost and easily available materials. Thus this thesis predominantly focused on preparation, development and investigation of various carbon based nanocomposite and their application in various part of DSSCs.

Chapter 1 of the thesis gives an introduction into the photovoltaics and provides a literature review of various types of photovoltaic cells and technological approaches with particular focus given to DSSCs. This chapter also outlines the motivation and objective of this work.

Chapter 2 describes the details of experimental procedures and characterization techniques used in this thesis. The characterisation techniques include Thermogravimetric Analysis, Raman spectroscopy, Power conversion efficiency measurements, Electrochemical impedance spectroscopy, Electrical conductivity measurements, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

Chapter 3 is dedicated to the development of new electrolyte materials for DSCCs. It describes the investigation and uses of graphene, SWCNTs and mixture of graphene in IL such as PMII. It was found that the power conversion efficiencies of DSSCs increased sharply (up to 2.10%) when 30 wt % of graphene was added into PMII. Moreover the power conversion efficiency was further improved to 2.50 % with hybrid quasi solid state electrolyte which contained SWCNTs (3 wt %) and graphene (12 wt

%) in PMII. Our results demonstrated the incorporation of carbon based nanomaterial into IL has enhanced the DSSC power conversion efficiency because carbon nanomaterials can serve simultaneously both as charge transporter in the ILs and as electrocatalysts for the reduction of I_3^- . Furthermore, in this work we have investigated the effect of the addition of iodine on three best formulations of each type quasi solid electrolyte/DSSC. We have also performed the stability study of three best formulations of each type quasi solid electrolyte the quasi solid state and compared the results with DSSCs containing only PMII. The stability study has also shown that these quasi solid state based DSSCs demonstrate higher efficiencies than pure PMII based DSSC under same condition. TGA studies have demonstrated that these electrolytes have high thermal stability up to 300 °C.

Chapter 4 is focused on the investigation of binary IL based electrolytes which were produced by using various combinations of EMISCN and PMII and utilized in DSSCs. Moreover, in this work we have developed the binary IL based quasi solid state electrolytes by the incorporation of graphene or SWCNTs or mixture of graphene and SWCNTs. Using new electrolytes the power conversion efficiencies were increased from 1.40% (optimized binary IL= EMISCN/PMII) to 2.04%, 2.24% and 3.07% with addition of SWCNTs, graphene and hybrid SWCNTs + graphene into binary IL based DSSCs respectively. We believe that power conversion efficiencies were increased due to fabrication of more homogeneous carbon based quasi solid state electrolytes in less viscous binary IL than pure PMII. Thus in this part of our work we have successfully developed the new efficient binary IL based quasi solid state electrolytes for DSSCs.

Chapter 5 is dedicated to the development of new materials for counter electrodes (CEs) in DSSCs. This part of the work includes the investigation of Pt free CEs for DSSCs. We have successfully replaced the Pt of CE with hybrid composite of GNPs type 3 plus MWCNTs into PEDOT: PSS matrix. These various carbon based materials were dispersed in conducting polymer PEDOT: PSS aqueous dispersion, via non-covalent approach that allowed the retention of their good electrical properties. These various kinds of composites CEs were deposited on FTO coated glass substrates. However only hybrid C coated on FTO/glass substrate-CE, which was contained GNPs type 3 (22 wt %) and MWCNTs (44 wt %) into PEDOT: PSS film, demonstrated a higher power conversion efficiency of 4.10% compared to standard Pt coated FTO/CE–

DSSC (3.90%). Furthermore, the hybrid CE were also tested in complete DSSCs with various type electrolytes system i.e. organic based electrolytes, ionic liquid electrolyte (PMII) and quasi solid state electrolyte. Hybrid-C-FTO/CE- DSSC with quasi solid state electrolyte and ionic liquid electrolyte demonstrated power conversion efficiencies of 1.88 % and 0.38 % respectively. The TGA study showed that GNPs and MWCNTs samples are highly thermally stable either in powder form or in composite film and the hybrid C-CE can be used as effective metal-free CE to replace Pt in high-performance DSSC.

Chapter 6 describes the development and investigation of the Pt and FTO free CEs with various composite films which were prepared with addition of three different types of GNPs into NMP doped PEDOT: PSS matrix. The highest power conversion efficiency of 3.70 % was achieved with GNPs type 2 plus NMP doped PEDOT: PSS composite film/glass-CE compared with the power conversion efficiencies of 1.35 % and 4.72 % for NMP doped PEDOT: PSS film/glass-CE and standard Pt/FTO/glass-CE/DSSCs respectively. Furthermore, the power conversion efficiency was further increased up to 4.29 % by optimizing the sintering temperature (150 °C) for GNPs type 2 plus NMP doped PEDOT: PSS composite film-CE.

Chapter 7 describes the effect of addition of GO and sintered GNPs type 2 into TiO₂ films of the WEs (photoanodes) in DSSCs. It was found that the power conversion efficiencies of DSSCs were decreased with addition of GO but increased with addition of sintered GNPs type 2 into TiO₂ films of the WE. The highest power conversion efficiency of 4.77 % was achieved with 0.6 wt % of GNPs into TiO₂ film/WE-DSSC compared to 3.75 % of pure TiO₂ film/WE-DSSC.

Chapter 8 provides the conclusion of this work, summaries the main achievements and outlines the future work. This chapter emphasizes that future work should focus on the optimization of the formulations and preparation processes of these new materials and corresponding DCCSs in order to further improve the photovoltaic performances of the cells. Particularly, it is important to expand the use of these materials and techniques for the “closed cell” fabrication approach, when the cell is initially assembled and sealed and then electrolyte is introduced into the cell under vacuum via a small hole, which then sealed with surlyn. This approach should potentially allow to

achieve much better efficiencies due to the minimal exposure of electrolytes to air and moisture.

In overall this thesis is expected to make a contribution to the further development of various components of DSSCs with potentially low-cost fabrication and enhanced power conversion efficiency.

Abbreviations

CE	Counter Electrode
DSSC	Dye Sensitized Solar Cell
0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
EIS	Electrochemical impedance spectroscopy
EETMs	Extended Electron Transfer Material
EMISCN	1-ethyl-3-methylimidazolium thiocyanate
E _g	Band Gap Energy
FTO	Fluorine tin oxide
FF	Fill Factor
GNPs	Graphene Nanoplatelets
HTM	Hole transport materials
I _{sc}	Short Circuit Current
ILs	Ionic Liquids
J _{sc}	Short Circuit Current Density
MWCNTs	Multi Walled Carbon Nanotubes
M	Molar Concentration
NMP	N-methyl-pyrrolidone
MMP	Maximum Power Point
nm	Nanometer

OPV	Organic Photovoltaics
Pt	Platinum
PMII	1-Methyl-3-Propylimidazolium Iodide
PV	Photovoltaic
Ru	Ruthenium
SWCNTs	Single walled carbon nanotubes
Si	Silicon
SEM	Scanning Electron Microscopy
TiO ₂	Titanium Dioxide
TCO	Transparent Conducting Oxides
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
μm	Micrometer
Voc	Open Circuit Voltage
WE	Working Electrode

Table of Contents

Chapter 1: Introduction

1.1 General Introduction	1
1.2 Solar Irradiance	2
1.3 History and Application of Photovoltaic Devices	3
1.4 Classification of Solar Cells	5
1.4.1 The First Generation Solar Cells	5
1.4.2 Second Generation Solar Cells	7
1.4.3 Third Generation Solar Cells	7
1.5 Dye Sensitized Solar Cell (DSSC)	8
1.5.1 Introduction to DSSC	8
1.5.2 General Structure of DSSCs	9
1.5.3 Main Part of DSSC	10
1.6 Operating principles of DSSCs	19
1.7 Introduction and Application of CNTs in DSSCs	21
1.7.1 Introduction to CNTs	21
1.7.2 Application of CNTs in DSS	24
1.8 Introduction and application of Graphene in DSSCs	26
1.8.1 Introduction to Graphene	26
1.8.2 Application of Graphene in DSSCs	27
1.9 Aims and objectives of thesis	30

1.10 References	32
Chapter 2: Experimental	
2.1 Starting materials	40
2.2 Experimental details for chapter 3	40
2.2.1 Preparation of carbon based quasi solid state electrolytes	40
2.2.2. Fabrication of DSSCs	41
2.3 Experimental details for chapter 4	42
2.3.1 Preparation of binary ionic liquid based quasi solid state electrolyte for dye sensitized solar cells	42
2.4 Experimental details for chapter 5	42
2.4.1 Preparation of PEDOT: PSS-carbon nanomaterial composites	42
2.4.2 Fabrication of carbon based CEs	43
2.5 Experimental details for chapter 6	43
2.5.1 Preparation of Pt and TCO free CEs for DSSCs	43
2.6 Experimental details for chapter 7	44
2.6.1 Sample preparation	44
2.6.2 Fabrication of sealed DSSCs	45
2.7 Characterization techniques	45
2.7.1 Thermogravimetric Analysis	45
2.7.2 Raman Spectroscopy	48
2.7.3 Scanning Electron Microscopy (SEM)	50
2.7.4 Transmission Electron Microscopy (TEM)	52
2.7.5 Power conversion efficiency measurements of DSSC	53

2.7.5.2 Solar simulator	55
2.7.6 Electrochemical impedance spectroscopy	56
2.7.7 Electrical conductivity measurement	57
2.8 References	58

Chapter 3: Graphene, Carbon nanotubes and Ionic liquid mixtures: Towards new Quasi Solid State Electrolytes for Dye Sensitised Solar Cells

3.1 Introduction	60
3.2 Preparation of Graphene	62
3.3 Characterizations of Graphene	63
3.3.1 Transmission electron microscopy (TEM)	63
3.3.2 Raman Spectroscopy	64
3.3.3 Electrical conductivity measurement	66
3.3.4 Scanning electronic microscopy (SEM)	66
3.4 Preparation and characterisation of DSSCs with new quasi solid state electrolytes	68
3.4.1 Preparation of graphene based quasi solid state electrolytes and corresponding DSSCs	68
3.4.2 Investigation of the Photovoltaic performance of DSSCs with graphene based quasi solid state electrolytes/DSSCs	69
3.4.3 Thermogravimetric analysis (TGA) of graphene based quasi solid state electrolytes	72
3.4.4 Investigation of the photovoltaic performance of DSSCs with SWCNTs based quasi solid state electrolyte/DSSCs	74
3.4.5 TGA of SWCNTs based quasi solid state electrolyte	76

3.4.6 Investigation of the photovoltaic performance of DSSCs with hybrid graphene - SWCNTs-PMII quasi solid state electrolyte	77
3.4.7 TGA of hybrid graphene–SWCNTs-PMII quasi solid state electrolyte	79
3.4.8 Investigation of photovoltaic performance of Pt free CE/DSSC with quasi solid state electrolytes (only FTO/glass)	80
3.4.9 Iodine (I ₂) effect on the photovoltaic performance of DSSCs with quasi solid state electrolyte	82
3.4.10 Comparative stability study of electrolytes in DSSCs	85
3.5 Conclusions	86
3.6 References	87

Chapter 4: Development of binary Ionic liquid based Quasi Solid State Electrolyte for Dye Sensitized Solar Cells

4.1 Introduction	91
4.2 Preparation of binary ionic liquid based quasi solid state electrolyte for dye-sensitized solar cells	92
4.3 TGA of hybrid graphene-SWCNTs in binary IL based quasi solid state electrolyte	92
4.4 Investigation of the Photovoltaic parameters of the DSSCs with various combinations (w/w) of binary IL based DSSC	93
4.5 Investigation of the Photovoltaic parameters of the DSSCs with incorporation of various carbon based material into binary IL electrolyte	95

4.6 Investigation of the photovoltaic parameters of the DSSCs with various molar concentration of guanidinium thiocyanate into hybrid SWCNTs- graphene based binary IL quasi solid state electrolyte	98
4.7 Conclusion	99
4.8 References	101

Chapter 5: Development of carbon based Counter Electrode for Dye Sensitized Solar Cells

5.1 Introduction	103
5.2 New Pt –free CE for DSSCs	105
5.2.1 Preparation of dispersions of carbon nanomaterials in PEDOT: PSS	105
5.2.2 Scanning Electron Microscopy of CEs	106
5.2.3 Raman Spectroscopy of carbon based composites for CEs	107
5.2.4 TGA analysis of materials for CEs	108
5.2.5 Electrical conductivity measurements	110
5.2.6 Investigation of photovoltaic performance of DSSCs with various carbon based CE/DSSC	112
5.2.7 Hybrid C-CE with FTO tested with different electrolytes systems in DSSCs	115
5.2.8 EIS studies of DSCCs with selected CEs	117
5.2.9 Photovoltaic performance of Pt and FTO free CE with selected carbon based materials	120
5.3 Conclusions	122
5.4 References	123

Chapter 6: Development of Pt and TCO free Counter electrodes for Dye Sensitized Solar Cells

6.1	Introduction	126
6.2	Preparation and characterization of Pt and TCO free CEs for DSSCs	128
6.2.1	Preparation of GNP based CEs	128
6.2.2	Raman Spectroscopy	128
6.2.3	Scanning Electron Microscopy of GNPs type 2 with NMP doped PEDOT: PSS composite film/CE	130
6.2.4	Thermo gravimetric analysis (TGA) of GNPs type 2 with PEDOT: PSS composite film/ CEs	132
6.2.5	Electrical conductivity measurement	133
6.2.6	Investigation of photovoltaic performance of Pt and TCO free CEs/DSSCs with various type of GNPs with NMP doped PEDOT: PSS composite films.	135
6.3	Effect of sintering on the properties of CE and performance of corresponding DSSCs	138
6.3.1	Effect of Sintering on the electrical conductivity of GNPs type 2 plus NMP doped PEDOT: PSS films/ CEs	138
6.3.2	Raman spectroscopy of GNPs type 2 plus NMP doped PEDOT: PSS films/CEs sintered at various temperatures	140
6.3.3	Effect of sintering temperature on the photovoltaic performance of DSSCs with GNPs type 2 with PEDOT: PSS composite films/CEs	141
6.3.4	Adhesion test	144
6.4	Conclusion	145

6.5 References	146
----------------	-----

Chapter 7: Development of GO and GNP modified photoanodes/working electrodes for DSSCs

7.1 Introduction	150
7.2 Preparation of photoanodes (WE)	152
7.3 Raman spectroscopy characterization	153
7.4 Thermogravimetric analysis	154
7.5 Scanning electron microscopy characterization	155
7.6 Electrical conductivity measurement	157
7.8 Investigation of the Photovoltaic performance of various weight % of GO into TiO ₂ film /working electrode/DSSC	158
7.7 Investigation of the Photovoltaic performance of various weight % of GNP type 2 into TiO ₂ films/ working electrodes of the DSSCs	160
7.9 Conclusion	162
7.10 References	163

Chapter 8 Conclusions and future work

8.1 Conclusion	166
8.2 Future work	170
8.4 References	171

List of Figures and Tables

Chapter 1: Introduction

Figure 1.1 World energy consumption by type [1].

Figure 1.2: A) Sun radiation reaches by the surface of the earth and absorb [2], and B) Solar energy distribution the surface of the earth [3].

Figure 1.3: Shows photovoltaic application A) solar panel installed in building [4] and B) solar panel installed on the roof of house [5].

Figure 1.4: shows A) single crystalline silicon solar cell [6] and B) Polycrystalline silicon solar cell [7].

Figure 1.5: A) P type and n type Si and B) general structural diagram Si (p-n junction) solar cell.

Figure 1.6: Shows A) Amorphous silicon solar cell module and B) Copper indium gallium selenide solar cell module.

Figure 1.7: A) Flexible DSSC [8] and B) Glass based DSSC [9].

Figure 1.8: General structure of assembled DSSC.

Figure 1.9: Chemical structures of the ruthenium-based dyes N3, N719 and 'black dye [10, 11].

Figure 1.10: Chemical structure of 1 Methyl-3-propylimidazolium iodide (PMII) [12].

Figure 1.11: Schematic energy diagrams and operating principle of DSSC.

Figure 1.12: A) SWCNTs and B) MWCNTs [13].

Figure 1.13: SWCNTs type A) armchair, B) zigzag and C) chiral.

Figure 1.14 A): Schematic structure of graphite [14] and B) Schematic structure of graphene [15].

Table 1.1: Shows the published reports of the Photovoltaic parameters of DSSCs fabricated with graphene based CE (grphene/TCO).

Chapter 2: Experimental

Figure 2.1: Pictures of A) dyed WE with spacer, B) Pt/FTO-CE and C) Assembled DSSC.

Figure 2.2: TGA and DTGA curves of CNTs, PEDOT, and CNT/PEDOT nanostructures [7].

Figure 2.3: A) Perkin Elmer Pyris 1 TGA [8] and B) Schematic diagram of a modern Thermogravimetric Analysis Instrument [9].

Figure 2.4: Raman spectra for graphite and graphene showing the G and G' bands [16].

Figure 2.5: The main types of electrons that can be detected. They are split into several groups depending on their origin and their range.

Figure 2.6: Carl Zeiss Ultra Plus Field Emission Scanning Electron Microscope [21].

Figure 2.7: Schematic of the illumination system in a TEM [23].

Figure 2.8: Shows IV curve of a DSSC which showing the open circuit voltage (V_{oc}), short circuit current (I_{sc}), and the maximum power point (MPP).

Figure 2.9: The solar simulator Oriel instruments model 92193.

Figure 2.10: Schematic diagram of an Oriel Solar Simulator model 92193 [25].

Figure 2.11: Nyquist plots of electrochemical impedance spectra (EIS) of DSSC [27].

Chapter 3: Graphene, carbon nanotubes and ionic liquid mixtures: towards new quasi solid state electrolytes for dye sensitised solar cells

Figure 3.1: Steps involved in graphene preparation.

Figure 3.2: Representative TEM images of graphene (A, B, C and D), represent multilayer (3 to 5 layers) of graphene sheets, (after 60 hours of sonication).

Figure 3.3: Raman spectra (A) Top side, B) Bottom side of graphene film and C) graphite powder.

Figure 3.4: SEM images of graphene, (A and B) top surface and (C and D) edge of film.

Figure 3.5: Schematic illustration for the charge-transport processes of graphene-based quasi solid state DSSC.

Figure 3.6: Pictures of vials with the different of graphene wt % in PMII, from left to right the graphene (wt %) increased in PMII.

Table 3.1: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes containing different amounts of graphene (wt %) in PMII. Measured at 78 mW/cm². Cell active area: 0.8 cm².

Figure 3.7: A. TGA curves of A). a. PMII, A) .b. graphene and A). c. graphene (30 wt %)+ PMII quasi solid state electrolyte . B) DTGA curve of B).a. PMII, B).b. graphene and. B).c. graphene (30 wt %) + PMII electrolyte.

Table 3.2: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes containing different amounts of SWCNTs in PMII. Measured at 78 mW/cm². Cell active area: 0.8 cm².

Figure 3.8: A) shows TGA curves of A) .a. PMII, A) b. SWCNT and A).c. SWCNTs (7 wt %) + PMII quasi solid state electrolytes. B) Shows DTGA of B).a. PMII, B).b. SWCNTs and B).c. SWCNTs (7%) + PMII quasi solid state electrolytes.

Table 3.3: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes containing different amounts of graphene and SWCNTS in PMII. Measured at 78 mW/cm². Cell active area : 0.8 cm².

Figure 3.9: Photovoltaic (J–V) curves of the DSSCs with A) hybrid B, B) Graphene (30 wt %), C) SWCNTs (7 wt %) and D) PMII only.

Figure 3.10: A).a. Shows TGA curves of PMII, A).b. SWCNTs, A).c. graphene and A).d. hybrid B. B) Shows DTGA of B).a. PMII, B).b. graphene B).c. SWCNTs and B).d hybrid B.

Table 3.4: The Photovoltaic parameters of the DSSCs with quasi solid state electrolytes with Pt free CE/DSSCs. Measured at 78 mW/cm². Cell active area : 0.8 cm²

Figure 3.11: The Photovoltaic (J–V) curves of the DSSCs with 1) Pure PMII without Pt free CE, 2) Graphene (30 wt %) quasi state electrolyte without pt free CE., 3) SWCNTs(7 wt %) quasi state electrolyte without Pt free CE, 4) hybrid B without Pt free CE and 5) PMII with Pt/CE/DSSCs.

Table 3. 5: The Photovoltaic parameters of the DSSCs with quasi solid state electrolytes with addition of 0.1 wt % of iodine (I₂). Measured at 78 mW/cm². Cell active area is 0.8 cm².

Figure 3.12: The Photovoltaic (J–V) curves of the DSSCs with addition of 0.1 wt % of Iodine(I₂) 1) Graphene (30 wt %) quasi state electrolyte, 2) SWCNTs (7 wt%) quasi state electrolyte and 3) hybrid B quasi solid state electrolytes/DSSCs.

Figure 3.13: Stability studies of DSSCs with various electrolytes of 1) graphene-based, 2) SWCNT-based, 3) hybrid B based and 4) reference DSSCs (PMII only).

Chapter 4: Development of binary ionic liquid based quasi solid state electrolyte for dye-sensitized solar cells

Figure 4.1: A. TGA curve A) and B) DTGA curve of hybrid SWCNTs (3 wt %) + graphene (12 wt %) into binary IL.

Table 4.1: The photovoltaic parameters of the DSSCs fabricated with different wt % of EMISCN into PMII. Measured at 100 mW/cm², Cell active area is 0.8/cm².

Figure 4.2: Representative (J–V) curves of DSSCs with 1) PMII 2) Binary IL (30/70) and EMISCN.

Table 4.2: The photovoltaic parameters of the DSSCs with SWCNTs, graphene and hybrid of graphene plus SWCNTs into binary IL based quasi solid state electrolytes. Measured at 100 mW/cm^2 , Cell active area is $0.8/\text{cm}^2$.

Figure 4.3: The photovoltaic (J–V) curves of 1) Binary IL (30/70), 2) A+ graphene, 3) A+ SWCNTs+graphene and 4) A+ SWCNTs based binary IL quasi solid state electrolytes DSSC.

Table 4.3: The photovoltaic parameters of the DSSCs with hybrid graphene-SWCNTs in binary IL based quasi solid state electrolytes using different compositions of GuSCN. Measured at 100 mW/cm^2 , Cell active area is $0.8/\text{cm}^2$.

Figure 4.4: The photovoltaic (J–V) curves of hybrid SWCNTs-graphene based binary IL quasi solid state electrolyte/DSSCs which contained 1) 0 wt % 2) 0.05M, 3) 1M and 4) 2M of GuSCN.

Chapter 5: Development of carbon based Counter Electrode for Dye Sensitized Solar Cells

Figure 5.1: Represented schematically the carbon based CE /DSSC.

Figure 5.2: Representative SEM images of A and B-PEDOT: PSS/CE, C and D - GNPs powders, and E and F-hybrid C/CE.

Figure 5.3: Raman spectra: A) Graphite powders B) GNPs powders C) MWCNTs powders, D) B hybrid/CE and (E) C hybrid/CE.

Figure 5.4: DTGA of A) hybrid composite of GNPs (22wt %) and MWCNTs (44 wt %) in PEDOT: PSS, B) MWCNTs powders, C) GNPs powder and D) dried PEDOT: PSS film.

Figure 5.5: The electrical conductivity of I) PEDOT: PSS film; II) GNPs (66 wt %) + PEDOT:PSS composite film; III) MWCNTs(66 wt %) + PEDOT:PSS film and IV) Hybrid C: MWCNTs (44wt%)+ GNPs(22 wt%)/PEDOT:PSS film, V) hybrid C: MWCNTs (33 wt%)+ GNPs(33 wt%)/PEDOT:PSS film and VI) MWCNTs (22wt%)+ GNPs(44 wt%)/PEDOT:PSS film.

Figure 5.6: The photovoltaic (J–V) curves of: 1) standard reference Pt-CE; 2) PEDOT: PSS-CE, 3) MWCNTs+ PEDOT-CE, 4) GNPs type 3 +PEDOT-CE; 5- A hybrid –CE, 6- B hybrid –CE and 7 C- hybrid-CE/DSSC.

Table 5.1 The photovoltaic parameters of the DSSCs with various types of CEs with FTO. Light intensity was 100 mW cm^{-2} . Cell active area is 0.8 cm^2 .

Table 5.2: The Photovoltaic parameters of the DSSCs with various type electrolytes system with C hybrid CEs with FTO. Measured at 100 mW/cm^2 . Cell active area: 0.8 cm^2 .

Figure 5.7: The photovoltaic (J–V) curves of C hybrid with FTO glass: 1) Organic solvent based electrolytes, 2) Quasi solid state electrolyte 3) Ionic liquid electrolyte (PMII).

Figure 5.8: shows I) the equivalent circuit and II) Nyquist plots for A) pure PEDOT/CE, B) A hybrid CE, C) B hybrid CE, D) C hybrid CE and E) Pt standard CE / DSSCs.

Table 5.3: The photovoltaic parameters of the DSSCs with C hybrid CE on glass substrate without FTO. Light intensity was 100 mW cm^{-2} . Cell active area is 0.8 cm^2 .

Figure 5.9: The photovoltaic (J–V) curves of DSSCs with: 1) C hybrid/Glass/CE, 2) PEDOT: PSS- glass/CE and 3- and GNPs/CE.

Chapter 6: Development of Pt and TCO free counter electrodes for Dye Sensitized Solar Cells

Table 6.1: Intensity ratios for D and G band (calculated from corresponding Raman spectra).

Figure 6.1: Raman spectra of (A) Graphite powders, B) GNPs type 1 powders, C) GNPs type 2 powders, D) GNPs type 3 powders.

Figure 6.2: Representative SEM images of GNPs type 2 plus PEDOT: PSS composite film/CE, A and B shows SEM images of surface. C, D, E and E shows of fractured edge of composite film/CE.

Figure 6.3: A. Shows DTGA curves of A.I) GNPs type 2 powder, A.II) pure PEDOT: PSS film and A.III) GNPs type 2 + NMP doped PEDOT: PSS composite film/CE. B shows TGA curves of B.I) GNPs type 2 powder, B.II) PEDOT: PSS film and B.III) GNPs type 2+ NMP doped PEDOT: PSS composite film/CE.

Figure 6.4: The electrical conductivity of A) pure PEDOT: PSS film; B) NMP doped PEDOT: PSS film, C) GNPs type 1 + NMP doped PEDOT: PSS composite film, D) GNPs type 2 plus NMP doped PEDOT:PSS film and E) GNPs type 3 + NMP doped PEDOT:PSS composite film.

Table 6.2: The photovoltaic parameters of the Pt and FTO free CEs- DSSCs with various types of GNPs plus PEDOT: PSS composite films. Light intensity was 100 mW cm^{-2} . Cell active area: 0.8 cm^2 .

Figure 6.5: The photovoltaic (J–V) curves of: 1) pure PEDOT: PSS 2) NMP doped PEDOT: PSS, 3) GNPs type 1+NMP doped PEDOT: PSS, 4) GNPs type 2+NMP doped PEDOT: PSS, 5) GNPs type 3+NMP doped PEDOT: PSS and 6) Pt/FTO/CEs-DSSCs.

Figure 6.6: The electrical conductivity of GNPs type 2 plus PEDOT: PSS composite film/CE which was sintered at A) 120°C , B) 150°C , 200°C D) 300°C and 400°C .

Figure 6.7: I) Raman Spectra of, I) II), III), IV), V) and Vi) shows GNPs type 2 + PEDOT: PSS composite films/CEs, sintered at 120°C , 150°C , 200°C 300°C and 400°C respectively.

Table 6.3: Intensity ratios for D and G band (calculated from corresponding Raman spectra).

Table 6.4: Shows the effect of sintering on the photovoltaic performance of the DSSCs with GNPs type 2 plus NMP doped PEDOT: PSS composite film /CEs. Light intensity was 100 mW/cm^2 . Cell active area is 0.8 cm^2 .

Figure 6.8: The photovoltaic (J–V) curves of GNPs type 2+NMP doped PEDOT: PSS film/CE-DSSCs which were sintered at 1)120 °C 2) 150 °C 3) 200 °C, 4) 300 °C 5) 400 °C.

Figure 6.9: Films adhesion test with Scotch tape, A and B) NMP doped PEDOT: PSS film, C and D) and E and F) Shows the GNPs plus NMP doped PEDOT: PSS composite films which sintered at 120 °C and 150 °C respectively.

Chapter 7: Development of GO and GNP modified photoanodes/working electrode for DSSCs

Figure 7.1: Raman spectra of A.1) Graphite powders, A.II) GO powders, B.I) Sintered GNPs type 2 powders B.II) supplied GNP type 2.

Figure 7.2: A) shows TGA curves of GO powders and B) sintered GNPs type 2 powders.

Figure 7.3: Representative SEM cross section images (K and M) of GNPs type 2 plus TiO₂ (0.6 wt %) composite films/WE.

Figure 7.4: Representative surface SEM images (A, B, C and D) of GNPs type 2 plus TiO₂ (0.6 wt %) composite films/WE.

Table 7.1: The photovoltaic parameters of DSSCs with various wt % of GO into TiO₂ films/WEs. Measured at 100 mW/cm². Cell active area: 0.8 cm².

Figure 7.5 : The photovoltaic (J–V) curves of TiO₂ film/WE containing 1) 0 wt%, 2) 0.3 wt %, 3) 0.6 wt %, 4) 1 wt%, 5) 3 wt % and 6) 5 wt% of GO.

Table 7.2: The photovoltaic parameters of DSSCs with various wt % of sintered GNPs 2 into TiO₂ films/WEs. Measured at 100 mW cm⁻². Cell active area: 0.8 cm².

Figure 7.6: The photovoltaic (J–V) curves of TiO₂ film/WE containing 1) 0 wt %, 2) 0.3 wt %, 3) 0.6 wt %, 4) 1wt, 5) 3 wt% and 6) 5 wt% of GNPs type 2.

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Abstract

Sunlight is the largest of all available carbon-neutral energy sources. Therefore, currently solar cell or photovoltaic cell based technologies, which can utilize solar energy, are of extreme importance. Gratzel et al. developed a new type of photovoltaic cell some 20 years ago, which is known as dye-sensitized solar cell (DSSC.) DSSCs are relatively easy to produce and they can work in very varied weather conditions (e.g. cloudy day) without a real drop of their efficiency, but these cells still have a very limited applications due the low efficiency and the presence of unstable, volatile and expensive components. The main goal of this thesis is to improve the power conversion efficiencies and long term stabilities of DSSCs by using low cost and easily available materials to replace existing electrolytes and electrodes in DSSCs. In this work we have developed new quasi solid state electrolytes by using carbon nanomaterials and ionic liquids (ILs). In this case graphene, Carbon nanotubes (CNTs) and combination of graphene and CNTs were incorporated into IL or binary IL to make gel or quasi solid state electrolyte for DSSC.

There is another problem is the cost of Platinum/Transparent Conducting Oxides (Pt/TCO) based Counter Electrode (CE) of the DSSC which accounts for approximately 25~35% of the overall price of DSSCs. To address this issue new electrode materials were prepared by the incorporation of CNTs or GNPs into conducting polymer (e.g. PEDOT: PSS) to develop potentially inexpensive, stable and efficient Pt and Pt/TCO free CEs for DSSCs. Finally in our work various weight % of carbon nanomaterials were also incorporated into the TiO_2 films of the WEs of the DSSC. These various carbon based quasi solid state electrolytes, various carbon based composites of Pt or Pt/FTO free CEs and carbon based modified WE have been studied using various instrumental technique including electrical measurements, photoelectrical measurements, thermal characterization and electron microscopy. In overall this research has made a contribution to the development of various components of DSSCs with potentially low-cost fabrication and enhanced power conversion efficiency.

Chapter 1: Introduction

1.1 General Introduction

Energy is one of the basic needs of today life. Energy powers our machineries, vehicles, aeroplanes and many household appliances. Generally energy is defined as, the ability to bring about change or to do work. Energy exists in many forms, such as heat, light, chemical energy and electrical energy etc. Energy resources mainly divided into two categories i.e. non-renewal energy resources and renewal energy resources. Fossil fuels such as coal, petroleum, and natural gas are examples of non-renewable energy resources. Currently, fossil fuels provide the most of the energy consumed worldwide at approximately 70 to 80% of all energy sources [1] as shown in figure 1.1. There is a rapid growth of the prices for fossil fuels and a great danger of the greenhouse effect due to the increased carbon dioxide emission from the burning of these fossil fuels. Fossil fuels will also be depleted one day and furthermore the energy needs of the planet will at least double within the next 50 years [2]. Therefore, there is an urgent demand for alternative energy resources. Renewable green energy such as hydro, wind and solar has been explored over the last several decades. Among all these renewable green energy sources, solar energy has emerged as a most practical long lasting alternative to conventional fossil fuels based energy sources. To utilise solar energy for variety of applications one would need to convert it into electricity. This can be done using photovoltaic cells which can convert sunlight into electricity. Photovoltaic cells also have another competitive advantage: they can be independent of the grid and therefore are useful in remote areas or for mobile applications. In addition the solar panels operate without noise and any toxic effects. At present mostly silicon based solar cells are commercially available and produce less than 0.1% of the world energy [3]. However, silicon solar cells are still too expensive for household/large scale production due to the costly fabrication process e.g. requires high temperatures and high vacuum conditions [4]. Therefore, the developments of inexpensive solar cells, which can convert maximum solar energy to electricity, are of extreme importance. In this chapter we provide an overview of current state of the art in photovoltaic cell area and formulate aims and objectives of our work.

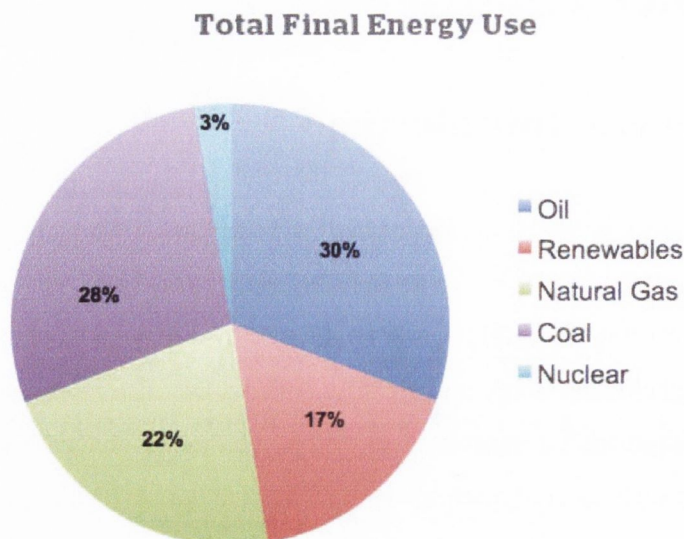


Figure 1.1: World energy consumption by type [5].

1.2 Solar Irradiance

The amount of solar power available per unit area is known as irradiance [6]. Radiation from the sun, which is more popularly known as sunlight or solar energy, is a mixture of electromagnetic waves which include Infrared (IR), ultraviolet rays (UV) visible light and X-rays. However, not all radiation of sun reaches the earth's surface. The atmosphere attenuates many parts of the spectrum e.g., X-rays are almost totally absorbed before reaching the earth's surface [7]. A good percentage of ultraviolet radiation is also filtered out by the atmosphere [7]. The atmosphere is a powerful absorber and can cut the sun's energy reaching the earth's atmosphere by around 50% [7]. Visible light (400–700 nm) and infrared radiation (700–2500 nm) constitute the major fraction of solar radiation reaching the earth's atmosphere, approximately 43 % of the radiation energy is visible light, 52% of infrared radiation and about 5% of the Ultraviolet radiation ((300–400 nm) energy reaching the earth's atmosphere (fig.1.2.B) [8]. When the rays reach the earth, some bounce off clouds back into space (Fig.1.2.A). The earth absorbs most of the radiant energy; this solar energy becomes thermal energy, which warms the earth. Fortunately, the sun power reaching the top of the earth's atmosphere is about 1400 Watts/m^2 or the supply of energy from the sun to the earth is gigantic, i.e., $3 \times 10^{24} \text{ J year}^{-1}$ or about 10^4 times more than what mankind

consumes currently [2, 9]. In other words, covering 0.1% of the earth’s surface with solar cells with an efficiency of 10% would satisfy our present needs [9].

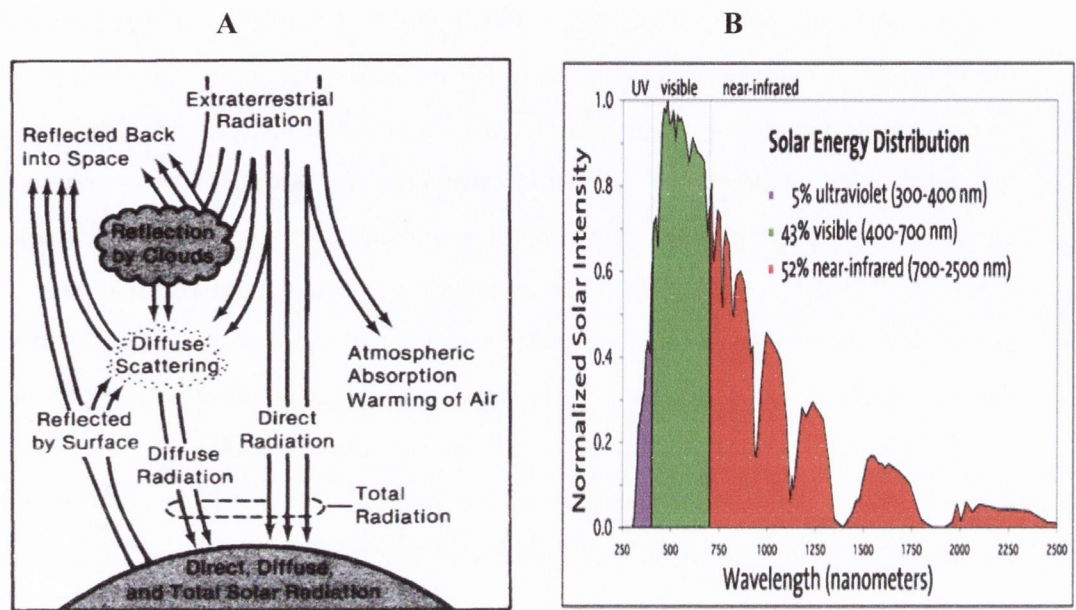


Figure 1.2: A) Sun radiation reaches by the surface of the earth and absorb [7], and B) Solar energy distribution at the surface of the earth [8].

1.3 History and Application of Photovoltaic Devices

Photovoltaic (PV) systems convert light directly into electricity. The term photo comes from the Greek phos, which means “light.” The term volt is a measure of electricity named for Alessandro Volta (1745-1827), a pioneer in the development of electricity. Photovoltaic literally mean light–electricity. French physicist Edmond Becquerel first described the photovoltaic effect in 1839 [10], and was the subject of scientific inquiry through the early twentieth century. However, a major step forward in solar-cell technology came more than 100 years later in the 1940s and early 1950s when a method (called the Czochralski method) was developed for producing highly pure crystalline silicon which can be used to produce silicon based solar cells [7, 11]. In 1954, work at Bell Telephone Laboratories resulted in a silicon photovoltaic cell with a 4% efficiency [7]. On March 17, 1958 the world’s first solar-powered satellite was

launched, Vanguard I, It carried two separate radio transmitters to transmit scientific and engineering data. The battery powered transmitter operated for only 20 days, but the solar cell powered transmitter operated until 1964 [12]. Vanguard I proved the merit of space solar cell power. Technology development of the solar cell has been a part of the space program ever since. At present PV cells are already an important part of our lives. The simplest PV systems power many of the small electrical devices e.g. mobile phone chargers, calculators and wrist watches etc. Larger PV systems provide electricity for pumping water, powering communications equipment, and even lighting homes and running appliances. Various vehicles (car and bus) are also run on solar power devices on trail basis. Even solar power boats are commercially available. PV devices also installed in building structures such as windows, skylights, roofs and walls to provide electric power for the building and save electric energy as shown in fig.1.3. Grid connected PV systems also entered the market with significant contribution [13]. At the end of 2009, the world's cumulative installed PV capacity was approaching 24 GW. One year later it was 40.7 GW and at the end of 2011 it was 71.1 GW. In 2012, more than 100 GW of PV were installed globally [13]. Although at present PV technology is still expensive but it is expected that development of cheap and efficient solar cells would further push the growth of PV market.

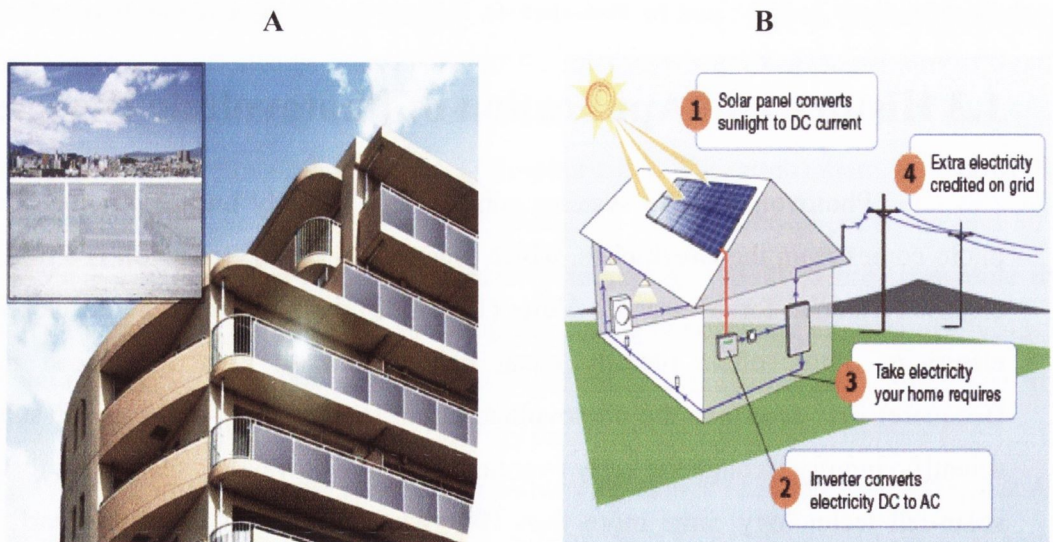


Figure 1.3: Shows photovoltaic application, A) solar panel installed in building and [14] B) solar panel installed on the roof of house [15].

1.4 Classification of Solar Cells

Solar cells are usually classified using three main categories i.e. 1) first generation 2) second generation and 3) third generation solar cell.

1.4.1 The First Generation Solar Cells

First generation solar cells are the most commercially available solar cells, currently making up about 90% of the photovoltaic market [16, 17]. First-generation technology consisted of a single-junction solar cell based on silicon wafers including single crystal (c-Si) (fig.1.4.A) or Poly-crystalline (p-Si) (fig.1.4.B) semiconductors. First generation solar cells have high efficiencies e.g. single crystal silicon solar cells show power conversion efficiency up to 25% and poly-crystalline silicon shows power conversion efficiency up to 20% [18]. Although the first generation solar cells have quite high efficiencies, but its production cost is very high, e.g. it requires highly pure silicon wafers with thicknesses of 200–250 μm which are accountable for a half of the cost of first-generation PV devices [18, 19]. Therefore, the electricity production cost of first generation solar cells technology is very high compared to the fossil fuels e.g. solar buzz, an international solar energy research and consulting reported that the residential price per kilowatt-hour of solar electricity in August 2010 was approximately 35 cents while electricity cost from coal power plants between 2 and 4 cents per kilowatt-hour [20].

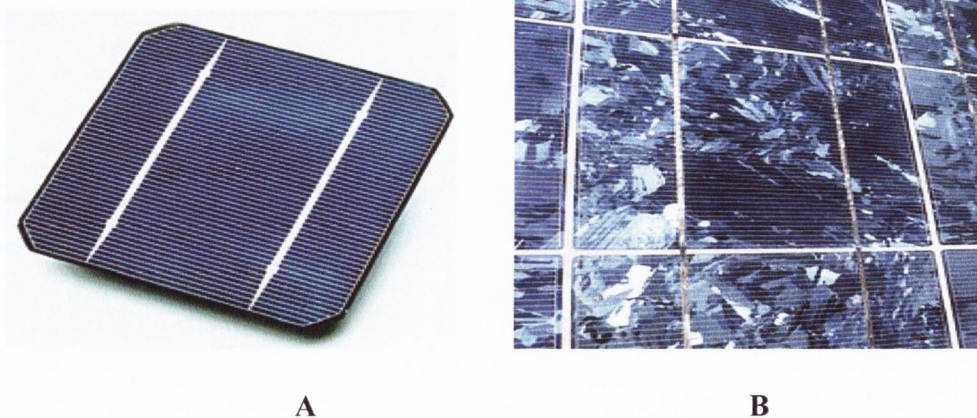


Figure 1.4: Shows **A)** single crystalline silicon solar cell [21] and **B)** Polycrystalline silicon solar cell [22].

The Si solar cells are designed from two types of doped semiconductor material, called "n-type" and "p-type" material as shown in Fig.1.5 A. The place between these two doped semiconductor layers is called p-n junction as shown in Fig. 1.5. B. When Si is doped with phosphorous, (have one extra valence electron than Si) is used to give a negative charge to the layer is called "n-type" material. On the other hand, when Si is doped with boron, (have one less valence electron than Si) is called "p-type" material. The light is absorbed by n-type side of Si cell and negative charges flow out of the electrode on the n-type side, through a load and perform useful work. The electrons then flow into the p-type side through external circuit, where they recombine with holes near the electrode [7].

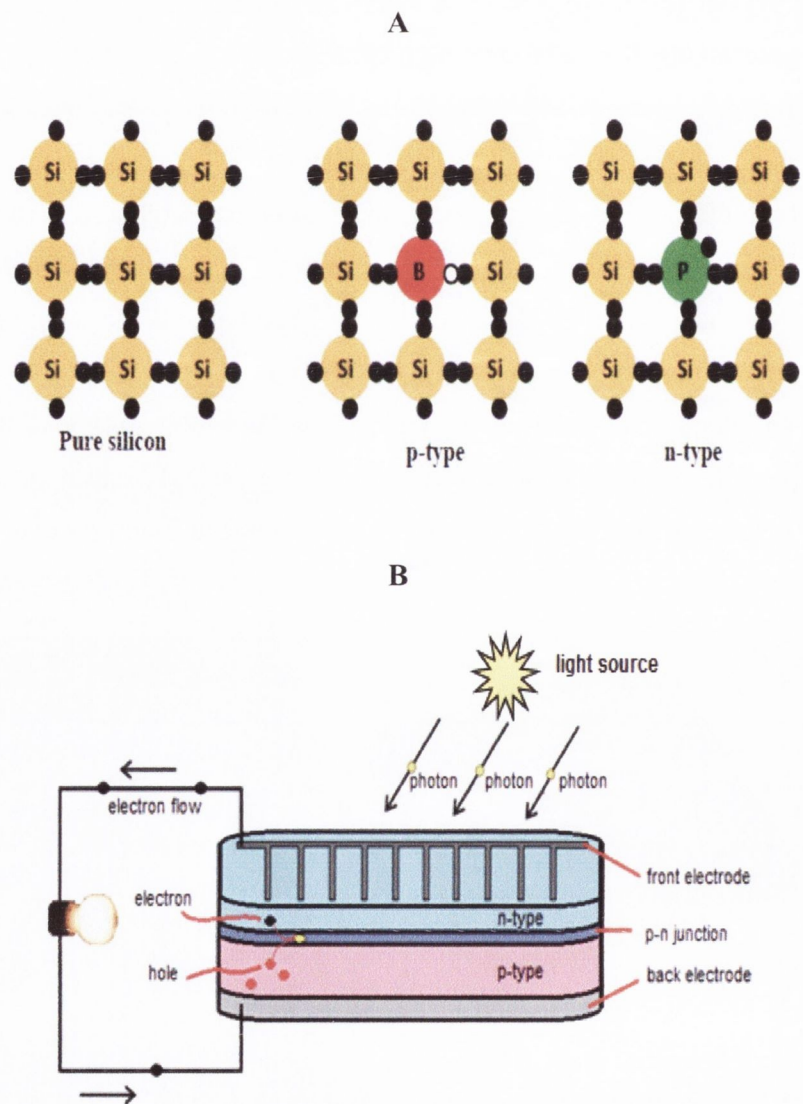


Figure 1.5: A) P type and n type Si and B) general structural diagram Si (p-n junction) solar cell.

1.4.2 Second Generation Solar Cells

Second-generation solar cells also known as thin film technology. The aim of second generation solar technology was to develop inexpensive material and method to produce a low cost and efficient solar cell [19]. The second generation solar cells include amorphous-Si (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) based devices. New manufacturing techniques such as vapour deposition and electroplating are advantageous as they reduce the need for processing solar cells at high temperatures. This technology uses only 1–10 μm of active material and absorbs the solar spectrum much more efficiently [19]. The second generation solar cells show conversion efficiencies typically in a range of 18–20% [17]. Although such conversion efficiencies have been able to meet the requirements for most uses in low power electrical appliances, the costs of the materials and their manufacturing are still somewhat too high and therefore limit practical application of these cells [17]. Therefore, this technology needs more research work and development to produce efficient, more stable and inexpensive devices/ technology.

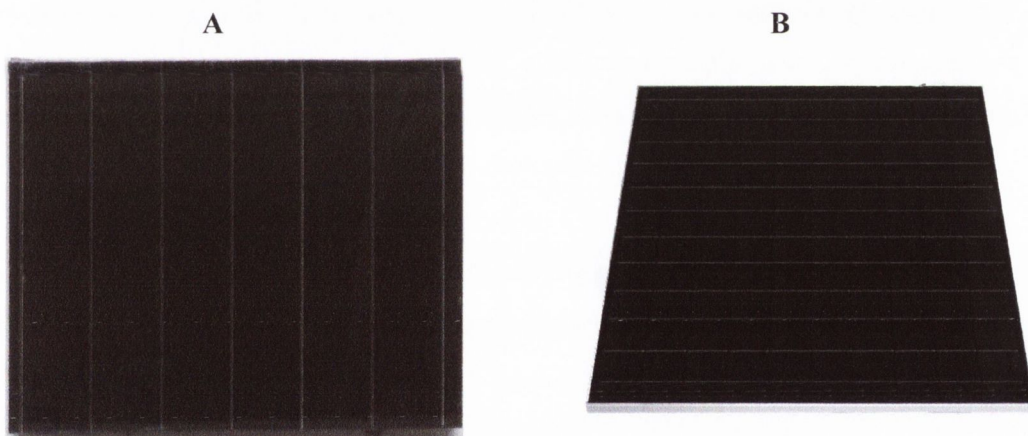


Figure 1.6: Shows **A)** Amorphous silicon solar cell module [23] and **B)** Copper indium gallium selenide solar cell module [24].

1.4 .3 Third Generation Solar Cells

The high cost of the first and second generation solar cells has motivated the development of third generation solar cells, based on new materials, structures and concepts [17]. Third generation solar cells was emerging as a novel PV-technology. Most of these cells are still in the research and development phase. All those solar cells

which are not directly related to a single p–n junction are referred to as third-generation solar cell [25]. There are several technologies in this generation include organic photovoltaics (OPVs) and dye-sensitized cells (DSSCs) etc. Organic photovoltaics use polymers for light absorption and dye-sensitized cells rely upon organic dyes or Ru bases dye. Both OPVs and DSSCs have relatively modest efficiencies; the highest recorded efficiencies are 8.3 % [26] and over 11 % [27] for OPV and DSSC respectively. However, the lack of chemical stability of the polymer materials under long term sunlight is still a problem for OPV [17]. However the lifetime of DSSCs has been demonstrated longer than 20 years in operating condition [28].

1.5 Dye Sensitized Solar Cell (DSSC)

1.5.1 Introduction to DSSC

The Dye sensitized solar cell (DSSC) is a type of third generation solar cell which represents one of the cheap potential options. For the first time a DSSC was developed by Gratzel et al. in 1991 [29]. Since then DSSCs have been widely investigated because of their potentially lower costs and simple manufacturing process compared to silicon (Si) solar cells [30]. DSSCs has some other advantages over Si solar cells due to their unique electrochemistry and physics e.g. the change in the light incident angle has a very small effect on the power conversion efficiency of DSSCs and the drop of the power conversion efficiency between 20 °C and 50 °C is negligible [31, 32]. So far, the highest reported power conversion efficiency for FTO/glass based DSSC (0.25 cm²) is 11.3% [2]. Although the power conversion efficiencies of DSSCs are lower than that of classical crystalline silicon cells, but the theoretical power conversion efficiency of the DSSC is expected to be over 20 %. Therefore, there is also a high potential for improvement in efficiency of DSSCs [33]. Beside the above advantages, DSSC can also fabricate on TCO coated flexible plastic e.g. polyethylene terephthalate sheet coated with tin-doped indium oxide (PET-ITO) [34]. Plastic based DSSCs has advantages over FTO/glass based DSSCs, such as low manufacturing cost, light weight, flexibility, transparency. Fig.1.7 shows A) Flexible DSSC B) glass based DSSC. These features attracted an interest of many research groups in recent years. The DSSC is also considered to be the most attractive alternative to silicon solar cells.

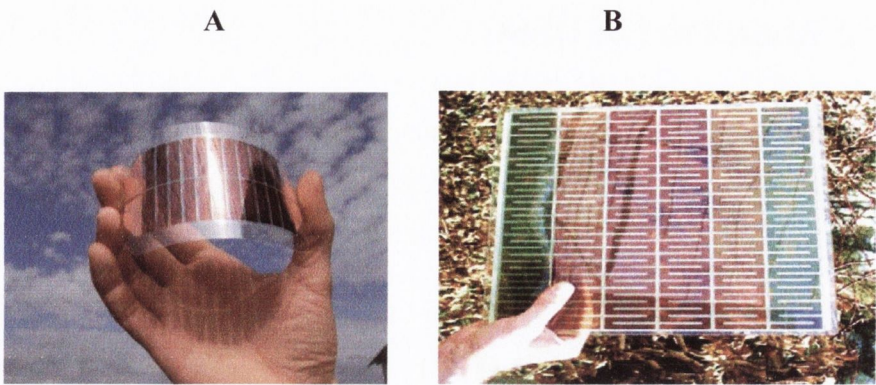


Figure 1.7: A) Flexible DSSC [35] and B) Glass based DSSC [36].

1.5.2 General Structure of DSSCs

DSSCs (Figure 1.8) generally consist of three main parts i.e. 1) working electrode (WE): is a transparent conductive oxide (TCO) coated glass with a photovoltaic layer such as mesoporous oxide (e.g. TiO_2) stained usually with an organometallic dye, 2) Counter electrode (CE) is again a TCO glass coated with platinum (Pt). The two electrode of DSSC are sealed by thermoplastic resin film. 3) The gap between these two electrodes is filled with an electrolyte which contains an organic solvent (e.g. acetonitrile) with iodide/tri-iodide redox couple [29].

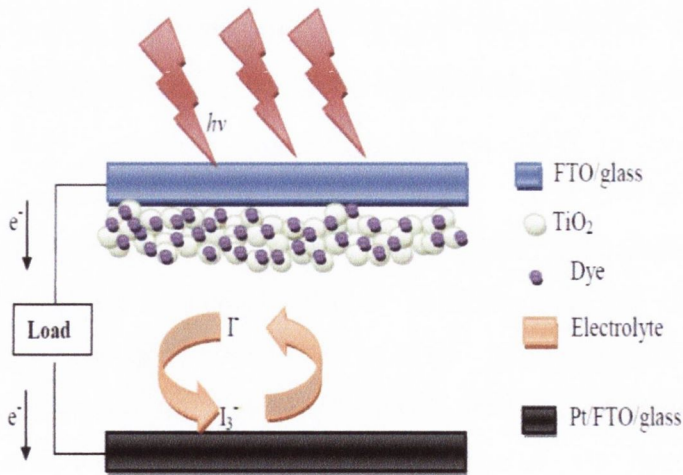


Figure 1.8: General structure of an assembled DSSC.

1.5.3 Main Part of DSSC:

In this section will discuss each component and each part of DSSC in more details to understand the ways to improve the power conversion efficiency and stability of DSSCs.

1.5.3.1 Working Electrode (WE)

The WE also knew as a photoanode. WE mainly consist of the following three components.

- A) Transparent conductive oxide (TCO)/glass or PET
- B) Mesoporous oxide semiconductor materials
- C) Photosensitizers (Dye)

A) Transparent Conducting Oxides (TCOs):

TCOs are both optically transparent and electrically conductive and mainly used in displays and in optoelectronics [37]. The indium tin oxide (ITO) [38], indium zinc oxide (IZO) [39], fluorine tin oxide (FTO) and antimony tin oxide (ATO) [40] are widely used as transparent conducting substrates. Traditionally, FTO deposited glass used as conducting substrate for WE as well as for CE in a DSSC. To obtain high DSSCs performance, the TCOs must have high conductivity, high transmittance, and high heat stability [41]. Among existing TCO materials, ITO has the highest transmittance in the visible range and the electrical conductivity [42] but the electrical conductivity of ITO substrate significantly decreases when it is sintered at high temperature over 400 °C [42, 43], which is required to remove organic components and to interconnect the TiO₂ particles of WE of the DSSC [44]. Therefore, ITO is not suitable for DSSCs application because its conductivity decreases at high temperature process, leading to significant reduction of power conversion efficiency of DSSCs [42]. Beside the above issues the ITO has some other disadvantages such as it is high price of indium metal. Also beside of the high cost, indium resources are depleting at very fast rate. Therefore researchers are intensively searching for an alternative material [45]. Particularly attractive would be to replace TCOs with inexpensive carbon based material such as graphene due to its high conductivity, high chemical, and thermal stability [46, 47].

B) Mesoporous Oxide Semiconductor Materials

TiO₂ is most widely used mesoporous oxide material in WE of DSSC. TiO₂ is a wide band gap semiconductor with a gap of around 3.2 eV. Although other wide-band gap semiconductor oxides such as ZnO, SnO₂ and Nb₂O₅ have also been employed but TiO₂ has been material of choice [2] with advantageous properties such as it is cheap, abundant and low toxic. The success of the TiO₂ material has also been attributed to the fast electron injection from the sensitizer to the TiO₂ (~ 50 fs) and a much slower reversal process [48]. There are three common crystal structures of TiO₂: anatase, rutile and brookite but anatase structure is considered the most suitable for DSSCs applications as it provides a better device performance because of its broader band gap [49]. TiO₂ deposition most commonly involves preparation of a paste and its application by doctor-blade or screen printing [50, 51]. Alternatively, the TiO₂ may be dispersed in a liquid medium and deposited by spin or linear coating [50]. After deposition, TiO₂ film of WE (photoanode) is normally sintered at 450 °C to 500 °C, to allow the removal of organic compounds and to provide a necessary adhesion to the substrate. Furthermore this processing results in a network of interconnected particles through which electrons can percolate. The thickness of the TiO₂ layer on TCO glass is mostly in the range of 10-14 μm. For high efficiency of DSSC it is necessary to produce the TiO₂ “double-layer” i.e. first layer consisting of nanocrystalline-TiO₂ particle of around 20 nm and second layer consisting of nanocrystalline-TiO₂ around 100 to 400 nm, which form the transparent and the light-scattering layers of the WE respectively. DSSC performance is improved by inclusion of a light scattering layer of larger TiO₂ particles which back scatter any light not absorbed by the active layer back through the cell resulting in an increased light capture [52]. For example, a WE composed of entirely 23 nm sized TiO₂ particles is reported to show performance of 7.62 %. This was increased to 8.95 % by additional use of scattering layer of particle size 100 nm deposited on top of the 23 nm particle transparent layer [53]. However, to further improve power conversion efficiency, reducing charge recombination at these interfaces is critical. The most common and effective methods to reduce the back electron transfer involve treatment of the WE substrate with a TiCl₄ solution before TiO₂ paste printing (under layer) and again following TiO₂ paste printing (over layer) in order to deposit a thin compact layer of TiO₂ particles on the surfaces. The deposition of a compact layer of TiO₂ by TiCl₄ treatment is found to increase power-conversion

efficiency compared to an untreated cell by ~24 %. Furthermore, interfacial adhesion between FTO and the nanoporous screen printed TiO_2 layer is also improved which increases both values the FF and J_{sc} [54].

Although high sintering temperature, TiO_2 based WE give high performance DSSCs but it is expensive process and only suitable for TCO coated glass substrate. Therefore, several process and methods have been explored in the preparation of low temperature WE (ITO/PET) for DSSCs. These methods include mechanical compression, hydrothermal necking and microwave sintering etc. Although the compression method in combination with ultraviolet UV- O_3 treatment has reported an efficiency of 7.6% but integration of such a process in large scale DSSC device fabrication remains challenging [55].

C) Photosensitizers (dyes)

TiO_2 is a wide band gap semiconductor (around 3.2) that can absorb only UV light (<400 nm) [56]. This is not significant as the domain of the UV light represents only a small part of the sun emission spectrum. A strategy to overcome this problem is to use a photosensitizer (dye) that can absorb light in visible and IR range. Photosensitizer of proper molecular structure is used to adsorb onto the TiO_2 surface which function is converting the maximum incident light into photocurrent. Therefore, photosensitizer is an essential component of the DSSC. The photosensitizers (dyes) are also one of the most expensive components of the DSSCs but since its amount in the solution is very small, typically of the order 10^{-4} M, therefore effect on the overall manufacturing costs of the cell remains reasonably low. First of all the ideal sensitizer for DSSC should be able to absorb radiation across a broad spectrum. The second is that sensitizer molecules or particles must be small enough to enter the pores in the nanoporous semiconductor lattice. The third is that once inside the lattice, must be able to firmly bind to the TiO_2 surface [57]. Furthermore, it should be stable enough to sustain at least 10^8 redox turnovers under illumination corresponding to about 20 years of exposure to natural light [58]. So far, various metal complexes/ organometallic and organic dyes as well as quantum dots have been utilized as sensitizers in DSSC but most of these requirements are met by some organometallic dyes such ruthenium complexes [59]. Figure 1.9 shows the chemical structure of three types of Ru-complexes dyes i.e. Commonly known as N3, black dye and N719, currently applied sensitizers in DSSCs because of broad adsorption spectra and rapid charge injection

rates. They are readily available commercially and show excellent efficiency levels up to 11% [60]. Most of these Ru-complexes dyes contains carboxylic group that has the ability to bind to TiO_2 surface by chemisorptions [61]. Researchers are trying to enhance the power conversion efficiencies of Ru dye-based DSSCs by modify the structure of Ru complexes to achieve wider absorption covering the whole visible region, including the near IR region, and/or achieve a higher molar extinction coefficient and stability [62].

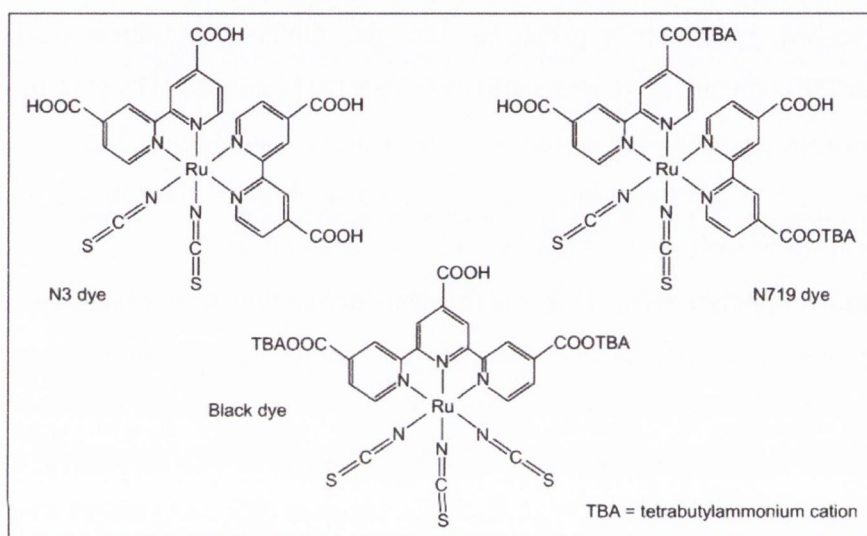


Figure 1.9: The chemical structures of the ruthenium-based dyes N3, N719 and ‘black dye’ [59].

1.5.3.2 Counter Electrode

The counter electrodes (CEs) or cathode is an important component of DSSCs, which traditionally consists of platinum (Pt) layer deposited on TCO substrate. The fabrication of CE can be achieved by dropping a solution of a platinum precursor (H_2PtCl_6) on the TCO coated glass substrate with subsequent heat treatment to 400 °C for 15 minutes [63]. The role of the counter electrode is to transfer electrons arriving from the external circuit back to the redox electrolyte and provide the reduction of the I_3^- to I^- in redox electrolytes, where the Pt serves as an electrocatalyst [64]. Though, Pt/FTO were the best counter electrode materials used in DSSCs so far because of its excellent electrocatalytic activity and good conductivity but both these materials (Pt and TCOs) are very expensive. Therefore Pt/FTO based CE accounts for approximately

25~35% of the overall price of DSSCs. Another disadvantage of Pt is that it slowly degrades in I^-/I_3^- medium [65]. Therefore it is extremely important to find new cost effective materials and approaches to replace the Pt and TCOs of CEs. The main requirements for a material to be used as an electrocatalyst in a DSSC are a low charge-transfer resistance and high exchange current densities for the reduction of the oxidized form of the charge mediator. Furthermore, such materials must possess chemical and electrochemical stability in the electrolyte system used in the cell. Various other materials rather than Pt, have also been used as electrocatalysts in DSSCs including CNTs,[66] graphite,[67] graphene, [66, 68] GNPs + graphene oxide, [69] carbon black,[70] conducting polymer PEDOT: PSS [71] and PEDOT:PSS+ graphene. Carbon nanotubes, graphene (or graphene nanoplates) are particularly attractive as they can be produced at relatively large scale, have good electric conductivity and high surface area.[72], as well as excellent mechanical strength and chemical resistance [73, 74]. Conducting polymers such as microporous polyaniline have also been employed as the components for counter electrode [75] and a power conversion efficiency of 7.1% has been achieved. In ideal case scenario a CE should be prepared with material which can act both as electrocatalyst and conducting material, to replace the Pt and TCO of CE [76]. In such an effort Lee et al. first time reported [76] TCO and Pt free CE for DSSC. They used conductive poly (3,4-alkylenedioxythiophene (PEDOT) films on a glass substrates as a counter electrode. They obtained in a power conversion efficiency of 5.08% compare to efficiency of 5.88% with a Pt/FTO counter electrode based DSSCs.

1.5.3.3 Electrolytes

The roles of the electrolytes are to provide electrons to regenerate the oxidized dyes to ground state. There are mainly four types of electrolytes employed in DSSCs so far as follow.

- A) Organic solvent based electrolytes
- B) Solid state materials/electrolytes
- C) Room temperature Ionic liquids (RTILs)
- D) Quasi solid state electrolytes

A) Organic Solvent based Electrolytes

Organic solvent based electrolytes mostly consist of an organic solvent containing iodide/tri-iodide redox couple and additives. The reported results shows that each component of these electrolyte plays a different role in the photovoltaic performance of DSSCs [77]. The organic solvent is a basic component in liquid electrolytes, it provides an environment/medium for iodide/tri-iodide ions dissolution and diffusion [77]. The ideal solvent should have low cost for commercial purpose, low viscosity, low volatility, should not desorb the dyes and should be non-toxic. Various kinds of organic solvent are used for the preparation of these kind of electrolyte such as acetonitrile (ACN), ethylene carbonate (EC), 3-methoxypropionitrile (MePN), propylene carbonate (PC), γ -butyrolactone (GBL), and N-methyl pyrrolidone (NMP) [78-83]. ACN has been shown to be the most successful and efficient organic solvent so far regarding the overall conversion efficiency, mainly due to its low viscosity (0.34 cp, 25 °C [84], and capability to dissolve organic components and additives in the electrolytes. Iodide/tri-iodide is the most efficient redox couple for regeneration of the oxidized dye so far employed but this redox couple is not suitable in some cases due to its severe corrosion for many sealing materials of DSSCs and the resulted DSSC is not stable for longer time [85]. Therefore, various type of redox couples such as Br^-/Br_2 , $\text{SCN}^-/\text{SCN}_2$, $\text{SeCN}^-/\text{SeCN}_2$ bipyridine cobalt (III/II) complexes have been investigated but these redox couples showed lower power conversion efficiencies than the iodide/triiodide redox couple, owing to their energy unmatchable with sensitized dyes or their intrinsic low diffusion coefficients in electrolyte [33, 86, 87]. There are also various kind of additives which were added to electrolytes such as 4-tert-butylpyridine, guanidinium thiocyanate, and guanidinobutyric acid [88] etc. These additives can also adsorb on the TiO_2 surface sites which are not occupied by the molecules dye to prevent recombination, i.e. electron leakage from the TiO_2 back to the electrolyte. Thus the addition of a small amount of these additives in electrolytes can enhance the photovoltaic performance of DSSCs. In summary of above discussion we can conclude that organic solvent based electrolyte containing iodide/tri-iodide redox couple shows high power conversion efficiency up to 11%. However, organic solvent based electrolytes face some problems such as leakage and volatility of the solvent which affect the long term performance of DSSCs.

B) Room Temperature Ionic liquids (RTILs or ILs):

The room-temperature ionic liquid (RTILs) are also called Ionic liquid (ILs). Ionic liquids (ILs) are molten salts made up of an anion and an organic cation and were discovered in 1914 by Paul Walden [89]. ILs can be both the source of iodide and the solvent itself due to its fluidic nature and can be used as electrolytes in dye sensitized solar cell [90, 91]. For the first time IL was tested in DSSC as electrolyte by Gratzel et al. in 1996 because of its good chemical and thermal stability, negligible vapor pressure, non flammability, and high ionic conductivity [92, 93]. Recently, growing attention has been paid to ILs especially those with 1,3-dialkylimidazolium cations due to their favorable properties [94], among the 1,3-dialkylimidazolium iodide compounds, 1-methyl-3-propylimidazolium iodide commonly known as PMII (Fig. 1.10) has the lowest viscosity, and its liquid domain extends down to -55 °C [95]. However, pure ILs usually has higher viscosity than that of organic solvent, which limits the iodide/triiodide diffusion /transport speed and the reduction of oxidized dye, so the photovoltaic performance of these DSSCs is lower than organic solvents based electrolyte [96]. The viscosity of highly viscous ILs can be lowered by mixing with low viscosity ILs. However, IL are still in the form of liquid, so facing same sort of problems of sealing and leaking like organic solvent based electrolytes in DSSCs. Thus the resulted DSSC is not stable for long time. Furthermore the overall power conversion efficiencies of ILs based electrolytes is lower than organic solvent based electrolytes/DSSCs. Therefore, researchers are investigating solid-state or quasi-solid-state electrolytes to replace liquid electrolytes of DSSC, to develop stable and efficient DSSCs.

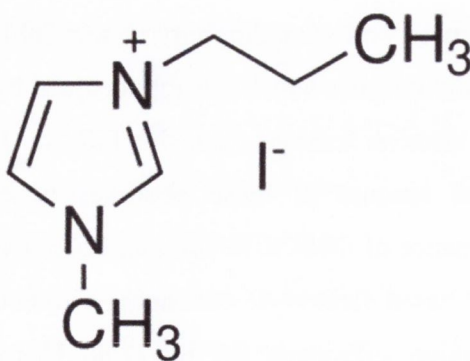


Figure 1.10: The chemical structure of 1 Methyl-3-propylimidazolium iodide (PMII) [97].

C) Solid State Electrolytes

There are mainly two kinds of solid state electrolytes used in DSSCs so far 1) Hole transport materials (HTMs) and 2) Solid state electrolyte containing iodide/tri-iodide redox couple.

C.1 Hole Transport Materials (HTMs)

These HTMs work as a mediator (electrolyte) in DSSC without the addition iodide/tri-iodide redox couple [77]. The original state of the dye is subsequently restored by electron donation from the hole conductor in DSSCs. The hole conductor is regenerated in turn at the counter electrode, and the circuit is completed via electron migration through the external load [98]. Inorganic hole transport materials such as CuI was used as HTM in DSSC and obtained power conversion efficiency of 2.4 %. Beside the lower power conversion efficiency, the inorganic HTMs stability is quite poor, even worse than the traditional organic based DSSCs. Organic material such as Spiro-OMeTAD used as HTM in DSSC and achieved power conversion efficiency of 3.2 %. Organic or inorganic HTM as a mediator for DSSCs cannot satisfy the practical application either due to their low power conversion efficiencies or stability issues.

C.2 Solid State Electrolyte containing Iodide/Tri-iodide redox couple

In this case a redox couple dispersed in solid state material and used as solid state electrolytes in DSSC for example Stergiopoulos et al dispersed I^-/I_3^- redox couple into binary polyethylene oxide (PEO) /TiO₂ nanoparticles mixture [99]. The addition of the titania filler into PEO matrix reduces the crystallinity of the polymer and enhances the mobility of the I^-/I_3^- redox couple and increasing the power conversion efficiency up to 4.2%. The I^-/I_3^- based solid state electrolyte showed higher photovoltaic performance than that using HTMs is due to the fact that the I^-/I_3^- can efficiently convert oxidized sensitizers to ground state [77]. This kind of solid state electrolyte show higher photovoltaic performance than HTMs is due to the fact that the I^-/I_3^- can efficiently revivify oxidized dyes but still its efficiency is much lower than organic based electrolytes DSSC.

D) Quasi Solid State Electrolyte or Gel Electrolyte

The quasi-solid state electrolyte, or gel state, is a particular state of matter, neither liquid nor solid or conversely both liquid and solid [77]. The incorporation of

organic materials (polymer) or inorganic material (SiO_2) or combination of both types of material either in organic solvent based electrolyte or in ionic liquids to solidify them is called quasi solid state electrolyte or gel electrolyte. Michael Gratzel et al. reported for the first time the incorporation of nanoparticles (SiO_2) into ionic liquids based liquid electrolytes achieving 7% of efficiency with ionic liquids based liquid electrolytes and 7% efficiency with SiO_2 nanoparticle based quasi solid state electrolytes [100]. After this several type of materials e.g. methacrylate or polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), poly ethylene oxide, PMMA and carbon based material e.g. CNT, graphite and carbon black were incorporated in liquid electrolytes and used as quasi solid state electrolytes in DSSC. Singh et al. [101], incorporated polyethylene oxide into ionic liquid (1-ethyl 3-methylimidazolium trifluoromethanesulfonate) and further added NaI and I_2 to this system and achieved power conversion efficiency of 2.45%. Li et al. prepared a quasi-solid electrolytes by using poly (acrylonitrile-co-styrene) as polymer matrix, acetonitrile and tetrahydrofuran as binary organic mixture solvent, NaI + I_2 as electrolyte, graphite powder and 1-methylimidazole as additives [102]. They obtained power conversion efficiency of 3.16 % and 3.25% with liquid electrolytes and quasi solid state electrolytes/DSSC respectively. The conversion of liquid electrolyte to gel or quasi solid state electrolytes has some advantages, for example, can stop the leakage and some nanomaterials (e.g. CNT or graphite) also increase the light conversion efficiency of DSSC. Therefore, quasi-solid state electrolytes/DSSCs have received much attention and widely investigated.

1.5.3.4 Sealing Materials of DSSC

Long-term stability is a key parameter for any type of solar cells. To meet this requirement, the cell must be intrinsically and extrinsically stable under elevated temperature, cyclic changing temperatures, exposure to humidity and prolonged illumination. Penetration of water and oxygen and escape of solvent molecules are typical examples for extrinsic factors [60]. The sealing material is needed to prevent the leakage of electrolyte and the evaporation of solvent. The sealing material should be chemically and photochemically stable against the electrolytes components such as iodine and the solvent present in electrolytes. Surlyn (Du Pont), a copolymer of ethylene and acrylic, meets these requirements [103]. The sealant frame place between WE and

CE and typically laminated together on a hot plate. Surlyn also acts as a spacer between WE and CE to prevent the cell from short circuiting. There is another method so-called glass frit technique, which could also be used but it requires high temperatures (400 °C), that is likely to cause the degradation of dye. So in this case the dye adsorption is done after sealing but this techniques required several step and components for dye and electrolytes filling. Therefore, this method is not really suitable for a large scale production. Due to the direct relevance to the manufacturing of commercial products, little is published about sealing issues [104]. The intrinsic stability of DSSC is related to test the thermal stability of the sensitizer, the electrolyte and the Pt-coated counter electrode under International Electrotechnical Commission (IEC) test standards [105]. In this case the stability is not directly related to sealing materials but the DSSC should be perfectly closed/sealed to find the intrinsic stability [60].

1.6 Operating Principles of DSSCs

This section describes the operating principles of DSSCs. Dye-sensitized solar cell (DSSC) device physics is different from traditional p-n junction type solar cells in many way. Figure 1.11 shows schematic energy diagram of a DSSC. We can summarize the the photo conversion process of a DSSC in following different steps [106].

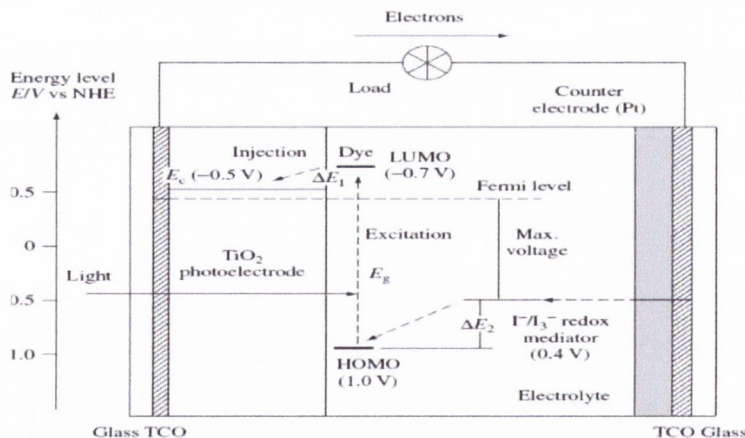
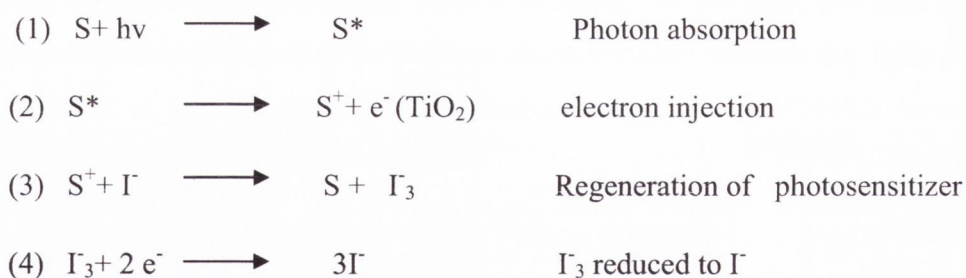


Figure 1.11: Schematic energy diagrams and operating principles of DSSC [107].

- Sunlight enters through the working electrode of a DSSC and the photosensitizers absorb the incident photon flux ($h\nu$).

- The photosensitizers are excited from the ground state (**S**) to the excited state (**S***), from where it inject, within femto seconds, an electron into the conduction band of the TiO_2 , resulting in the oxidation of the photosensitizer (**S⁺**).
- Injected electrons in the conduction band of TiO_2 are transported between TiO_2 nanoparticles with diffusion toward the back contact (TCO) and consequently reach the counter electrode through the external load and wiring.
- The oxidized sensitizers (**S⁺**) accept electrons from the I^- ion redox electrolyte and regenerating the ground state of sensitizers (**S**), and I^- is oxidized to I_3^- state.
- The I_3^- diffuses toward the counter electrode where it is reduced to I^- ions.

The chemical reactions going on in the DSSC can be summarized as follows.



Overall, electric power is generated without permanent chemical transformation. The performance of a DSSC is predominantly based on four energy levels of the component: the excited state (approximately LUMO) and the ground state (HOMO) of the photosensitizer, the Fermi level of the TiO_2 electrode, which is located near the conduction-band level, and the redox potential of the mediator (I^-/I_3^-) in the electrolyte. The photocurrent obtained from a DSSC is determined by the energy difference between the HOMO and the LUMO of the photosensitizer, analogous to the band gap, E_g , for inorganic semiconductor materials. The smaller the HOMO–LUMO energy gap, the larger the photocurrent will be because of the utilization of the long-

wavelength region in the solar spectrum. The energy gap between the LUMO level and the conduction-band level of TiO_2 , ΔE_1 , is important, and the energy level of the LUMO must be sufficiently negative with respect to the conduction band of TiO_2 to inject electrons effectively. In addition, substantial electronic coupling between the LUMO and the conduction band of TiO_2 also leads to effective electron injection. The HOMO level of the complex must be sufficiently more positive than the redox potential of the I^-/I_3^- redox mediator to accept electrons effectively (ΔE_2). The energy gaps, ΔE_1 and ΔE_2 , must be larger than approximately 200 mV as driving force for each of the electron-transfer reactions to take place with optimal efficiency [108]. A series of recombination reactions compete with the forward reactions in the DSSC. When electrons injected from the excited state of the dyes into the conduction band of the TiO_2 . The injected electrons have two possible recombination pathways, either reduce to 1) the oxidized dye molecules to ground state 2) or I_3^- ion to I^- ion [109]. Such charge recombination leads to losses in both the short-circuit current (J_{sc}) and the open-circuit voltage (V_{oc}), resulting in the decrease in efficiency of DSSC [110]. Various approach were introduced to reduce the possible charge recombination pathways occurring at the semiconductor/ dye/electrolyte interface such use of additives which have been co-adsorbed onto the semiconductor surface to improve the photovoltaic performance (J_{sc} and V_{oc}) of DSSCs [110].

1.7 Introduction and Application of CNTs in DSSCs

1.7.1 Introduction to Carbon Nanotubes (CNTs)

The word carbon has been derived from Latin carbo meaning coal or charcoal [111]. Carbon as charcoal, soot and coal has been used since prehistoric times. For centuries, carbon was considered to have two crystalline allotropic forms i.e. diamond and graphite. However, in recent decades many more allotropes and forms of carbon have been discovered such as wrapped 0D buckyballs (fullerenes), the rolled 1D nanotubes and 2D sheet of graphene [112]. The carbon atoms in diamond are arranged of sp^3 bonds (which arises from the mixing of one s and three p orbitals). While carbon atoms in graphite, CNTs and graphene are arranged of sp^2 bonds, and the fourth electron in unhybridized P_z orbital allowed to be delocalized among all atoms. Carbon nanotubes (CNTs) have been discovered and characterized in 1991 by Iijima from NEC

laboratories [113]. CNTs are sheets of graphene rolled up as hollow cylinders. CNTs can be classified as 1) Single walled carbon nanotubes (SWCNTs) (Fig.1.12.A) and multiwalled carbon nanotubes (MWCNT) (Fig.1.12.B). A single walled carbon nanotube is a single rolled graphene sheet. The diameter of a SWCNT is between 0.4–4 nm [114]. MWCNTs, with several concentric shells (2-50 layers) [115]. MWCNTs can have diameters from 2 nm-100 nm and lengths of up to micrometers [116]. Based on the rolling up pattern of graphene sheet there are three possible types of CNTs. Shown in Figure 1.13 A, B, C are the armchair, zigzag and chiral CNTs respectively. The structure of SWCNTs strongly influences their electronic properties. SWCNTs are either electrically conductive or semiconducting. Two-thirds of zigzag and chiral nanotubes behave like a semiconductor, whereas one-third of these nanotubes (with different diameters), and all armchair nanotubes (independent of diameter), have electrical conductivity as good as that of a metal [117]. Therefore, SWCNT is known to exhibit metallic or semiconducting property. This is, however, not the case for MWCNT which consist of two or more concentric rolled graphene sheets, all MWCNTs have metallic nature [118]. Because of its large diameter, the shells of an MWCNT would be conductive even if they are of semiconducting chirality [116]. CNTs are unique nanoscale objects with the combined advantages of large surface area, high electrical conductivity, and chemical stability [119] that make them excellent candidates for a variety of application.

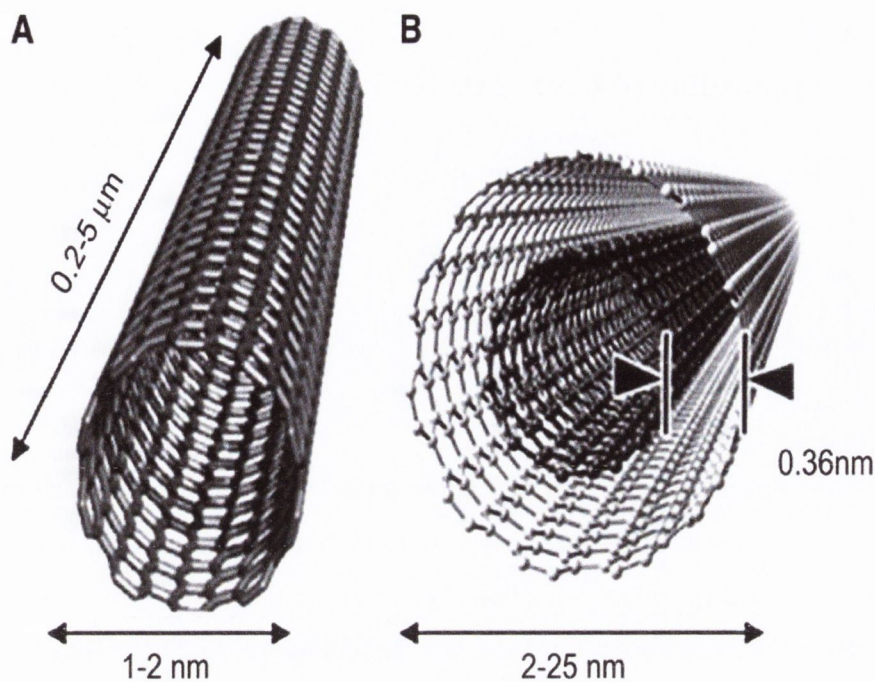


Figure: 1.12.A) SWCNTs and B) MWCNTs [120].

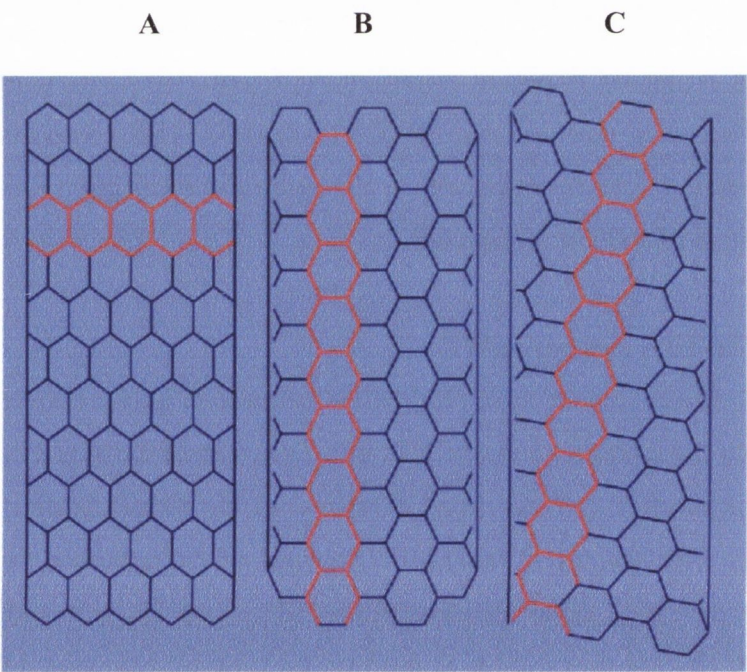


Figure 1.13: SWCNTs type A) armchair, B) zigzag and C) chiral [121].

1.7.2 Application of CNTs in DSSC

CNTs have found following application in DSSC so far.

- 1) As a electrocatalyst in CE
- 2) CNTs-TiO₂ composite/WE
- 3) As a filler in electrolytes

1) As a Electrocatalyst in CE

Several research groups reported CNTs as an electrocatalysts in CE for DSSC due to their rapid electron transfer kinetics, large surface area, and electrocatalytic activity toward tri-iodide reduction. Lee et al. reported that MWCNTs can be used as efficient electrocatalysts for tri-iodide reduction in DSSCs. They achieved power conversion efficiencies of 7.67 % and 7.83 % with MWCNTs/FTO and Pt/FTO based CEs/DSSCs respectively [119]. Various CNTs based composites materials were also used as electrocatalysts in CE of the DSSC [122]. Yun et al. used MWCNTs and conducting polymer (PEDOT: PSS) composite as electrocatalysts in CE. The DSSC with MWCNT/PEDOT: PSS composite /FTO-CE showed power conversion efficiency of 5.4 % compared to power conversion efficiency of 7.1 % with Pt/FTO based CE [123]. They also reported that MWCNTs-PEDOT: PSS composite /CE shows good performance due to improvement in the electrical conductivity and catalytic activity than pristine PEDOT: PSS film/CE.

2) CNTs-TiO₂ composite/WE

Several papers have reported an increase in power conversion efficiencies of DSSCs by the incorporation of CNTs into TiO₂ film of the WE. Lee et al. reported that incorporation (0.1 wt %) MWCNTs into TiO₂/WE increased power conversion efficiency from 4% to 5.02% [124]. The value of J_{sc} increased from 7.96 mA/cm² to 9.08 mA/cm², Voc value increased from 761 mV to 781 mV and FF increased from 0.68 to 0.70. The researchers found that the charge recombination between injected electrons and electron acceptors in the redox electrolyte, I₃⁻ was remarkably retarded. Weng et al. reported TiO₂ and MWCNTs (0.3 wt %) nanocomposite WE for DSSC which was obtained by the modified acid-catalyzed sol-gel procedure [125]. MWCNTs would improve the roughness factor (from 834 to 1267) of the WE and the reduced

charge recombination of electron. However, a higher loading of MWNTs causes light-harvesting competition that affects the light adsorption of the dye-sensitizer, and consequently reduces the cell efficiency.

3) As a Filler in Electrolytes

CNT have also been incorporated in ionic liquid electrolytes to prepare gel or quasi solid state electrolytes. Usui et al. dispersed SWCNTs (1 wt %) and MWCNTs (1 wt %) individually into 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (EMIm-TFSI) ionic liquid electrolyte by grinding [126]. The resulted gel electrolytes of CNTs- EMIm-TFSI shows increased in their viscosity as well as their electric conductivity also increased. The power conversion efficiencies were increased from 4.21 % (pure ionic liquid) to 4.60 % with SWCNTs and 4.79 % with MWCNTs based gel electrolyte-DSSCs. Ikeda et al. [127] fabricated quasi solid-state electrolytes by incorporation of SWCNTs (6.97 wt %) and MWCNTs (6.97 wt %) to the IL, 1,3-diethyleneoxide derivative of imidazolium iodide and they obtained power conversion efficiencies of 1.63% and 1.01% with SWCNTs and MWCNTs based quasi solid state/DSSCs respectively. The mixing yielded CNT-EOImI composite in the form of a highly viscous black paste which is clay-like solid state and is free of volatile components. They obtained power conversion efficiencies of 1.63% and 1 % with SWCNTs and MWCNTs based quasi solid state electrolytes/DSSCs respectively. They found that SWCNTs works best over other kinds of carbon based quasi solid state/DSSC. By adsorption of oxygen in air, semiconducting SWCNT tends to exhibit p-type nature in conduction and current rectification [128, 129]. This would indicate that the SWCNTs can function like a hole conductor in junction with the surface of dye-coated n-type TiO_2 . It has also been shown that SWCNTs also works as an efficient electrocatalyst in the CE of the DSSC[130]. While MWCNTs has lack current rectification ability, back electron transfer (short-circuiting) matters at the surface of carbon in contact with dye coated TiO_2 , which significantly reduce the J_{sc} value. This is assumed to be a main reason why SWCNTs enable to achieve relatively high performance in J_{sc} and V_{oc} .

1.8 Introduction and Application of Graphene in DSSCs

1.8.1 Introduction to Graphene

The remarkable properties of graphene include high specific surface area [131], high mechanical strength, unparalleled thermal and electricity conductivity [132-134]. Furthermore, it was reported that the production cost of graphene in large quantities could be much lower than that of CNTs [135], therefore graphene has emerged as a rapidly rising star in the field of material science [136]. It is the thinnest known and the strongest ever measured material in the universe [137]. Graphene (fig.1.14 A) is a one-atom-thick planar sheet of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice [138]. Graphene is extracted from graphite while graphite consists of layers of carbon atoms arranged in a hexagonal lattice (1.14 B). Each carbon layer in graphite is bonded to a carbon layer above and a carbon layer below through van der Waals forces while each carbon atom is covalently bonded (sp^2 -bonded carbon) to three other atoms within each graphite layer. Graphene can be also considered as a basic building block for carbon nanomaterials of all other dimensionalities including the wrapped 0D buckyballs (fullerenes) the rolled 1D nanotubes and the stacked 3D graphite [138].

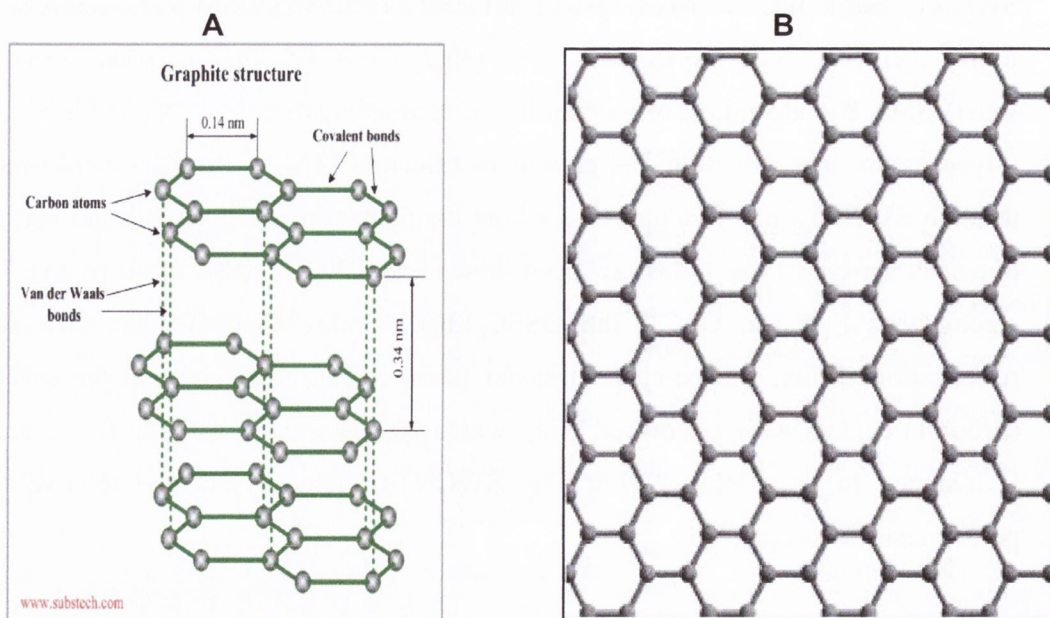


Figure 1.14: A) Schematic structure of graphite [139] and B) schematic structure of graphene [140].

Until now, several physical and chemical methods have been developed to produce individual graphene or chemically modified graphene. For example ‘The Scotch Tape Method’ which was developed in 2004 by a group of researchers in the University of Manchester [141], remains to be the most popular and successful in producing single or few layers of graphene. Although graphene can be obtained by this method but the yield is extremely low [136]. Graphene can be synthesised by oxidization of graphite, followed by exfoliation in water, to give aqueous dispersions of graphene oxide (GO) [142]. GO faces some significant disadvantages such as GO is a poor electrical conductor [143]. The oxides can be removed by using reducing chemical agents [144] (such as hydrazine hydrate, dimethyl hydrazine and hydroquinone), and thermal reduction [143]. The reduction of GO results in graphene but it cannot remove many structural defects introduced by the oxidation process [143] making this material unsuitable for many applications. Therefore all these mentioned methods are not suitable for practical application either due to very low production or structural defects formation in graphene. Recently Khan et al [145] have developed a method to prepare graphene dispersions at high concentrations, up to 1.8 mg/ml, with yields of up to 4 wt % monolayers without oxidation and defect formation. This process relies on low-power sonication for long time. This method has some advantages such as low cost and simple preparation process make them a best choice for certain application. The graphene and graphened based material research is still in its relative infancy, and the application of graphene has just begun. Thus, many properties of graphene are not fully understood. Therefore diverse applications are yet to be explored [136].

1.8.2 Application of Graphene in DSSCs

Graphene have found following application in DSSC so far:

- 1) As a transparent electrode in WE
- 2) As catalyst in CE

1) Transparent Conductive Electrode/WE

Graphene might replace the TCO of WE in the DSSCs because graphene films shows excellent electrical conductance, reasonable transparency in both the visible and near-infrared regions, furthermore graphene shows high chemical and thermal stabilities [146]. Xuan et al. used exfoliated graphite oxide as starting material,

followed with thermal reduction, they obtained a graphene film with a thickness of 10 nm with transparency of higher than 70% and a conductivity of 500 S cm^{-1} [46]. They used this transparent electrode as WE in DSSC, this was the first attempt to use graphene film to replace the FTO of the WE. Although the photovoltaic performances of this graphene-based WE was not as good as that of the FTO-based WE (reference DSSC). However the authors suggested that there is still large room left for further improvement in the graphene based transparent electrode for WE of the DSSCs.

2) Graphene as Electrocatalyst in CE

Graphene was also expected to be a promising material for CE in DSSC due to its excellent electrical conductivity and good catalytic activity toward iodide-tri-iodide redox couple [147]. Therefore, several groups have explored graphene-based Pt free CEs for DSSCs. The power conversion efficiencies of graphene based counter electrodes-DSSC vary from 0.7 to 6.8% as shown in Table 1.1. The variation in the power conversion efficiencies with graphene based CE is mainly due to the utilization of different methods and techniques for graphene synthesis and graphene film preparation respectively. W. Zhang et al. reported graphene based CE for DSSC and they achieved power conversion efficiency of 6.8 % compared to the power conversion efficiency of 7.59 % with standard Pt based CE/DSSC [148]. Graphene nanosheets (GNs) were synthesized by a hydrazine reduction of exfoliated graphene oxide and the GNs were dispersed in a mixture of terpineol and ethyl cellulose and deposited FTO glass substrate by screen-printed process, followed by annealing at various temperature in air. In this work the authors claimed that the annealing temperature used for the graphene-based counter electrode exhibited a remarkable effect on the performance of DSSCs. They reported that optimized annealing temperature was 400°C , at which the best power conversion efficiency (6.8%) was achieved. The researchers also found that there was a trade-off between enhancing the adhesion and increasing the electrical conductivity of the graphene film on the FTO glass substrate by the annealing treatment in air. When the annealing temperature was higher than 400°C , the GNS film was easier to peel off from the FTO substrate due to the presence of fewer organic binders (terpineol and ethyl cellulose), which were burned out at high temperatures, causing a higher R_{ct} in the CE of the DSSC. Kaniyoor et al. also reported graphene based CE for DSSC where graphene was prepared by thermal reduction of graphite oxide. Graphene were dispersed in nafion and ethanol solution and deposited on FTO glass substrates by

drop casting. They achieved power conversion efficiencies of about 2.82% and 3.4% with graphene based CE and Pt-based CE/ DSSCs respectively [68].

Table 1.1: Shows the published reports of the photovoltaic parameters of DSSCs fabricated with graphene based CE (graphene/TCO).

CE type	Jsc(mA/cm ²)	Voc(V)	FF	Efficiency%	Ref.
Graphene	16.98	0.747	0.53	6.98	[148]
Graphene	6.12	0.640	0.56	2.19	[149]
Graphene	5.60	0.700	0.60	2.30	[150]
Graphene	7.70	0.680	0.54	2.82	[68]
Graphene	6.42	0.700	0.16	0.74	[151]

Various graphene based composites were also used as electrocatalyst in the CE of the DSSCs. Lee et al. used graphene/PEDOT composite as CE in DSSC. The DSSC with such a graphene/PEDOT composite counter electrode showed a power conversion efficiency of 6.26%. The incorporation of graphene into PEDOT increased the electrical conductivity as well as electrocatalytic activity of the composite film.[152] Bajai et al. deposited Pt nanoparticles on graphene layers and revealed that the amount of Pt loading had a remarkable influence on the efficiency of the resulting DSSCs [153]. An optimal Pt loading (27.43%) was found. The DSSC with the optimized Pt/graphene counter electrode not only contained a lower amount of Pt, but it also exhibited improved conversion efficiency. The efficiency improvement was attributed to the increase in the graphene sheet defects caused by Pt.

3) Graphene-TiO₂ Composite / WE

The performance enhancement of DSSCs as a result of the graphene incorporation into TiO₂ semiconductor was demonstrated by several groups [154-156]. Yang et al. reported chemically reduced graphene oxide-TiO₂ composite/WE for working electrode in DSSC [155]. They found that 0.6 wt%, the graphene incorporation in TiO₂ layer led to a faster electron transport and a lower recombination, together with a higher light scattering. On the basis of these advantages, graphene-TiO₂ composite based WE has shows increased in the short circuit current density by 45% without

sacrificing the open-circuit voltage and obtained the power conversion efficiency of 6.97%, which was increased by 39%, compared to power conversion efficiency of 5.01% with pure TiO_2 based WE/DSSC.

1.9 Aims and Objectives of Thesis

It is well established that the commercialisation of DSSCs requires improvement in three areas: power conversion efficiency, long-term stability, and low fabrication costs. Thus, the main goal of this thesis is to improve the power conversion efficiencies and long term stabilities of DSSCs by using low cost and easily available material. Traditionally DSSCs use organic solvent based electrolytes which gave higher power conversion efficiency up to 11 % but the use of organic solvent based electrolytes has facing some serious issue of stability which is limiting the long term performance and practical use of DSSCs. Lee et al. reported incorporation of SWCNTs in to binary ionic liquids and resulted quasi solid state electrolytes was tested in DSSC and they achieved the power conversion efficiency of 3.49 % [157]. Although SWCNTs based quasi solid state in DSSC showed superior stability than organic based electrolyte based DSSC but SWCNTs is very expensive. So the challenge is to replace SWCNTs with low cost material. Hence one of the objectives of our work is to replace the SWCNTs of IL bases quasi solid state electrolytes with low cost but effective material. Graphene was our choice material as it has remarkable properties including high specific surface area, thermal and electricity conductivity [132, 158-162]. Furthermore, it was reported that the production cost of graphene in large quantities could be much lower than that of CNTs. Graphene was prepared according to procedure developed by Khan et al. [145]. Therefore we plan to use graphene, SWCNTs and mixture of SWCNTs plus graphene as additives (filler) to IL, 1-propyl-3-methylimidazolium iodide (PMII) to make quasi solid state electrolytes for DSSCs.

Another objective of our work is exploring the mixture of ILs as potential electrolyte for DSSCs. We plan to use the low viscosity IL (EMISCN) to mix it at various wt % with high viscosity IL (PMII) in order to find the optimal binary IL combination for efficient DSSC. We aimed to develop new quasi solid state electrolytes, which could be prepared by the addition of SWCNTs, graphene, hybrid SWCNTs+ graphene into optimized binary IL. It is expected that dispersion of various carbon based nanomaterials should improve in binary IL based quasi solid state

electrolytes. Also we anticipate that the enhanced diffusion and redox processes in new electrolytes and as a result the further improvement of power conversion efficiencies of DSSCs.

There is another problem which should be overcome i.e. cost of CE of the DSSC. For example, Pt based CE accounts for approximately 25~35% of the overall price of DSSCs [163] and its high cost limits the mass production of DSSCs. Therefore it is extremely important to find new cost effective materials and approaches to replace the Pt of the CEs. Carbon based nanomaterials such as carbon nanotubes and graphene has been used as electrocatalyst materials in CE of the DSSC. However the power conversion efficiency of DSSCs using carbon nanomaterial based CEs has been found to be lower as compared to Pt ones [164]. Furthermore, carbon based nanomaterials (CNTs or GNPs) have a very low adhesion to TCO and glass substrate surfaces [165]. Thus, our aim is to address these issues by introducing and investigating composite films of CNTs, GNPs type 3 and hybrid of CNTs + GNP type 3 plus PEDOT: PSS composite as electrocatalysts to replace Pt of the CE of the DSSC. It is expected that the addition of PEDOT: PSS could enhance the adhesion and electrocatalysts properties of these various carbon based composite films.

Another objective of our work is to investigate various types of composite films by addition of three types of GNPs into PEDOT: PSS dispersion, which should simultaneously replace the Pt as well as TCO of the CEs of the DSSCs. It is well known that an addition of organic solvents with high boiling point significantly improves the electrical conductivity of PEDOT: PSS by up to 2 or 3 orders of magnitude [166-169]. Therefore, we plan to add the NMP (10 vol %) to PEDOT: PSS dispersions and then add various types of GNPs to these NMP diluted dispersions. We believe, that the addition of NMP to the PEDOT: PSS dispersion will also improve the dispersion of GNPs and as a result the composite films should show enhanced conductive properties compared to pure PEDOT: PSS film/CE.

To further improve the power conversion efficiency of DSSC, it is necessary to provide an efficient electron transport across the TiO_2 film and to reduce or eliminate the charge carriers recombination process. Therefore, our other aim to investigate the effect of GO and GNPs type 2 onto the TiO_2 film of the WE in order to enhance the power conversion efficiency of DSSC. It is expected that the introduction of highly electrically conductive GNPs into TiO_2 film/WE should reduce the charge recombination at the TiO_2 nanoparticle-electrolyte interface due to a faster electron

transport. Furthermore it is also expected that GNPs type 2 would also enhance the conductivity within TiO₂ nanoparticle film and facilitate an electron transport between the TiO₂ and the FTO substrate.

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Chapter 2: Experimental

2.1 Starting Materials

Powdered graphite was purchased from Branwell (Branwell natural graphite). 1-Methyl-3-propylimidazolium iodide (PMII) and 1-ethyl-3-methylimidazolium thiocyanate was purchased from Io-li-tec and used as received. Organic solvent based High Performance Electrolyte (HPE), TiO₂ pastes, DSL 18 NR-T (average TiO₂ nanoparticle size 20 nm), Thermoplastic Sealant (25 μ m) and dye (N-719) were purchased from Dyesol Ltd. Sealant/spacer (Meltonix 1170-60 series) and Ti-Nanoxide D paste (average TiO₂ nanoparticle size 15-20 nm and 100 nm) were purchased from Solaronix SA. SWCNTs were supplied by Elicarb (SWCNT, PR 0925). N-Methylpyrrolidone (NMP) was supplied by Sigma-Aldrich. Graphene nanoplatelets (GNPs) type 1, type 2 and type 3 was purchased from Cheap Tubes Inc, USA (www.cheaptubesinc.com), with surface area: GNPs type 1 =50 m²/g, GNPs 2 =100 m²/g and GNPs type 3 =600-750 m²/g, and diameter: GNPs 1 = 5 μ m, GNPs 2 = 5 μ m and GNPs 3= 2 μ m). MWCNTs were purchased from MER Corporation (Catalog # MRGC, have 8-30 graphene layers, 6-20 nm in diameter and 1-5 microns in length. PEDOT: PSS aqueous dispersion (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. FTO/glass (~13 Ω /sq) was purchased Sigma Aldrich. Guanidinium thiocyanate was purchased from Merck. Iodine (I₂) was purchased Sigma Aldrich. Working electrodes (TiO₂ layer with ~10 μ m thickness), counter electrode (Pt coated) were purchased from Dyesol Ltd. Working electrodes (TiO₂ layer with ~14 μ m thickness), counter electrode (Pt coated) were purchased from Solarprint Ltd.

2.2 Experimental Details for Chapter 3

2.2.1 Preparation of carbon based quasi solid state electrolytes

Graphene was prepared according to Khan et al procedure [1]. Then the resulting graphene was placed into an oven at 60 °C for 48 hours to remove any trapped solvent left after ambient drying. The graphene samples were triturated in a vial and dried in an oven for 4 hours at 65 °C to remove the traces of NMP if any remaining in graphene powders. After that the dried graphene powders was dispersed in the PMII as concentrations of 1 %, 10 %, 15 %, 20 %, 25 %, 30 %, 35 % and 40 % by weight in glass vials. In all cases the graphene was added step by step in small quantities,

followed by sonication for 30 minutes. After each sonication a further small amount of graphene was added. This process was repeated until the desired quantity of graphene powder was dispersed. After this, all samples were sonicated in the ultrasonic bath Grant XB6 (200 W) for further 4 hours in closed glass vial. A second type of quasi solid state electrolytes were prepared using SWCNTs. SWCNTs were dispersed in PMII in quantities of 1 %, 7 %, 10 %, 13 % and 16 % by weight in glass vials. Each sample was sonicated by ultrasonic tip Bandelin Sonopuls HD 2200 at 20% power for 10 minutes. Then all samples were sonicated in the ultrasonic bath Grant XB6 (200 W) for further 4 hour in closed glass vials. Two kinds of graphene and SWCNTs hybrid quasi solid state electrolytes were also prepared, one with 12 % of graphene and 3 % of SWCNTs by weight were dispersed in PMII. While second one with 12 % SWCNTs and 3 % graphene by weight were dispersed in PMII. Both type samples were sonicated by ultra sonic tip at 20 % power for 10 minutes and then sonicated in ultrasonic bath Grant XB6 (200 W) for further 8 hours.

2.2.2. Fabrication of DSSCs

TiO₂ coated electrodes /WEs (dyesol Ltd) were sintered at 450 °C in an oxygen atmosphere in a furnace and cooled to 80 °C, then soaked in 3×10^{-4} M solution of N719 (dye) in ethanol in a closed container at room temperature for 24 hours. After dye adsorption white TiO₂ film became reddish as shown in Fig.2.1 A. Dyed TiO₂ films were washed with ethanol to remove the excess of dye which are not firmly bound to the surfaces of TiO₂. Then a 60 µm thick surlyn spacer (Sealant/spacer (Meltonix 1170-60 series) was coated around uncoated TiO₂ film and then various type of the quasi solid state electrolytes were sandwiched between the TiO₂ working electrode and platinum counter electrode as shown figure Fig.2.1 C.

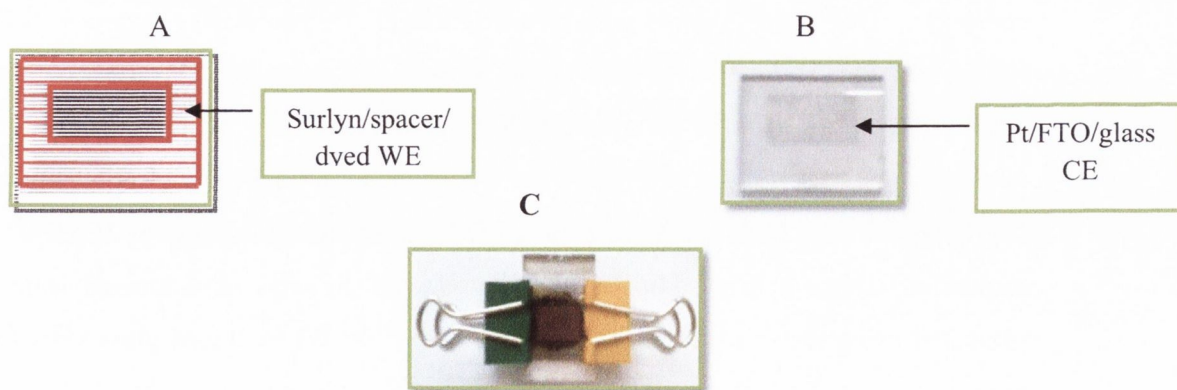


Figure 2.1: Pictures of **A)** dyed WE with spacer, **B)** Pt/FTO- CE and **C)** Assembled DSSC.

2.3 Experimental Details for Chapter 4

2.3.1 Preparation of binary ionic liquid based quasi solid state electrolyte for dye-sensitized solar cells

The EMISCN at 10 wt%, 30 wt%, 50 wt% and 70 wt % was added separately to the PMII under sonication in ultrasonic bath Grant XB6 (200 W) for 30 minutes. Graphene was prepared according to the Khan et al method [1]. The graphene (30 wt %), SWCNTs (7 wt%) and hybrid SWCNTs (3 wt%) and graphene (12 wt %) were dispersed in binary IL (EMISC (30 wt %)/PMII (70 wt%)) according to our previously published procedure [2]. Guanidinium thiocyanate (GuSCN) at 0.05M, 0.1M, 0.2 M were added to hybrid of SWCNTs (3 wt%) and graphene (12 wt %) of into binary IL(EMISCN 30 wt %/PMII) and sonicated for 3 hours in ultrasonic bath Grant XB6 (200 W). The DSSCs with these various type binary IL and quasi solid state electrolytes) were fabricated according to procedure described in the section 2.2.2 (with Solarprint ltd WEs and CEs).

2.4 Experimental Details for Chapter 5

2.4.1 Preparation of PEDOT: PSS-carbon nanomaterial composites

The MWCNTs (at 66 wt % of solid PEDOT: PSS content) and GNPs type 3 (at 66 wt % of solid PEDOT: PSS content) were added separately to two aqueous PEDOT: PSS dispersions. Both samples were diluted with 20 wt% of deionised water (Millipore). Both samples were sonicated in closed glass vials for 24 hours in ultrasonic bath Grant XB6 (200 W). Also, three type of hybrid samples of GNPs type 3 and MWCNTs were prepared: Hybrid A, MWCNTs (at 22 wt % of solid PEDOT: PSS content) + GNPs type 3 (at 44 wt% of solid PEDOT: PSS content) + aqueous PEDOT: PSS dispersion; Hybrid B, MWCNTs (at 33 wt% of solid PEDOT: PSS content) + GNPs type 3 (at 33 wt% of solid PEDOT: PSS content) + aqueous PEDOT: PSS dispersion and Hybrid C, MWCNTs (at 44 wt % of solid PEDOT: PSS content) + GNPs type 3 (at 22 % wt % of solid PEDOT: PSS content) aqueous PEDOT: PSS dispersion. These hybrid sample were diluted with 20 wt% of deionised water and sonicated using the in ultrasonic bath Grant XB6 (200 W) in closed glass vials for 24 hours.

2.4.2 Fabrication of carbon based CEs

FTO coated glass was cut in small pieces (3 x 2 cm) and sonicated in deionised water (Millipore) for 20 minutes and then sonicated in ethanol for further 20 minutes in ultrasonic bath Grant XB6 (200 W). This was followed by heating in an oven at 80 °C to remove any residual solvent traces. After cleaning and drying, adhesive tape was applied on the all sides of the conductive surface of the FTO glass. The purpose of the tape was to avoid over flow and hold a certain volume of liquid dispersion on each substrate. Various samples of dispersions which were already prepared were applied on FTO glass with help of a pipette and each FTO glass was covered with petri dish and left for 12 hours at room temperature to slowly evaporate the water from samples. After initial drying, the adhesive tape (3 M tape) was removed from each CE. Then these counter electrodes were heated at 80 °C in a furnace for 10 minutes and finally heated at 120 °C for a further 20 minutes. The film thickness of the composite film was controlled by squash tape or volume dropped. The thicknesses of these were in the range of 6 µm to 8 µm measured by SEM cross sectional characterization. The DSSCs with these carbon based CEs and reference CE with standard Pt/FTO/glass were fabricated with WEs (Solarprint ltd) according to procedure mentioned in section 2.2.2.

2.5 Experimental Details for Chapter 6

2.5.1 Preparation of Pt and TCO free CEs for DSSCs

The three aqueous PEDOT: PSS dispersions were diluted with 10 Vol% of NMP and 20 Vol% of deionised water (Millipore). This was split into three equal parts and GNPs type 1, GNPs type 2, GNPs type 3 were added to each part at 66 wt % of solid PEDOT:PSS content, to make three sample of dispersions. Each sample was sonicated in closed glass vials for 3 hours the in ultrasonic bath Grant XB6 (200 W) to make homogeneous dispersions. To prepare CE for above dispersion a non-conducting glass (NCG) substrate was used. The NCG was cleaned by sonicated in deionised water (Millipore) for 20 minutes and then sonicated in ethanol for further 20 minutes. This was followed by heating in an oven at 80 °C to remove any residual solvent traces. After cleaning, adhesive tape was applied on the all four edges of NCG substrate. Various samples of dispersions which were already prepared were drop casted on the

NCG substrate using a pipette, then each sample was covered with petri dish and left for 2 hours at room temperature to stabilize. After that these GNPs based CEs were dried by heating at 80 °C in an oven for 40 minutes and finally heated at 120 °C for a further 20 minutes to remove any residual solvent. The thickness of the composite film was controlled by squash tape or volume dropped. The thicknesses of these films were in the range of 15 µm to 20 µm measured by SEM cross sectional characterization. The DSSCs with these various GNPs based CEs and reference CE with standard Pt/FTO/glass were fabricated with WEs (Solarprint ltd) according to procedure mentioned in section 2.2.2.

2.6 Experimental Details for Chapter 7

2.6.1 Sample preparation

GO was prepared according to the modified Hummer's process [3-5] and GNPs type 2 powders was purchased from cheap tube. GNPs type 2 powders were sintered at 400 °C for 30 minutes. GO and GNPs type 2 was dispersed separately in NMP at 1 mg/ml by sonication in ultrasonic bath Grant XB6 (200 W) for 1 hour. TiO₂ pastes, DSL 18 NR-T and Ti-Nanoxide D paste at 2:1 and diluted with ethanol (30 wt %) and sonicated for 4 hours. Various weights % (0 to 5 wt%) of GO dispersion and sintered GNPs type 2 dispersion separately added to already prepared diluted TiO₂ paste mixture and all sample were further sonicated for 4 hours. FTO glass (3 cm x 2 cm) was cleaned by sonication in deionised water (Millipore) for 20 minutes and then it was sonicated in ethanol for further 20 minutes. This was followed by heating in an oven at 80 °C to remove any residual solvent traces. After cleaning, adhesive tape (Scotch magic tape) was applied on the all four edges of FTO glass substrate. The purpose of the tape was to avoid over flow and hold a certain volume of TiO₂ paste on FTO glass substrate. WEs were left at room temperature for two hours and then sintered at 450 °C in air for 1 hour and then cooled to 80 °C. Now these GO and GNPs plus TiO₂ composite films/WEs and pure TiO₂/Film/WE were soaked in 3×10^{-4} M solution of N719 (dye) in ethanol in a closed container at room temperature for 24 hours. Dyed TiO₂ films were washed with ethanol to remove the excess of dye which are not firmly bound to the surfaces of TiO₂.

2.6.2 Fabrication of sealed DSSCs

For fabrication of sealed DSSCs, CEs (Solarprint ltd) were first drilled from non-conductive glass side to make a small hole and then washed with ethanol and dried in an oven at 80 °C. Then GO and GNPs type 2 plus TiO₂ (dyed) composite films/WEs and drilled CEs were sealed with Surlyn (25 µm) by heating at 100 °C. The organic electrolyte (HPE) was introduced through small hole in CE under vacuum with the following steps:

1. The sealed electrodes (WE +CE) placed in a glass desiccator and then few drops of organic solvent based electrolyte were placed at the top of small hole of the CE.
2. The desiccator was then swiftly closed up. The mechanical vacuum pump connecting to the desiccator was subsequently turned on.
3. As the air in the desiccator evacuated by vacuum pump, air bubbles appear in the electrolyte. This is an indication of air coming out from the space between the electrodes in the device.
4. After a few seconds, when there was no more bubbles coming out from the device, the vacuum pump was turned off. Air was slowly introduced back into the desiccators.
5. The small hole in the CEs was sealed with a piece cover glass and Surlyn (25 µm).

2.7 Characterisation Techniques

2.7.1 Thermogravimetric Analysis

All thermogravimetric analysis in this work was done using a Perkin Elmer Pyris 1 TGA set up. Each of the sample was heated from 30 °C to 900 °C at rate of 10 °C/min. In this technique, the mass of a sample was monitored as function of temperature and plotted as a TGA curve and derivative TGA curve (DTGA) as shown in Fig. 2.2. TGA can be run under a range of atmospheres e.g. oxygen, nitrogen or other gas. TGA is commonly used to determine selected thermal characteristics of materials and content of some components that exhibit either mass loss or gain [6]. A modern TGA instrument consists of a number of parts. Weight is monitored by a sensitive

thermo balance. A digital recorder records variation in weight during a TGA run. A heating furnace made up of ceramic material which can withstand high temperature. Temperature is precisely controlled by a temperature programmer and a computer monitor displays the data. These components represented through a simple schematic diagram in Fig.2.3.B. Thermal stabilities of materials can be measured and compared under the required atmosphere.

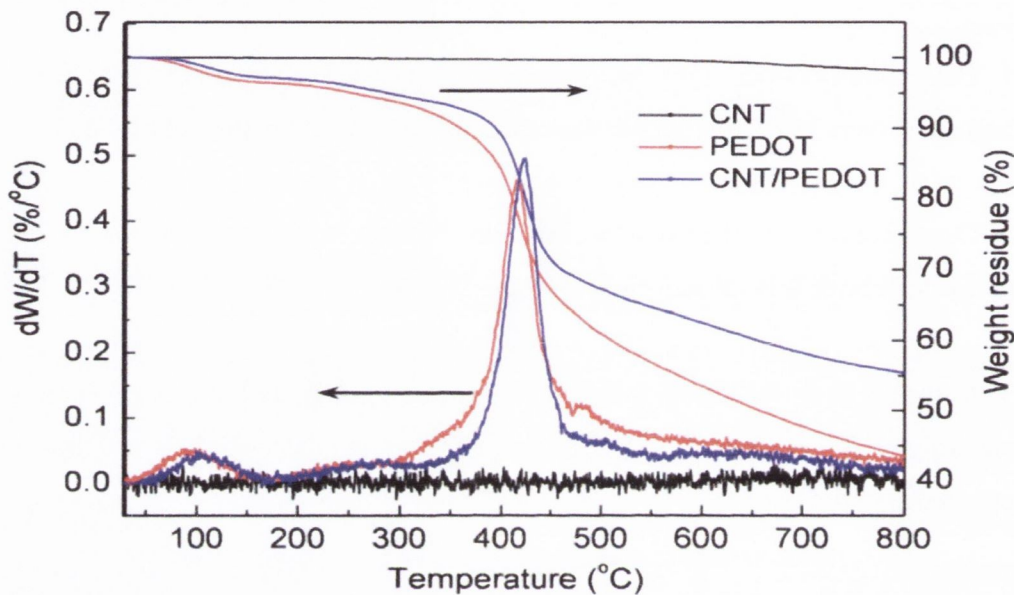


Figure.2.2: TGA and DTGA curves of CNTs, PEDOT, and CNT/PEDOT nanostructures [7].

Application of TGA:

- Oxidation or reduction of materials can be monitored using TGA.
- Life spans of materials can be estimated with TGA.
- The presence of volatile components in a sample can be determined from a TGA.

- TGA can be used for analysing the kinetic features of all types of weight loss or gain, either with a view to predictive studies, or to understand the controlling thermochemistry.
- It can be used to find the presence of trapped solvent and the effect of this solvent on thermal stability of samples.

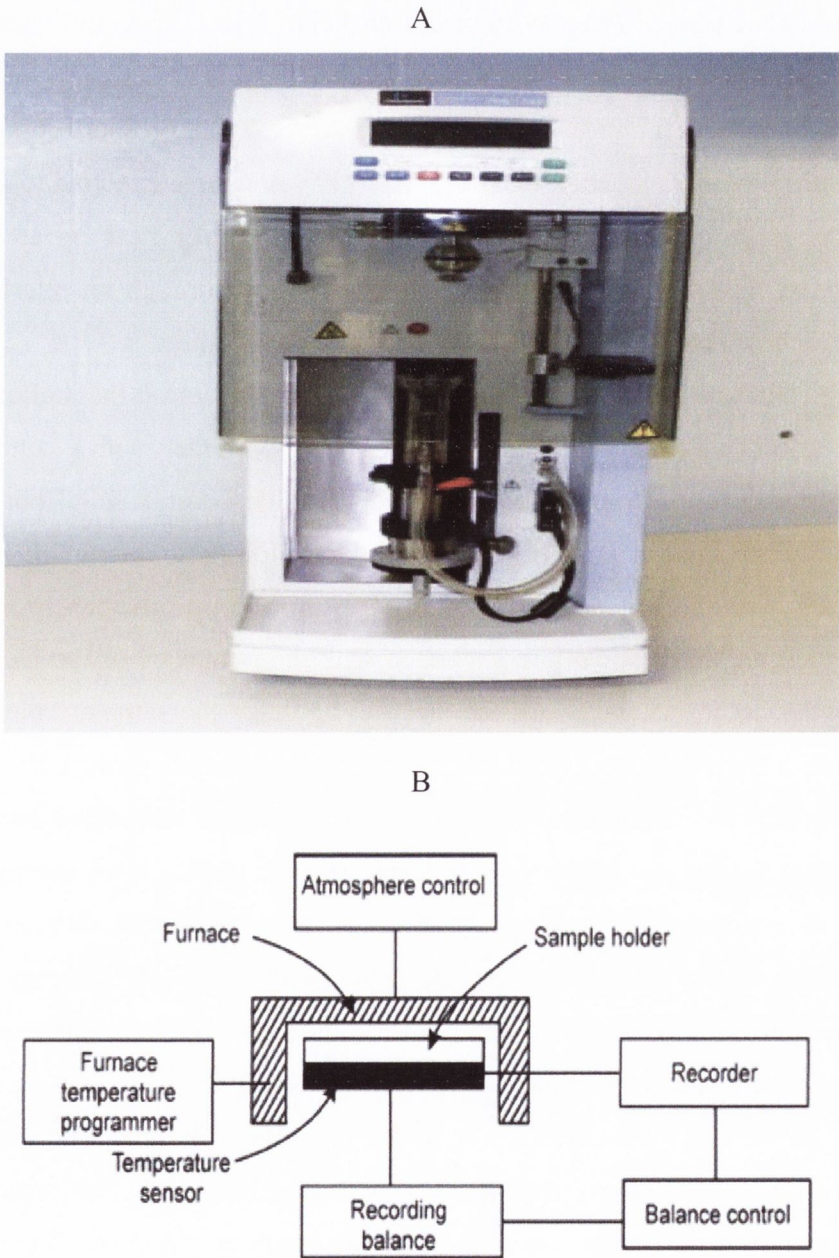


Figure 2.3: **A)** Perkin Elmer Pyris 1 TGA [8] and **B)** Schematic diagram of a modern Thermogravimetric Analysis Instrument [9]

2.7.2 Raman Spectroscopy

In our work Raman measurements were performed using Horiba Jobin Yvon LabRAM HR spectrometer with a 100 x objective lens and 633 nm laser excitation. Raman spectroscopy is a non-destructive, fast, characterising technique which is commonly used for the characterization of carbonaceous materials, including distinguishing between graphene and graphite. Furthermore, it can provide valuable information about defects and stacking of the graphene layers [10]. All allotropic forms of carbon are active in Raman spectroscopy [11]. A Raman system typically consists of four major components: 1) Excitation source (Laser). 2) Sample illumination system and light collection optics. 3) Wavelength selector (Filter or Spectrophotometer) and 4) Detector (Photodiode array, CCD or PMT) [12]. A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through an interference filter or spectrophotometer to obtain a Raman spectrum of a sample.

Raman spectroscopy is a technique which relies on the inelastic scattering of laser light of a sample. When monochromatic light interacts with a sample, the majority of photons are elastically (Rayleigh) scattered. However a small portion (~ 1 in 10^7 photons) is shifted in wavelength through interactions with the sample material. This is referred to as the Raman effect. During this process, the frequency of the photons is either shifted up or down in comparison with the frequency of the incident light. The incident photons interact with the electric dipole of the sample molecules causing a change in the molecules vibrational, rotational or electronic energy. Rayleigh scattering occurs if the excited molecule returns back to its original vibrational state. If the excited molecule returns to a higher energy level, then the photon loses energy on interaction with the sample. This is known as Stokes Raman scattering. Similarly, Anti-Stokes scattering occurs when an excited molecule returns to a lower energy level, meaning the photon gains energy. The energy distribution gives us information on the chemical bonds present and is like a fingerprint of the material [13].

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wavenumbers, cm^{-1}). The main features in graphite /graphene Raman spectra are represented by the D, G and 2D or G' peaks as shown in figure 2.4 [14]. In graphene, the D peak occurs at $\sim 1350 \text{ cm}^{-1}$ and is associated with defects and also edge effects

[15]. In graphene, the G band occurs at around 1582 cm^{-1} and this occurs because of vibrations between neighbouring carbon atoms.

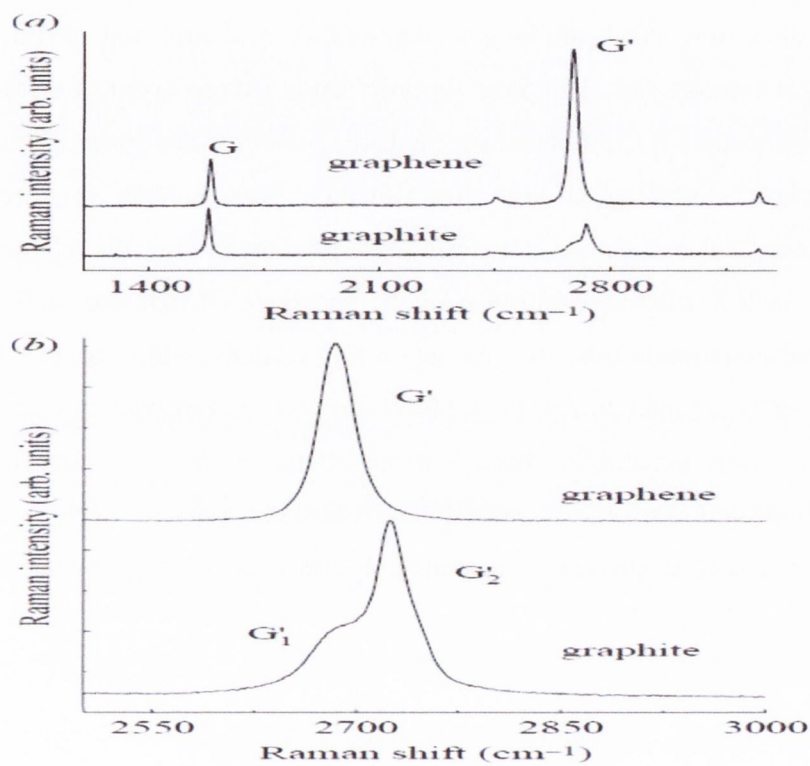


Figure 2.4: Raman spectra for graphite and graphene showing the G and G' bands [16].

An up shift of 5 cm^{-1} occurs if single layer graphene is present. Up shifts show a $1/n$ dependence where n is the number of graphene layers [16]. At 2700 cm^{-1} , the 2D band is present. This is also known as the G' band. This band is seen for all sp^2 hybridised carbon materials. The 2D peak changes shape width and position with increasing number of graphene layers [17]. For graphene, only one G' peak is seen here but for graphite two distinct peaks G'1 and G'2 will be present. For graphene, the intensity of the 2D (or G') band is much larger than the G band with a ratio of 4. This is in contrast with graphite in which the G band is larger than the 2D band (figure 2.4) which is also the case for nanotubes [16].

2.7.3 Scanning Electron Microscopy (SEM)

SEM was performed using a Carl Zeiss Ultra Plus Field Emission Scanning Electron Microscope. Up to 8 conventional SEM samples can be mounted in the chamber at once in Carl Zeiss Ultra Plus Field Emission SEM. SEM can provide information on surface topography, crystalline structure, and chemical composition (EDX) of samples [18, 19]. SEM benefits from a large depth of field so most of the specimen surface is simultaneously in focus whatever the surface roughness. Optical microscopes operating at high magnification have a very small depth of field. Large specimens (200 mm diameter wafers, or even larger in specially adapted SEMs), SEM permits non-destructive evaluation of the specimen (if it is conductive). Very short specimen preparation time (maybe only a few seconds) while the specimen is attached to a “stub” (specimen holder) [19]. SEM consists of seven primary operational systems: vacuum, beam generation, beam manipulation, beam interaction, detection, signal processing, and display and record. The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern [20].

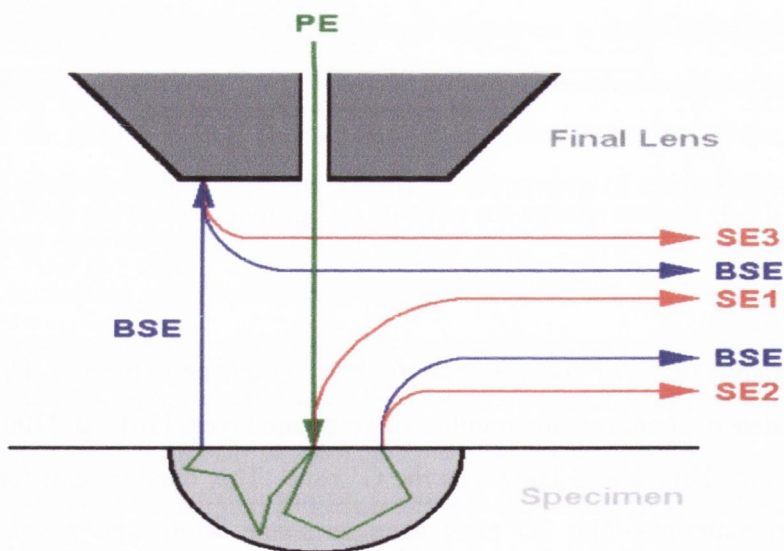


Figure 2.5: The main types of electrons that can be detected. They are split into several groups depending on their origin and their range.



Figure 2.6: Carl Zeiss Ultra Plus Field Emission Scanning Electron Microscope [21].

When the electron beam interacts with the sample, secondary electrons (SE), back scattered electrons (BSE), Auger electrons and X rays are produced, collected in various detectors and an image is produced [19]. Generally the most common or standard detection mode is SE imaging. Fig. 2.5 shows the main types of electrons that can be detected. When electrons are scattered from the inner core or from the electrons of the sample, inelastic scattering occurs resulting in secondary electrons. These are low energy electrons (<50 eV). SE1 electrons come from the spot centre, SE2 electrons undergo some scattering and these leave the sample further from the spot centre, SE3 electrons are not generally used for imaging and these electrons come from backscattered electrons. Secondary electrons can be detected using the in-lens detector on this machine which is ideal for surface imaging. Electrons with energies higher than this are known as backscattered electrons. These occur from the elastic scattering off the sample at a much deeper range. The backscattered electron (BSE) detector is useful for seeing elemental contrast between different parts of a sample. Both secondary and backscattered electrons can be detected using the SE2 detector. The secondary electrons account for 90% of the electrons with the backscattered electrons contributing to the rest. This detector can be used at a higher voltage range than the in-lens detector and is effective for looking at material contrast.

2.7.4 Transmission Electron Microscopy (TEM)

The TEM samples were prepared by pipetting the dispersion of graphene in NMP directly onto a holey or lacey carbon support mesh on a copper TEM grid. The grids were allowed to dry in air or dried in a vacuum oven, depending on the solvent used. Transmission electron microscopy was carried out using a Jeol 2100 TEM operated at 200 kV. The TEM machine consists of an electron source, electromagnetic lens, and various apertures and a phosphor screen/CCD camera. The illumination system controls the incident beam on the sample, and is made up of a condenser, aperture and lens. These produce a parallel beam of coherent electrons along the optic axis, to interact with the sample (fig.2.7) [22]. Upon interaction, the beam undergoes transmission or is either scattered elastically or inelastically.

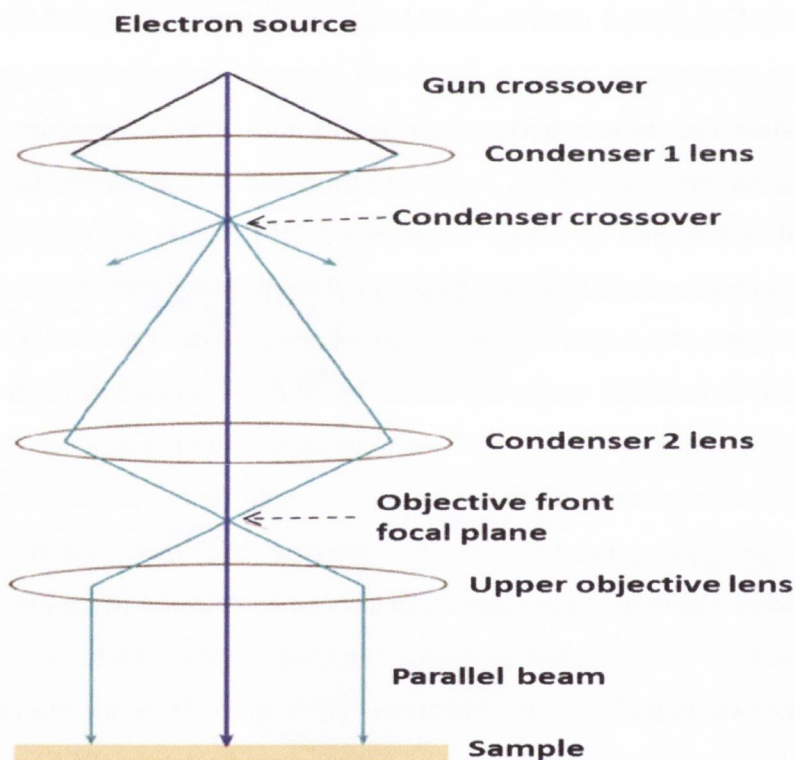


Figure 2.7: Schematic of the illumination system in a TEM [23].

After the beam has passed through the sample, the objective aperture only allows the unscattered electrons to travel to the projection lens system, is magnified and focused onto an imaging device, such as a photographic film, a fluorescent screen, or detected

by a CCD camera. Bright field imaging is the most commonly used imaging technique and this mode was used for imaging these samples. The darker areas of an image correspond to areas where fewer electrons could pass through and these areas correspond to a larger number of graphene layers [24]. TEM of folding at the edges or within the free-hanging sheets gives the number of layers by direct visualization [17].

2.7.5 Power Conversion Efficiency Measurements of DSSC

2.7.5.1 Current-voltage (IV) curve measurements

Current-voltage (IV) curve measurements are the most frequently used characterization method to determine the photovoltaic device performance. The IV curve provides information about open circuit voltage (V_{oc}), the short-circuit current (I_{sc}) and the fill factor (FF) of a solar cell. Measurements of I–V curves were performed using a digital source meter (Keithley 2400) and a standard solar simulator (Oriel 92193).

Open Circuit Voltage (V_{oc})

The open circuit voltage (V_{oc}) is the voltage across the solar cell when the current through the solar cell is zero and it is the maximum voltage available from the solar cell (V (at $I=0$) = V_{oc}). To read the open circuit voltage from the graph, locate the point on the voltage axis where the current is zero as shown fig.2.8.

Short Circuit Current (I_{sc})

The short circuit current (I_{sc}) is the current through the solar cell when the voltage across the solar cell is zero (I (at $V=0$) = I_{sc}). To read the short circuit current from the graph (fig2.8), locate the point on the current axis where the voltage is zero. Divide this current by the active area of the solar cell under test, to obtain the short current density, J_{sc} (mA/cm^2).

Fill Factor (FF)

The FF is defined as the ratio of the maximum power point to the product of V_{oc} and I_{sc} . An ideal FF should have value of 1, an ideal value 1 is not possible in a solar cell since resistive losses always exist. FF can also be interpreted graphically as the ratio of

the rectangular areas depicted in Fig.2.8. FF of a DSSC can calculate according to the equation 1.

Power conversion efficiency (%) (η)

The light or power conversion efficiency (%) (η) is defined as the ratio of the maximum electric power extracted to the radiation power incident on the solar cell surface. The power conversion efficiency of a DSSC can calculate according equation 2.

Equation 1:

$$FF = \frac{\text{Maximum power point}}{V_{oc} I_{sc}} \text{ or } \frac{V_{max} I_{max}}{V_{oc} I_{sc}}$$

V_{max} = Voltage at the maximum power.

I_{max} = Current at the maximum power.

Maximum power output or point = Product of V_{max} and I_{max} .

Equation 2:

$$\eta = \frac{V_{oc} I_{sc} FF}{A_c L} \times 100$$

η = The power conversion efficiency (%).

L = The light intensity of the incident light.

A_c = The surface area of the cell.

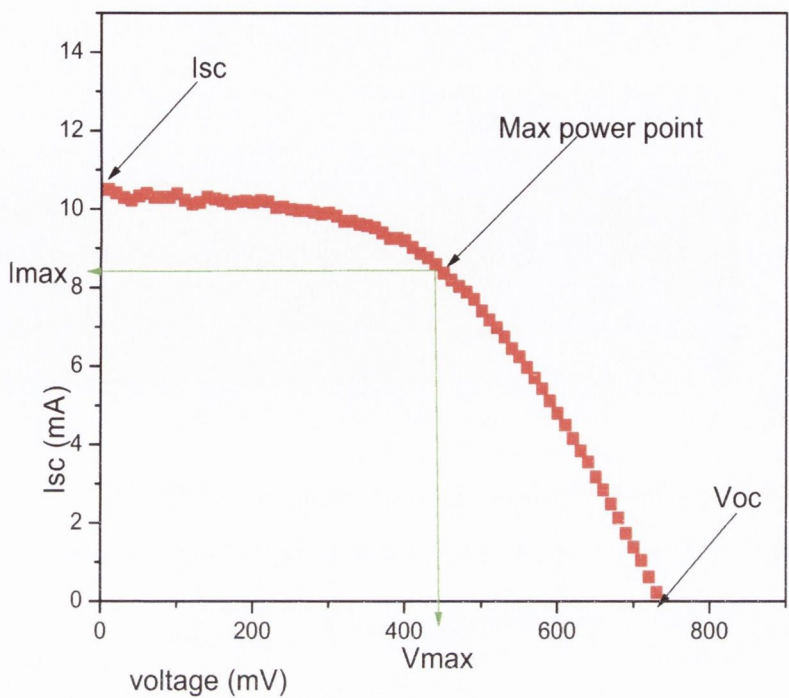


Figure 2.8: IV curve of a DSSC which showing the open circuit voltage (V_{oc}), short circuit current (J_{sc}), and the maximum power point (MPP).

2.7.5.2 Solar Simulator

Solar simulator is a device that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells and other materials and devices. The solar simulator Oriel instruments model 92193 (fig.2.9) was used to measure the IV curves in this work. This instrument was equipped with a 1.5G air mass filter and 1300W Xenon lamp bulb and was calibrated with a silicon-based reference cell. Fig.2.10 shows diagram of an Oriel solar simulator instruments model 92193.



Figure 2.9: The solar simulator Oriel instruments model 92193.

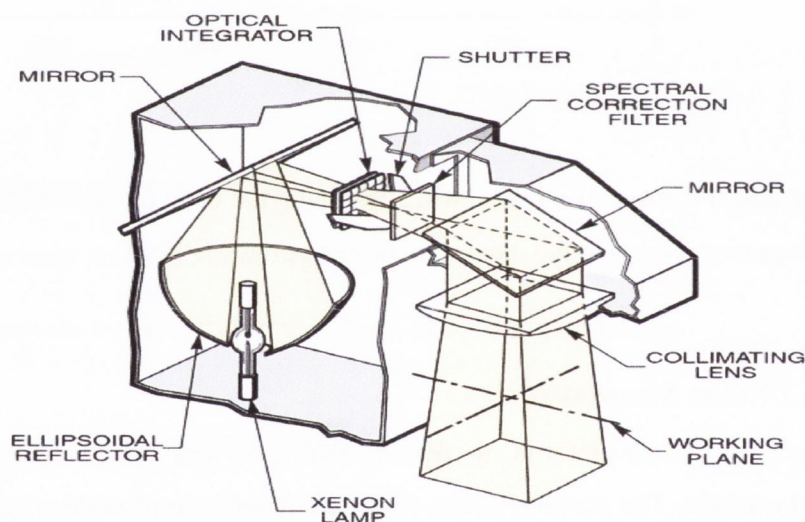


Figure 2.10: Schematic diagram of an Oriel Solar Simulator model 92193 [25].

2.7.6 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) analysis is a basic tool that provides deeper information about charge transfer phenomena in DSSC. EIS analysis has been widely used to explore the reduction of I_3 ions on CEs, and a well-supported equivalent circuit [26]. The impedance data is typically presented as a Nyquist plot. Fig.2.11 presents examples of Nyquist plots [27]. Generally, EIS spectra exhibit three

semicircles in the Nyquist plot, which describes the different impedances of DSSC [28]. Each semicircle can be assigned based on the model circuits (equivalent circuit) for a DSSC. The first semicircle of EIS spectra is attributed to the impedance of the charge transfer resistance at the counter electrode/electrolyte interface (R_{ct}) which is labelled as Z_1 in fig. 2.11, the second semicircle one (labelled as Z_2) and the last tailing one (labelled as Z_3) are related to charge transfer process at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (R_{ct2}) and Warburg diffusion process of I^-/I_3^- in the electrolyte (R_{diff}) respectively [29]. The EIS experiments can be conducted in dummy cells or real DSSC by using a computer-controlled potentiostat in the dark or under light intensity. The Electrochemical Impedance spectroscopy was performed with a potentiostat (Auto lab PGSTAT128N with FRA2 module) (in chapter 5). Electrochemical impedance spectroscopy (EIS) was determined in the frequency range from 10 mHz to 65 kHz under 5 mW /cm² over an open circuit potential V_{oc} . The equivalent circuit model used to interpret the EIS data.

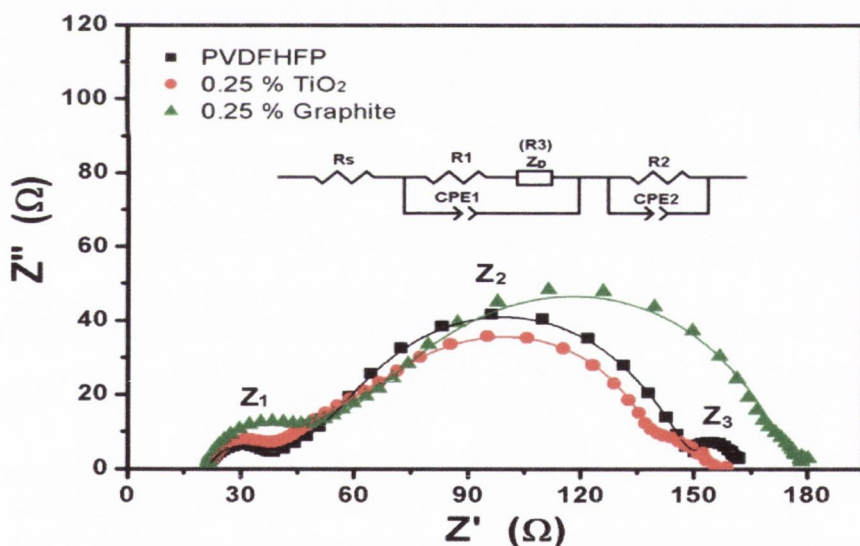


Figure 2.11: Nyquist plots of electrochemical impedance spectra (EIS) of DSSC [27].

2.7.7 Electrical Conductivity Measurement

For electrical conductivity measurement, silver paint were applied at both the end of each sample and then two piece of silver wire were attached to each strip with help of silver paint, to ensure proper flow of current through samples. And the samples were left for few minutes at room temperature to dry the silver paint. The samples were

then connected to a Keithley 2400 source meter through silver wire to measure the IV curves of each sample. The two-probe resistance was determined under V bias = 0.1 to 1V. The bulk conductivity of all samples was calculated according equation 3 .The electrical conductivity (σ_{dc}) was then found as the inverse of the product of sheet resistance R_s and thickness (t) by using the Equation 3 [30].

Equation 3:

$$\sigma_{dc} = \frac{1}{R_s t}$$

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Chapter 3: Graphene, Carbon Nanotubes and Ionic liquid mixtures: Towards new Quasi Solid State Electrolytes for Dye Sensitised Solar Cells

3.1 Introduction

The roles of the electrolyte is to provide electrons from CE to the WE of the DSSC, in order to regenerate the oxidized dye to ground state [1]. Therefore, the electrolyte is one of the essential components of the DSSC technology and its development is particularly important for further development and commercialisation of DSSCs. In order to get high cell power conversion efficiencies, the electrolyte has to fulfil certain criteria including appropriate viscosity, high diffusion coefficient, high electrochemical and thermal stability, low vapour pressure and ease of sealing [2, 3]. Traditional DSSC technology uses a volatile solvent based electrolyte [4, 5]. These electrolytes are characterized by low viscosities and high diffusion coefficients. However, the liquid electrolytes cause a number of problems during manufacturing that limit their applications. The main problems include leakage of electrolytes, corrosion of cells over time, high temperature instability (outdoor conditions) and additional complexity in trying to contain liquids in a solar cell device during manufacturing [6-8]. These drawbacks, as well as the fact that the liquid electrolytes are quite aggressive and can permeate plastics, are serious obstacles for large-scale outdoor application of DSSCs and their integration into flexible structures [9]. To resolve the above problems, alternative components such as Ionic liquids (ILs) have been investigated as a replacement for volatile organic solvent based electrolytes. ILs have good chemical and thermal stability, negligible vapour pressure, non flammability and high ionic conductivity [10]. However, the power conversion efficiencies obtained with ionic liquids at a full air mass (AM 1.5) solar irradiance have been much lower than those achieved with organic solvent-based electrolytes [11]. Very few examples are reported where reasonable power conversion efficiencies were obtained with ILs for example power conversion efficiency of 7.2% were achieved for DSSC with binary ILs

electrolytes i.e. 1-propyl-3-methyl-imidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIB(CN)) [12]. M. Gratzel et al has also reported a solvent free electrolyte with mixture of three types of ILs i.e. 1, 3-dimethylimidazolium iodide, 1-ethyl-3-methylimidazolium iodide and 1-ethyl-3-methylimidazolium tetracyanoborate. They have demonstrated power conversion efficiency up to 8.2% in their work [13]. In summary, the use of ILs is still limited either due to low power conversion efficiency, sealing issues, or high costs. To address these issues, the development of a new type of electrolyte is needed. Replacing the liquid electrolytes in the DSSCs with a solid or gel/quasi solid state electrolyte is expected to solve these problems [14]. The conversion of a liquid electrolyte to a gel or quasi solid state electrolytes has some advantages, for example the quasi solid state electrolytes can stop the leakage or flow of liquid electrolytes and some cases stop the leakage of liquid electrolytes as well as increased the power conversion efficiencies of DSSCs. Therefore, gel/quasi-solid state electrolytes for DSSCs have received much attention and are widely investigated. Various approaches have been made to prepare gel/ quasi solid state electrolytes for DSSCs. For example Gratzel et al. [15] reported the incorporation of nanoparticles of SiO₂ (5 wt%) in to IL (PMII) and they achieved same power conversion efficiencies of 7% for liquid electrolyte and corresponding quasi solid state electrolyte /DSSCs, this result shows that the presence of SiO₂ has no adverse effect on the conversion efficiency and the only advantage these electrolytes are free of leakage. However there some papers reported about increased in power conversion efficiencies with incorporation of various carbon based material in to ionic liquid electrolytes/DSSCs [16]. Lee et al. [17] reported a new promising quasi-solid state electrolyte for DSSCs, which was produced by utilizing an IL i.e. 1-ethyl-3-methylimidazolium iodide (EMMI) and SWCNTs (10 wt %) as filler. This research resulted in a cell with a relatively high power conversion efficiency of 1.88 % as compared to pure an IL (EMII) (0.41%). Ikeda et al [18] fabricated quasi solid-state electrolytes by incorporation of SWCNTs (6.97 wt %) and MWCNTs (6.97 wt %) to the IL, 1,3-diethyleneoxide derivative of imidazolium iodide and they obtained power conversion efficiencies of 1.63% and 1.01% with SWCNTs and MWCNTs based quasi solid state/DSSCs respectively. Though these cells would have many advantages (as discussed above) the drawback would be high cost and availability of CNTs in large quantities. A cost effective alternative to CNTs will be graphene. Graphene is another

material with remarkable properties including high specific surface area thermal and electricity conductivity [19-24]. There are many ways of graphene preparation [25-27] but the most cost effective and scalable method of graphene preparation is developed by Khan et al. [28], in this method graphene can be derived from naturally occurring graphite which is readily available in nature with very low cost compare to CNTs. Graphene has another advantage compare to CNTs i.e. its large surface area, hence one would expect graphene based quasi solid state electrolytes would give better performance than CNTs. Further more because of the 2D nature graphne could potentially make a better contact with TiO_2 of working electrode (WE) as well as to Pt of the counter electrode (CE) compare to curved CNTs and as a result electrons would transfer more efficiently from the CE toward the WE, resulting in higher power conversion efficiency. Therefore the use of the graphene would not only make the IL to a gel or quisi state and will also improve power conversion efficiencies of the DSSCs. Though SWCNTs are expensive they were used as comparison or baseline to graphene. Graphene can be incorporated to many ILs however, in our work IL, 1-propyl-3-methylimidazolium iodide (PMII) has been selected because amongst various types of /iodide salts that form room-temperature ionic liquids, 1- (PMII) has the lowest viscosity [13]. Also there are reports that the addition SWCNTs to graphene/graphite can have synergetic effect of various properties [29, 30]. Therefore, SWCNTs were also added to graphene/PMII. Our objectives were to develop cost effective quasi solid state electrolyte for DSSCs and evaluate whether the graphene and the resulting based quasi solid state electrolytes will show high efficiency and long-term stability that makes them commercially interesting for inexpensive applications. In this work we evaluate various mixtures of graphene and/or SWCNTs in ILs as potential quasi-solid state for the DSSCs.

3.2 Preparation of Graphene

Graphene was prepared according to the procedure outline by Khan et al (Figure 3.1) [28]. Graphite powder was added to N-methyl- pyrrolidone (NMP) at a concentration of 3.3 mg ml^{-1} in a 500 ml round bottomed flask. The dispersion was then sonicated for 60 hours. After sonication, the dispersion was transferred into vials and centrifuged at 1500 rpm for 45 minutes (Hettich Universal 32). After centrifugation, the

supernatant was carefully transferred to a glass bottle (500ml). The dispersion was vacuumed filtered onto a filter membrane (0.45 μ m). The resulting graphene film on filter membrane was left at room temperature for four hours and the filter membrane and film was then placed into a 60 °C oven for 48 hours to remove any trapped solvent left after ambient drying. After drying, graphene film was removed from membrane.

Exfoliation of Graphene

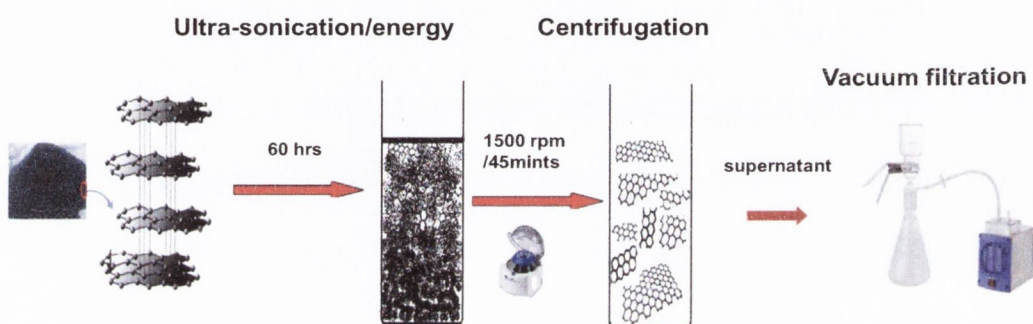


Figure 3.1: Steps involved in graphene preparation.

3.3 Characterisation of Graphene

3.3.1 Transmission electron microscopy (TEM)

Graphene was prepared by solvent exfoliation according the procedure outline by Khan et al al. [28] as explained in section 3.2. The quality of exfoliated graphene was examined using TEM. TEM analysis was employed to determine the typical thicknesses of the exfoliated graphene in dispersion. TEM of folding at the edges or within the free-hanging sheets gives the number of layers by direct visualization [31]. In TEM experiments a drop of the diluted (by factor of 30) dispersions of graphene/NMP and graphene/PMII was dropped on a holey carbon grid (400 mesh). This type of TEM

grid allowed flakes to be captured while the solvent was free to percolate through the membrane. The grid was then dried in a vacuum oven. As shown in figure 3.3 TEM images confirmed the exfoliation few layered graphene in dispersions (3 to 5 layers).

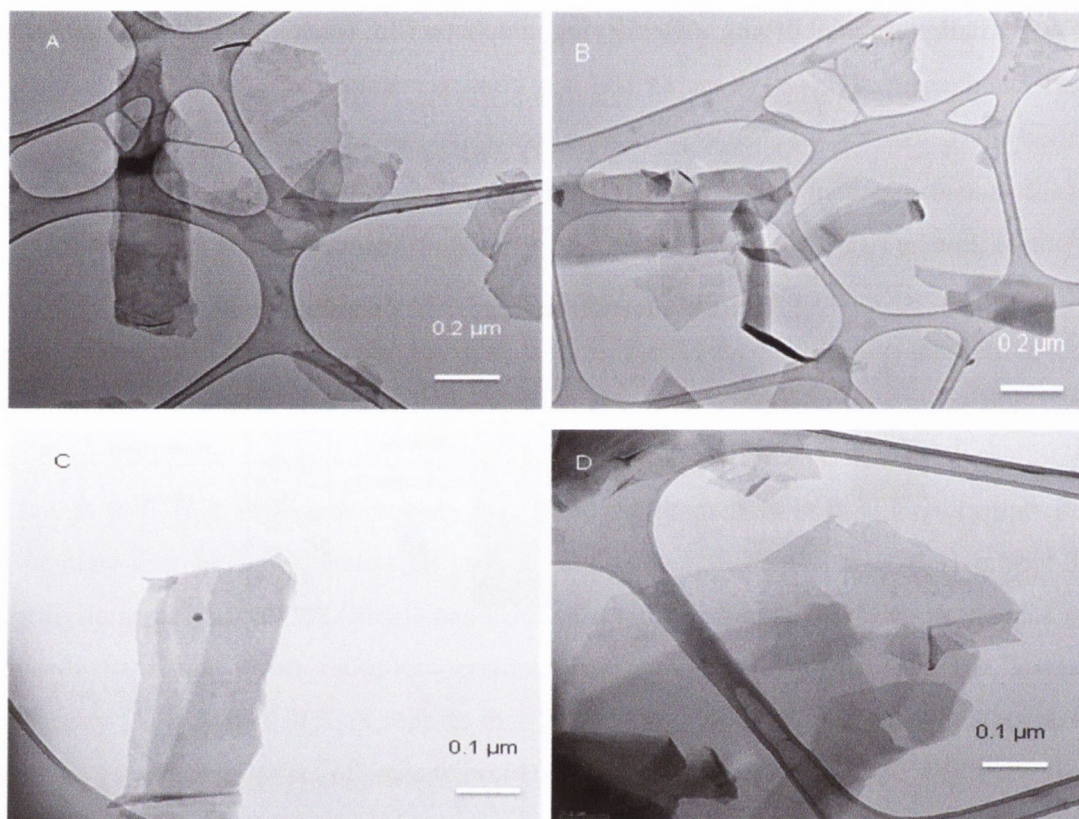


Figure 3.2: Representative TEM images of graphene (A, B, C and D), represent multilayer (3 to 5 layers) of graphene sheets, (after 60 hours of sonication).

3.3.2 Raman Spectroscopy

Further studies of the nature of exfoliated graphene were performed using Raman spectroscopy. Raman spectroscopy is commonly used for the characterization of carbon nanomaterials such as graphite, graphene and CNTs etc [32]. This is a non destructive, fast, characterising technique which enables to determine the number of graphene layers and their quality. In order to prepare the samples from graphene/NMP dispersion the solvent was removed and free standing films were obtained. Raman spectroscopy was done on both top, bottom sides of films as well as on graphite powder for comparison. The main features in graphite/graphene Raman spectra are represented

by the D, G and 2D peaks [33]. The D peak, so called after defects, can be found ~ 1350 cm^{-1} . The graphite powders displayed a small D band (~ 1330 cm^{-1}).

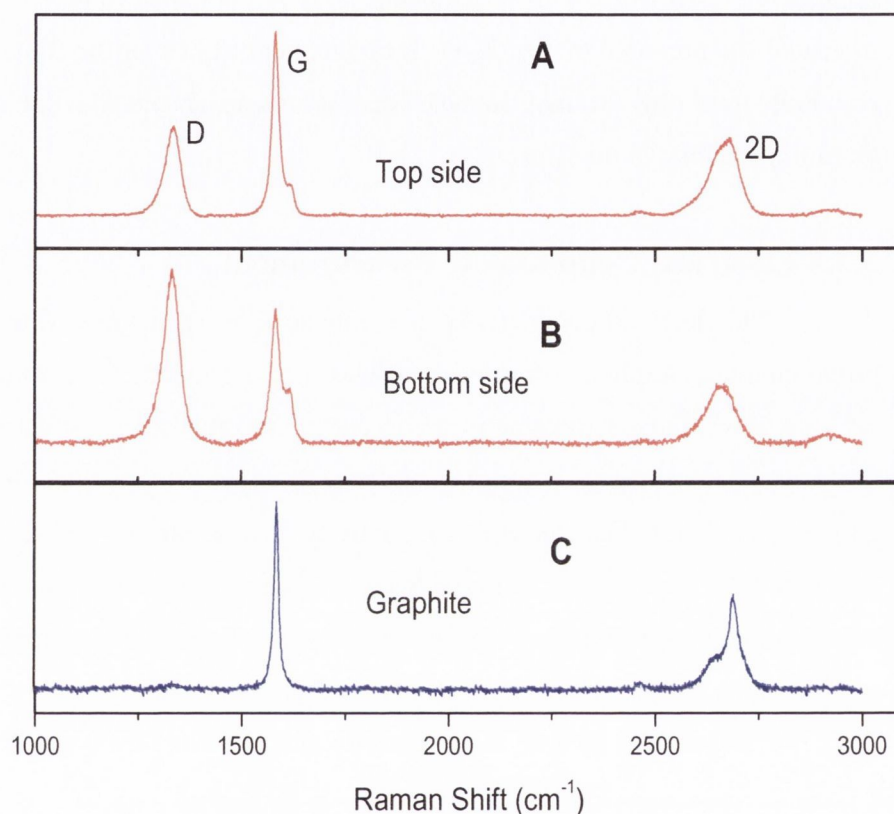


Figure 3.3: Raman spectra **A)** Top side **B)** Bottom side of graphene film and **C)** graphite powder.

The D band is indicative of defect or edges. The graphitic G peak located at ~ 1580 cm^{-1} and 2D peak located at ~ 2700 cm^{-1} always observed in graphite samples [34]. The graphite's 2D band (~ 2700 cm^{-1}) always have a shoulder at ~ 2650 cm^{-1} is representative of graphite [31]. While the absence of shoulder in 2D band of the film spectra represent the few layer graphene. Furthermore the shape and height /intensity of of the 2D band can be used to distinguish between single and multilayered graphene in a sample. In monolayer graphene the 2D peak evolves to be roughly 4 times more intense than the G peak [31]. Shown in Figure 3.3 C, Raman spectra of graphite powder showed negligible D peak. This suggests that there were no defects in the starting materials or due to bigger flake size of graphite, while a shoulder was in 2D peak was observed as

one would expect in graphite. Raman spectroscopy of our films showed a large D peak which can either be due to the defect created during sonication of the samples or most likely because of smaller flakes i.e. edge effect [28]. The shape of 2D peak spectra with no shoulder is consistent in all graphene film as shown in figure 3.3 A and B, which indicated the presence of few layer thick graphene sheets in the film, thus we can also conclude from this Raman analysis that graphene sheets did not re-aggregate into graphitic stacking in the film.

3.3.3 Electrical Conductivity Measurement

The electrical conductivity of graphene film was measured using the two point probe method. Graphene film thickness was measured using a micrometer screw gauge which was $\sim 20 \mu\text{m}$. Graphene film was cut up into five strips. Silver paint was applied to the each end of the strip and then silver wire was used to connect with Keithley model 2400 source meter. The electrical conductivity of five samples was determined and then calculated the average electrical conductivity, which was 110 S/cm. This study further confirmed that that graphene sheets did not re-aggregated into graphitic stacking as in the literature the electrical conductivity of graphene film in the range of 72 to 381 S/cm [35, 36] and the electrical conductivity of a graphite film is around 50 S/cm [37].

3.3.4 Scanning Electronic Microscopy (SEM)

SEM of graphene films allowed us to see their morphology and arrangement in the films. We have carried out SEM investigations both on the top and edge surfaces of the films. The SEM images showed that these films consisted of multiple layer of graphene sheet in all cases. Representative images of graphene films are shown in figure 3.4.

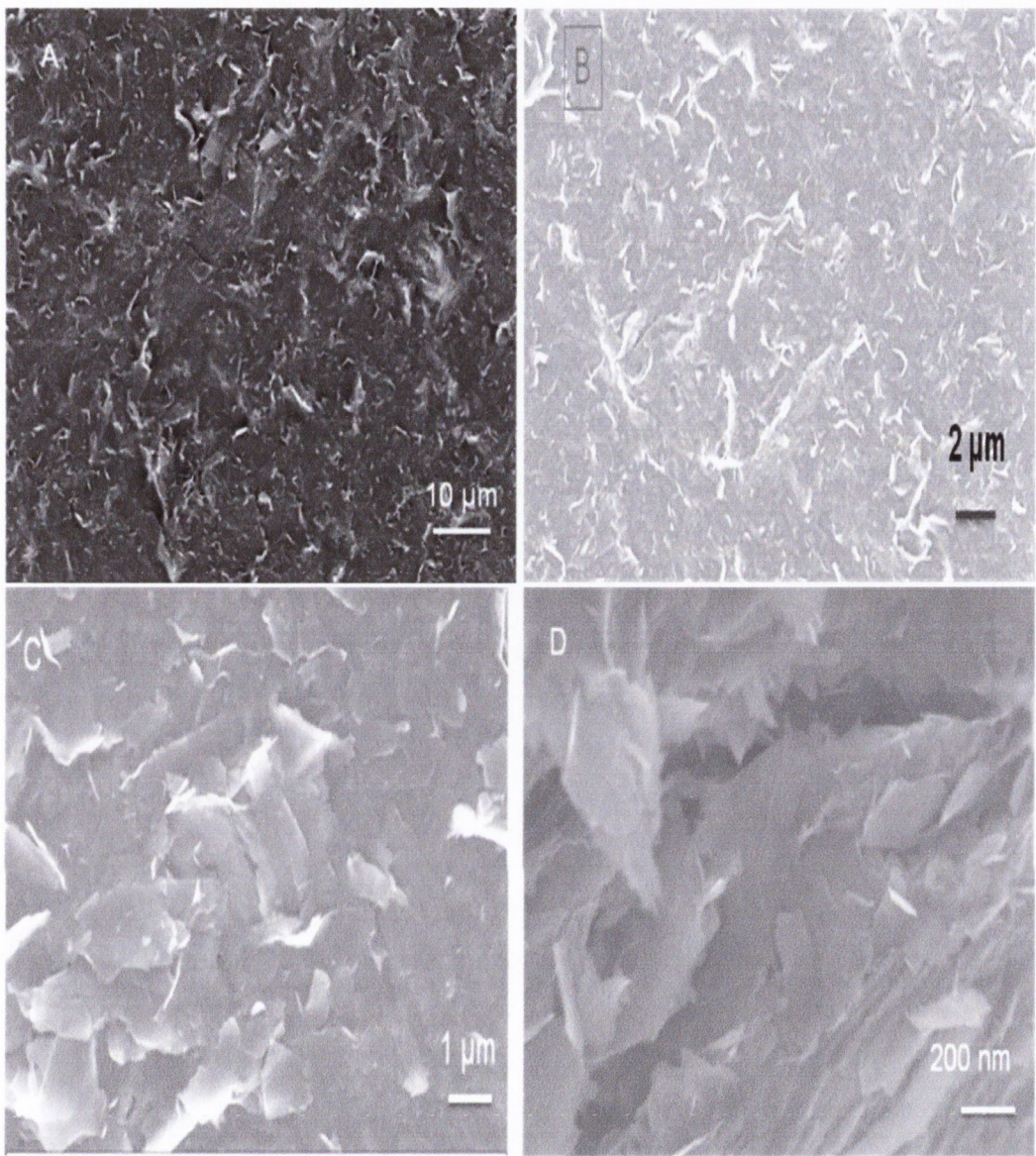


Figure 3.4: SEM images of graphene, (A and B) top surface and (C and D) edge of film.

3.4. Preparation and Characterisation of DSSCs with new Quasi Solid State Electrolytes

3.4.1 Preparation of graphene based quasi solid state electrolytes and corresponding DSSCs

DSSCs consist of many components and all parts effect the photovoltaic properties of the cell. Various factors that affect the photovoltaic properties of DSSCs are: (1) fabrication process (2) contamination and (3) humidity etc. It's very important to keep all parameters and conditions constant for each experiment. However, in case of graphene based quasi solid state electrolytes, more precaution is required because these graphene based electrolytes are highly conductive compared to pure ILs and there is a good chance that front working electrode and counter electrode can get short circuit using these electrolyte. Keeping this in mind this all uncoated FTO area was covered with an insulator (surlyn) 60 μm thick. Besides preventing short circuit, the spacer also has another advantage that it provides enough space between WEs and CEs to hold enough quantity of quasi solid state electrolyte. It also serves to keep the constant space between two electrodes in each cell. Our quasi solid state/DSSC consisting of graphene and PMII can be represented schematically as shown in Figure 3.5. Graphene was dispersed in PMII in various amounts (wt %) as described in experimental section.

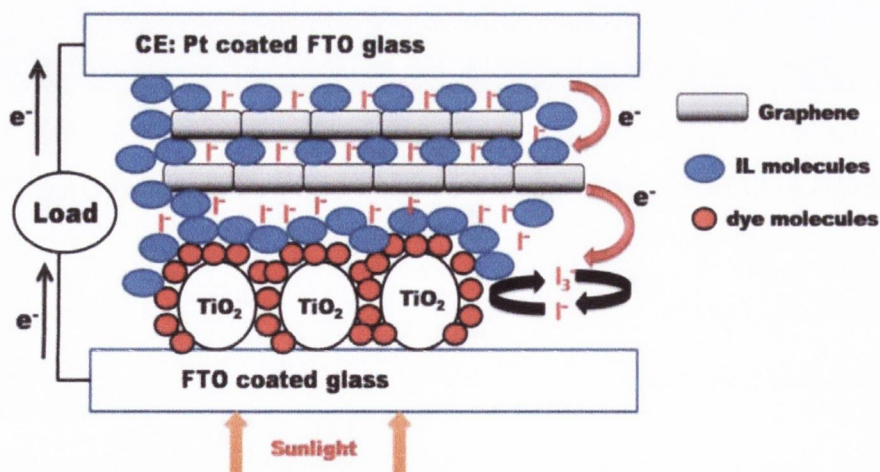


Figure 3.5: Schematic illustration for the charge-transport processes of graphene-based quasi solid state DSSC.

The addition of only 1 wt % of graphene changes the colour of PMII from yellow to black. Graphene was dispersed very well in PMII therefore a small quantity of graphene changed the colour of PMII. It was found that 1-15 weight % of graphene has almost no visible effect on flow of PMII but they can only make a gel like material and and at 20-40 wt % resulting in quasi solid state electrolyte as shown in Figure 3.6. The role of PMII is to fill the mesoscopic interior of sensitised porous TiO_2 layer where no space is available for graphene to occupy as well as PMII functions as a carrier mediator between sensitised porous TiO_2 and graphene. We expected that this kind of quasi solid state electrolytes would create perfect contact between the sensitised porous TiO_2 layer of the WE and Pt of the CE of the DSSC.

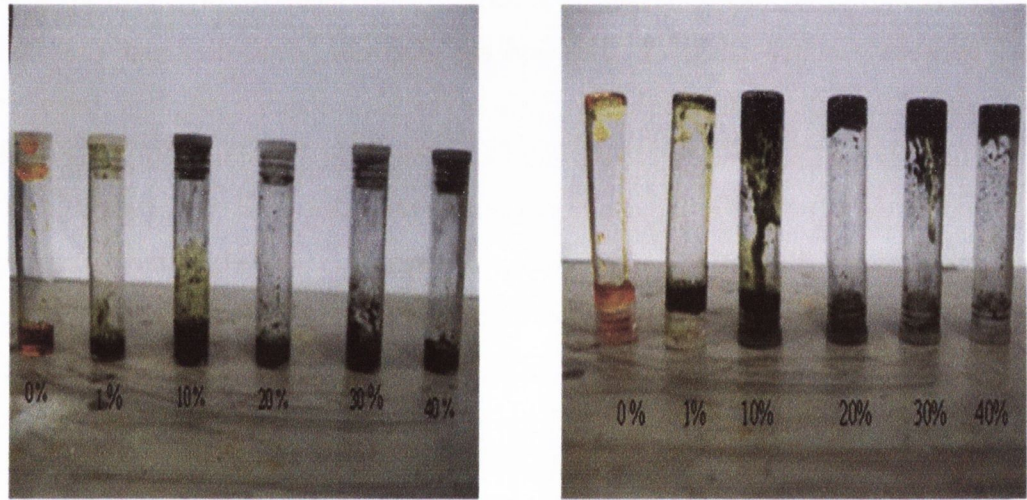


Figure 3.6: Pictures of vials with the different of graphene wt % in PMII, from left to right the graphene (wt %) increased in PMII.

3.4.2 Investigation of the Photovoltaic Performance of DSSCs with Graphene based Quasi solid state electrolytes/DSSCs

Table 3.1 presents a summary of photovoltaic parameters including short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency % of quasi solid state electrolytes containing different amounts (wt %) of graphene and the reference DSSC with PMII only. The power conversion efficiency of

the reference DSSC without graphene was found to be 0.16%. Initially we tried to keep graphene at a low concentration, significantly below the percolation threshold. After the addition of 1 to 10 wt % of graphene the power conversion efficiencies of DSSCs increased very little (up to 0.2 %). However the power conversion efficiencies of DSSCs increased sharply (up to 2.1%) when 30 wt % of graphene was added into PMII. At low concentrations the graphene flakes are away from each other and do not provide sufficient charge transfer. As the concentration increased the graphene flakes come closer to each other i.e. above the percolation threshold and as a result fast electrons transferred from the CE toward the WE, hence viscous quasi solid state electrolytes show higher power conversion efficiency. The power conversion efficiencies increased from 0.16 % (without graphene) to 2.10 % with 30 wt % of graphene concentration. It is known that the incorporation of a carbon based material in ILs make a direct link between counter electrode and working electrode, thus they reduced the physical diffusion path of tri-iodide ion (I_3^-) so called extended electron transfer material (EETM) for example SWCNTs etc [17]. The tri-iodide ion (I_3^-) is reduced back to iodide ion (I^-) by Pt at the counter electrode ($I_3^- + 2e^- \longrightarrow 3I^-$) of a DSSC. Therefore, physical diffusion of tri-iodide ion in the electrolyte, as well as the charge transfer on the TCO-Pt/electrolyte interface are important parameters that influence the performance of a DSSC [38]. Therefore, it is expected that incorporation of graphene in PMII also acts as an EETM and the resulted quasi solid state DSSCs would more efficient than other carbon based material because of its high surface area. The increase of power conversion efficiency of the cell with graphene is attributed to the dual functions of graphene, i.e. mediating charge transfer in the electrolyte and catalyzing the I_3^- reduction. Further increase of graphene in PMII (35% to 40% wt %) had reduce the power conversion efficiencies of DSSCs. When the amount of graphene was increased up to 35 to 40 wt %, the power conversion efficiencies had decreased to 0.59 % and 0.48 % respectively. This reduced power conversion efficiencies are most likely due to the reason that at 35 to 40 wt % graphene cannot be properly dispersed in PMII and thus homogeneity of composite electrolyte decreased and cannot provide enough PMII penetration into the sensitized porous TiO_2 layer and inhibits the diffusion of I^- and I_3^- ions in electrolyte.

Table 3.1: The Photovoltaic parameters of the DSSCs with various carbon based quasi solid state electrolytes with three different type of WE.

Graphene content (wt %)	Jsc (mA/cm ²)	Voc (V)	FF	Efficiency %
0 % (onlyPMII)	0.37	0.575	0.64	0.16 ± 0.01
1%	0.85	0.507	0.30	0.16 ± 0.01
5%	0.74	0.561	0.36	0.18 ± 0.01
10%	0.79	0.561	0.39	0.21 ± 0.02
15%	3.91	0.538	0.31	0.79 ± 0.02
20%	4.00	0.521	0.34	0.90 ± 0.05
25%	4.80	0.535	0.37	1.20 ± 0.06
30%	5.30	0.624	0.49	2.10 ± 0.10
35%	3.91	0.460	0.27	0.59 ± 0.02
40%	3.52	0.464	0.24	0.48 ± 0.02

It can be noticed that Jsc of DSSCs increased with increased the amount of graphene (wt %) in PMII, which indicted that an increased amount of graphene also increased conductivity of PMII in quasi solid state DSSC. Kang et al [39] have described that Jsc

is strongly dependent on the ionic conductivity of the electrolyte. The highest FF (0.49) was obtained with 30 wt % of graphene. This reflects that internal electric resistance of DSSC also decreased with 30 wt % of graphene based quasi solid state electrolyte. While V_{oc} values also increased from 0.575 to 0.624 V at 30 wt % of graphene. While the value for V_{oc} was decreased when the amount of graphene was increased to 35 to 40 wt%, which shows that up to 30 wt % graphene provide enough PMII to penetrate in to TiO_2 layer and further increase of graphene wt % cannot provide enough PMII to penetrate into the sensitized porous TiO_2 layer. It is believe that graphene based IL electrolyte is a facile and low-cost alternative to iodine-containing liquid and other quasi-solid electrolytes. In addition to promising photovoltaic parameters above this highly viscous electrolyte can hold together both electrodes and does not show any leakage even without sealing. Finally, this method of quasi solid-state DSSC can be applied for large scale fabrication of DSSC using the screen-printing method. We conclude on the basis of above results that graphene is a promising material as a filler to solidify/gelify the PMII.

3.4.3 Thermogravimetricanalysis (TGA) of Graphene Based Quasi Solid State Electrolytes

Thermal stability of graphene, PMII and the graphene (30 wt %) based quasi solid state electrolytes which gave the best result were selected for thermogravimetric analysis (TGA). The samples were heated from 26 °C temperature to 900 °C at a rate 10 °C per minutes. TGA curves are plotted in Figure 3.7 A and derivative TGA (DTGA) curves are shown in Figure 3.7. B. The DTGA curve of PMII (Figure 3.7 B .a) displayed three peaks in the region of 55 °C, 302 °C, and 724 °C. There was a loss of 4.2 wt% at 55 °C. This initial loss is due to the presence of moisture in the sample. Due to the hygroscopic nature of the PMII, moisture may be absorbed during transferring of the sample to the TGA pan. Most of the weight was (85.80 wt %) lost at 302 °C. A further 9.85% weight was lost at 724 °C. Shown in Fig 3.7 B. b) is the DTGA curve of graphene film. The absence of peak in low temperature region (up to 250 °C) indicates that there is almost no solvent trapped in film and film is suitable dry. Furthermore the curve revealed that graphene degradation begun at 650 °C and maximum weight lost occurred at 818 °C. Figure 3.7 B.c) shows the DTGA curve of quasi solid state

electrolytes which contain 30 % weight of graphene. This DTGA curve shows four peaks in the region of 52 °C, 302 °C, 575 °C and 659 °C. Initially 7.9 % weight was lost

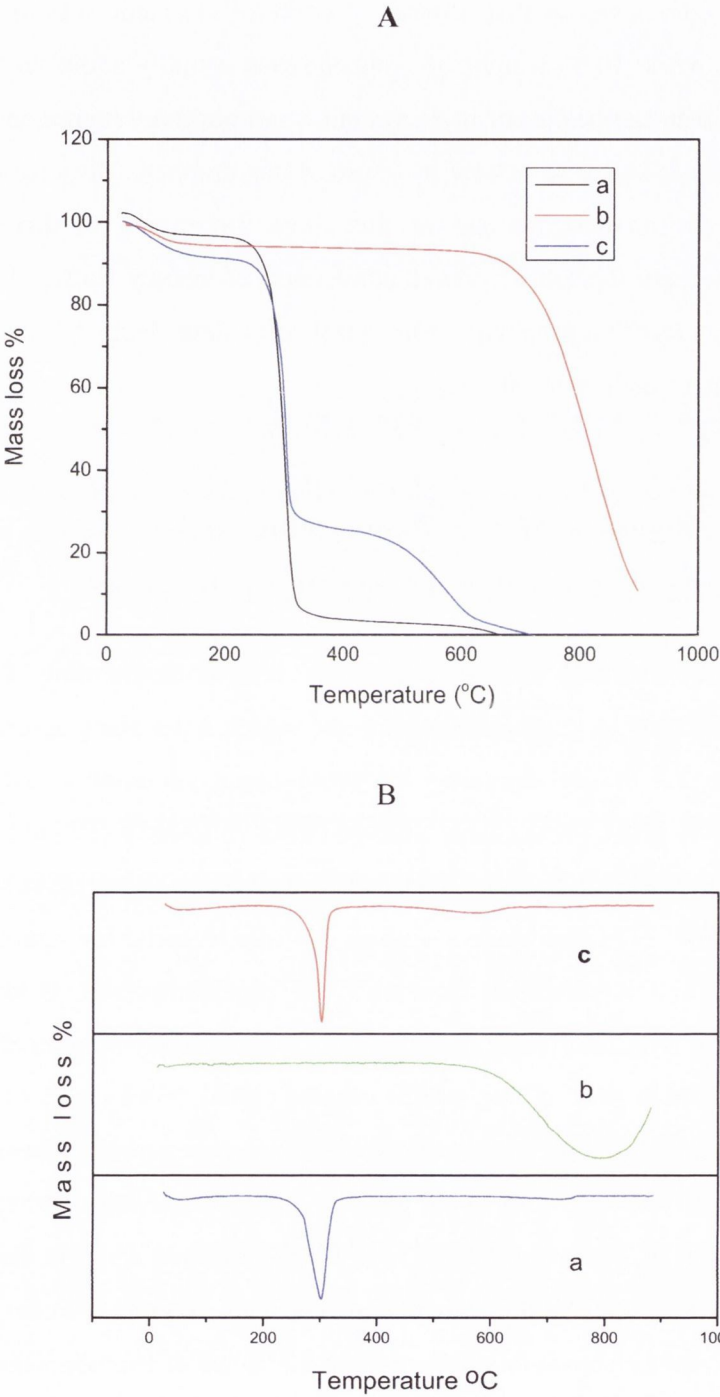


Figure 3.7: **A)** TGA curves of A.a), PMII, A.b) graphene and A.c) graphene (30 wt %) + PMII quasi solid state electrolyte. **B)** DTGA curve of B.a) PMII, B.b) graphene and B.c) graphene (30 wt %) + PMII electrolyte.

at 52 °C this can be attributed to the absorbed moisture. While 62.40 wt% was lost at 302 °C. A further 24.48 % weight was lost at 575 °C and 4.5 % weight was lost at 659 °C. DTGA curves shows that around 22 wt % of graphene was present in quasi state electrolytes while 30 % weight of graphene was actually added to PMII. TGA results shows that even our best electrolyte system is not perfectly homogenised. Therefore, we believe it is necessary somehow to improve our graphene dispersion in ILs. However this is a quite challenging task at this stage. Improving of dispersion quality will certainly increase the DSSC power conversion efficiency further. Finally, from TGA analysis it is clear that graphene based quasi solid state electrolytes are quite stable even at high temperature (up to 300 °C).

3.4.4 Investigation of the Photovoltaic performance of DSSCs with SWCNTs Based Quasi Solid State Electrolyte/DSSCs

SWCNTs-PMII based electrolytes and corresponding DSSCs have been prepared similarly to graphene based ones, which have been described above section 3.4.1. Table 3.2 present summary of photovoltaic parameters including short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency % of SWCNTs based quasi solid state electrolytes/DSSCs. It was found that 1 % wt of SWCNTs can make a viscous gel like material but cannot stop the flow of PMII as no visible effect on flow of PMII been observed. It has previously been reported that SWCNTs form specific bucky gels with structured network in ionic liquids (SWCNTs gels of ILs, which may be called “bucky gels of ionic liquid) [40]. Therefore the addition of 1 % wt of SWCNTs increased power conversion efficiency of DSSCs from 0.16 % to 0.25 % for PMII and quasi solid state electrolytes respectively. The dispersion of 7 % wt of SWCNTs in PMII produced a highly viscous black gel, the resulted gel was a quasi solid state electrolyte. This is quite different from the graphene based solid state electrolyte system where 10 % wt of sample would still have lower viscosity as no visible effect on flow was observed as shown in figure 3.6. The highest power conversion efficiency (1.43%) was achieved with 7 % wt of SWCNTs, which is an increase by the ~ 9. This increase in power conversion efficiency can be explained

by the fact that this high wt % and good dispersion SWCNTs provide very good electron transfer. The conductivity of PMII with SWCNTs increases hence a high J_{sc} (5.19 mA/cm^2) was observed. The increase of power conversion efficiency of the cell with 7 wt % is also attributed to the dual functions of SWCNTs, i.e. mediating charge transfer in the electrolyte and catalyzing the I_3^- reduction [17]. Furthermore, at 7 % wt of SWCNTs, there is enough PMII in electrolyte system to penetrate into the sensitized porous TiO_2 layer. However, further increase of SWCNTS loading from 10-16 wt % produced an even more viscous gel, but 10 wt %, 13 wt %, 16 wt % of SWCNTs quasi state electrolytes gave power conversion efficiencies of 0.56 %, 0.46 % and 0.40 % respectively. This is most likely because the dispersion of SWCNTs was not good at concentration above 7 wt % in PMII. The SWCNTs aggregates can easily be seen even by naked eye. That may be the reason that very low power efficiencies were obtained at higher loading of SWCNTs (10 to 16 wt %). In addition perhaps at high loading SWCNTs quasi state electrolytes cannot provide sufficient PMII penetration into the sensitized porous TiO_2 layer of the WE of the DSSCs.

Table 3.2: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes containing different amounts of SWCNTs in PMII. Measured at 78 mW/cm^2 . Cell active area: 0.8 cm^2

SWCNT content (wt %)	$J_{sc} \text{ (mA/cm}^2\text{)}$	$V_{oc} \text{ (V)}$	FF	Efficiency %
0 % (only PMII)	0.370	0.575	0.64	0.16 ± 0.01
1%	0.524	0.573	0.70	0.25 ± 0.01
7%	5.19	0.540	0.41	1.43 ± 0.13
10%	2.15	0.616	0.36	0.56 ± 0.02
13%	1.64	0.614	0.41	0.46 ± 0.02
16%	2.09	0.541	0.32	0.40 ± 0.02

3.4.5 TGA of SWCNTs Based Quasi Solid State Electrolyte

For TGA study the most efficient quasi solid state electrolytes i.e. contained 7 wt % of SWCNTs was selected and for comparison the TGA of SWCNTs was also performed.

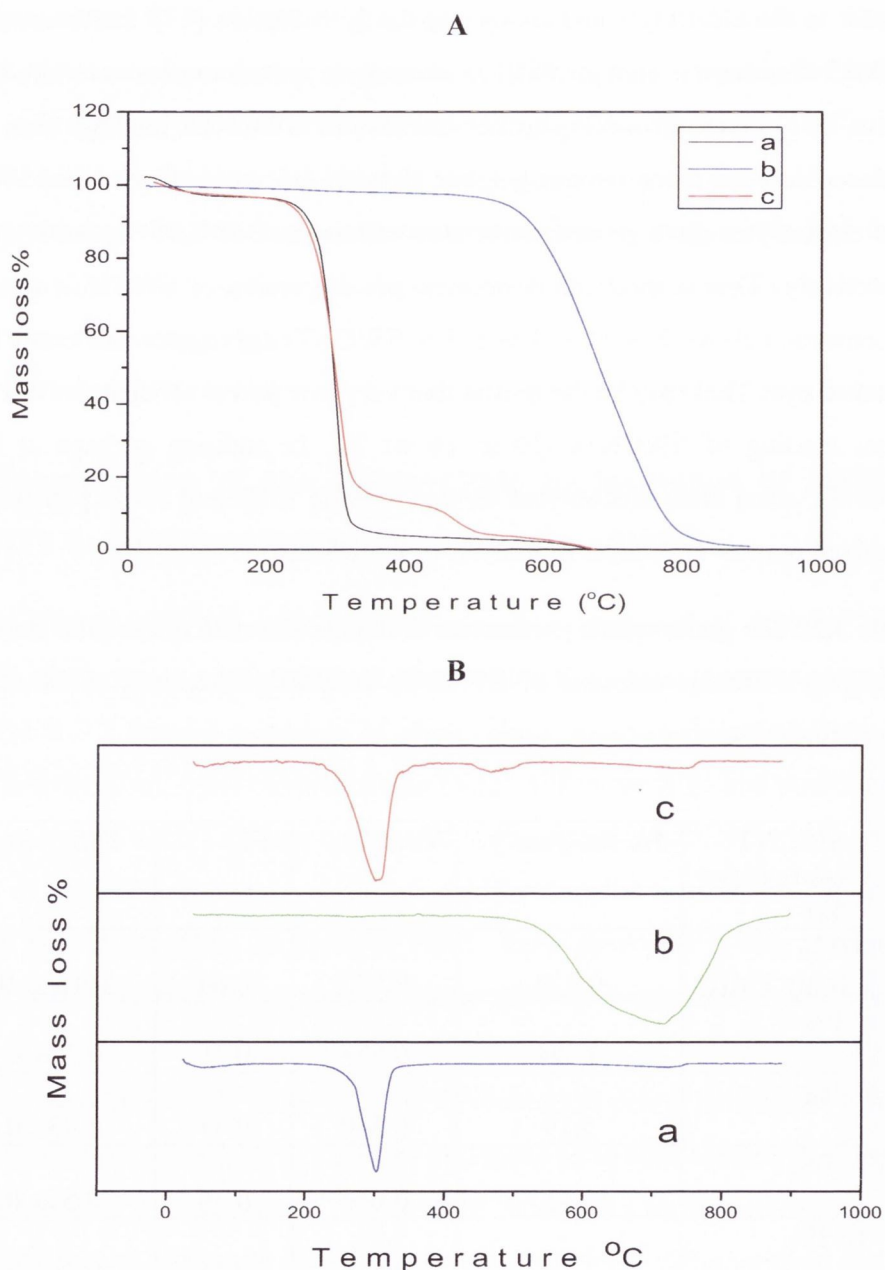


Figure 3.8: A) shows TGA curves of A.a) PMII, A.b) SWCNT and A.c) SWCNTs (7 wt %) + PMII quasi solid state electrolytes. B) Shows DTGA of B.a) PMII, B.b) SWCNTs and B.c) SWCNTs (7%) + PMII quasi solid state electrolytes.

Figure 3.8 B. b) shows the DTGA curve of SWCNTs which indicate that maximum weight (97 %) was lost at 717 °C. Figure 3.8.B.c) shows the DTGA curve of quasi solid state electrolytes which contained 7 wt % of SWCNTs. There was an initial 2 % wt loss observed at 52 °C, which shows the presence of some absorbed solvents and moisture in sample as have been discussed above 3.4.3. Then the main 77% wt was lost at 300 °C. Also 8 % wt loss was observed at 467 °C and 9 % wt was lost at 744 °C. The DTGA curve shows that around 15 % SWCNTs was present in this quasi solid state electrolyte while actually 7 % wt of SWCNTs was added. From TGA analysis it is clear that SWCNTs based quasi solid state electrolytes are also quite stable even at high temperature (300 °C).

3.4.6 Investigation of the Photovoltaic Performance of DSSCs with Hybrid Graphene-SWCNTs/PMII Quasi Solid State Electrolyte

Two kinds of hybrid quasi solid state electrolytes were produced with different graphene to SWCNTs ratio. Hybrid A consisted of 3 wt % of graphene and 12 wt % of SWCNTs and Hybrid B consisted of 3 wt % of SWCNTs and 12 wt % of graphene in PMII. Table 3.3, summarizes photovoltaic parameters of the DSSCs with hybrid graphene and SWCNTs based quasi solid state DSSCs. A highest power conversion efficiency of 2.50% was obtained with 3 wt % of SWCNT and 12 wt % of graphene quasi state electrolytes/DSSC. This is remarkable increased in power conversion efficiency by the factor of 15 increase compare to pure PMII. This increase is higher than both pure graphene- PMII or pure SWCNT- PMII based quasi state electrolytes. It is reported in literature that conductivity of graphite/graphene composite can be increased by addition of small quantities of SWCNTs [37]. That might be the reason in our case as well. These kinds of composite are more conducting than sample 1 and sample 2 hence this allows for faster electron transport through the electrolyte. This is further shown in the Jsc data obtained. The highest Jsc ($7.32\text{mA}/\text{cm}^2$) which was higher than graphene ($5.30\text{ mA}/\text{cm}^2$) and SWCNTs($5.19\text{ mA}/\text{cm}^2$) based quasi solid state electrolyte/DSSC as shown in Table 1 and Table 2 respectively. Therefore the ionic conductivity of this particular electrolyte (hybrid B) is higher than all other types quasi solid state electrolytes prepared in this work. Figure 3.9 shows the representative JV

curves of three best efficient quasi solid state of each type sample and reference (PMII) DSSCs which were fabricated in this work.

Table 3.3: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes containing different amounts of graphene and SWCNTs in PMII. Measured at 78 mW/cm². Cell active area: 0.8 cm²

SWCNT/Graphene weight content %	Jsc (mA/cm ²)	Voc (V)	FF	Efficiency %
0 (only PMII)	0.370	0.575	0.64	0.16 ± 0.01
SWCNT (3 %) + Graphene (12%) (Hybrid B)	7.32	0.594	0.44	2.50 ± 0.10
SWCNT (12%) + Graphene (3%) (Hybrid A)	4.66	0.561	0.43	1.39 ± 0.10

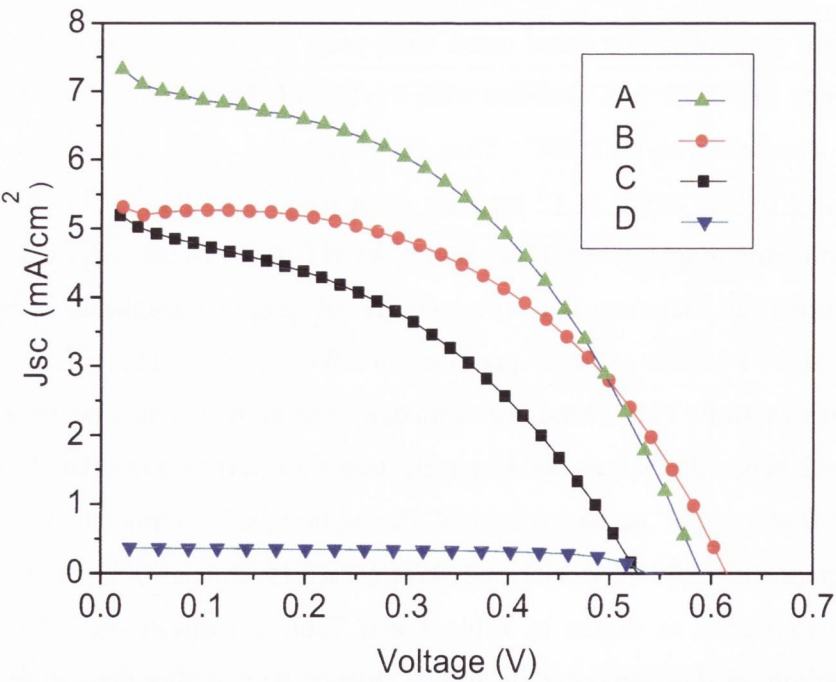


Figure 3.9: The photovoltaic (J–V) curves of the DSSCs with A) hybrid B, B) Graphene (30 wt %), C) SWCNTs (7 wt %) and D) PMII only.

3.4.7 TGA of Hybrid Graphene–SWCNTs-PMII Quasi Solid State Electrolyte

TGA of hybrid B based quasi solid state electrolytes (Fig 3.10.) showed four peaks in the region of 53 °C, 299 °C and 484 °C and 588 °C. Initially 4.3 % wt was lost at 55 °C this can be attributed to absorbed solvents and moisture as discussed in previous sections.

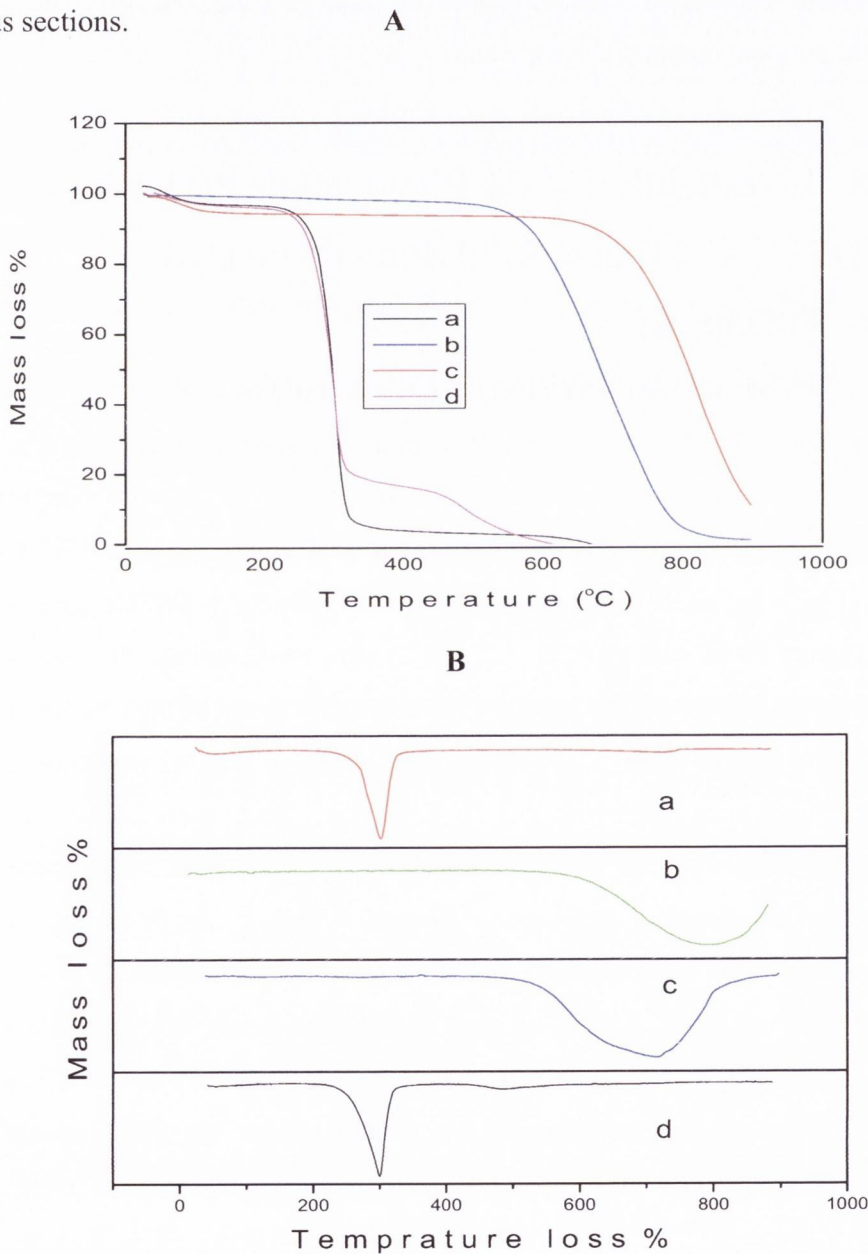


Fig 3.10: **A)** Shows TGA curves of A.a) PMII, A.b) SWCNTs, A.c) graphene and A.d) hybrid B. **B)** shows DTGA of B.a) PMII, B.b) graphene B.c) SWCNTs and B.d) hybrid B.

There was 76 % wt loss was recorded at 299 °C, a further 14 % wt loss at 484 °C and 6 % wt was lost at 588 °C. The DTGA curve shows that around 18 wt % graphene +SWCNTs were present in this electrolytes system while actually 15 wt % graphene (12 wt %) +SWCNTs (3 wt %) were added in to PMII. The TGA study shows that these kinds of quasi solid are more homogeneous than SWCNTs and graphene based quasi solid state electrolytes. These stable at high thermal condition because all their components and composite were stable up to 300 °C.

3.4.8 Investigation of the Photovoltaic Performance of Pt free CE/DSSC with Quasi Solid State Electrolytes (only FTO/glass)

Four identical FTO/glass (3 cm x 2 cm) was washed with DI water and then washed with ethanol and dried at 80 °C in a oven then used us as Pt free-CE in DSSC with three best formulations of quasi solid electrolyte i.e. with Graphene (30 wt%) +PMII, SWCNTs (7wt%) + PMII and SWCNTs (3wt%) + Graphene (12 wt%)+PMII=hybrid B and for comparison two references DSSCs were also fabricated with 1) pure PMII with Pt/FTO- CE and 2) pure PMII without Pt , only FTO/glass-CE as shown in Table 3.4. The power conversion efficiency of 0.01 % was achieved with pure PMII without Pt/FTO -CE/DSSC and 0.16 % of power conversion efficiency was obtained with pure PMII with Pt/FTO-CE/DSSC. This power conversion efficiency is higher by factor of 2.28 than PMII with Pt free CE–DSSC. This increase in power conversion efficiency is attributed to catalytic activity of the Pt for the reduction of tri-iodide ion on the FTO/glass-CE/DSSC. This result shows that Voc is more or less independent of Pt as Voc value was slightly decreased from 0.575V to 520 V. In contrast, both FF and Jsc show strong dependence on the Pt of the CE as FF decrease from 0.65 to 0.07 and Jsc decreases from 0.387 mA/cm² to 0.230 mA/cm². The power conversion efficiency of Pt free CE with graphene based quasi solid state /DSSC increased from 0.07 % (without Pt/CE with only PMII) to 0.92%. This result confirmed that graphene act as EETM in quasi solid state DSSC as increase was seen in Jsc (2.68 mA/cm²) and FF (0.50). Similarly, the power conversion efficiency of Pt free CE with SWCNTs based quasi solid state DSSC increased to 0.70% due to improvement in Jsc

(2.94mA/cm²) and FF (33). However the highest power conversion efficiency of Pt free CE was obtained with hybrid B quasi solid state electrolyte/ DSSC. The highest Jsc value (3.56mA/cm²) obtained with hybrid B quasi solid state electrolytes/DSSC, this shows that this electrolytes is more catalytic active and more conductive than all other quasi solid state/ DSSCs which are tested in this work. In conclusion, all three carbons based quasi solid state/DSSCs shows a great increase in conversion efficiencies than pure PMII with Pt/FTO and Pt free CE/DSSCs. However, these power conversion efficiencies are lower than those which were obtained with carbon based quasi solid state electrolytes with Pt/FTO CE/DSSCs as discussed in early sections, as the quasi solid state electrolytes are in loosely sandwich between WE and CE of the DSSC while Pt is firmly attached to FTO surface. Therefore, it is expected that electron efficiently transfer to carbon based quasi solid electrolytes and thus shows excellent performance the presence of the Pt in CEs/ DSSCs. These results confirmed the importance of carbon based material in ILs and confirmed that these carbon based materials work as EETM in ILs in DSSCs, therefore photovoltaic parameter of DSSC increased than pure PMII with Pt/FTO CE and pure PMII without Pt CE (only FTO)/DSSCs. Figure 3.11 shows the JV curves of Pt free CE/DSSCs which were fabricated in this work.

Table 3.4: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes with Pt free CE/DSSCs. Measured at 78 mW/cm². Cell active area: 0.8 cm²

Electrolytes Type	CE type	Jsc (mA/cm ²)	Voc (V)	FF	Efficiency %
only PMII	Pt/FTO	0.370	0.575	0.64	0.16 ± 0.01
Only PMII	FTO	0.230	0.520	0.07	0.01 ± 0.01
Graphene+PMII	FTO	2.68	0.532	0.50	0.92 ± 0.01
SWCNTs +PMII	FTO	2.94	0.565	0.33	0.70 ± 0.01
Hybrid B	FTO	3.56	0.521	0.50	1.18 ± 0.01

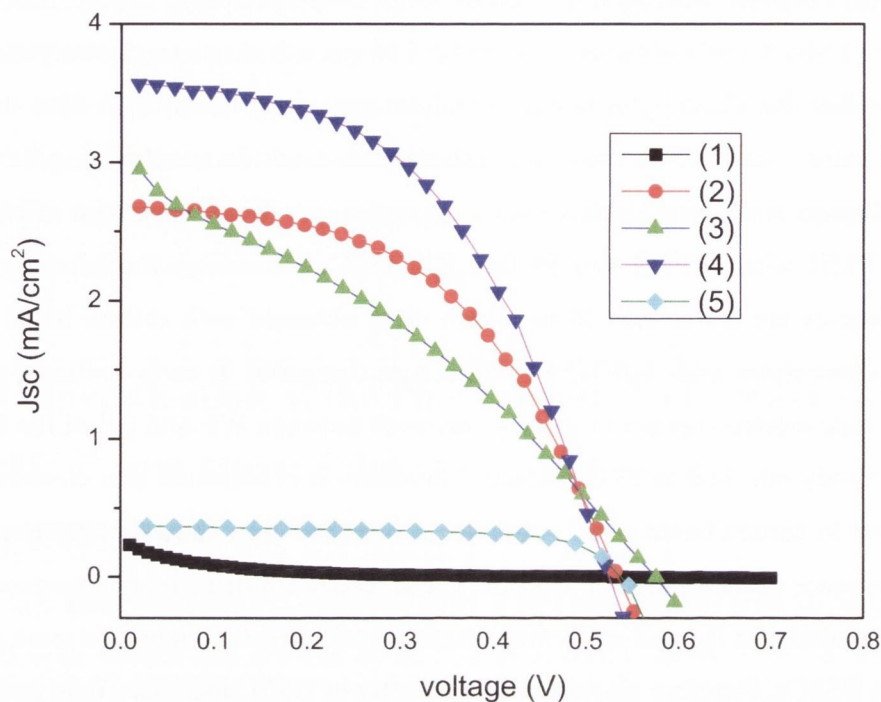
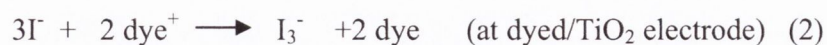
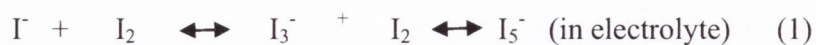


Figure 3.11: The photovoltaic (J–V) curves of the DSSCs with 1) Pure PMII without Pt free CE, 2) Graphene (30 wt %) quasi state electrolyte without Pt free CE, 3) SWCNTs (7 wt %) quasi state electrolyte without Pt free CE, 4) hybrid B without Pt free CE and 5) PMII with Pt/CE/DSSCs.

3.4.9 Iodine (I_2) effect on the Photovoltaic Performance of DSSCs with Quasi Solid State Electrolyte

It is well-known that I_2 exists in the electrolyte containing iodide in the form of polyiodides such as I_3^- or I_5^- (eq 1) [41]. An efficient transport/diffusion of I^- and I_3^- ion in the electrolyte is necessary for a good performance of the DSSC because the oxidized state of the dye (dye^+) should be regenerated by I^- ion efficiently after the electrons from the excited state of the dye are injected into the conduction band of TiO_2 under illumination (eq 2). Meanwhile, the electrons accumulated at the counter electrode by the external circuit will lead to concentration over potentials for the electrolyte at the electrode and loss of energy of the DSSC if the electrons are not transferred by I_3^- efficiently (eq 3).



It has been previously reported that the introduction of I_2 into liquid or gel electrolytes could increase the conductivity of the electrolyte [41-44]. Therefore, in this study, three best formulations were selected from each type quasi solid electrolyte i.e. with Graphene (30 wt%) + PMII, SWCNTs(7wt%)+PMII and SWCNTs (3wt%) + Graphene (12 wt%)+PMII 0.1 wt % of Iodine (I_2) was added to each sample as shown in Table 3.5. The tests demonstrated that the addition of I_2 resulted in the decrease of the power conversion efficiency in all cases mainly due to the decreased V_{oc} and J_{sc} values with the addition I_2 (0.1 wt %). This study and other reported work [6, 17, 45] suggested that the iodide anion in IL based carbon based quasi solid state electrolyte/DSSCs, can provide sufficient I^- for the regeneration of the oxidized dye under illumination (eq 2) I^- in turn oxidizes to I_3^- which can be reduced back to I^- at the EETM (eq 3). Therefore, the addition of I_2 can increase concentration of polyiodides in the porous dye-coated TiO_2 layer and thus it can facilitate recombination of injected conduction band electrons with polyiodides [6, 17]. Furthermore, addition the I_2 content also enhances light absorption even in the visible range [41]. This decreases the light-harvesting of dye molecules [41]. These results demonstrate that theses carbon based quasi solid state electrolytes works most effectively without the addition I_2 due to above reasons. Figure 3.12 shows the JV curves of DSSCs which were fabricated in this work.

Table 3. 5: The photovoltaic parameters of the DSSCs with quasi solid state electrolytes with addition of 0.1 wt % of iodine (I₂). Measured at 78 mW/cm². Cell active area: 0.8 cm²

Electrolytes type	Jsc (mA/cm ²)	Voc (V)	FF	Efficiency %
Graphene+PMII	4.38	0.596	0.31	1.06 ± 0.01
SWCNTs +PMII	3.45	0.559	0.38	0.90 ± 0.09
Graphene+SWCNTs +PMII	4.14	0.569	0.4	1.16 ± 0.10

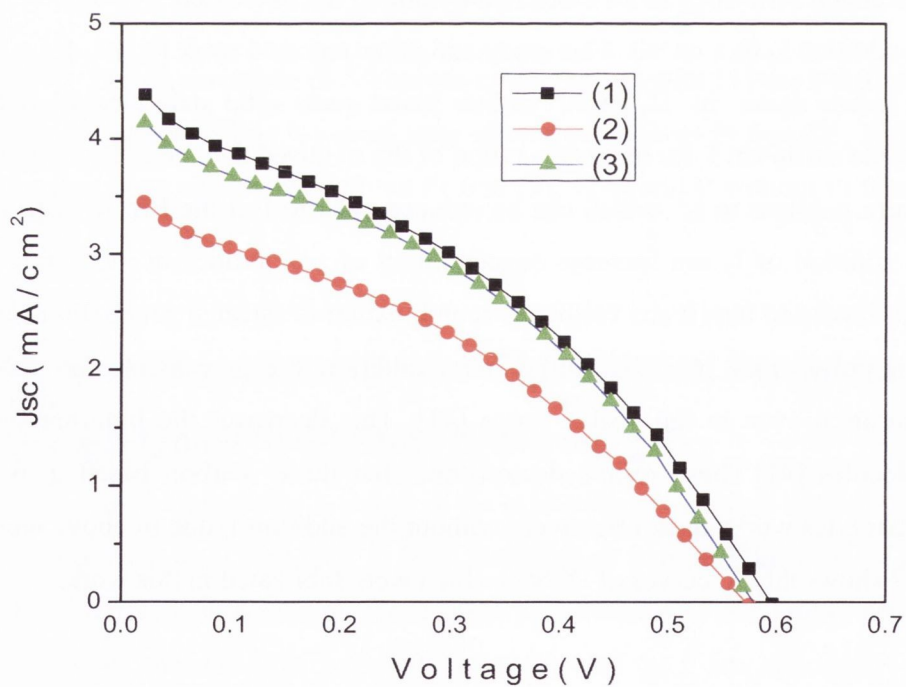


Figure 3.12: The photovoltaic (J–V) curves of the DSSCs with addition of 0.1 wt% of Iodine(I₂) 1) Graphene (30 wt %) quasi state electrolyte, 2) SWCNTs (7 wt%) quasi state electrolyte and 3) hybrid B quasi solid state electrolytes/DSSCs.

**3.4.10 Comparative Stability Study of quasi solid state
DSSCs**

To investigate the stability of the quasi solid state DSSCs, the three best and most efficient quasi solid state DSSCs were selected from each type of sample. In addition one reference DSSC was also fabricated with PMII only. These four DSSCs (open cell) were stored in a desiccator. Figure 3.13 shows a summary of the stability of quasi solid state electrolytes used in DSSCs. The J-V curves of the all DSSCs were measured at intervals of 120 hours for 1000 hours. It was noticed that the cell efficiency in all cases was decreased after five days and then stabilized for some period of time. This was followed by another gradual decrease as shown in Figure 3.13. These results indicate that the overall power conversion efficiencies of the quasi solid state electrolyte with SWCNTs 2) graphene and 3) hybrid B were decreased from 1.43% to 1.02 %, 2.10% to 1.61% and 2.50 % to 1.55% respectively after 1000 hours.

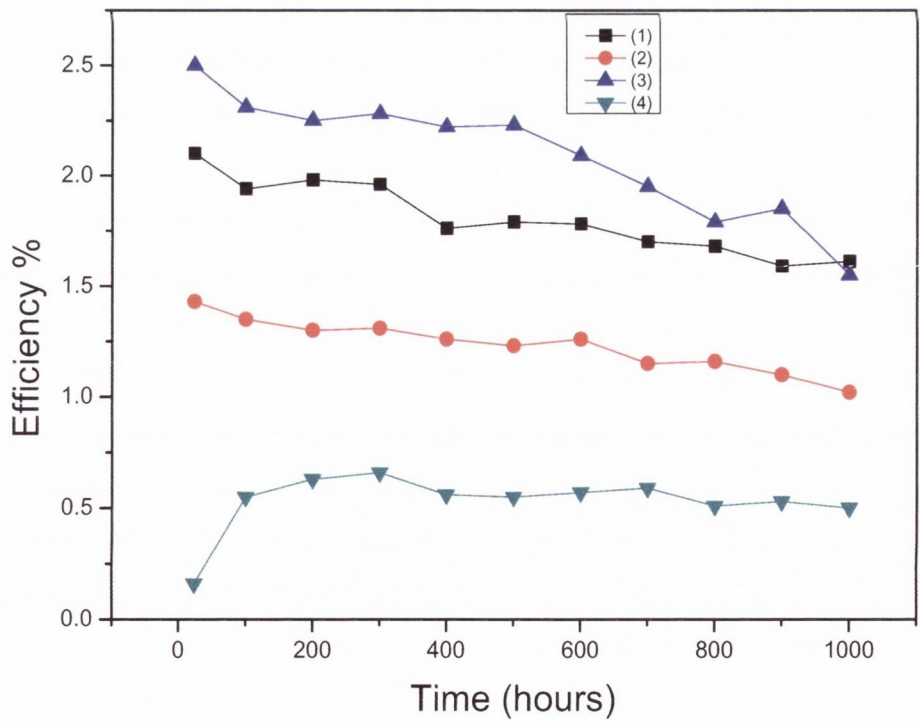


Figure 3.13: Stability studies of DSSCs with various electrolytes of 1) graphene-based, 2) SWCNT-based, 3) hybrid B based and 4) reference DSSCs (PMII only).

The power efficiency of the reference cell made with PMII was initially increased after 120 hours, this might be due to the deeper penetration of PMII into TiO_2 of WE but then gradually decreased and reached to 0.50 % after 1000 hours. Among all the various types quasi solid state DSSC the graphene based based DSSCs was the most stable. One reason for the stability could be that graphene makes a protective layer over the dyed TiO_2 layer. The 2 D structure of graphene firmly adheres to TiO_2 layer and thus protects the dyed TiO_2 and PMII from moisture/ humidity and other contaminations. From the first glance apparently it looks like the DSSC made using pure PMII is more stable than the rest. However it is clear that even at 1000 hours of aging all the nano-carbon filled electrolyte samples still have much higher power conversion efficiencies that of only PMII at the same aging level.

3.5 Conclusions

In conclusion this part of work resulted in the development of new electrolytes for DSSCs. Series of quasi solid state electrolytes were prepared by the incorporation of: (1) graphene or (2) SWCNTs or (3) a combination of SWCNTs+graphene into PMII. Using these new electrolytes significant increases in power conversion efficiencies of DSSCs were achieved comparing to pure PMII. The maximum power conversion efficiency in graphene based quasi state electrolytes was 2.10 %. This is an increase of a factor of 13 (an increase from 0.16%). While in case of SWCNTs based quasi state electrolytes the power conversion efficiency showed an increase from 0.16 to 1.43%. However, the best power conversion efficiency of 2.50% (an increase by a factor of ~15) achieved when SWCNTs (3 wt %) and graphene (12 wt %) were mixed in PMII (hybrid B). The incorporation of carbon based nanomaterials has enhanced the DSSC power conversion efficiency, apparently due to an improved electron transfer from the counter electrode to the PMII (ILs) resulting in reduced charge diffusion length i.e. new electrolytes serve as an extended electron transfer material (EETM). It was established that carbon nanomaterials serve simultaneously both as charge transporter in the ILs and as an electrocatalyst for the electrochemical reduction of I_3^- . It was also demonstrated

that DSSC can be constructed without Pt with a moderate efficiency (1.16%) as graphene and CNT can act as an electrocatalyst in hybrid B quasi solid state electrolytes/DSSCs. The aging/stability study revealed that these quasi solid state DSSCs cells still possess the higher efficiencies than pure PMII DSSC under same condition. At all processing stages the quality of dispersions were monitored by various characterization techniques. TEM revealed the formation of exfoliated graphene. Raman data suggests the presence of few layered graphene even in dry form in the films. The thermal stability of each component in the quasi solid state electrolyte and the best efficient quasi solid state electrolyte of each sample were characterized by a thermogravimetric analyzer (TGA). TGA studies demonstrated that these electrolytes have high thermal stability up to 300 °C. This research provides a useful approach for the fabrication of the stable quasi solid state electrolytes and corresponding DSSCs. It is believed that further optimization of these quasi solid state electrolytes as well as photovoltaic cell optimization will enable to get higher power conversion efficiencies for cost-effective production of DSSCs.

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Chapter 4: Development of Binary Ionic liquid Based Quasi Solid State Electrolyte for Dye Sensitized Solar Cells

4.1 Introduction

Ionic liquids (IL) can serve as both iodide ion source and solvent and therefore can be used as electrolytes in dye sensitized solar cell (DSSCs) [1, 2]. ILs exhibit low vapour pressure and better stability than organic solvent based electrolytes [2]. However, the power conversion efficiencies obtained with ILs at a full air mass (AM 1.5) solar irradiance have been much lower than those achieved with organic solvent-based electrolytes [3]. The use of ILs is still limited either due to low power conversion efficiency, sealing issues, or high costs. Therefore, the focus of research on DSSCs has shifted recently from those based on liquid electrolytes to quasi solid-state electrolytes [4]. ILs based imidazolium salt has been widely used as solvent and iodide source of electrolyte for the fabrication of DSSCs but unfortunately pure imidazolium ionic liquids containing I^-/I_3^- redox couple have high viscosity as compared to the volatile organic solvent based electrolytes, which suppresses the diffusion of redox ions, hence show lower power conversion efficiency [5]. The viscosity of highly viscous IL can be lowered by mixing them with low viscosity IL [6]. As a result the diffusion of I^-/I_3^- redox couple increases, resulting in an improved DSSC performance [7]. This kind of systems is generally called binary IL electrolyte. Binary IL electrolyte, usually composed of an imidazolium iodide and another IL with relatively low viscosity, exhibited high power-conversion efficiencies. The IL 1-methyl-3-propylimidazolium iodide (PMII) which shows an appreciable conductivity of 0.58 mS cm^{-1} at room temperature, to further increase this value, a net decrease of its high viscosity (1000 cP at 25°C) [8] is necessary; for this purpose, PMII is usually mixed with alkyl substituted imidazolium-based ionic liquids of much lower viscosities that employ anions other than iodide such as fluorine-free tetracyanoborate $[B(CN)_3]^-$, dicyanamide $[N(CN)_2]^-$ and tricyanomethanide $[C(CN)_3]^-$ (with viscosities lower than 25 cP at 25°C [9-11]. In order to reduce the fluidity of IL-based electrolytes, various materials are dispersed into of IL to produce gel or quasi-solid-state electrolytes for DSSC to increase their robustness and stability of the DSSC. Chen et al. [4] reported the preparation of quasi solid solid-state electrolyte by mixing polyaniline-loaded carbon black (PACB) (11.1 wt%) into PMII and mixture of PMII and 1-ethyl-3-

methylimidazolium thiocyanate (EMISCN) at volume ratio 35/65. They achieved power conversion efficiencies of 5.81% with PMII+PACB based quasi solid solid-state electrolyte and 6.15 % with binary IL (PMMI+EMISCN) +PACB quasi solid solid-state electrolytes compared to power conversion efficiency of 0.18 % with mixture of binary ILs without the addition of PACB. They believed that the power conversion efficiency was increased because PACB acting as an extended electron transfer surface (EETS) that reduced the diffusion length for I^- and I_3^- ions in the electrolyte, and also simultaneously serves as a charge-transporter and a catalyst for I_3^- reduction. The power conversion efficiency was further increased with the addition of EMISCN, this increase was attributed to the less viscous nature of the EMISCN, which provided better penetration of the composite electrolyte into TiO_2 film/WE and also showed better conductivity of the electrolyte for I^- and I_3^- ions.

In our previous chapter 3 we reported the development of various types of quasi solid state electrolytes by the incorporation of: (1) graphene or (2) SWCNTs or (3) hybrid SWCNTs + graphene into PMII [3]. Using these new quasi solid state electrolytes significant increases in power conversion efficiencies of DSSCs were achieved comparing to pure PMII. However, PMII has very high viscosity (1000 cP at 25 °C), therefore we expected that the addition of low viscosity IL EMISCN (25 cP at 21 °C) to our previously reported quasi solid state formulations could increase the dispersion of SWCNTs or graphene or hybrid SWCNTs+ graphene in binary ILs and diffusion rates and result in the further improvement of power conversion efficiencies of quasi solid state based DSSCs.

4.2 Preparation of Binary Ionic liquid Based Quasi Solid State Electrolyte for DSSC

The EMISCN various wt % was added separately to the PMII and then The graphene (30 wt %), SWCNTs (7 wt%) and hybrid SWCNTs (3 wt%) plus graphene (12 wt %) were dispersed into optimized binary IL as explained in experimental chapter 2.

4.3 TGA of hybrid Graphene-SWCNTs in Binary IL Based Quasi Solid state Electrolyte

Thermal stability of hybrid graphene-SWCNTs-binary quasi solid state electrolyte was investigated by TGA. TGA curves are plotted in Figure 4.1.A and derivative TGA (DTGA)

curves are shown in Fig.4.1. B. The DTGA curve of hybrid graphene-SWCNTs-binary quasi solid state electrolyte which contain 3 wt% of SWCNTs of and 12 wt% of graphene shows three peaks in the region of 55 °C, 301°C, 610 °C. Initially around 1.50 % wt was lost at 52 °C, this can be attributed to the absorbed moisture. While around 82 % wt was lost at 302 °C due to the thermal decomposition of ILs. A further 14 % wt was lost at 610 °C. DTGA curves shows that around 12.62 wt% of graphene+SWCNTs was present in quasi state electrolytes actually 15 wt % graphene (12 wt%) +SWCNTs (3 wt%) were added in to binary ILs. Thus the TGA study showed that the hybrid graphene-SWCNTs-binary quasi solid state electrolytes are stable up to 300 °C.

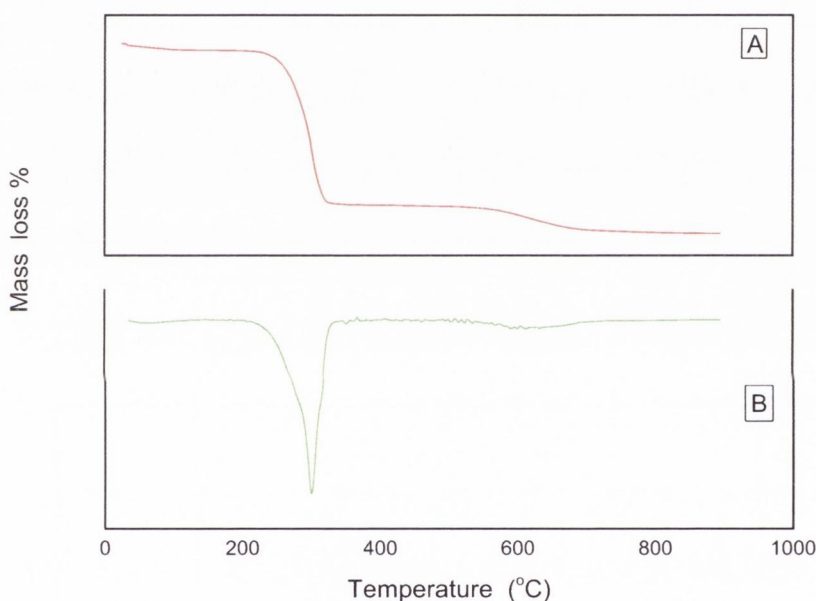


Figure 4.1: A. TGA curve A) and B) DTGA curve of hybrid SWCNTs (3 wt %) + graphene (12 wt %) into binary IL.

4.4 Investigation of the Photovoltaic Parameters of the DSSCs with various Combinations (w/w) of Binary IL Based DSSC

Table 4.1 summarises the photovoltaic parameters i.e. open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiencies of all DSSCs which were fabricated using different wt% of EMISCN into PMII. DSSC fabricated with the pure PMII showed power conversion efficiency of 0.47 %. The power conversion efficiency was increased from 0.47 % (only PMII) to 0.78 % with the addition of 10 wt% of

EMISCN into PMII. The power conversion efficiency was further increased to 1.40 % after the addition of 30 wt % of EMISCN into PMII. However the power conversion efficiency

Table 4.1: The photovoltaic parameters of the DSSCs fabricated with different wt% of EMISCN into PMII. Measured at 100 mW/cm², Cell active area: 0.8/cm².

EMISCN/PMII (w/w ratio)	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency %
0/100	640	2.82	0.26	0.47 ± 0.02
10/90	680	3.83	0.30	0.78 ± 0.04
30/70	680	4.93	0.41	1.40 ± 0.08
50/50	660	4.75	0.40	1.25 ± 0.06
70/30	670	3.65	0.38	0.92 ± 0.05
100/0	520	1.78	0.31	0.29 ± 0.02

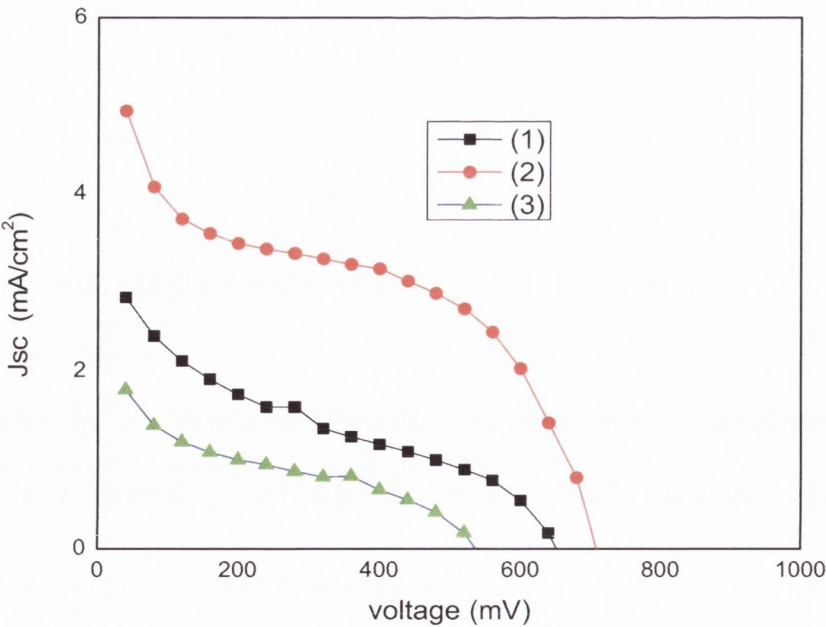


Figure 4.2: Representative photovoltaic (J–V) curves of 1) PMII, 2) Binary IL (30/70) and EMISCN.

dropped from 1.40 % (EMISCN 30 wt% /PMII) to 1.25 % and 0.92 % after the addition of 50 wt% and 70 wt % of EMISCN into PMII respectively. The J_{sc} value was increased from 2.86 mA/cm^2 to 3.83 mA/cm^2 , 4.93 mA/cm^2 , 4.75 mA/cm^2 and 3.65 mA/cm^2 with addition of 10 wt% and 30 wt%, 50 wt and 70 wt% EMISCN into PMII respectively. The highest J_{sc} value (4.93 mA/cm^2) was obtained with the addition of 30 wt% of EMISCN into PMII demonstrating that this particular binary IL combination has better ionic conductivity than all others binary IL which were prepared in this work. Furthermore the increase in J_{sc} values showed that the addition of all wt % EMISCN into PMII increased their ionic conductivity of all binary IL. The FF values were also increased from 0.26 to 0.30, 0.41, 0.40 and 0.38 with addition of 10 wt%, 30 wt%, 50 wt% and 70 wt% of EMISCN into PMII respectively. The V_{oc} values have also raised from 640 mV to 680 mV, 680 mV, 660 mV and 670 mV with addition of 10 wt%, 30 wt%, 50 wt% and 70 wt% of EMISCN into PMII respectively. These results demonstrated that the addition of lower weight % (30 wt%) of EMISCN into PMII gave the best result. This can be attributed to the less viscous nature of the EMISCN (25 cP at 21 °C) than only PMII (1000 cP at 20 °C), which provides better penetration of the binary IL into TiO_2 film/WE and also better conductivity of the electrolyte and diffusion of I^- and I_3^- ions. The advantages of EMISCN with regard to the improvement of the apparent diffusion coefficients and with regard to faster diffusion rates have been also reported [4, 12]. However, when the composition of EMISCN increased to 50 wt% and 70 wt% into PMII then power conversion efficiency start to decrease going below one for the binary IL which contained 30 wt% of EMISCN into PMII. This might be due to the increase of the probability of electron capture resulting in an increased recombination rate [13].

4.5 Investigation of the Photovoltaic Parameters of the DSSCs with incorporation of various Carbon Based Material into Binary IL Electrolyte

The best binary IL combination of EMISCN (30 wt%) into PMII was selected for further investigations. Three types of binary IL based quasi solid electrolytes were prepared by the addition SWCNTs (7 wt%), graphene (30 wt %) and hybrid of SWCNTs (3 wt%) plus

graphene (12wt%) similarly as described in the chapter 3 [3]. Table 7.2 summarises the photovoltaic parameters i.e. Voc, Jsc, FF, and power conversion efficiencies of all DSSCs which were fabricated using binary IL based quasi solid state electrolytes/DSSC. DSSC fabricated with the only binary ILs show power conversion efficiency of 1.40 %. However power conversion efficiencies was increased to 2.04 %, 2.24% and 3.07% with addition of SWCNT, graphene and hybrid graphene + SWCNTs into binary IL respectively. The incorporation of carbon based nanomaterial has enhanced the DSSC power conversion efficiency, due to an improved electron transfer from the counter electrode to the binary IL resulting in reduced charge diffusion length i.e. serve as an extended electron transfer material (EETM). It was previously established that carbon nanomaterials can serve simultaneously both as charge transporter in the ILs and as an electrocatalyst for the electrochemical reduction of I_3^- [3, 4, 14]. The power conversion efficiencies of all three type quasi solid state were mainly improved due to increase in Jsc and FF values than pure binary IL based DSSC. The Jsc value was increased from 4.93 mA/cm² to 7.36 mA/cm², 7.85 mA/cm² and 8.22 mA/cm² after the addition of SWCNTs, graphene and hybrid graphene plus SWCNTs into binary IL respectively. The increased in Jsc value shows that the addition of SWCNTs, graphene and hybrid graphene + SWCNTs increased the ionic conductivity of the binary IL. The highest Jsc values was obtained with hybrid of graphene plus SWCNTs into binary ILs, this shows this particular quasi solid state electrolytes has highest ionic conductivity than SWCNTs and graphene based binary IL quasi solid state electrolytes/DSSCs. The FF value was also increased from 0.41 to 0.45, 0.47 and 0.58 after the addition of SWCNTs, graphene and hybrid SWCNTs plus graphene into binary IL respectively. This reflects the fact that internal electric resistance was also decreased with addition of SWCNTs, graphene and hybrid graphene and SWCNTs into binary IL. The Voc values of 600 mV, 640 mV and 0.640 mV were achieved with addition of SWCNTs, graphene and hybrid of graphene plus SWCNTs into binary IL respectively. Overall the addition of SWCNTs, graphene and hybrid of graphene plus SWCNTs into binary IL did not affect too much the Voc values of DSSCs compared to Voc value of 680 mV for the pure binary IL/DSSC.

Table 4.2: The photovoltaic parameters of the DSSCs with SWCNTs, graphene and hybrid of graphene plus SWCNTs into binary IL bas quasi solid state electrolytes. Measured at 100 mW/cm², Cell active area: 0.8/cm².

Electrolytes type	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency %
EMISCN/PMII=A	680	4.93	0.41	1.40 ± 0.08
A+ SWCNTs	600	7.36	0.45	2.04 ± 0.10
A+graphene	600	7.85	0.47	2.24 ± 0.10
A+graphene+ SWCNTs	640	8.22	0.58	3.07 ± 0.11

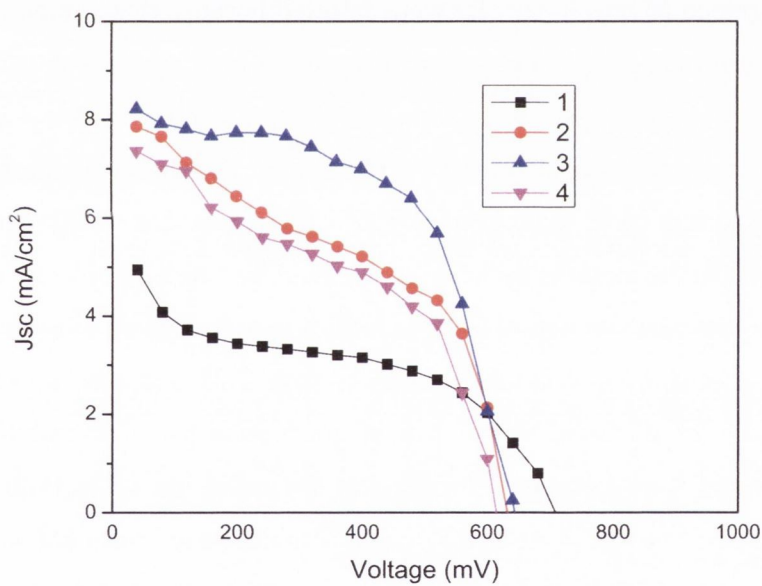


Figure 4.3: The photovoltaic (J–V) curves of 1) Binary IL (30/70=A), 2) A+ graphene,3) A+ SWCNTs+graphene and 4) A+ SWCNTs based binary IL quasi solid state electrolytes DSSCs.

4.6 Investigation of the Photovoltaic Parameters of the DSSCs with various Molar Concentration of Guanidinium Thiocyanate into Hybrid SWCNTs-Graphene Based binary IL quasi solid state electrolyte

It has been previously reported that the introduction of guanidinium thiocyanate (GuSCN) into ionic liquid electrolyte improved the photovoltaic performance of DSSCs [13, 15]. It was reported that GuSCN cations are adsorbed together with the dye molecules facilitating the formation of a compact monolayer. This monolayer of GuSCN cations and dye molecules prevents the recombination causing a surface passivation effect and positive shift in TiO_2 conduction band probably increasing the injection efficiency of the excited dye molecules [9, 16, 17]. For this study, hybrid quasi solid of state electrolytes which contained SWCNTs plus graphene of into binary IL were selected because this combination gave the best photovoltaic performance as discussed in the section 4.4. 0.05M, 0.1M, 0.2M of GuSCN was added separately to these quasi solid state electrolytes samples (Table 4.3). The power conversion efficiencies were increased from 3.07 % to 3.60 % with the addition of 0.05 M of GuSCN to hybrid quasi solid state electrolyte. The power conversion efficiency was improved mainly due to the increase in J_{sc} value 8.22 mA/cm^2 to 8.89 mA/cm^2 and V_{oc} from 650 mV to 680 mV after the addition of 0.05M GuSCN to hybrid quasi solid state electrolyte. However, the power conversion efficiencies reduced from 3.07% to 2.86% and 2.19 % with addition of 1M and 2M of GuSCN into hybrid quasi solid state electrolyte. The power conversion efficiencies were decreased mainly due the reduction of J_{sc} values from 8.22 mA/cm^2 to 8.05 mA/cm^2 to 6.88 mA/cm^2 , V_{oc} was also decreased from 650 mV to 600 mV and 600 mV with the addition of 1M and 2M of GuSCN into hybrid quasi solid state electrolyte respectively. This might be explained by the decrease in photon absorption by dye molecules after the addition of 1M and 2M of GuSCN [13]. The FF values were little increased from 0.58 to 0.59 and 0.59 with addition of 0.05M and 1M of GuSCN to hybrid quasi solid state electrolyte. However the FF value was further reduced to 0.54 with addition of 2M of GuSCN to hybrid quasi solid state electrolyte.

Table 4.3: The photovoltaic parameters of the DSSCs with hybrid graphene-SWCNTs in binary IL based quasi solid state electrolytes using different compositions of GuSCN. Measured at 100 mW/cm². Cell active area: 0.8/cm².

Molarity of GuSCN (M)	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency %
0	650	8.22	0.58	3.07 ± 0.11
0.05	680	8.90	0.59	3.60 ± 0.10
1	600	8.05	0.59	2.86 ± 0.08
2	600	6.78	0.54	2.19 ± 0.08

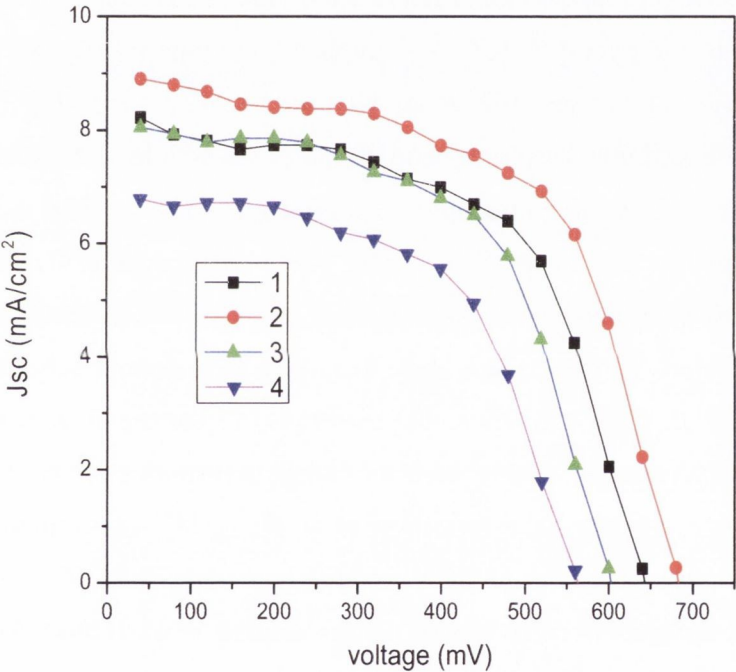


Figure 4.4: The photovoltaic (J–V) curves of hybrid SWCNTs-graphene based binary IL quasi solid state electrolyte/DSSCs which contained 1) 0M 2) 0.05M, 3) 1M and 4) 2M of GuSCN.

4.7 Conclusion

In summary, dye sensitized solar cells (DSSCs) were fabricated using various combinations (W/W) of EMISCN and PMII (binary IL electrolytes). We have demonstrated

that the DSSC with binary IL electrolytes consisting of 30 wt% of EMISCN and 70 wt% of PMII gave the best power conversion efficiency. The power conversion efficiency was increased from 0.47% (PMII) to 1.40 % with binary IL/DSSC. This is around 197 % increase comparing with pure PMII based DSSCs. We believe that in this case the increase in power conversion efficiency can be attributed to the addition of low viscosity IL EMISCN, that resulted in an increase of the diffusion rate and therefore in the raise of the V_{oc} and J_{sc} values was observed with optimized binary IL based DSSC [13]. Quasi solid state electrolytes were also fabricated by the addition of graphene, SWCNTs and hybrid SWCNTs plus graphene into optimized binary IL electrolytes similarly to the work described in chapter 3. The use of these new electrolytes enabled us to achieve increases in the power conversion efficiencies: from 1.40% (optimized binary IL) to 2.04% and 2.24% and 3.07% with addition of SWCNTs, graphene and hybrid SWCNTs + graphene into binary IL/DSSCs respectively. In this case the power conversion efficiencies were increased around 45% (with addition SWCNTs), 60% (with addition graphene) and 119% (with addition of hybrid SWCNTs+ graphene) comparing to those for pure optimized binary IL-DSSCs. The incorporation of carbon based nanomaterials has enhanced the DSSC power conversion efficiency, apparently due to an improved electron transfer from the counter electrode to the binary IL resulting in reduced charge diffusion length. In this case carbon nanomaterials served as extended electron transfer materials (EETMs). As it was mentioned in the previous chapter 3 carbon nanomaterials can serve simultaneously both as charge transporter in the ILs and as an electrocatalyst for the electrochemical reduction of I_3^- [3, 4, 14]. In addition the effect of addition of various concentrations of GuSCN into the best quasi solid state electrolytes i.e. hybrid of SWCNTs plus graphene into binary IL was studied. It was found that the addition of 0.05M of GuSCN into binary IL gave the best power conversion efficiency (3.60%). The power conversion efficiencies increased around 17% over hybrid SWCNT+graphene based binary IL/quasi solid state electrolytes/DSSC. This might be explained by the more efficient surface passivation preventing electron recombination reactions at the TiO_2 /dye/electrolyte interface. TGA studies demonstrated that these electrolytes have relatively high thermal stability up to 300 °C. It is believed that that further optimization of these quasi solid state electrolytes as well as photovoltaic cell optimization should potentially allow to achieve higher power conversion efficiencies and cost-effective production of DSSCs.

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Chapter 5: Development of Carbon Based Counter Electrode for Dye Sensitized Solar Cells

5.1 Introduction

Traditionally the counter electrode (CE) in DSSCs is a TCO substrate coated with Pt. The gap between the two electrodes is filled with an electrolyte which contains an organic solvent with the iodide/tri-iodide (I^-/I_3^-) redox couple [1]. The Pt deposited TCO substrate has been widely used as the standard counter electrode (CE) for DSSCs [2] but both these materials (Pt and TCOs) are very expensive. Therefore Pt based CE accounts for approximately 25~35% of the overall price of DSSCs [3]. It is extremely important to find new cost effective materials and approaches to replace the Pt and TCOs of CEs of the DSSCs. Various other materials rather than Pt, have also been used as electrocatalysts in DSSCs so far such as CNTs, [4] graphite, [5] graphene, [4, 6] GNPs + graphene oxide, [7] carbon black, [8] conducting polymer PEDOT: PSS [9] and PEDOT:PSS+ graphene. Carbon nanotubes, graphene or graphene nanoplates are particularly attractive of these materials as they can be produced at large scale, have good electric conductivity and high surface area [10], and in addition excellent mechanical strength and chemical resistance [11, 12]. These properties make them very attractive for use in CEs of the DSSCs. However the power conversion efficiency of DSSCs using CNT based CEs has been found to be lower as compared to Pt ones [13]. Therefore, various approaches have been used to increase the catalytic activity of carbon based nanomaterials such as a hybrid composite of MoS₂–graphene nanosheet (GNS) which was used as a CE in DSSC [14]. These studies enabled to achieve power conversion efficiencies of 4.15 %, 2.68 %, 5.81 % and 6.24 % with MoS₂, GNS, hybrid MoS₂ plus GNS composite CEs and standard Pt based CE/DSSCs respectively. There has been also a report of a graphene and MWCNTs composite CE/ DSSC, [15] in which the authors reported that they achieved a higher power conversion efficiency with the composite CE (7.55%) compared to graphene (4.62%) and MWCNTs (6.62%) alone as a CE/DSSC but still lower than the Pt/CE (8.8 %) standard DSSC. One other challenge in use of such materials in CE is their good and homogeneous dispersion of in a system. Generally, MWCNTs or GNPs are insoluble and non-dispersible in water

[16, 17]. Two approaches are commonly used to disperse the CNTs or GNPs in a solvent 1) covalent or 2) non covalent approach. The non covalent approach for the dispersion of CNT or GNPs allows the retention of their good electrical properties as in this case the π -electron cloud in the carbon ring does not change. Surfactants and polymers are widely used for CNTs and GNPs dispersion via the non covalent approach [18]. These materials adsorb onto the GNPs and CNTs surface, rendering them soluble in aqueous or organic solvents [18]. Surfactants are usually used to enhance CNTs dispersion in aqueous media [19-21] and thus dispersion with high volume fractions could be prepared but surfactants can also impart unwanted properties to a composite [22, 23]. For example most of the surfactants are insulating in nature, upon deposition from liquid dispersions, surfactant becomes trapped between the CNTs or GNPs particles/flakes and as a result the resultant composite may have reduced electrical conductivity [24]. One of other hurdle to overcome to use these material in CE, is that carbon based nanomaterials (CNTs or GNPs) have a very low adhesion to TCO and glass substrate surfaces [25]. As a result weakly adhered CNTs/GNPs may easily detach from the TCO or glass substrate as they contact with electrolyte in DSSCs. To address these two issues i.e. good dispersion and good adhesion a novel approach was adopted. It is well know that some polymers have very good adhesion properties. Also polymer in solution can bind to nanoparticles and can exfoliate and stabilize carbon nanomaterials [13, 26, 27]. The down side is most of the common polymer are insulating in nature, which will again reduce electrical conductivity. This implies that ideally one would need a system/polymer which not only disperse these nanomaterials but also does not reduce electrical properties of the system. If we look at polymer list there certain conjugated polymers which are electrically conducting e.g. PEDOTS: PSS etc. PEDOT: PSS has received ever-accelerating interest from scientists throughout the world due to its high conductivity, electrochemical stability, and catalytic ability [28]. This polymer is commonly available in liquid dispersion. CNT or graphene can be dispersed effectively in it [13, 26]. This implies that it can serve all the purposes we need i.e. as an adhesive material and as a dispersant/stabilizer for CNTs and GNPs. Furthermore it is well established that by addition of CNTs or graphene to polymer it is not only mechanically reinforces the system but also significantly enhance the electrical and catalytic properties of the composite film comparing to original pristine polymer [13, 26].

Therefore in this work we use PEDOT: PSS as matrix, dispersant/stabilizer for CNTs and GNPs to improve the adhesion and enhance mechanical properties of the composite film. This chapter not only describes the use of these materials as electrocatalysts with strong adhesion properties but importantly it has been shown that CE can prepare without FTO. We also report our studies of these new hybrid carbon based nanomaterials as CEs in DSSCs.

5.2. New Pt –free CE for DSSCs

5.2.1 Preparation of dispersions of carbon nanomaterials in PEDOT-PSS

First of all, concentration of PEDOT: PSS in aqueous dispersion was determined by filtering 3 g of PEDOT: PSS aqueous dispersions through a nylon membrane which was then dried in an oven (120 °C) for an hour. The filtered mass of PEDOT: PSS was measured by careful weighing the filter membrane (Ohaus Discovery Analytical balance), which was 1.10 wt%. After this the MWCNTs GNPs and hybrid of these two nanomaterial (at 66wt% of solid PEDOT: PSS content) were added to aqueous PEDOT: PSS suspension and various type of carbon based CE were fabricated after that various type DSSCs were fabricated with these new carbon based CEs and reference Pt based CE as explained in experimental section (fig.5.1 Represented schematically the carbon based CE /DSSC).

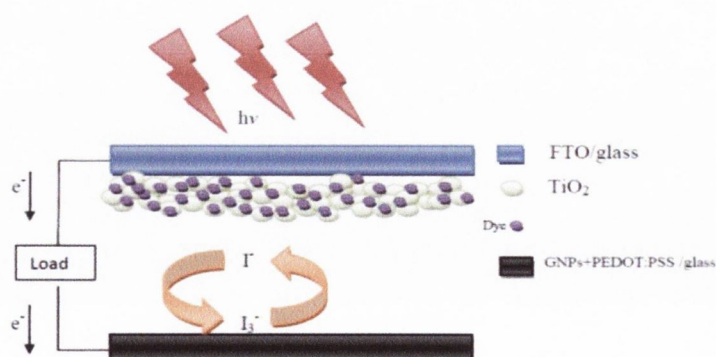


Figure 5.1: Represented schematically the carbon based CE /DSSC.

5.2.2 Scanning Electron Microscopy of CEs

SEM of the selected hybrid materials was performed to characterise the morphology of the films for CEs. SEM was carried out to investigate selected CEs: the hybrid C based CE and for comparison GNPs powder and PEDOT: PSS films. These images are used primarily to determine structural information for hybrid film and to understand the distribution of MWCNTs and GNP in hybrid C-CE. Fig.5.2 panels A and B show representative SEM images of the PEDOT: PSS CE, panels C and D show images of GNPs powder 3 and panels E and F show the SEM images of hybrid-C-CE. According SEM investigation, the MWCNTs were well dispersed, as single tube can be seen in Fig.5.2 E and F and suggesting that GNPs interconnection with the MWCNTs in hybrid C-CE.

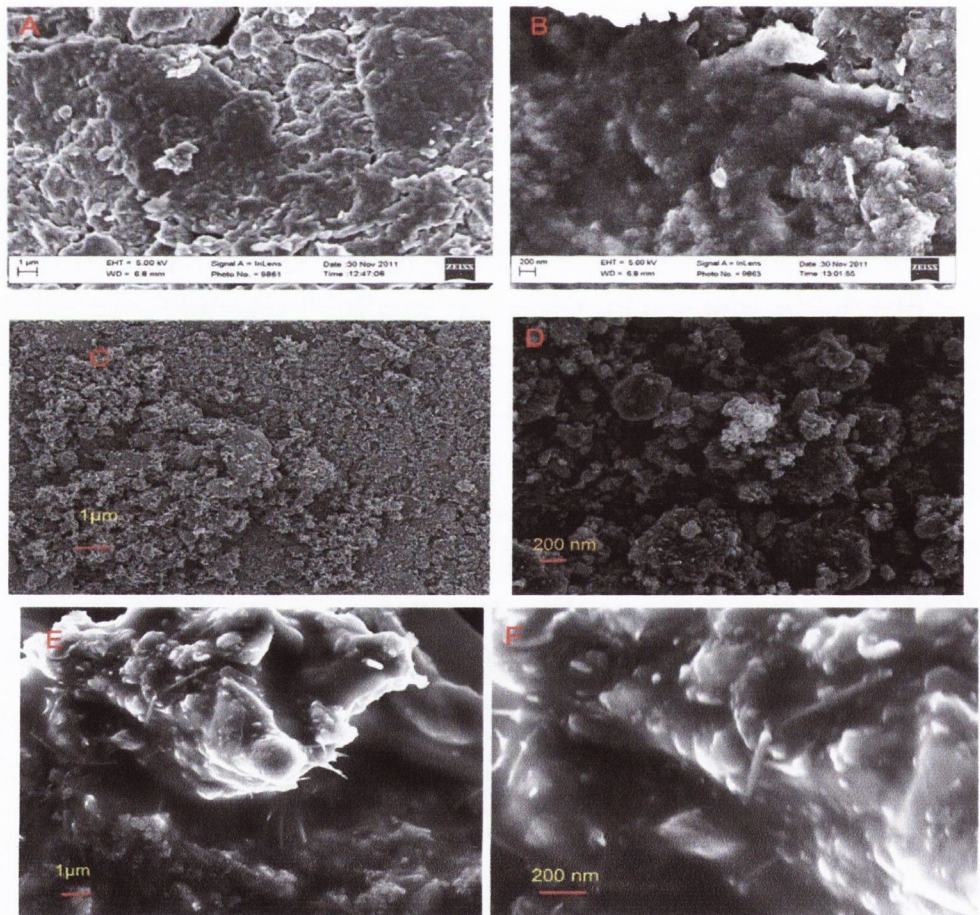


Figure 5.2: Representative SEM images of A and B-PEDOT: PSS/CE, C and D-GNPs powders, and E and F-hybrid C-CE.

5.2.3 Raman Spectroscopy of Carbon Based Composites for CEs

The distribution and conformation of GNPs/MWCNTs in PEDOT: PSS in the film were further characterized by Raman spectroscopy. Raman spectroscopy is a non destructive, fast, characterising technique which is commonly used for the characterization of carbonaceous materials, especially distinguishing between graphene and graphite. All allotropic forms of carbon are active in Raman spectroscopy [29]. Raman spectra of graphitic materials was investigated for almost 47 years , even before the discovery of graphene [30, 31]. Thus Raman spectroscopy can identify a single layer and few (less than five) layers of graphene flakes [32]. Raman spectra for graphite powder, GNPs powder, MWCNTs powder, hybrid B-CE, and hybrid C-CE are shown Fig.5.3 A, B, C, D and E respectively. Raman spectra (Fig.5.3.A) of graphite powder showed negligible D peak. While a shoulder in the 2D peak was observed at $\sim 2650\text{ cm}^{-1}$ is representative of graphite [33]. Raman spectra (Fig.5.3.B) of GNPs powder showed a large D peak at $\sim 1330\text{ cm}^{-1}$, which can either be due to the defect or most likely because of the presence of smaller flakes, i.e. edge effect [34, 35]. The shape of 2D peak spectra without any shoulder as shown in Fig.5.3. B confirmed that these are few layer thick graphene flakes. Furthermore from the intensity of the 2D can be used to distinguish single and multilayered graphene in a sample. In monolayer graphene the 2D peak evolves to be roughly 4 times more intense than the G peak [31, 33][31, 33][31, 33][31, 33][31, 33]. The intensity of the 2D peak in Fig.5.3.B shows that these GNPs consist 4 to 5 layers of graphene sheets. Fig.5.3.C shows Raman spectra of the pristine MWCNTs. The main features of the MWCNTs Raman spectra are represented by three peaks [36] at D ($\sim 1332\text{ cm}^{-1}$) and G ($\sim 1580\text{ cm}^{-1}$) and 2D ($\sim 2643\text{ cm}^{-1}$) bands as shown in Fig. 5.3.C. Fig.5.3.D and E shows the Raman spectra of hybrid B-CE and hybrid C-CE respectively. In fig.5.3.D, the 2D band confirmed the presence few layer thick graphene nanosheets in hybrid C-CE. While the D band in Fig. 5.3.D is more intense than the G band in 5.3.B and 5.3.C, this is possibly due small flake or edge effect or might some defect or to the combined effect of GNPs and MWCNTs in the nanocomposite film (hybrid C-CE).

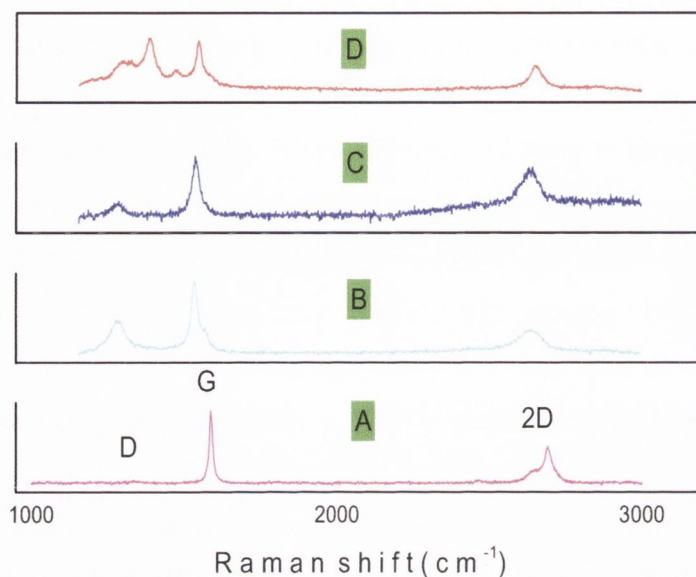


Figure 5.3: Raman spectra: (A) Graphite powders (B) GNPs powders (C) MWCNTs powders, (D) B- hybrid CE and (E) C-hybrid CE.

5.2.4 TGA Analysis of Materials for CEs

The thermal stability of hybrid C composite sample was also investigated by TGA and compared with the TGA of a PEDOT: PSS dried film, GNPs powders and MWCNTs powders. Derivative Thermogravimetric analysis (DTGA) curves are plotted in figure 5.4. DTGA curve of hybrid C composite sample (Fig.5.4.A) displayed 4 peaks in the region of 50 °C to 852 °C. DTGA curve of hybrid composite C sample shows initial 5 % wt was lost between 50 °C and 163 °C. This initial loss is due to the presence of water/solvent content in the film, similar to already published reported for a PEDOT–PSS dried film [37] and also similar to DTGA of pure PEDOT:PSS dried film as shown in Fig. 5.4.D. The second peak of wt loss (13.16 % wt) was between 258 °C and 437 °C and third wt loss (15.13%) was between 527 and 627 °C are consistent with the

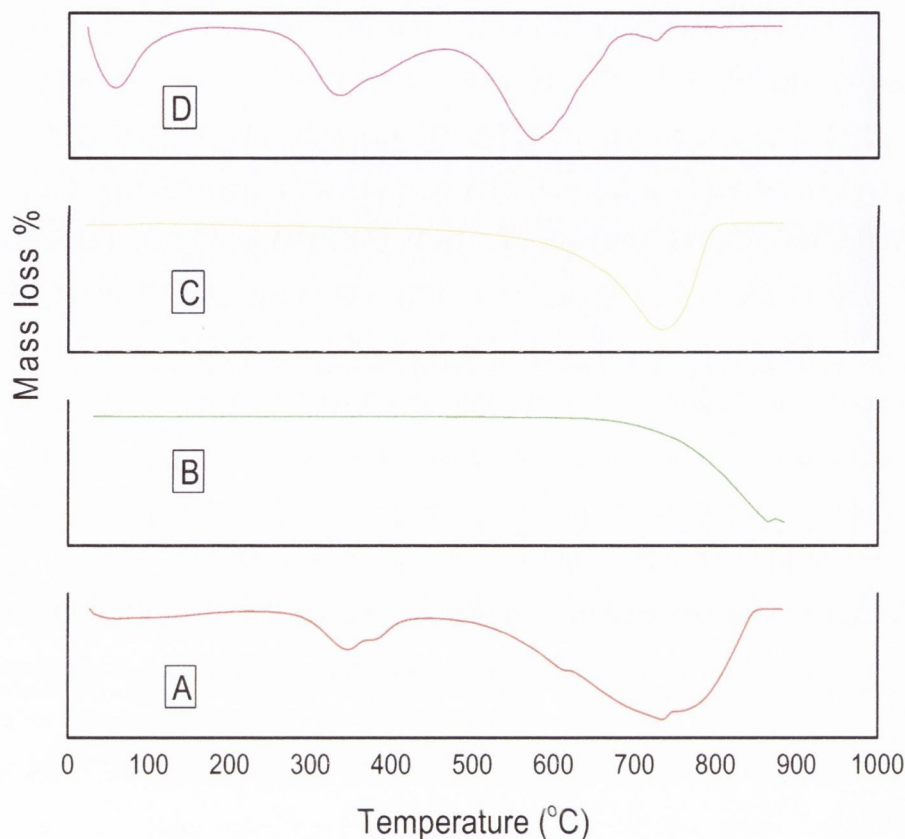


Figure 5.4: DTGA of A) hybrid C composite of GNPs (22wt %) and MWCNTs (44 wt%) in PEDOT: PSS, B) MWCNTs powders, C) GNPs powders and D) dried PEDOT: PSS film.

degradation of PEDOT: PSS in the hybrid composite film [38]. The further wt loss (61.44%) was between 631°C to 852°C. This wt loss shows the degradation of GNPs and MWCNTs as the DTGA of GNPs (Fig. 5.4 C) and MWCNTs (Fig. 5.4 B) showing maximum degradation at 733 °C and 863 °C respectively. These results demonstrated that GNPs and MWCNTs samples are highly thermal stable either in powder form or in composite form and confirmed the presence of GNPs and MWCNTs in hybrid composite of GNPs and MWCNTs in PEDOTS: PSS

5.2.5 Electrical Conductivity Measurements

For electrical conductivity measurements corresponding films were prepared : I) pure/Pristine PEDOT: PSS, II) GNPs (66 wt% of solid content of PEDOT:PSS) plus PEDOT: PSS composite, III) MWCNTs (66 wt%) plus PEDOT: PSS composite, IV) hybrid A: GNPs(44 wt%) and MWCNTs (22 wt%) plus PEDOT: PSS composite, V) hybrid B: GNPs (33 wt%) and MWCNTs (33 wt%) plus PEDOT: PSS and VI) hybrid C with GNPs (22 wt%) and MWCNTs (44 wt%) plus PEDOT: PSS composite. Electrical measurements were performed by two point probe method. From each film, three identical samples were selected and used for electrical measurements and then calculated the average electrical conductivity as shown in Fig.5.5. Pristine PEDOT: PSS film shows conductivities in the range of 10–1000 S/m [45-47]. This reveals that untreated PEDOT PSS would not be a good candidate for use in CE of the DSSC. Various approaches were used to increase the conductivity of PEDOT: PSS including the addition of polar organic compound with high boiling point, such as ethylene glycol (EG) or dimethyl sulfoxide (DMSO), into PEDOT:PSS aqueous solution [48-50]. However in this work we only diluted the aqueous PEDOT: PSS solution with deionised water and none of the above solvent was added to our samples. The conductivity enhancement of PEDOT: PSS film was totally depend on the addition of GNPs, MWCNTs and hybrid of these two materials. The average values of electrical conductivity was found to be 211 S/m, 933 S/m, 1170 S/m, 2060 S/m, 1840 S/m and 1350 S/m, for samples I, II, III, IV, V, and VI respectively (Fig. 5.5). Due to the high surface area and high electrical conductivity of MWCNTs network [13] in PEDOT: PSS composite showed increased electrical conductivity by a factor of 4.5 (an increase from 211 S/m of pure PEDOT: PSS. Similarly the GNPs addition in to PEDOT: PSS film also show increase in conductivity by factor of 3.4. These results confirmed the addition of MWCNTs or GNPs to PEDOT: PSS increased the power conversion efficiencies of DSSCs due to improvement in electrical conductivity of PEDOT: PSS films. Furthermore these results suggest that MWCNTs-PEDOT composite films were more electrical conductive than GNPs-PEDOT: PSS composite films, therefore, should show high photovoltaic performance in DSSC than pure PEDOT: PSS film. Hybrid composite film A showed little increased in electrical conductivity (1350 S/m) compared to GNPs-PEDOT: PSS composite (933 S/m) and MWCNTs composite (1170

S/m) films. Hybrid B showed increases in electrical conductivity by factor of 7.7 compared to pure PEDOT: PSS film. However hybrid composite C showed the highest electrical conductivity compared to all composite films which were prepared in this work, it was increased by factor of 8.7 compared pure PEDOT: PSS film. These results suggest that the addition of lower wt % of GNPs showed increased the electrical conductivity in hybrid films. This reveals that due to its high electrical conductivity of the hybrid C composite of GNP and MWCNTs/PEDOT: PSS/CE should demonstrate higher power conversion efficiency in DSSC.

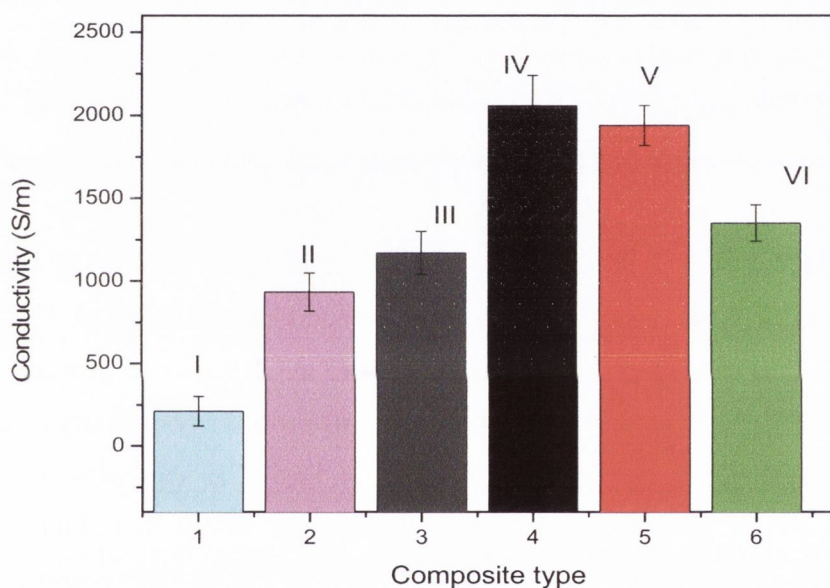


Figure 5.5: The electrical conductivity of I) PEDOT: PSS film; II) GNPs (66 wt%) + PEDOT:PSS composite film; III) MWCNTs(66 wt%) + PEDOT:PSS composite film, IV) Hybrid C: MWCNTs (44wt%) + GNPs(22 wt%)/PEDOT:PSS film, V) Hybrid B: MWCNTs (33 wt%)+ GNPs(33 wt%)/PEDOT:PSS film and VI) Hybrid A: MWCNTs (22wt%) + GNPs (44 wt%)/PEDOT:PSS film.

5.2.6 Investigation of the Photovoltaic Performance of DSSCs with various Carbon Based CE/DSSC

The CE is an essential part of a DSSC and the quality of CE greatly influences the performance of a DSSC. The roles of the counter electrode are to transfer electrons arriving from the external circuit back to the redox electrolyte (performed by the Pt and TCO) and to catalyze the reduction of the I_3^- to I^- in the electrolytes where the Pt serves as the catalyst, ($I_3^- + 2 e^- \rightarrow 3I^-$) [39] and thus completes the cycle of operation of the cell. High catalytic ability, excellent electrical conductivity, and high corrosion resistance are indispensable for the functioning of a good CE in DSSC [40]. The photocurrent density–voltage (J–V) characteristics of the DSSCs with various carbon nanomaterial based composite CEs which were obtained through the use of GNPs, MWCNTs and hybrid of these two material in PEDOT: PSS are shown in fig.5.6 and the corresponding photovoltaic parameters including short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency are shown in Table 5.1. Two kinds of reference cells were fabricated: one with standard Pt/FTO/CE based DSSC and the second kind with PEDOT: PSS/FTO/CE based DSSC. The DSSC with the conventional Pt/FTO/CE showed a power conversion efficiency of 3.90 %. Due to the high sheet resistance and the poor catalytic activity of the pure PEDOT: PSS the DSSC with PEDOT: PSS /CE showed a lower power conversion of 2.32 %. The addition of MWCNTs (66 wt %) to PEDOT: PSS-CE, power conversion efficiencies improved from 2.32 % to 2.81 %. This power conversion efficiency was improved mainly due to increases in FF value from 0.34 (pure PEDOT) to 0.39 and V_{oc} value from 0.710 to 0.760 V. This result shows that addition of MWCNTs to PEDOT: PSS could increased the conductivity and catalytic activity of the CE [26]. Another DSSC which was prepared with GNPs (66 wt %) plus PEDOT: PSS/CE demonstrated small increases in power conversion efficiencies from 2.32% to 2.53 % compared to MWCNTs (66 wt %) to PEDOT: PSS-CE. The power conversion efficiency was improved mainly due increases in J_{sc} value from 9.63 mA/cm^2 (pure PEDOT) to 9.82 mA/cm^2 and V_{oc} value from 0.710 V to 0.770 V. While almost the same FF of 0.33 (pure PEDOT: PSS=0.34) was achieved with GNPs (66 wt %) plus PEDOT: PSS composite /CE. This result shows that addition of GNPs to PEDOT: PSS also increased the conductivity and catalytic activity of the CE. These results demonstrated that MWCNTs-PEDOT: PSS composite /CE showed increase in FF and

V_{oc} values while GNPs-PEDOT: PSS composite /CE displayed increase in J_{sc} and V_{oc} of the DSSCs. On the basis of these results, we decide to investigate the hybrid nanocomposite of these two nanomaterial at various wt % in PEDOT: PSS composite films. Previously it was also reported that by combining 2D graphene and 1D CNT, a synergistic effect in conductivity can be established due to its structural arrangements [41, 42].

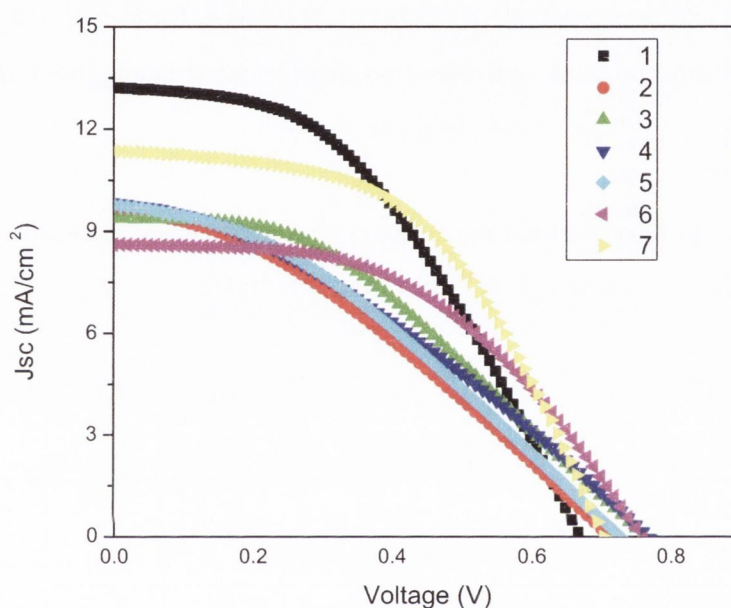


Figure 5.6: Photovoltaic (J–V) curves of: 1) standard reference Pt-CE; 2) PEDOT: PSS-CE, 3) MWCNTs+ PEDOT-CE, 4) GNPs +PEDOT-CE; 5) A-hybrid –CE, 6) B-hybrid –CE and 7 C-hybrid-CE/DSSC.

It has been reported that hybrids composite of pristine single walled carbon nanotubes and pristine, unoxidised graphene /graphite, display electrical conductivity that are better than those of either nanotube only or graphene only films [42]. It would be more interesting and potentially more rewarding to study mixtures of pristine MWCNTs and pristine GNPs in PEDOT: PSS composite films and use as CEs in DSSCs. This would allow the study of the synergistic effects of these nano-carbon hybrid materials in CE of the DSSCs. So, next the three types of hybrid CEs consisting of mixture of GNPs and MWCNTS in PEDOT: PSS solution (hybrids A, B and C) were prepared and tested in completed DSSCs. Due to the high wt% of GNPs (44 wt %) in the hybrid A-CE, it

shows a similar power conversion efficiency (2.47%), FF (0.34), J_{sc} (9.74 mA/cm²) to DCCS with GNPs/PEDOT based CE. This indicates that in hybrid A, the high wt % of GNPs did not produce any synergistic effect as no photovoltaic parameter of DSSC was increased. Hybrid B-CE showed increases in power conversion efficiencies from 2.32 % to 3.20 %. The power conversion efficiency increased due to the improvement in FF value from 0.32 to 0.48. These results demonstrated that synergistic effect was obtained by nanohybrid material in hybrid B-CE, this suggest the electrical conductivity was increased of hybrid B-CE. However, J_{sc} was slightly decreased from 9.63 to 8.65 mA/cm², this indicates that there is good chance to further improve the catalytic activity of these nano hybrid based

Table 5.1: The Photovoltaic parameters of the DSSCs with various types of CEs with FTO. Measured at 100 mW cm⁻². Cell active area: 0.8 cm².

CE type	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Efficiency %
Pt/FTO/glass	13.21	0.671	0.44	3.90 ± 0.13
PEDOT:PSS/FTO/glass	9.63	0.710	0.34	2.32 ± 0.10
MWCNTs (66 wt%) + PEDOT:PSS/FTO/glass	9.38	0.760	0.39	2.81 ± 0.10
GNPs (66 wt %) + PEDOT:PSS/FTO/glass	9.82	0.770	0.33	2.53 ± 0.12
A hybrid/FTO/glass	9.74	0.730	0.34	2.47 ± 0.13
B hybrid/FTO/glass	8.61	0.760	0.48	3.20 ± 0.11
C hybrid/FTO/glass	11.35	0.703	0.51	4.10 ± 0.15

CE/DSSC. Hybrid C-CE showed a power conversion efficiency of 4.10 %. This power conversion efficiency is higher than all the CEs which were prepared in this work while also marginally higher than the Pt/CE based DSSC, which were prepared by us using open cell fabrication approach. Hybrid C-CE demonstrated increases in the FF from 0.34 (pure PEDOT) to 0.51. J_{sc} value also improved from 9.32 mA/cm^2 (pure PEDOT) to 11.32 mA/cm^2 . This shows that catalytic activity also increases than all other CEs which were prepared in this work. Hybrid C-CE showed that the addition of a lower ratio of GNPs (22 wt %) to MWCNTs into PEDOT: PSS gave an improved result because the smaller quantity of GNPs might be exfoliated and dispersed very well in solution and upon deposition on a substrate, the GNPs and MWCNTs properly interconnect to each other and increase the conductivity of the hybrid C-CE and reduce charge transfer resistance. In addition there is a catalytic activity increase due to raise of available active surface areas for reduction of I_3^- to I^- in nanographene-MWCNT composite/CE. Overall the addition of GNPs or MWCNTs and mixture of these two nanomaterials into PEDOT: PSS CE/ DSSC did not significantly affect the V_{oc} value of DSSCs. Pure PEDOT/CE showed V_{oc} of 0.710 V. While A, B and C hybrid CEs show V_{oc} of 0.730 V, 0.760 V and 0.703 V respectively.

5.2.7 Hybrid C-CE with FTO tested with different Electrolytes system in DSSCs

For further study the best performing hybrid C materials was selected and deposited on FTO glass substrate and used as CEs in DSSCs. The system was tested with three different electrolytes system i.e. 1) conventional organic based electrolytes (HPE), 2) ionic liquid electrolytes (PMII) 3) Carbon nanomaterials quasi state electrolyte (SWCNTs(3 wt%) + graphene (12 wt%) /PMII), which was described in the Chapter 3. Table 5.2 summarises the photovoltaic parameters of C hybrid/CE-DSSCs with these various type electrolytes systems. Shown in Fig.5.7 the photocurrent density–voltage (J–V curves) characteristics of the DSSCs. The ionic liquid electrolytes (PMII) based DSSC with C hybrid CE showed power conversion efficiency of only 0.38% with a low value of FF (0.26) but J_{sc} (2.65 mA/cm^2) and V_{oc} (0.640 V) values were good in comparison to published works, usually pure PMII based DSSC with

standard Pt/CE shows power conversion efficiency around 0.60 % with FF value of 0.38 [43, 44]. Quasi solid state electrolyte with C hybrid CE DSSC showed a power conversion efficiency of 1.88 %. The efficiency was increased due to increase in J_{sc} value from 2.26 mA/cm² to 7.96 mA/cm² and FF value increased from 0.26 to 0.40. However V_{oc} was decreased from 0.640 to 0.560 V. Hybrid C CE DSSC with organic solvent based electrolytes demonstrated a quite high power conversion efficiency of 4.10 %.

Table5.2: The photovoltaic parameters of the DSSCs with various type electrolytes system with C hybrid CEs with FTO. Measured at 100 mW/cm². Cell active area: 0.8 cm²

CE	Electrolyte type	Jsc(mA/cm ²)	Voc (V)	FF	Efficiency %
C hybrid/FTO	OSE	11.35	0.703	0.51	4.10 ± 0.15
C hybrid/FTO	PMII	2.26	0.640	0.26	0.38 ± 0.01
C hybrid/FTO	QSE	7.96	0.560	0.40	1.88 ± 0.10

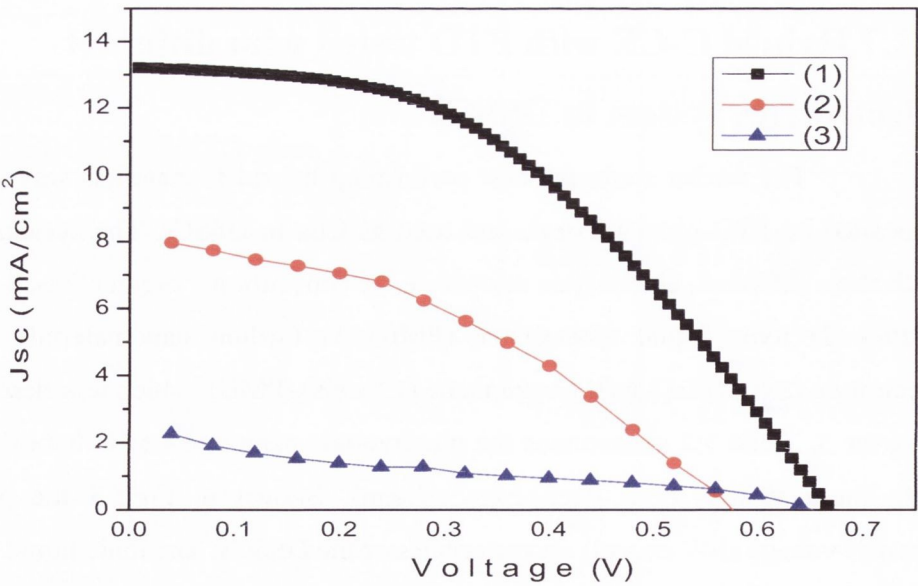


Figure 5.7: The photovoltaic (J–V) curves of hybrid-C/FTO glass: 1) Organic solvent based electrolytes, 2) Quasi solid state electrolyte 3) Ionic liquid electrolyte (PMII).

Over all the power conversion efficiency of hybrid C with quasi solid state electrolytes was improved by factor of 3.94 from pure ionic liquid electrolyte (PMII) but lower than hybrid C CE/DSSCs with organic solvent based electrolyte by factor of 2.22. The reason most likely associated with the fact that organic solvent based electrolytes could easily penetrate in the mesoporous TiO_2 layer of WE due their low viscosity. Therefore, the C hybrid CE with organic solvent based electrolytes can show better performance than PMII and quasi solid state based DSSCs. However in overall these results demonstrated that there is good chance that hybrid of MWCNTs and GNPs into PEDOT: PSS composite could replace Pt of the CEs either with organic based electrolytes or quasi solid state electrolytes DSSCs.

5.2.8 EIS Studies of DSSCs with Selected CEs

Electrochemical impedance spectroscopy (EIS) analysis is a basic tool that provides detailed information about charge transfer phenomena in DSSC. EIS analysis has been widely used to explore the reduction of I_3^- ions on CEs, and a well-supported equivalent circuit [45]. Generally, EIS spectra exhibit three semicircles in the Nyquist plot, which describes the different impedances of DSSC [46]. Each semicircle can be assigned based on the model circuits (equivalent circuit) for DSSC. The first semicircle of EIS spectra is attributed to the impedance of the charge transfer resistance at the counter electrode/electrolyte interface (R_{ct}), the second semicircle one and the last tailing one are related to charge transfer process at the TiO_2 /dye/electrolyte interface (R_{ct2}) and Warburg diffusion process of I^-/I_3^- in the electrolyte (R_{diff}) respectively [47]. We also performed electrochemical impedance spectroscopic (EIS) studies using the reference Pt/CE, PEDOT/CE, A hybrid, B hybrid and C hybrid CEs in DSSCs as shown in figure 5.8.II and equivalent circuit was used for fitting the EIS data as shown in figure 5.8.I. A low R_{ct} corresponds to a high exchange current density, which is essential for a DSSC with good performance [48]. The first semicircle of Fig 5.8.II.A shows an R_{ct} value of $109\ \Omega$ for the PEDOT/CE. Fig.5.8.II.B shows an R_{ct} value of $75\ \Omega$ for hybrid A CE. This demonstrates that the addition of GNPs + MWCNTS decreases the R_{ct} value of the CE /DSSC. Figure.5.8.II.C displays the R_{ct} value of hybrid B CE/DSSC reduced to $2.92\ \Omega$. Fig.4.8.II.D shows that the R_{ct} value is further reduced to $2.33\ \Omega$ for the hybrid C CE. This value is lower than the R_{ct} values of all the

CEs which were fabricated in this work while also slightly lower than R_{ct} value of Pt/CE/DSSC ($R_{ct}=3.86 \Omega$) as shown in fig 6.II.E. EIS investigation confirmed that due to the low R_{ct} value of hybrid C this gave higher power conversion efficiency. The lower R_{ct} value of hybrid C-CE shows that there are less losses at the electrolyte/counter electrode interface than all the CEs tested in this work. Due to the lower R_{ct} value of the hybrid C-CE it gave a higher FF (0.51) than all the other CEs tested in DSSCs. Therefore, the hybrid C-CE/DSSC shows a slightly improved performance compared to the Pt /CE-DSSC. From the R_{ct} value we can find the exchange current density (J_o) of the CE according to equation 1 below [49].

Equation 1:

$$J_o = \frac{RT}{nFR_{ct}}$$

where **R** is the universal gas constant, **T** is the absolute temperature, **F** is the Faraday constant and **n** is the stoichiometric number of electrons involved in the reaction (**n** = 2 for the reaction $I_3^- + 2e = 3I^-$). For the higher performance of DSSCs a higher exchange current density is required. DSSC with the hybrid C based CE showed an exchange current density of $11.07 \Omega/\text{cm}^2$ while the one with Pt standard CE demonstrated an exchange current density of $6.68 \Omega/\text{cm}^2$

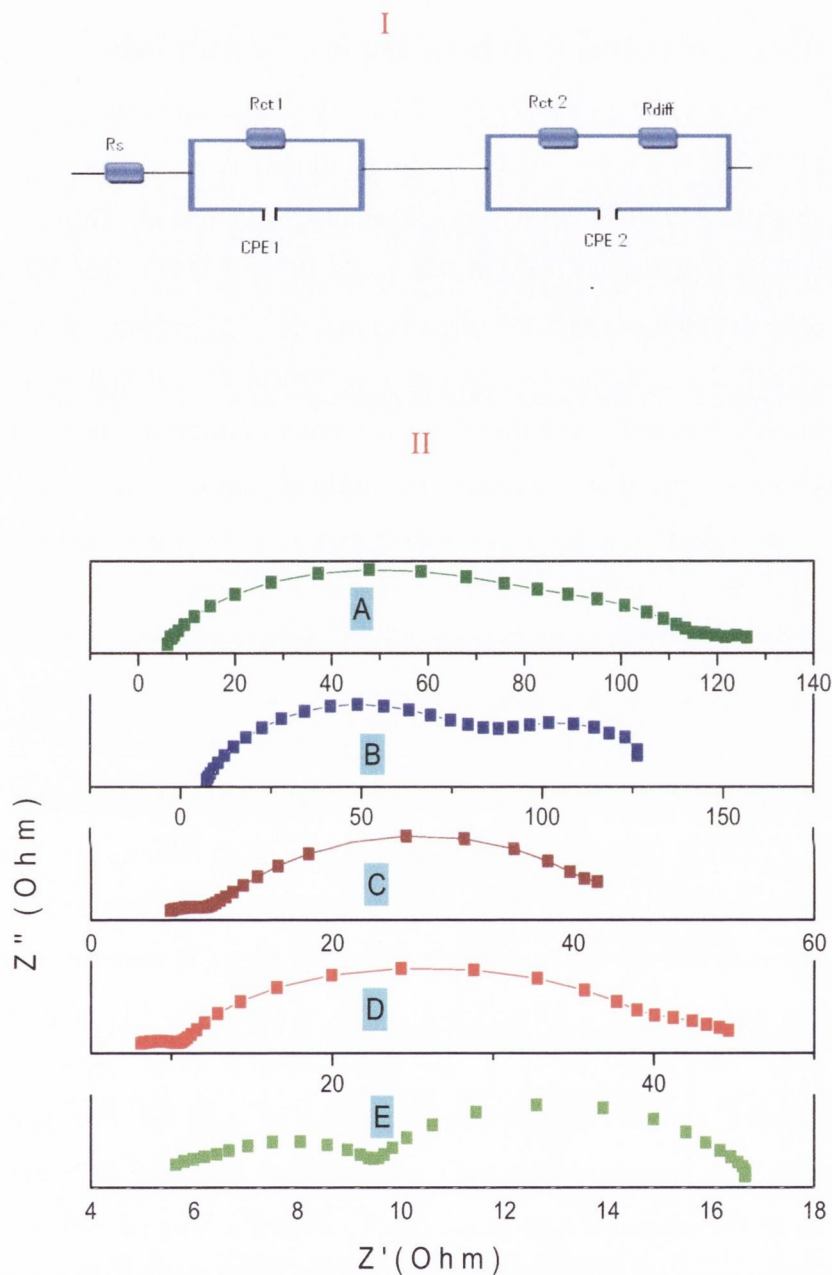


Figure 5.8: shows I) the equivalent circuit and II) Nyquist plots for **A)** pure PEDOT/CE, **B)** A hybrid-CE, **C)** B-hybrid-CE, **D)** C-hybrid-CE and **E)** Pt standard CE / DSSCs.

5.2.9 The Photovoltaic Performance of Pt and FTO free CE with Selected Carbon Based Materials

Selected Pt and FTO free CEs have been fabricated by drop casting of PEDOT/PSS mixtures with carbon nanomaterials on glass substrates. Corresponding DSSCs have been fabricated and tested. Table 5.3 summarises photovoltaic parameters of DSSCs with Pt and FTO free CEs which were fabricated in this work and the photocurrent density–voltage (J–V) characteristics of the DSSCs are shown in Fig.5.9. The hybrid C material was chosen for the fabrication for Pt and FTO free CE, on a non conducting glass substrate because the hybrid C has demonstrated the highest conductivity and highest power conversion efficiency on FTO substrate/CE with the organic solvent based electrolyte as discussed in above sections. For comparison pristine GNPs and pristine PEDOT: PSS were deposited non conducting glass substrate and used as Pt and FTO free CE in DSSC. These three types of Pt and FTO free CEs were tested with organic solvent based electrolytes in complete DSSC. Pristine PEDOT: PSS/CE/DSSC showed poor photovoltaic performance due the fact pristine PEDOT: PSS has much lower, electrical conductivity. The lower power conversion efficiency of 0.11 % can be attributed to lower values of J_{sc} (0.686 mA/cm^2) and V_{oc} (0.400 V). The Pt and FTO free CE with pristine GNPs type 3 demonstrated a J_{sc} of 2.46 mA/cm^2 , V_{oc} of 0.600 V, FF of 0.34 and a power conversion efficiency of 0.71 %. The hybrid C CE DSSC (without FTO) demonstrated a power conversion efficiency of 2.48 %. The power conversion efficiency was increases comparing to pristine PEDOT: PSS and GNPs based CEs due to the improvement in J_{sc} (8.27 mA/cm^2), V_{oc} (0.640 V) and FF (0.47). The performance of the hybrid C-CE without FTO is inferior compared to the hybrid C-CE with FTO but these results are still very promising and potentially after further optimisation it is highly likely that this hybrid material could potentially replace both Pt and TCO components of the CE in DSSC in the future.

Table 5.3: The photovoltaic parameters of the DSSCs with C hybrid CE on glass substrate without FTO. Measured at 100 mW/cm². Cell active area: 0.8 cm².

CE type	Jsc (mA/cm)	Voc (V)	FF	Efficiency %
C hybrid/Glass	8.275	0.640	0.47	2.48 ± 0.13
PEDOT:PSS/glass	0.686	0.400	0.40	0.11 ± 0.01
GNPs/ glass	2.66	0.790	0.34	0.71 ±0.05

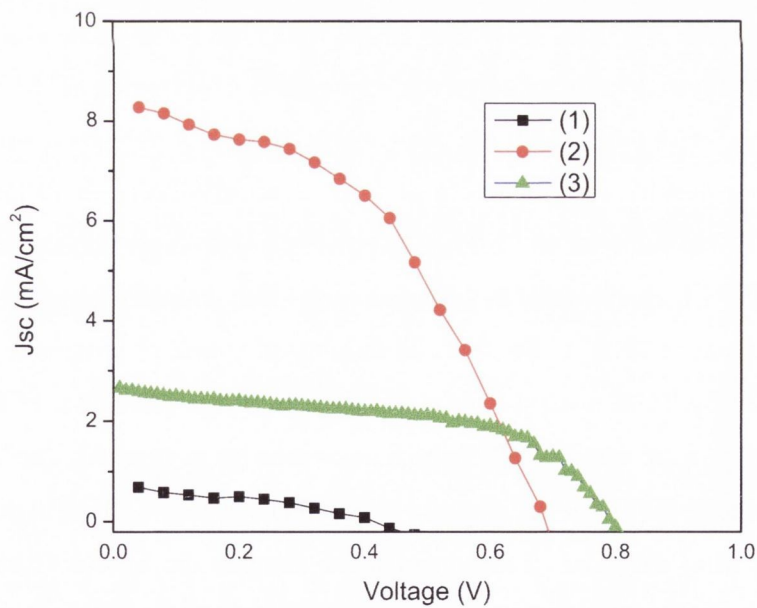


Figure 5.9: The photovoltaic (J–V) curves of: 1) C hybrid/glass/CE, 2) PEDOT: PSS-glass/CE, 3- and GNPs/CE.

5.3 Conclusions

In the present work we have demonstrated the synergistic effect of hybrid GNPs and MWCNTs with PEDOT: PSS media in counter electrodes for DSSCs. Various kinds of counter electrodes/DSSCs were prepared by the dispersion of: 1) GNPs, 2) MWCNTs and 3) a various combination of MWCNTs and GNPs into PEDOT: PSS aqueous dispersions. Various kinds of counter electrodes for DSSCs were prepared by a simple drop cast method. This study demonstrated that the addition of GNPs to MWCNTs composite increased the electrical conductivity and reduced the R_{ct} of the CE/DSSC. As result some CEs such as hybrid C FTO/CE demonstrated a higher power conversion efficiency of 4.10%, which was even higher than the standard Pt/CE DSSC. While the similar Pt and FTO free CE showed a power conversion of 2.48 % with the same material combination which was used for hybrid C composite CE with FTO. The power conversion efficiency of Pt and FTO free CE was 36 % and 39 % lower than standard Pt/FTO/CE and hybrid C CE (with FTO) DSSC respectively. Furthermore, the hybrid CEs with FTO also tested in complete DSSCs with various type electrolytes system i.e. organic based electrolytes, ionic liquid electrolyte (PMII) and quasi solid state electrolyte. Hybrid-C-FTO/CE- DSSC with Quasi solid state electrolyte and ionic liquid electrolyte demonstrated power conversion efficiencies of 1.88 % and 0.38 % respectively. Both these value are comparable to already published work [43, 44]. This work shows that hybrid composite of GNPs and MWCNTs in PEDOT: PSS can be used as efficient catalysts in CE/DSSCs especially with organic based electrolyte. Thus, the hybrid C-CE can be used as effective metal-free counter electrodes to replace Pt in high-performance DSSCs. The thermal stability of hybrid C composite sample was also investigated by TGA analysis and for comparison the TGA of a PEDOT: PSS dried film, GNPs powder and MWCNTs powder, were also performed. The TGA study show that GNPs and MWCNTs samples are highly thermal stable either in powder form or in composite film. SEM was carried out to investigate the hybrid C based CE and for comparison SEM of GNPs powder and PEDOT: PSS film was also performed. Which suggest that GNPs interconnection with the MWCNTs in hybrid C-CE. We must notice that all values of power conversion efficiencies have been achieved for DSSCs, which were produced using the “open cell” method. This fabrication technique normally results in solar cells with lower efficiency than sealed DSSC. Therefore, we believe that further optimization of the carbon based hybrid CE and corresponding photovoltaic cell

fabrication will enable to achieve higher power conversion efficiencies on glass substrate without Pt and FTO layers. We also expect that the conversion efficiency of CE could be further potentially increased by the addition of organic solvent (e.g. DMSO or EG) to the carbon based aqueous PEDOT: PSS dispersions.

5.4 References

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Dye Sensitized Solar Cells

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Chapter 6: Development of Pt and TCO free Counter Electrodes for Dye Sensitized Solar Cells

6.1 Introduction

The Pt deposited TCO substrate is widely used as the standard counter electrode (CE) for DSSCs [1]. However it has been reported that the Pt coated TCO-CE is the most expensive component in a DSSC [2, 3] and its high cost limits the mass production of DSSCs. The development of a cost-effective counter electrode should simultaneously replace the Pt as well as TCO of the CEs of the DSSCs [4]. It is important to develop new low-cost CEs using materials that are simultaneously abundant, non toxic and enabling production of relatively high power conversion efficiency in DSSCs. An ideal CE should have high electrical conductivity and high electrocatalytic activity towards the iodide/tri-iodide redox reaction (I^-/I_3^-). Furthermore these CE materials should be chemically stable in the electrolyte systems used in DSSCs. There are few reports where they completely replace Pt as well as the TCO of CEs of the DSSCs with various materials [4-6]. For example Veerappan et al. used graphite film to make Pt and FTO free CE. They showed power conversion efficiencies of 5.0 % and 6.8 % with graphite/glass based CE and with standard Pt/FTO/glass-CE/DSSCs respectively [7]. Lee et al. used conducting polymer PEDOT as a Pt and FTO free CE, they achieved power conversion efficiencies of 5.08 % and 5.88% with PEDOT/glass-CE and Pt/FTO/glass-CE/DSSCs respectively [5]. Similarly Zhang et al. also reported TCO and Pt-free CE, they used PEDOT: PSS film as conductive substrate and electro deposited PEDOT layer as the electrocatalytic layer (PEDOT/PEDOT: PSS/glass), showed a high power conversion efficiency of 8.33%, which was comparable to that of the standard Pt/FTO/glass-CE/DSSC (8.75%) [8]. Recently Jiang et al. [9] reported a graphene and Pt/graphene based TCO and Pt free CEs/DSSCs, they achieved power conversion efficiencies of 2.16% (with graphene/glass) and 6.09 % (Pt/graphene/glass) compared to 5.76 % with standard Pt/FTO/glass-CE/DSSCs.

These studies show that graphene film/paper has sufficient electrical conductivity to replace the TCO of the CE of the DSSC but its electrocatalytic activity is much lower than Pt.

There are reports on high-performance and low platinum loading Pt/Carbon black CE [10] and Graphene-Pt/ITO CE with significantly reduced Pt loading and enhanced charge transfer [11], which have been used in DSSCs. However, ultimately Pt free CEs are necessary to achieve a significant cost reduction. Cruz et al. have prepared stand-alone graphene-based CEs for DSSCs by spray deposition and chemical reduction of GO, followed by thermal annealing under an inert atmosphere. This work resulted in transparent electrodes with transmittance higher than 80%, which have been used to produce DSSCs with energy conversion efficiency of 2.64% [12]. Another Pt-free CE was produced from vertically-aligned carbon nanotube forests. The use of this CE enabled to fabricate DSSCs with relatively high efficiency of 5.2 % which was close to the power conversion efficiency (6.6 %) of the similar Pt based cells [13].

In this work we used three different type of graphene nano-platelet (GNPs) based Pt and TCO free CEs for DSSCs. Although pure graphene (unoxidised and defect free graphene) is an attractive material due to it is good electrical conductivity, thermal stability and high surface area [14, 15] but it still may possess a limited number of active sites for I_3^- electrocatalysis [16]. We expect that the addition of an electrically conductive polymer i.e. PEDOT: PSS to GNPs film should result in an increase of the electrical conductivity as well as electrocatalytic activity of the Pt and FTO free CEs/DSSCs [17]. It is well known that an addition of organic solvents with high boiling point, such as ethylene glycol (EG) Dimethyl sulfoxide (DMSO), and N-Methyl-2-pyrrolidone (NMP) etc, significantly improves the electrical conductivity of PEDOT: PSS by up to 2 or 3 orders of magnitude [18-21]. Among these various organic solvents, NMP has lower viscosity (1.7 cP) compared to viscosity of EG (16.9 cP) and DMSO (1.99 cP). Therefore, in this work we added the NMP (10 vol %) to PEDOT: PSS dispersions and then added various type of GNPs to theses dispersions. We believe, that addition of NMP to the PEDOT: PSS dispersion will also enhance the dispersion of GNPs and as a result the composite film/CE will show enhanced in electrical conductivity compared to NMP doped PEDOT: PSS film/CE. These various types of GNPs plus NMP doped PEDOT: PSS composite films were deposited on non-

conducting glass substrates by simple drop casting method. Their performances were compared with standard Pt/FTO/glass-CE/DSSC under the same conditions. In addition, we investigated the adhesion of the more efficient GNPs plus NMP doped PEDOT: PSS composite film/CE and compared it with the pure NMP doped PEDOT: PSS film. In this chapter we report the new GNPs based composite materials, which can simultaneously act as an electrocatalyst for I_3^- reduction and charge transport material in CE / DSSC.

6.2 Preparation and Characterisation of Pt and TCO free CEs for DSSCs

6.2.1 Preparation of GNPs Based CEs

Three aqueous PEDOT: PSS dispersions were diluted with 10 vol% of NMP and 20 vol% of deionised water (Millipore). This was divided into three equal parts. GNPs type 1, GNPs type 2, GNPs type 3 was added to each part at 66 wt% of solid PEDOT: PSS content, to make three dispersions. After that various types of DSSCs were fabricated with this new carbon based CEs and reference Pt based CE as explained in experimental section.

6.2.2 Raman Spectroscopy

Raman spectroscopy has historically played an important role in the structural characterization of graphitic materials, in particular providing valuable information about defects and stacking of the graphene layers [22]. Initially Raman spectroscopy of GNPs type 1, GNPs type 2 and GNPs type 3 powders was done as well as on graphite powders for comparison (figure 6.1). Raman spectroscopy can clearly distinguish a single layer, few layers thick graphene and unexfoliated graphite [23]. The main features in graphite/graphene Raman spectra are represented by the D, G and 2D peaks [24]. The graphitic G peak located at $\sim 1580\text{ cm}^{-1}$ and 2D peak located at $\sim 2700\text{ cm}^{-1}$ are always observed in graphite samples [25]. The graphite's 2D band ($\sim 2700\text{ cm}^{-1}$) always have a shoulder at $\sim 2650\text{ cm}^{-1}$ is representative of graphite [23] as shown figure 6.1. A. The graphite powders displayed a small D band ($\sim 1330\text{ cm}^{-1}$). The D band is indicative of defect or edges. The ratio of the intensity of the D band, ($\sim 1300\text{ cm}^{-1}$) to

that of the G band ($\sim 1580 \text{ cm}^{-1}$) band usually indicates the structure, size, and defects of the carbon material [7, 26, 27]. Figure 6.1.A,B and C shows Raman spectra of GNP type 1, GNPs type 2 and GNP type 3 respectively, all three type GNPs powders showed a large D peak compared to the D peak of graphite (Fig.6.1.A) which can either be due to the defect or most likely because of smaller flakes i.e. edge effect. ID/IG ratio was measured as shows in Table 6.1. One would expected that smaller flake (GNPs type 3) would show higher ID/IG ratio than large flakes GNPs (type 2 and GNPs type 1) [26]. However, the ID/IG ratio of GNPs type 3 powder was (0.40) similar to GNPs type 1 powder (0.40) and little higher than GNPs type 2 powders (0.34). This suggests that GNPs type 1 and type 2 might have some defect or might have some edge functional groups. The shape of the 2D peak spectra with no shoulder is consistent for all three types of GNPs powder as shown in figure 6.1 B,C, and D. This indicates the presence of few layer thick graphene flakes in all three types of powders. In conclusion the Raman spectroscopy analysis confirmed that all three types of GNPs are few layer thick graphene flakes.

Table 6.1: Intensity ratios for D and G band (calculated from corresponding Raman spectra.

Powder type	ID/IG
Graphite powder (Reference)	0.02
GNPs type 1	0.40
GNPs type 2	0.34
GNPs type 3	0.40

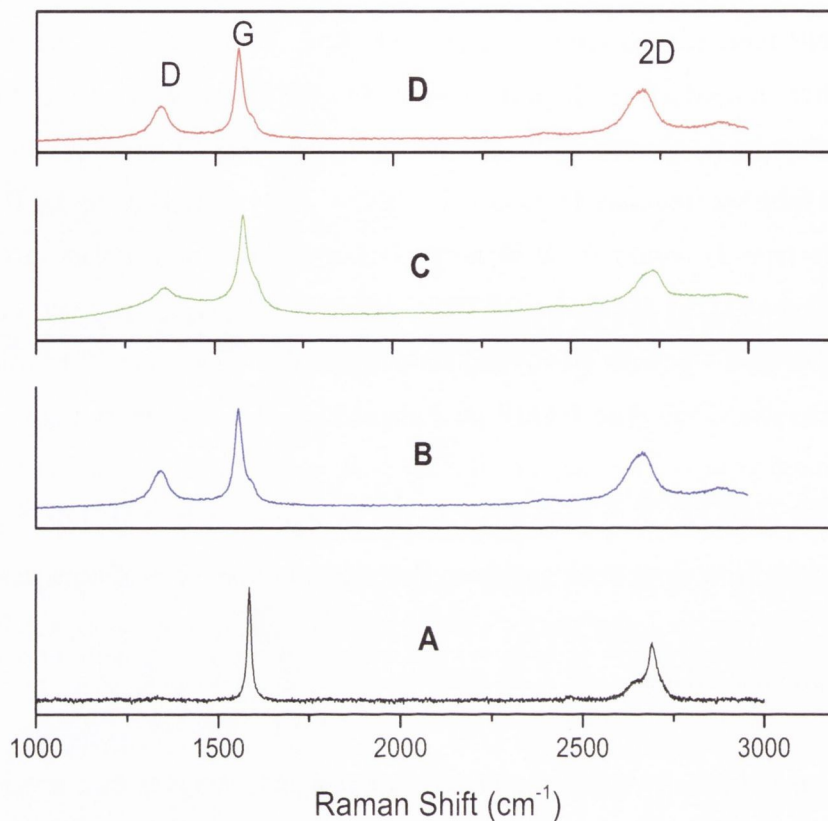


Figure 6.1: Raman spectra of powder (A) Graphite powders, B) GNPs type 1 powders, C) GNPs type 2 powders and D) GNPs type 3 powders.

6.2.3 Scanning Electron Microscopy of GNPs type 2 with NMP Doped PEDOT: PSS Composite film/CE

SEM was done on the best performance sample i.e. GNPs type 2 with NMP doped PEDOT: PSS composite film/CE. SEM was performed to investigate the morphology of the GNPs type 2 plus NMP doped composite film/CE. SEM of the surface as well as of fractured edge composite film/CE was also performed. Fig.6.2 panels A and B show representative SEM images of the surface and panels C, D, E and F show of fracture edge of GNPs type 2 plus NMP doped PEDOT:PSS composite film/CE. In both surface and fracture images of GNPs plus NMP doped PEDOT: PSS,

SEM investigation reveals, that GNPs were homogeneously dispersed suggesting that GNPs are interconnected in composite film/CE.

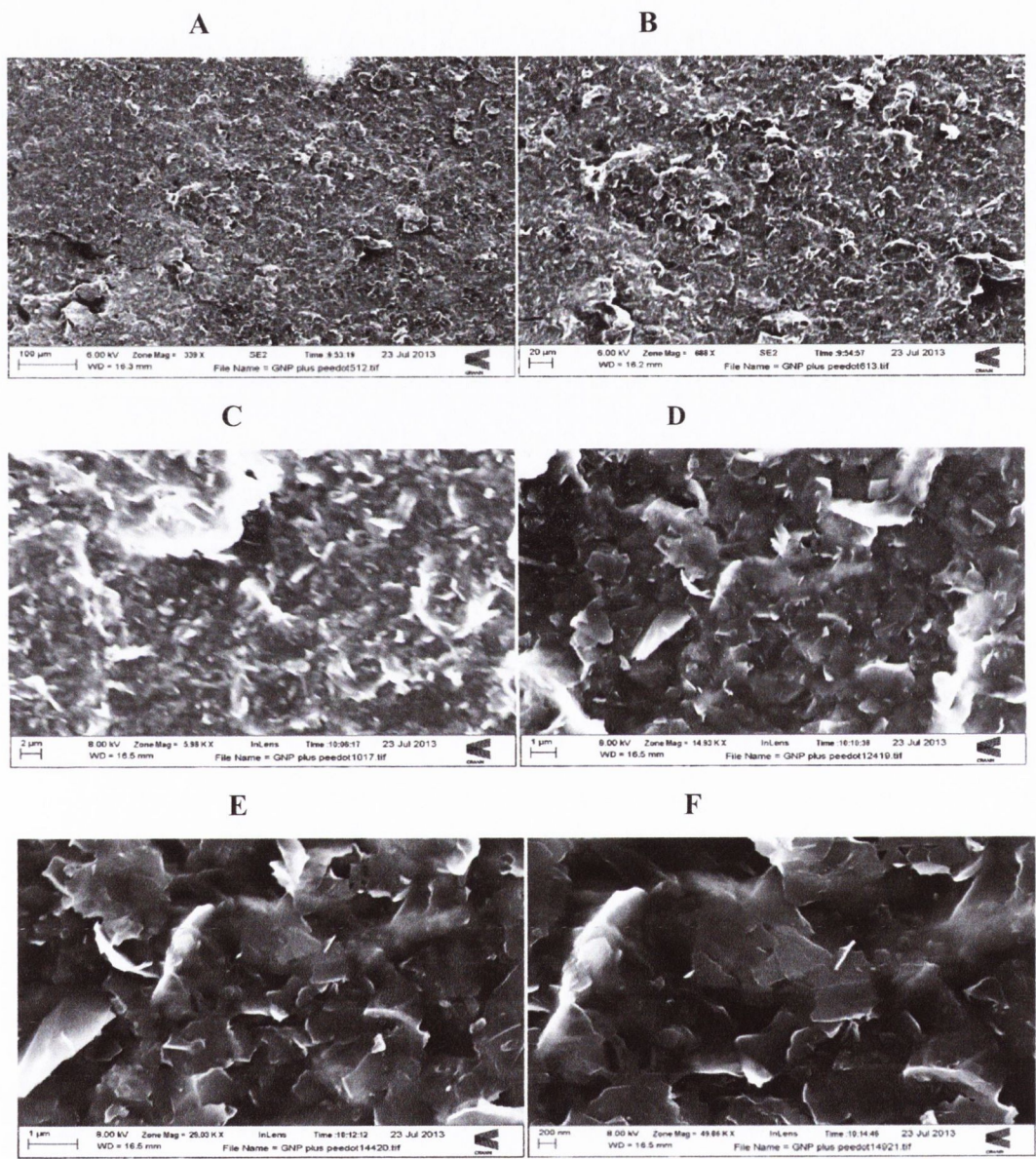


Figure 6.2: Representative SEM images of GNPs type 2 plus PEDOT: PSS composite film/CE, A and B shows SEM images of surface. C, D, E and E shows of fractured edge of composite film/CE.

6.2.4 Thermogravimetric Analysis (TGA) of GNPs type 2 with PEDOT: PSS composite film/ CE

The thermal stability of GNPs type 2 powders, pure PEDOT: PSS film and GNPs type 2 plus NMP doped PEDOT: PSS composite film was investigated by TGA. Figure 6.3.A shows Derivative TGA (DTGA) curves and figure 6.3 B shows TGA curves.

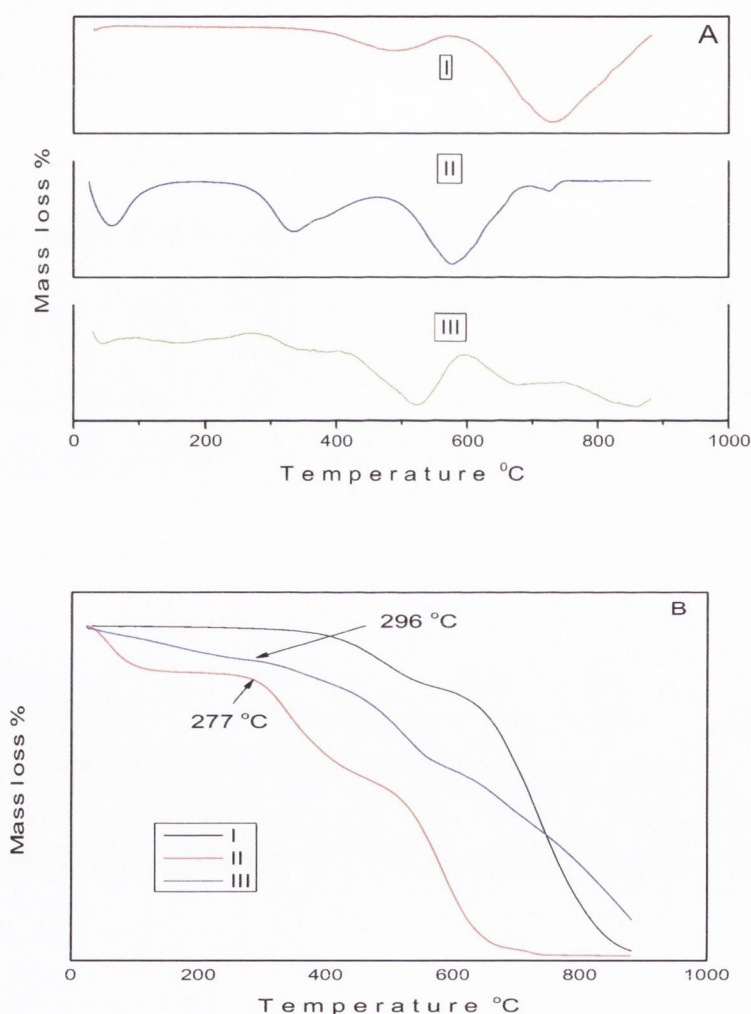


Figure 6.3: A. shows DTGA curves of A.I) GNPs type 2 powder, A.II) pure PEDOT: PSS film and A.III) GNPs type 2 + NMP doped PEDOT: PSS composite film/CE. B shows TGA curves of B.I) GNPs type 2 powder, B.II) PEDOT: PSS film and B.III) GNPs type2+ NMP doped PEDOT: PSS composite film/CE.

DTGA (6.3.A.I) curve of GNP type 2 powder demonstrated an initial weight loss of 14 % between 390°C and 581°C, suggesting the removal of some functional groups [28-30], further weight loss between 587 °C to 881 °C can be attributed to the degradation of GNPs. DTGA curve (Fig.6.3.A.III) of GNPs type 2 plus NMP doped PEDOT: PSS composite film showed initial 6 % wt was lost between 30 °C to 162 °C. This initial loss is due to the presence of some organic solvent and water in the film, similarly to publish reported for PEDOT: PSS film [31, 32] and also similar to DTGA of pure PEDOT: PSS film as shown in figure 6.3.A.II. The second wt lost (8.4%) between 296°C to 419 °C and third wt lost (28.47%) between 419 °C to 596 °C are revealing the degradation of PEDOT: PSS. Further weight loss (50 wt %) between 607 °C to 881 °C is revealing the degradation of GNPs type 2 as DTGA curve (fig.6.3.A.I) of pure GNP type 2 powder shows maximum degradation at 733°C. TGA curve showed that the GNPs type 2 plus PEDOT: PSS composite film (Fig.5.5.B.III) is thermally more stable than that PEDOT: PSS dried film (Fig.6.3.B.II), as degradation of PEDOT: PSS started in GNPs type 2 plus NMP doped composite film at 296 °C while is 19 °C higher than that degradation of PEDOT: PSS film (277°C) [32]

6.2.5 Electrical Conductivity Measurement

The electrical conductivity was measured using the two point probe technique and an average of the measured values was taken and a standard deviation was calculated. The results are presented in fig.6.4. The thickness of the films in the range 15 µm to 20 µm was measured by digital micrometer calliper. Initially two types of PEDOT: PSS films were prepared, 1) pure PEDOT: PSS film and 2) NMP (10 vol %) doped PEDOT: PSS film. The electrical conductivity of the NMP doped PEDOT: PSS film was increased from 2.11 S/cm (pure PEDOT: PSS film) to 33 S/cm. The electrical conductivity of the NMP doped PEDOT: PSS film enhanced by around 15 orders of magnitude compared to pure PEDOT: PSS film. The electrical conductivity enhancement might have been related to the better connections between the conducting PEDOT chains by removing insulating PSS from the PEDOT: PSS film [33]. The electrical conductivity of GNPs type 1, GNPs type 2 and GNPs type 3 plus NMP doped PEDOT: PSS composite films were also measured. As a result the electrical conductivities were dramatically increased by the addition of all three types of GNPs to

PEDOT: PSS composite films compare to NMP doped PEDOT: PSS film. However the highest electrical conductivity of 190 S/cm is obtained with GNP type 2 plus NMP doped PEDOT: PSS composite film. The electrical conductivities of GNPs type1 plus NMP PEDOT: PSS and GNPs type 3 plus PEDOT: PSS composite films were 175 S/cm and 164 S/cm respectively. These results indicate that the addition of all types of GNPs strongly influences the electrical conductivity of NMP doped PEDOT: PSS films. However, it was expected from Raman spectroscopy investigation that GNPs type 3 powder has the lowest level of defects vice versa for type 1 and type 2 powders but GNPs type 3 plus NMP doped PEDOT: PSS shows the lowest electrical conductivity among these three GNPs type plus PEDOT: PSS composite film.

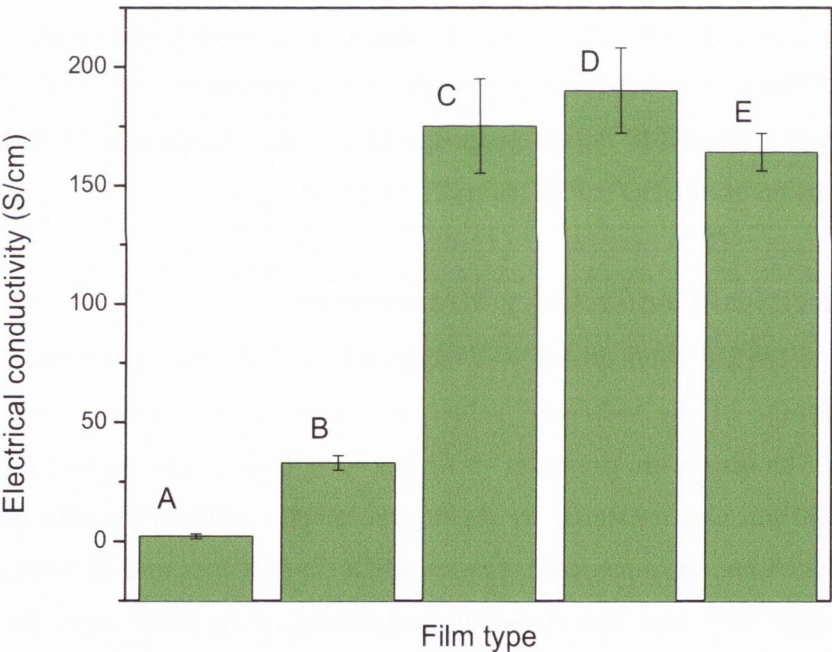


Figure 6.4: The electrical conductivity of **A)** pure PEDOT: PSS film; **B)** NMP doped PEDOT: PSS film, **C)** GNPs type 1 + NMP doped PEDOT: PSS composite film, **D)** GNPs type 2 plus NMP doped PEDOT:PSS film and **E)** GNPs type 3 + NMP doped PEDOT:PSS composite film.

Thus these results suggest that electrical conductivity of GNPs plus NMP doped PEDOT: PSS composites films greatly depends on the diameter and surface area of

GNPs. GNPs type 1 and type 2 have similar average diameter (up to 5 μm) but different surface area (GNPs 1 = 50 m^2/g and GNPs 2 = 100 m^2/g). Thus we can say that electrical conductivity of GNPs type 2 is greater than GNPs 1 due to its higher surface area. GNPs type 3 has very high surface (600–750 m^2/g) but shows lower electrical conductivity (164 S/cm) than GNPs type 1 and GNPs type 2 plus NMP doped PEDOT: PSS composites films. This is thought to be due to the large contact resistance between small-size GNPs type 3 (diameter = 2 μm) which as a result shows a lower electrical conductivity than GNPs type 1 and GNPs type 2 based films. These results show that large diameter GNPs (GNPs type 1 and GNPs type 2) have a higher electrical conductivity than small diameter GNPs type 3 in NMP doped PEDOT: PSS composite films.

6.2.6 Investigation of the Photovoltaic performance of Pt and TCO free CE/DSSCs with various types of GNPs with NMP Doped PEDOT: PSS composite films

Table 6.2 summarises photovoltaic parameters i.e. open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiencies of all DSSCs which were prepared in this work. The photocurrent density–voltage (J – V) characteristics of the DSSCs with various CEs are shown in Fig. 6.5. Three kinds of reference DSSCs were fabricated: one with standard Pt/FTO/glass-CE and the second kind is Pt and FTO free CE with pure PEDOT: PSS/glass and third one is also Pt and FTO free CE with NMP doped PEDOT: PSS/glass. The Pt/FTO/glass-CE/DSSC showed a power conversion efficiency of 4.72 %. The power conversion efficiency of NMP doped PEDOT: PSS–CE/DSSC without Pt and FTO was increased from 0.11% (pure PEDOT: PSS/glass-CE) to 1.35%. Most likely the power conversion efficiency was increased due to improvement in electrical conductivity of PEDOT: PSS film as discussed in the previous section. Three types of composite films were prepared i.e. A) GNPs type 1 plus NMP doped PEDOT: PSS, B) GNPs type 2 plus NMP doped PEDOT: PSS and C) GNPs type 3 plus NMP doped PEDOT: PSS and used as Pt and TCO free CEs in DSSCs. The addition of all three types of GNPs to PEDOT: PSS film resulted in the further increase of the power conversion efficiencies of Pt and FTO free CEs-DSSCs. The addition of GNPs type 1 to NMP doped PEDOT: PSS film/CE

improved the power conversion efficiencies from 1.35 % (NMP doped PEDOOT: PSS/glass-CE) to 3.36 %. This power conversion efficiency was improved mainly due to increases in FF from 0.31 to 0.41 and J_{sc} from 5.67 mA/cm² to 11.4 mA/cm². The addition of GNPs type 2 to NMP doped PEDOT: PSS film/CE also improved the power conversion efficiencies from 1.35 % (NMP doped PEDOOT: PSS/glass-CE) to 3.70 %. Again the improvement of power conversion efficiencies of GNPs type 2 plus NMP doped PEDOT: PSS was mainly due to the increase in FF from 0.31 to 0.43 and J_{sc} from 5.67 mA/cm² to 12.45 mA/cm². The addition of GNPs type 3 to NMP doped PEDOT: PSS film/CE improved the power conversion efficiencies from 1.35 % (NMP doped PEDOOT: PSS/glass-CE) to 2.78 %. The power conversion efficiencies of GNPs type 3 plus NMP doped PEDOT: PSS was mainly increased due to the rise in J_{sc} from 5.67 mA/cm² to 12.80 mA/cm² while FF (0.33) was almost similar to NMP doped PEDOT: PSS film/glass-CE/DSSC. These results show that addition of all three types of GNPs to NMP doped PEDOT: PSS in general resulted in an increase of the electrocatalytic activity of CE as J_{sc} was increased in all cases. However, the GNPs type 1 and type 2 plus NMP doped PEDOT: PSS composite films/CEs shows increase in FF as well as in J_{sc} , this suggest that these two composite film/CEs are more conductive than GNPs type 1 with NMP doped PEDOT: PSS composite film/CE as this was also confirmed and discussed in the section above (6.2.5).

The power conversion efficiencies are changing in the following order: Pt/FTO/glass > GNPs type 2 plus NMP doped PEDOT: PSS/glass > GNPs type 1 plus NMP doped PEDOT: PSS/glass > GNPs type 3 plus NMP doped PEDOT: PSS/glass > NMP doped PEDOT: PSS/glass and PEDOT:PSS/glass -CEs/DSSCs. The two main factors that are responsible for power conversion efficiencies are electrical conductivity and electrocatalytic activity of the CE. The highest J_{sc} value (13.12 mA/cm²) and FF (0.49) was obtained with Pt/FTO/glass-CE/DSSC. This shows that the Pt/FTO/glass-CE is more electrically conductive and more electrocatalytically active than the GNP type plus NMP doped PEDOT: PSS composite films/CEs. In the case of the GNPs filled samples, type 2 and 1 plus NMP doped PEDOT:PSS composite film/glass-CE have power conversion efficiencies of 3.70 % and 3.36 % respectively. The fact that type 2 has higher power conversion efficiency is due to the higher surface area of type 2 that results in higher electrical conductivity and higher electrocatalytic activity.

In general, graphitic materials, such as CNTs and graphite, have basal and edge planes. Basal planes exhibit slow electron transport, whereas edge planes exhibit fast electron transport [34, 35]. Among these three GNPs type the GNPs type 3 has high surface, which mean GNP type 3 might have many edge planes or surfaces available for reduction of tri-iodide ion in electrolytes. Therefore, it was expected that GNP type 3 with NMP doped PEDOT: PSS composite film /CE would more electrocatalytic active than GNP type 1 and GNP type 2 plus NMP doped PEDOT: PSS composite/glass- CE /DSSC. The lower power conversion efficiency of GNPs type 3 plus NMP doped PEDOT:PSS composite film/CE could be due to large contact resistances because of involvement of large number of small size of GNPs per unit volume compared to GNP

Table 6.2: The photovoltaic parameters of the Pt and FTO free CEs-DSSCs with various types of GNPs plus PEDOT: PSS composite films. Measured at 100 mW/cm². Cell active area: 0.8 cm²

CE type	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency %
Pt/FTO/glass	730	13.12	0.49	4.72 ± 0.10
Pure PEDOT: PSS/glass	686	0.400	0.40	0.11 ± 0.01
NMP doped PEDOT:PSS/ glass/CE	760	5.67	0.31	1.35 ± 0.05
GNPs type 1 + NMP doped PEDOT:PSS/glass	710	11.4	0.41	3.36 ± 0.06
GNPs type 2+NMP doped PEDOT:PSS/glass	690	12.45	0.43	3.70 ± 0.10
GNPs type 3 + NMP doped PEDOT:PSS/glass	690	12.80	0.31	2.78 ± 0.08

of type 1 and type 2. This large contact resistance per unit volume can have a negative effect on the electrical transport properties of GNPs 3 and result in lower electrical conductivity hence lower power conversion efficiency than GNP type 1 and GNP type 2. Overall the addition of all three types of GNPs into NMP doped PEDOT: PSS CE/ DSSC did not significantly affect the Voc in comparison to standard Pt/FTO/glass-CE /DSSCs. The standard Pt/FTO/glass-CE shows Voc of 0.730 mV while pure PEDOT:PSS, NMP doped PEDOT:PSS, GNPs type 1 plus NMP doped PEDOT:PSS

composite/glass-CE,GNPs type 2 plus NMP doped PEDOT:PSS composite/glass-CE and type 3 plus NMP doped PEDOT:PSS composite/glass-CE/DSSCs shows Voc of 0.686, 0.760,0.710,0.690 and 0.690 respectively.

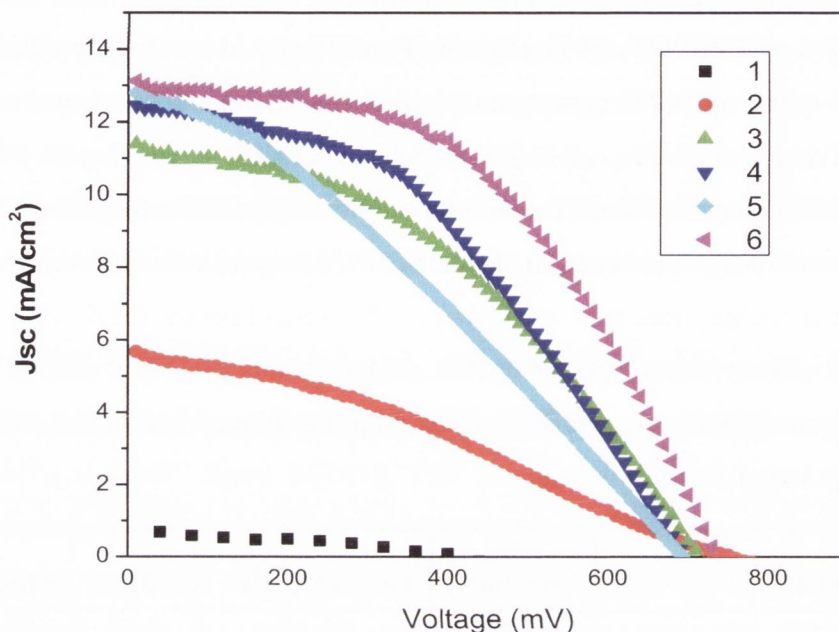


Figure 6.5: The photovoltaic (J–V) curves of: 1) pure PEDOT: PSS 2) NMP doped PEDOT: PSS, 3) GNPs type 1+NMP doped PEDOT: PSS, 4) GNPs type 2+NMP doped PEDOT: PSS, 5) GNPs type 3+NMP doped PEDOT: PSS and 6) Pt/FTO/CEs-DSSCs.

6.3 Effect of sintering on the Properties of CE and Performance of the Corresponding DSSCs

6.3.1 Effect of Sintering on the Electrical Conductivity of GNPs type 2 plus NMP Doped PEDOT: PSS films/ CEs

The electrical conductivity of GNPs type 2 plus NMP doped PEDOT: PSS composite films/CEs, which were sintered at: 120 °C, 150 °C, 200 °C, 300 °C and 400 °C for 20 minutes, were measured and the results are presented in fig.6.6. The electrical conductivity of GNPs type 2 plus NMP doped PEDOT: PSS composite films/CE which

was sintered at 120 °C is 190 S/cm. The electrical conductivity was increased to 196 S/cm for type 2 plus NMP doped PEDOT: PSS composite films/CEs which sintered at 150 °C. However electrical conductivity of the sample was decreased to 176 S/cm as it was sintered temperature up to 200 °C. The electrical conductivity was further decreased to 143 S/cm and 132 S/cm with sintered temperature at 300 °C and 400 °C respectively. This shows that PEDOT: PSS starts decomposing in the temperature range of 277°C to 400°C which consistent with TGA data (section.6.2.4). In summary, the electrical conductivity investigation demonstrated that around 150 °C is an optimal sintering temperature for GNPs type 2 plus NMP doped composite film/CE at which GNPs are properly interconnected in composite film and that result in the efficient electron transfer from one GNP to another on and hence in high electrical conductivity.

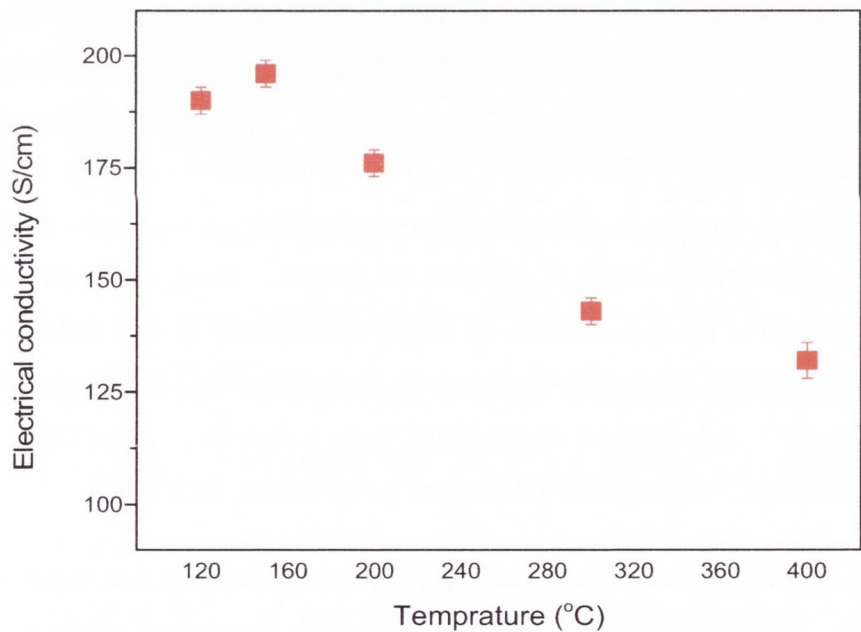


Figure 6.6: The electrical conductivity of GNPs type 2 plus PEDOT: PSS composite film/CE which was sintered at A) 120 °C, B) 150 °C, 200 °C D) 300 °C and 400 °C.

6.3.2 Raman Spectroscopy of GNPs type 2 plus NMP Doped PEDOT: PSS films/CEs Sintered at various Temperatures

Raman spectroscopy was employed to investigate a change in the graphitic structure during the sintering process of GNPs type 2 plus NMP doped PEDOT: PSS composite films/CEs as shown in Fig.6.7. Raman spectroscopy was performed on GNPs type 2 plus NMP doped PEDOT: PSS composite films/CEs which were sintered at 120 °C, 150 °C, 200 °C 300 °C and 400 °C. The defect in graphite samples are generally characterised by the ratio of the intensity of the defect band (D band, ~1300 cm^{-1}) to that of the G band (~1580 cm^{-1}), ID/IG. ID/IG was measured as it is shown in the Table 6.3. ID/IG for GNP type 2 was 0.34. The ID/IG was decreased to 0.23 for GNPs type 2 plus NMP doped PEDOT: PSS composite film/CE sintered at 120 °C. In addition, a G peak position of the GNPs type 2 plus NMP doped PEDOT: PSS composite film was downshifted by 6 cm^{-1} compared to GNPs powder, suggesting a non-covalent functionalization of PEDOT on the graphitic structure of GNPs [36]. The ID/IG ratio of GNPs plus NMP doped PEDOT: PSS composite films/CEs which were sintered at 150 °C, 200 °C 300 °C and 400 °C were further decreased to 0.13, 0.13, 0.02 and 0.06 respectively. These results suggest that as supplied GNPs type 2 is partially oxidised/functionalised graphene i.e. that have some edge functional groups. And the sintering process reduces the attached functional groups and thus results in decrease of the ID/IG for GNPs type 2 in composite film/CE. In summary, Raman studies confirm that electrical conductivity hence power conversion efficiency can be further increased if the initial GNPs powder is pre-sintered at 300 °C.

Table 6.3: Intensity ratios for D and G band (calculated from corresponding Raman spectra.

Sintering temperature	ID/IG
GNPs 2 type powder (Reference)	0.34
120 °C	0.23
150 °C	0.13
200 °C	0.13
300 °C	0.02
400 °C	0.06

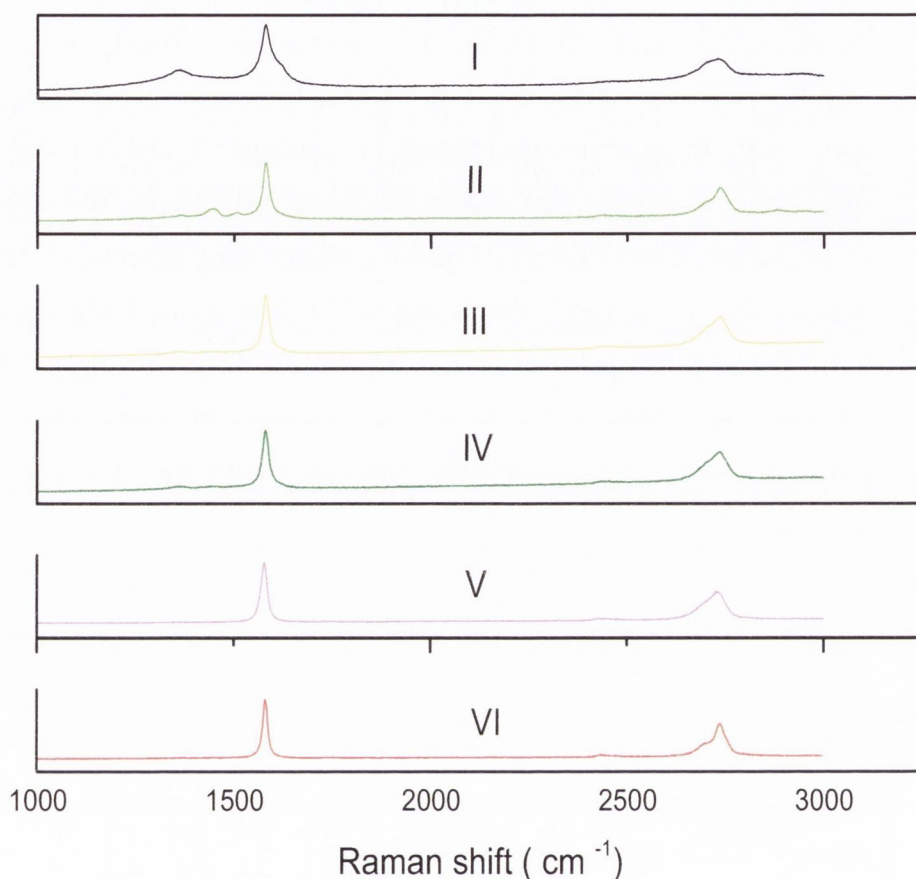


Figure 6.7: I) Raman Spectra of, I), II), III), IV), V) and VI) shows GNPs type 2 + PEDOT: PSS composite films/CEs, sintered at 120 °C, 150 °C, 200 °C 300 °C and 400 °C respectively.

6.3.3 Effect of Sintering Temperature on the Photovoltaic Performance of DSSCs with GNPs type 2 with PEDOT: PSS composite films/CEs

GNPs type 2 plus NMP doped PEDOT: PSS composite film gave the best power conversion efficiency and higher electrical conductivity in comparison to GNP type 1 and GNPs type 3 plus NMP doped PEDOT: PSS composite films. Therefore for further investigation GNPs type 2 plus PEDOT: PSS composite film was selected. GNP type 2 plus PEDOT: PSS composite films were sintered at various temperatures for 20

minutes as shown in Table 6.4. The purpose of this investigation to find out the optimal sintering temperature at which the GNPs type 2 plus PEDOT composite film/CE has the best performance. The highest power conversion efficiency of 4.29 % was observed for CE which was sintered at 150 °C. The power conversion efficiency of GNPs type 2 plus NMP doped composite film/ CEs (sintered at 200 °C) decreased to 3.23%. However power conversion efficiencies were dramatically decreased to 1.35 % and 0.84 % for GNP2/PEDOT: PSS/CEs which were sintered at 300 °C to 400 °C respectively. These result shows that GNPs type 2 and NMP doped PEDOT: PSS film/CE was properly dried at 150 °C and PEDOT: PSS, degradation start at high sintering temperature (274°C to 400 °C), therefore the power conversion efficiencies were decreased at high temperature sintering as this was confirmed by DTGA study (section 6.2.4)

Table 6.4: Shows the effect of sintering on the photovoltaic performance of the DSSCs with GNPs type 2 plus NMP doped PEDOT: PSS composite film /CEs. Measured at 100 mW/cm². Cell active area: 0.8 cm².

CE type	Sintering Temperature °C	Voc (mV)	Jsc (mA/cm ²)	FF	Efficiency %
GNPs 2 type 2+ NMP doped PEDOT:PSS/CE	120	690	12.45	0.43	3.70± 0.10
As above	150	710	13.75	0.44	4.29± 0.12
As above	200	710	11.28	0.40	3.23± 0.09
As above	300	720	7.66	0.24	1.35± 0.08
As above	400	720	6.03	0.18	0.84± 0.05

These results demonstrated that the optimum temperature for sintering of GNP 2 plus NMP doped PEDOT: PSS is 150 °C for 20 minutes. The Jsc value of GNPs grade 2 plus NMP doped composite film/CE was also initially improved from 12.45 mA/cm² (sintered at 120 °C) to 13.75 mA/cm² (sintered at 150 °C) but the Jsc values were

linearly decreased to 11.28 mA/cm² (sintered at 200 °C), 7.66 mA/cm² (sintered at 300 °C) and 6.3 mA/cm² (sintered at 400 °C). Voc values did not significantly affect by sintering temperature, the Voc value of 0.690 mV, 0.710 mV, 0.710 mV,0.720 and 0,720 mV were observed for GNPs grade 2 plus NMP composite film/CEs which were sintered at 120 °C, 150 °C, 200 °C,300 °C and 400 °C respectively. The FF values (0.43) initially remained stable for GNPs grade 2 plus NMP doped composite films/CEs which were sintered at 120 °C and 150 °C but FF values were greatly decreased to 0.40, 0.22 and 0.18 for CE which were sintered at 200 °C, 300 °C and 400 °C respectively. This reveals that the internal resistance of the CE/ DSSC was increased at high sintering temperature due the degradation of PEDOT: PSS in composite film/CE, therefore the FF values decreased accordingly. This demonstrated the importance of PEDOT: PSS in GNPs grade 2 composite films/CEs, that PEDOT is well adhered on the surfaces of GNPs, therefore the GNP are properly interconnected and as a result the electrons are efficiently transferred from one GNP to another as well as an increase in the electrocatalytic activity of the composite film/CE.

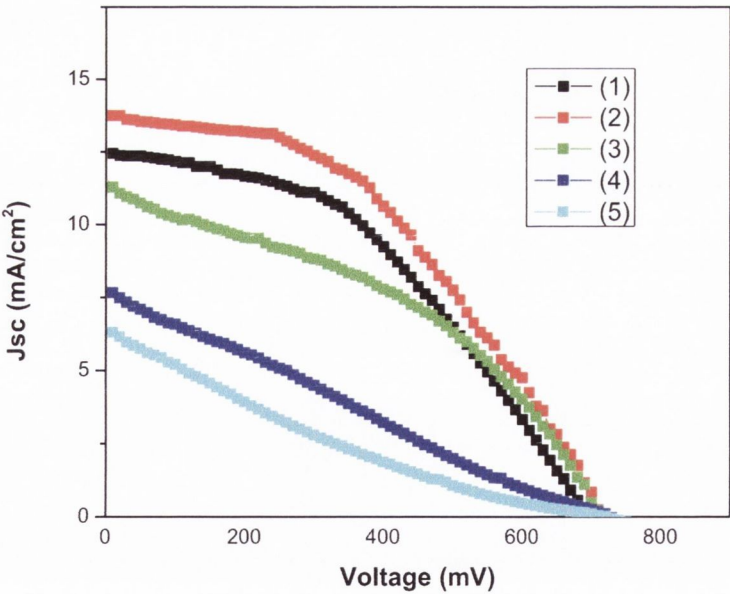


Figure 6.8: The photovoltaic (J–V) curves of GNPs type 2+NMP doped PEDOT: PSS film/CE-DSSCs which were sintered at 1)120 °C 2)150 °C 3)200 °C, 4) 300 °C 5) 400 °C.

6.3.4 Adhesion test

For the adhesion test, the two most efficient GNPs type 2 plus NMP doped PEDOT: PSS composite films were selected. These films were sintered at 120 °C and 150 °C and for comparison the NMP doped PEDOT: PSS film was also tested. The adhesion test was measured according to published report using the Scotch tape test [37, 38]. First, 3M tape was adhered on the surface of the films as shown in fig.6.9.

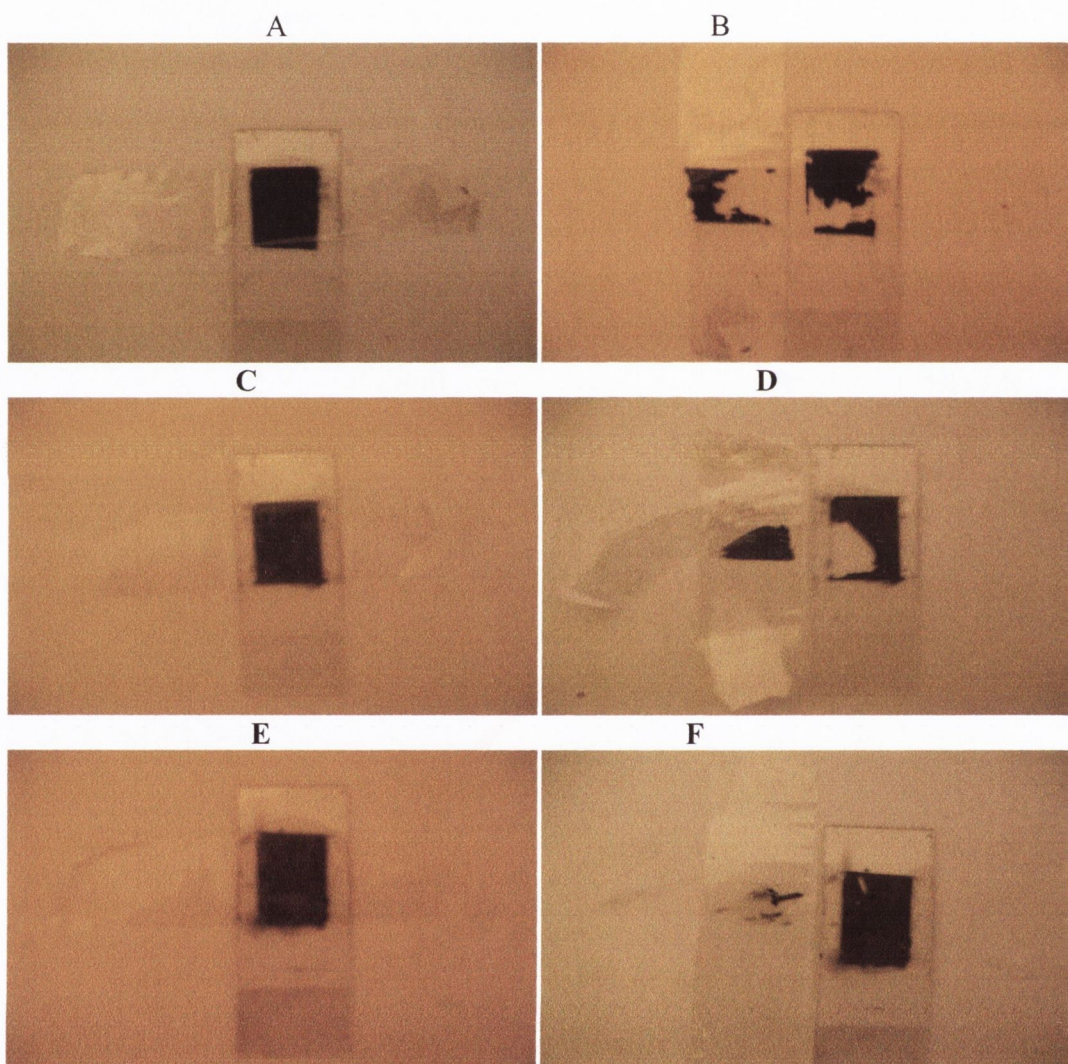


Figure 6.9: Films adhesion test with Scotch tape, A and B) NMP doped PEDOT: PSS film, C and D) and E and F) Shows the GNPs plus NMP doped PEDOT: PSS composite films which sintered at 120 °C and 150 °C respectively.

The tape was drawn from both sides of the films. The GNPs type 2 plus NMP doped PEDOT: PSS composite films (fig.6.9.E and F), which was sintered at 150 °C shows good adhesion as show little visible crack compare to GNPs type 2 plus PEDOT: PSS composite film which was sintered at 120 °C (fig.6.9.C and D) and NMP doped PEDOT: PSS film (fig.6.9.A and B). The result showed that GNPs also improved the adhesion of the NMP doped PEDOT: PSS film on non conducting glass as compared to the NMP doped PEDOT: PSS film.

6.4 Conclusion

In this part of our work, we have prepared and investigated Pt and TCO free counter electrodes with three different types of graphene nanoplatelets (GNPs), which were dispersed into a NMP doped/diluted PEDOT: PSS/H₂O matrix. These formulations were deposited onto a non conducting glass substrate. Using these new Pt and FTO/glass/CE the power conversion efficiencies of DSSCs were increased in all three cases and were higher than only pure NMP doped PEDOT: PSS film/glass-CE. However the highest power conversion efficiency of 3.70 % was achieved with GNPs type 2 plus NMP doped PEDOT: PSS composite film/glass-CE compared with the power conversion efficiencies of 1.35 % and 4.72 % for NMP doped PEDOT: PSS film/glass-CE and Pt/TCO/glass-CE/DSSCs respectively. The power conversion efficiency of GNPs type 2 plus NMP doped PEDOT: PSS composite film-CE was increased by a factor of 2.27 compared to the only NMP doped PEDOT: PSS film/glass-CE/DSSC due to the improvement in the electrical conductivity of the composite film. However the power conversion of efficiency of GNPs type 2 plus NMP doped PEDOT: PSS composite film/CE was 21 % lower than standard Pt/FTO/glass-CE/DSSC. While in case of GNPs type 1 and type 3 plus NMP doped PEDOT: PSS composite film-CEs the power conversion efficiencies also improved from 1.35 % to 3.36% and 2.78 % respectively, which is an increase by a factor of 2.48 for (GNPs type 1) and 2.05 for (GNPs type 3) compared to a power conversion efficiency of 1.35 % for NMP doped PEDOT: PSS film/glass-CE/DSSC. An electrical conductivity study of the composites revealed that all three types of GNPs increased the electrical conductivity of

NMP doped PEDOT: PSS composite films/CEs but GNPs type 2 plus PEDOT: PSS composite film/CE showed the highest conductivity of 190 S/cm.

The power conversion efficiency was further increased to 4.29 % by optimizing the sintering temperature for GNPs type 2 plus NMP doped PEDOT: PSS composite film-CE which was optimal at 150 °C. Electrical conductivity studies demonstrated that the effect of sintering temperature on the GNPs type 2 plus NMP doped PEDOT: PSS composite films/CEs which show that highest conductivity (196 S/cm) was achieved at 150 °C. The morphology GNPs type 2 plus NMP doped PEDOT: PSS composite film-CE electrodes was studied by scanning electron microscopy (SEM) which showed that GNPs type 2 were well dispersed and interconnected to each other in the composite film. The thermal stability of the GNPs type 2 plus NMP doped and GNPs type 2 powders and NMP doped was also investigated by TGA which showed that GNPs type 2 plus PEDOT: PSS composite film is more stable than only PEDOT:PSS film. The Raman spectroscopy demonstrated that some defects were present in GNPs type 2 composite films/CEs, which was decreased at a high sintering temperature as the lowest ID/IG value of 0.02 and 0.06 were obtained for GNPs type 2 plus PEDOT: PSS composite films which were sintered at 300 °C and 400 °C respectively. Therefore we believe that the power conversion efficiency can be potentially further improved upon by sintering the initial GNPs powder at high temperature to prepare the counter electrode as described above. The adhesion test was also performed for GNPs type 2 plus PEDOT: PSS composite films/CEs. This test demonstrated that type 2 plus PEDOT: PSS composite films/CE has a better adhesion in comparison to only NMP doped PEDOT: PSS film on non conducting glass substrate under identical conditions.

6.5 References

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Chapter 7: Development of GO and GNP Modified Photoanodes/Working Electrodes for DSSCs

7.1 Introduction

TiO₂ is the most widely used mesoporous oxide material in WE of the DSSC. TiO₂ is a wide band gap semiconductor with a band gap of around 3.2 eV, although other wide-band gap semiconductor oxides such as ZnO, SnO₂ and Nb₂O₅ have also been employed. However, TiO₂ has been material of choice [1, 2]: with advantageous properties such as its low price, high abundance and low toxicity [3, 4]. Its quality affects the loading of the dye molecules, the electron injection from the dye molecules to the TiO₂ nanoparticles, and the electron transport across the TiO₂ film [5, 6]. The WEs of DSSCs is typically fabricated using thick films (10 to 15 μm) of TiO₂ nanoparticles [7, 8], since the incorporation of TiO₂ nanoparticles into WE, the power conversion efficiency of DSSCs has remarkably increased [9-11]. The enhanced performance is due to increased dye adsorption in the nanostructured TiO₂ film and suitable electronic structure of TiO₂ [12]. However, electron transport in disordered TiO₂ nanoparticles proceeds by a trap-limited diffusion process [8], in which injected electrons travel through a large number of colloidal particles and grain boundaries before reaching the collecting electrode. Such a random transit path for the photo generated electrons increases the chance of carrier recombination and thus decreases the power conversion efficiencies of DSSCs [7, 8, 13]. To further improve the power conversion efficiency of DSSC, a more efficient electron transport process is required in the TiO₂ film, this will eliminate or reduce the charge recombination process. Therefore, various approaches are being investigated to improve the power conversion efficiencies of DSSCs. Many studies have sought to enhance the electron mobility and transport by incorporating conductive materials, such as SnO₂ or a variety of carbon based nanomaterials into TiO₂ film of the WE/DSSC [14-16]. The incorporation of carbon based nanomaterials, such as carbon nanotubes (CNTs) [17-19] and graphene sheets [11, 20, 21] into TiO₂ film of the WE of the DSSC has shown promising results. However, graphene has recently received more interest than other carbon based

nanomaterials [13], because it displays a high specific area, great mechanical strength, chemical stability and high electron mobility [22-24]. Various graphene-TiO₂ composite films/WEs have been fabricated by various method including solvothermal [11], microwave-assisted [25], electro spinning [26], chemical exfoliation [12] and by direct mixing of graphene into TiO₂ paste through mechanical grinding [27]. Yang et al. reported the incorporation of graphene (0.6 wt %) and CNTs (0.4 wt %) individually into TiO₂ film/WE and they achieved the power conversion efficiencies of 6.97 % (with graphene) and 0.58 % (with CNTs) compared that of 5.01 % with pure TiO₂ film/WE-DSSC [10]. They believed that higher performance of graphene due to their 2D nature which create better contact with the TiO₂ nanoparticles than 1D CNTs. Their device showed a 45% increase in short circuit current density compared of that pure TiO₂ film/WE-DSSC. This may be due to a lower recombination and a faster electron transport with the introduction of graphene. Tsai et al. reported the fabrication of graphene-TiO₂ composite film /WE by spin coating and they achieved high power conversion efficiency of 6.86 % with incorporation 1 wt% graphene into TiO₂ film, compared to 5.98% with pure TiO₂ film /WE-DSSC [28]. They believed that graphene content involved in TiO₂ film reduces the loss of electrons by suppressing their recombination, and also enhancement the dye adsorption on the graphene-TiO₂ composite film surface and this results in a significant increase in the short-circuit current density and power conversion efficiency of the DSSC. Kim et al. reported the incorporation of graphene (1 wt%) into TiO₂ film/WE and they achieved power conversion efficiencies of 6.05 % (with graphene) compared to 4.42 % with pure TiO₂ film/WE-DSS [29]. Their device showed increased short circuit current density from 8.69 mA/cm² (pure TiO₂ film/WE) to 12.89 mA/cm². They reported that the addition of graphene (1 wt%) into TiO₂ film decreased the resistance in graphene-TiO₂ composite film/WE compared to that of the pure TiO₂ film/WE-DSSC. Furthermore they reported that the larger amounts of dye molecules are also adsorbed, and more light is transmitted through and scattered in the graphene-TiO₂ composite film/WE than in the pure TiO₂ film/WE. Recently Cheng et al. also reported graphene-TiO₂ composite films which were fabricated by a hydrothermal method and deposited by on FTO glass substrate by the dr blade technique. The incorporation of 1.6 wt % of graphene into TiO₂ film/WE, enabled to achieve a high power conversion of 7.68 % compared to power conversion efficiency of 4.78 % for the pure TiO₂ based film/WE-DSSC [30].

Neo et al. has reported the incorporation of graphene oxide (GO) into TiO_2 nanoparticles film/WE [27]. They found that GO facilitates binding of TiO_2 nanoparticles together through the interactions between functional groups on GO and the surface species of TiO_2 nanoparticles. They reported that the presences of 0.8 wt% GO in the TiO_2 paste is sufficient to fabricate thick and crack-free TiO_2 films via single printing. These researchers achieved the power conversion efficiency of 7.70 % which is almost the same as that of control devices with the TiO_2 film/WE fabricated from the conventional TiO_2 paste without GO via four-fold printings. However, it is still remains a great challenge to develop an alternative route to fabricate graphene- TiO_2 composite film/WE. In order to enhance the power conversion efficiency of DSSC especially to explore novel, simple and effective method [30, 31].

In this chapter we report a facile method to enhance the power conversion efficiency of DSSC by introduction of GNPs type 2 into TiO_2 film of the WE and for comparison GO was also incorporated into TiO_2 film/WE by direct mixing into mixture of two types commercially available TiO_2 paste and was deposited by the dr blade technique. It was expected that the introduction of highly electrically conductive GNPs type 2 into TiO_2 film/WE would reduce charge recombination at the TiO_2 nanoparticle-electrolyte interface due to a faster electron transport. Furthermore it was also expected that GNPs type 2 would also enhances conductivity within TiO_2 nanoparticle film and facilitates conduction between the TiO_2 film and the FTO substrate. The amount of GNPs type 2 and GO in composite film varied from 0 wt% to 5 wt%. The photovoltaic performance of the GNPs or GO - TiO_2 /dye (N719)/WEs- DSSCs was compared with that of a pure TiO_2 film/(N719)/WE-DSSC.

7.2 Preparation of Photoanodes (WE)

GO was prepared according to a modified Hummer's process [32-34] and GNPs type 2 powders [35] were sintered at 400 °C for 30 minutes and then various weights % (0 to 5 wt%) of GO and sintered GNPs type 2 based WE were prepared as explained in experimental section. These new GO and GNPs plus TiO_2 composite films/WEs were then tested in DSSC and compared with pure TiO_2 which was also tested under same condition.

7.3 Raman spectroscopy Characterisation

Raman spectroscopy was done on graphite powders and GO powders as shown in Fig. 7.1.A before the use of these materials in WEs. Raman spectroscopy was also done on as supplied GNP type 2 powder and sintered GNPs powders as shown in Fig. 7.1.B. Raman spectra of GO showed a typical D band located around 1330 cm^{-1} and G band located at around 1588 cm^{-1} ,

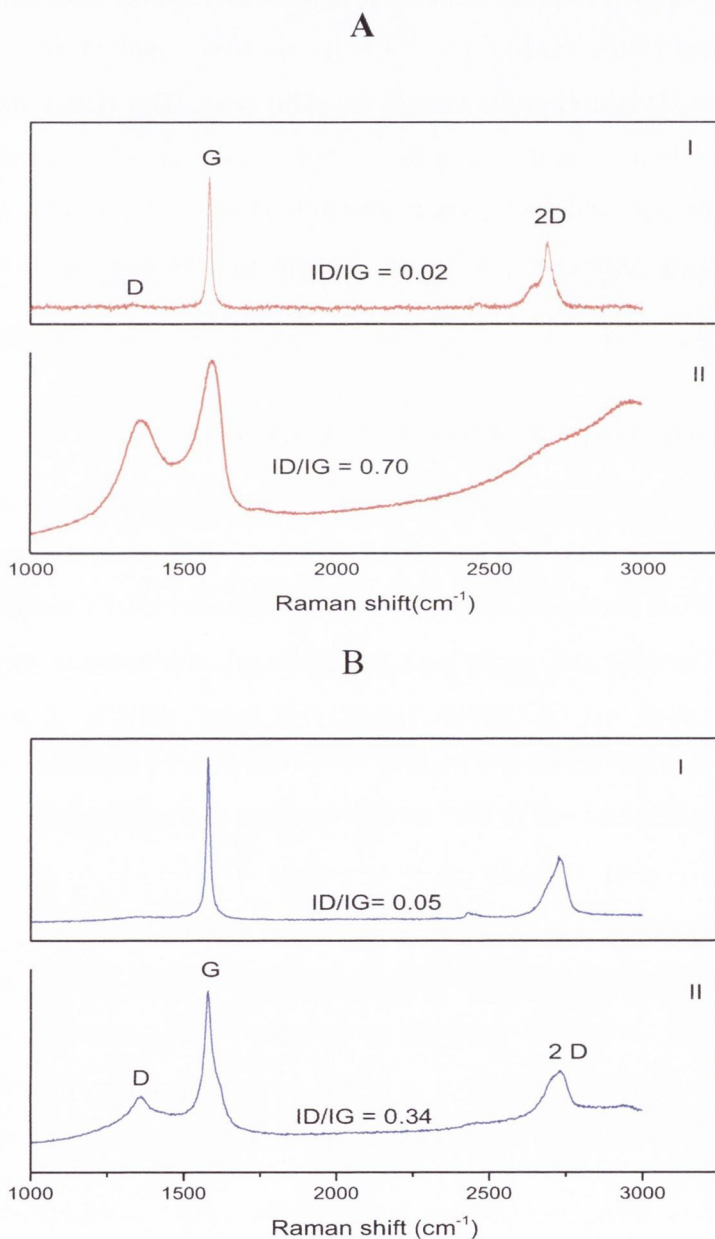


Figure 7.1: Raman spectra of A.I) Graphite powders, A.II) GO powders, B.I) Sintered GNPs type 2 powders B.II) supplied GNP type 2.

which correspond to the presence of sp^3 defects and tangential vibration of sp^2 carbon atoms in the hexagonal plane, respectively [36]. GO Raman spectra (fig.7.1.A.II) also shows two prominent D and G band at 1350 cm^{-1} and 1600 cm^{-1} respectively. While the intensity ratio of D and G bands (ID/IG) of GO is around 0.76 for GO. The ID/IG (0.76) confirmed the successful oxidation of graphite as the ID/IG ratio was around 0.02 for graphite as shown in fig.7.1.A.I. The enhanced ID/IG ratio value for GO can be attributed to the increased number of defects in graphitic structure [37]. Raman spectra of sintered GNPs type 2 (fig.7.1.B.II) show a small D peak which is located at 1348 cm^{-1} . While G peak located at 1580 cm^{-1} . The ID/IG ratio for GNPS type 2 powders was 0.34 as shown in fig.7.1.B.II. However, after sintering the ID/IG ratio of GNPs type 2 powders were decreased to 0.05 as shown in fig.6.2.B. I. This shows that the sintering process reduces the remaining attached functional groups and thus decreased the ID/IG ratio for GNPs type 2 powder

7.4 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) have been performed under air for graphene oxide (GO) powders and sintered GNPs type 2 powders as shown in figure 6.2. The TGA curve of GO (fig.7.2.A) shows some initial 7 weight % between $40\text{ }^{\circ}\text{C}$ to $110\text{ }^{\circ}\text{C}$. The obtained results were in agreement with previous reported works [38, 39]. This indicated that GO powders contained some quantity of water molecules which were evaporated in the low heating step [38]. Further degradation around 35 weight % was occurred between $124\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$. This second weight loss is associated to the decomposition of oxygen-containing groups. The final decomposition of 58 weight % occurred between $510\text{ }^{\circ}\text{C}$ to $877\text{ }^{\circ}\text{C}$. and it was attributed to the oxidation of carbon [38]. TGA curve of GNPs type 2 powders shows negligible weight loss from $200\text{ }^{\circ}\text{C}$ to $510\text{ }^{\circ}\text{C}$. This shows that sintering process has mostly removed the attached functional groups (Explained in chapter 6 in detail). However maximum weight was lost between $600\text{ }^{\circ}\text{C}$ and $800\text{ }^{\circ}\text{C}$, which correspond to the thermal degradation of GNPs type 2.

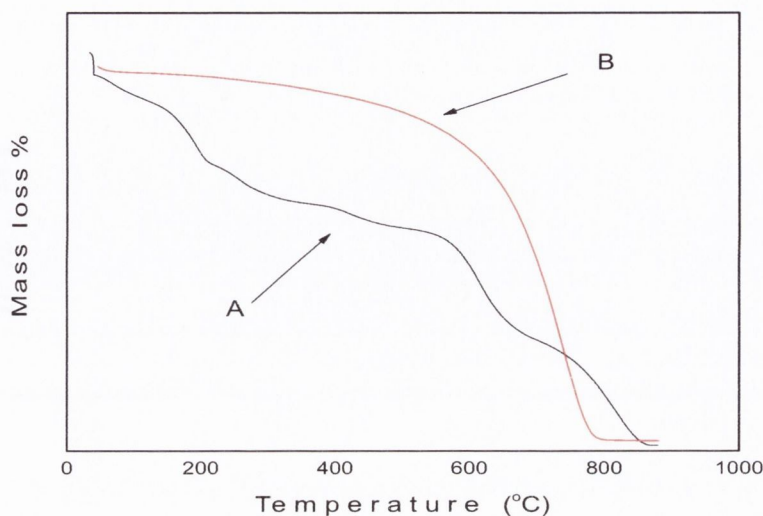


Figure 7.2: A) shows TGA curves of GO powders and B) sintered GNPs type 2 powders.

7.5 Scanning Electron Microscopy Characterisation

The surface and cross section morphology of GNPs type 2 (0.6 wt %) plus TiO_2 composite films/WEs has been examined using SEM. Fig.7.3. K and M shows cross sectional images of GNPs type 2 plus TiO_2 plus composite film/WE which shows their thickness was around 16 to 18 μm . Fig.7.4. A,B, C, E, F and G shows SEM images of the surface GNPs type 2 plus TiO_2 composite film/ WE. According to SEM GNPs type 2, was uniformly dispersed and attached to TiO_2 particles.

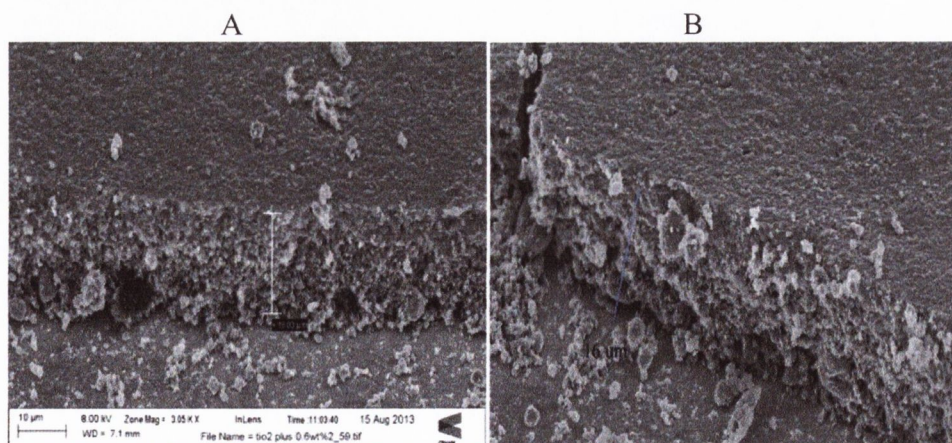


Figure 7.3: Representative SEM cross section images (K and M) of GNPs type 2 plus TiO_2 (0.6 wt %) composite films/WEs.

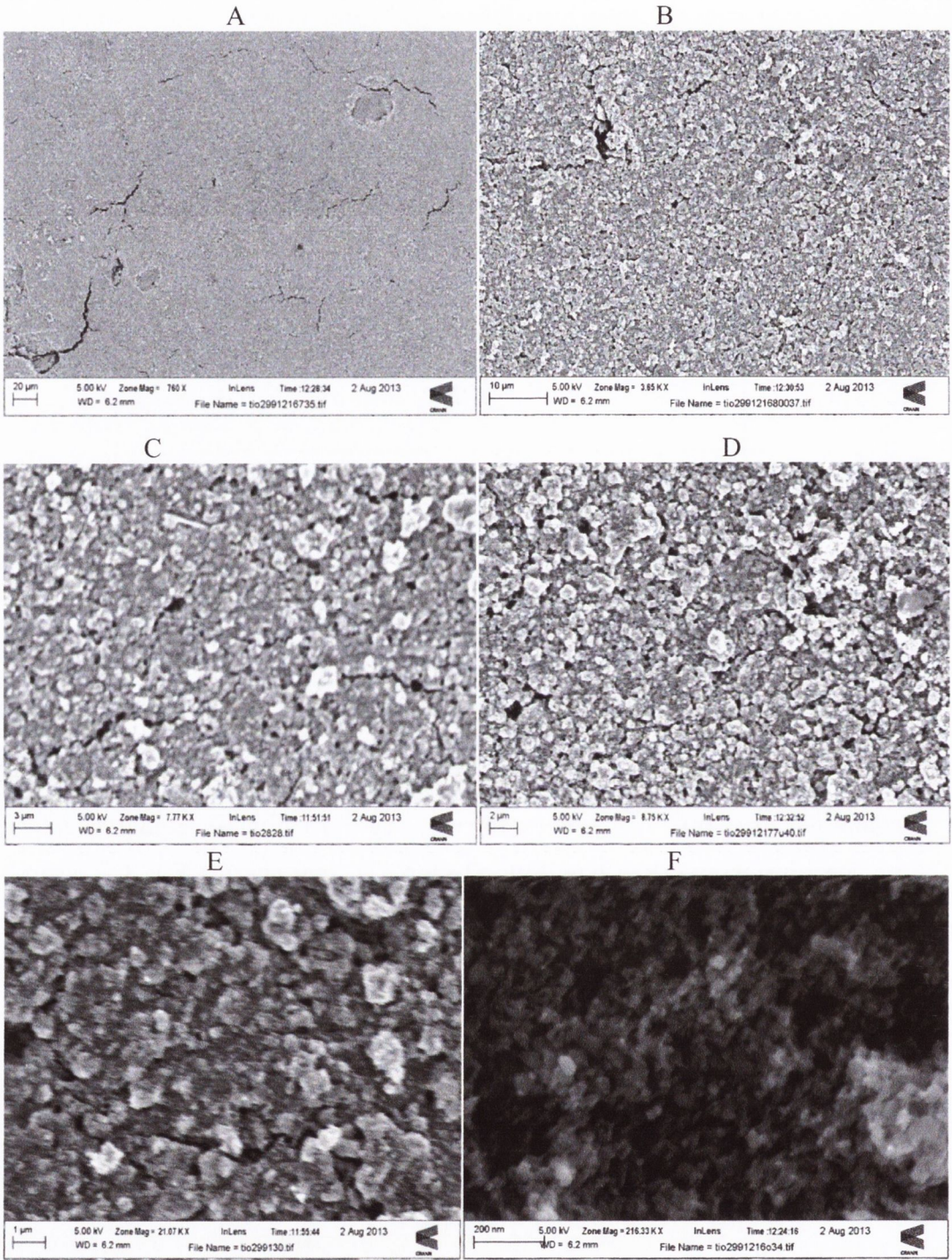


Figure 7.4 Representative surface SEM images (A, B, C and D) of GNPs type 2 plus TiO₂ (0.6 wt %) composite films/WE.

7.6 Electrical Conductivity Measurement

For electrical conductivity measurement the reference sample (pure TiO₂ film) and samples with various wt % of GNPs type 2 and TiO₂ composites films were deposited on non-conducting glass substrates. The electrical conductivity was measured using the two point probe technique and an average of the measured values was taken. The results are presented in fig.7.5. The thickness of the films was in the range 16 μm to 18 μm according to SEM cross section images. The TiO₂ nanoparticle film showed a very low electric conductivity in the range of 1 x 10⁻⁶ to 1 x 10⁻¹¹ S/m [39-42]. However, the incorporation of graphene sheet into the TiO₂ nanoparticle film significantly improved the film electrical conductivity [12]. The addition of 0.3 wt %, 0.6 wt % and 1 wt % of GNPs type 2 in to TiO₂ films resulted in the rise of electrical conductivity from 1.43 x 10⁻⁴ S/m (pure TiO₂ film) to 1.93 x 10⁻⁴ S/m, 2.20 x 10⁻⁴ S/m and 2.87 x 10⁻⁴ respectively. The electrical conductivity was also further increased to 3.86 x 10⁻⁴ S/m and 4.40 x 10⁻⁴ S/m with addition of 3 wt % and 5 wt % of GNPs type 2 in to TiO₂ films respectively.

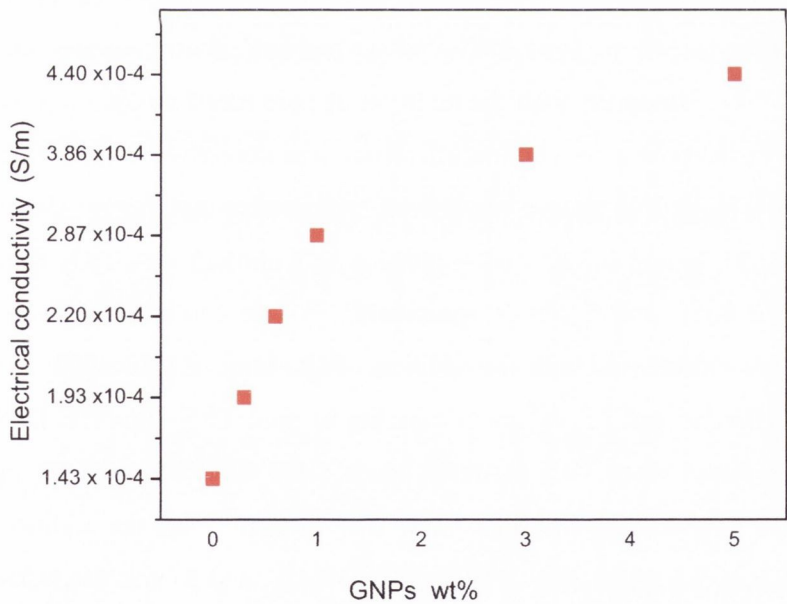


Figure 7.5: Electrical conductivity of GNPs type 2 plus TiO₂ composite films as a function of GNPs wt %.

These results clearly demonstrate that the incorporation of high electrically conductive sintered GNPs type 2 into TiO_2 films enhances the electrical conductivity due to fast electron transport via graphene sheets within the composite films. It is expected that the photovoltaic performance improved due to the increase in electrical conductivity of GNPs type 2 plus TiO_2 composite film/WE-DSSC.

7.7 Investigation of the Photovoltaic performance of various weight % of GO into TiO_2 films/Working Electrodes of the DSSCs

To investigate the effect of the addition of GO component into TiO_2 film/Working electrode (WE), a series of WEs were prepared with various wt% of GO into TiO_2 films and used as WEs in DSSCs. Table 7.1 summarises the photovoltaic parameters i.e. open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiencies of all DSSCs which were prepared in this work. The photocurrent density–voltage (J – V) characteristics of the DSSCs with various WEs are shown in Fig. 7.6. The power conversion efficiency of pure TiO_2 film/WE were 3.75 %. However, with the addition of pure small amount 0.3 wt % of GO to TiO_2 film/WE, the power conversion efficiency was decreased from 3.75 % (pure TiO_2 film/WE) to 1.33 %. The power conversion efficiencies were further decreased to 1.13 %, 1.16 %, 0.53 % and 0.30 % with addition GO content into TiO_2 film/WEs at 0.6 wt%, 1 wt%, 3 wt%, and 5 wt% respectively. As we can see the power conversion efficiencies were decreased with the addition of GO into TiO_2 film/WE in all cases due to decreased the J_{sc} and FF values comparing to pure TiO_2 film/WE-DSSCs. The J_{sc} value were reduced from 10.5 mA/cm^2 (pure TiO_2 film/WE) to 6.08 mA/cm^2 , 5.21 mA/cm^2 , 5.66 mA/cm^2 , 2.67 mA/cm^2 and 1.39 mA/cm^2 with the addition of GO into TiO_2 film/WE at 0.3 wt %, 0.6 wt%, 1 wt%, 3 wt%, and 5 wt% respectively. The FF values dropped from 0.49 (pure TiO_2 film/WE) to 0.32, 0.31, 0.30, 0.29 and 0.29 with addition of GO into TiO_2 film/WE at 0.3 wt %, 0.6 wt %, 1 wt%, 3 wt%, and 5 wt% respectively. The V_{oc} values decreased from 730 mV (pure TiO_2 film/WE) to 700 mV, 690 mV, 680 mV, 690 mV and 610 mV with addition of GO into TiO_2 films/WEs 0.3 wt %, 0.6 wt %, 1 wt %, 3 wt %, and 5 wt % respectively. It was expected that during

the sintering process at 450 °C the GO in TiO₂ composite film/WE could be potentially reduced to graphene and at result graphene-TiO₂ composite film/ WE were expected to show better performance than pure TiO₂ film/WE.

Table 7.1: The photovoltaic parameters of DSSCs with various wt % of GO into TiO₂ films/WEs. Measured at 100 mW cm⁻². Cell active area:0.8 cm².

GO content (Wt %)	Voc (mV)	Jsc(mA/cm ²)	FF	Efficiency %
0	730	10.5	0.49	3.75 ± 0.10
0.3	700	6.08	0.32	1.33 ± 0.06
0.6	690	5.21	0.31	1.13 ± 0.05
1	680	5.66	0.30	1.16 ± 0.05
3	690	2.67	0.29	0.53 ± 0.04
5	610	1.39	0.29	0.30 ± 0.04

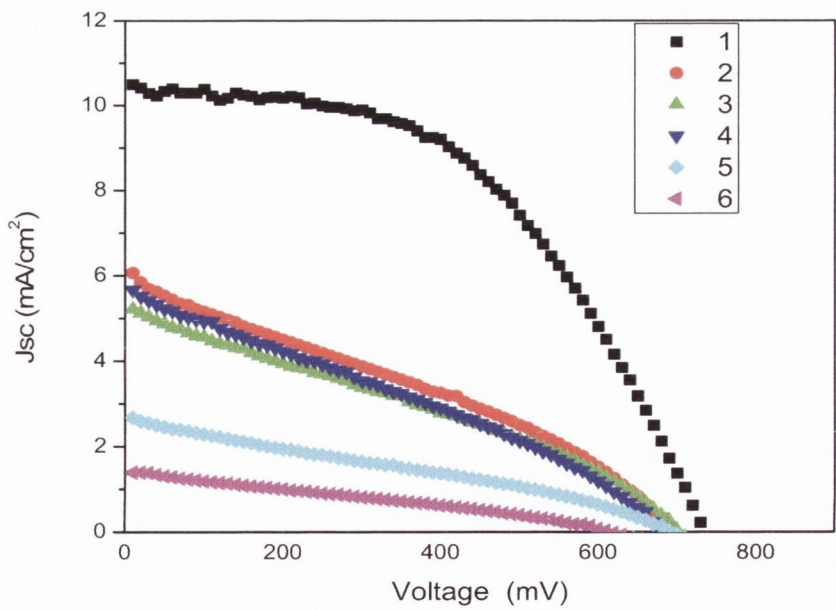


Figure 7.6: The photovoltaic (J–V) curves of TiO₂ film/WE containing 1) 0wt %, 2) 0.3 wt %, 3) 0.6 wt %, 4) 1wt, 5) 3 wt % and 6) 5 wt % of GO.

However, the poor photovoltaic performance of GO-TiO₂ film/WE demonstrated that the reduction of GO did not occur and the selected method and GO are not suitable for the preparation of an efficient WE for DSSC.

7.8 Investigation of the Photovoltaic performance of various weight % of GNPs type 2 into TiO₂ film /Working electrode/DSSC

To investigate the effect of the addition of GNPs type 2 into the TiO₂ film/WE, a series of WEs with various wt % of sintered GNPs type 2 in TiO₂ films were prepared and used as WEs in DSSCs. Table 7.2 summarises the photovoltaic parameters i.e. Voc, Jsc, FF, and the power conversion efficiencies of all DSSCs which were prepared in this work. The photocurrent density–voltage (J–V) characteristics of the DSSCs with various WEs are shown in Fig. 7.7. The power conversion efficiency of DSSC with pure TiO₂ film/WE was 3.75 %. The addition of a small amount (0.3 wt%) of GNPs type 2 into TiO₂ film/WE increased the power conversion efficiency from 3.75 % (pure TiO₂ film/WE) to 4.06 %. The power conversion efficiency was further increased to 4.77 % with the addition of 0.6 wt% of GNPs type 2 in TiO₂ film/WE. The power conversion efficiencies of GNPs type 2 plus TiO₂ film were mainly improved due to increase in Jsc and FF values comparing to those for pure TiO₂ film/WE-DSSCs. However, the power conversion efficiency decreased from 4.77 % (with 0.6 wt% of GNPs type 2) to 4.21 % with the addition of 1 wt % of GNPs type 2 into TiO₂/WE. Further increasing of the wt% (3 wt% and 5 wt%) of GNPs type 2 into TiO₂ /WE resulted only in further reduction of the power conversion efficiencies from 3.75 % (pure TiO₂ /WE) to 3.38 % and 2.90 % respectively. These results indicate that only a small optimal amount of GNPs type 2 (0.3wt % to 1 wt %) can effectively improve the DSSC performances. This can be explained by the fact that small amount of GNPs type 2 can be dispersed properly into TiO₂ film/WE and as a result enhance the dye adsorption due to high specific surface area of GNP. These results clearly demonstrate that a small wt% of GNPs into TiO₂ film/WE is sufficient to enhance the electron injection and electron transfer rate in the DSSC operation. Although, electrical conductivity measurement (see section 7.6) showed that the electrical conductivity

Electrodes for DSSCs

linearly increased as wt % of GNPs type 2 increased in TiO₂ film. However, the photovoltaic investigation showed that power conversion efficiencies decreased at high wt % (3 to 5 wt %) of GNPs type 2 into TiO₂ film, this might due short circuit the DSSC from inside. The J_{sc} values increased from 10.5 mA/cm² (pure TiO₂ film /WE) to 11.51 mA/cm² to 12.66 mA/cm² and 11.39 mA/cm² with addition of 0.3 wt % 0.6 wt % and 1 wt % of GNPs type 2 respectively. This shows that the incorporation of GNPs type 2 into TiO₂ film/WE enhanced the dye adsorption as it was reported that the increment of J_{sc} resulted from the enhancement in amount of dye absorption through high surface area of WE materials [40]. However J_{sc} values reduced to 9.12 mA/cm² and 8.88 mA/cm² with addition 3 wt % and 5 wt % of GNPS type 2 into TiO₂ film/WE respectively. The J_{sc} results clearly demonstrate that a small wt% (0.3 wt% to 1 wt %) of GNPS type 2 in the composite WE is sufficient to enhance the electron transport in composite film/WE. The FF values increased from 0.49 (pure TiO₂ film/WE) to 0.52, 0.51 and 0.50 with addition 0.3 wt % and 0.6 wt % and 1 wt % of GNPs type 2 into TiO₂ film/WE respectively. The FF values were 0.51 and 0.48 with addition of 3 wt % and 5 wt% of GNPS type 2 into TiO₂ film/WE respectively. The Voc values of 680 mV, 730 mV, 740 mV,730 and 680 mV were achieved with 0.3, 0.6,1,3 and 6 wt % of GNPs into TiO₂ film/WE compared to Voc value of 730 mV with pure TiO₂ film/WE-DSSC.

Table 7.2: The photovoltaic parameters of DSSCs with various wt % of sintered GNPs 2 into TiO₂ films/WEs. Measured at 100 mW cm⁻². Cell active area:0.8 cm².

GNPS Type 2 content (wt %)	Voc (mV)	Jsc(mA/cm ²)	FF	Efficiency %
0	730	10.50	0.49	3.75 ± 0.10
0.3	680	11.51	0.52	4.06 ± 0.09
0.6	730	12.66	0.51	4.77 ± 0.10
1	740	11.39	0.50	4.21 ± 0.11
3	730	9.12	0.51	3.38 ± 0.10
5	680	8.88	0.48	2.90 ± 0.08

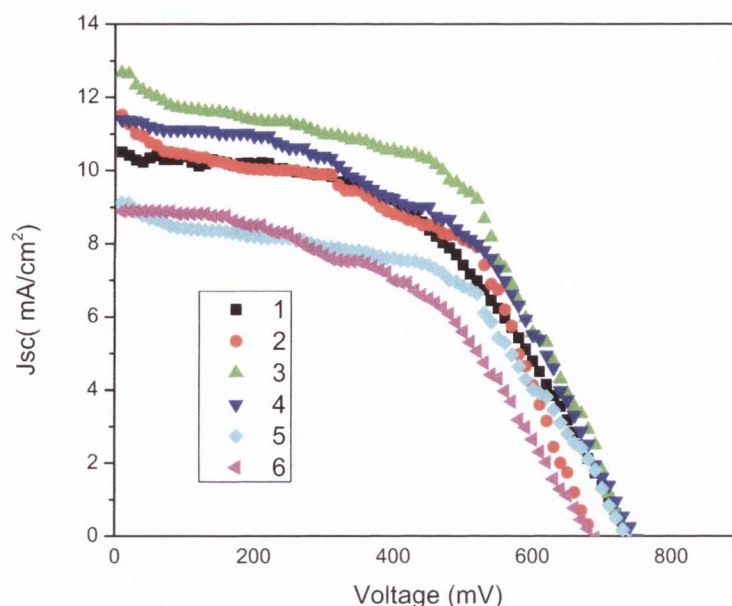


Figure 7.7: Photovoltaic (J–V) curves of TiO₂ film/WE containing 1) 0wt %, 2) 0.3 wt %, 3) 0.6 wt %, 4) 1 wt, 5) 3 wt % and 6) 5 wt% of GNPs type 2.

7.9 Conclusion

In this part of our work, various weight % of GO and sintered GNPs type 2 were incorporated into TiO₂ films to produce new WEs for DSSCs. The photoconductivity studies have shown that the power conversion efficiencies of DSSCs decreased with addition of GO into TiO₂ films/WEs in all cases. However the power conversion efficiencies were increased with addition of GNPs type 2 into TiO₂ films/WEs. The highest power conversion efficiency of 4.77 % was achieved with 0.6 wt% of GNPs into TiO₂ film/WE-DSSC compared to 3.75 % of pure TiO₂ film/WE-DSSC. The power conversion efficiency of GNPs type 2 plus TiO₂ composite film was increased around 27% than pure TiO₂ film /WE-DSSC. Raman spectroscopy was done on as supplied GNP type 2 and sintered GNPs type 2 powders which show that the ID/IG was decreased from 0.34 to 0.06, this shows that sintering process removed the attached functional groups and thus decreased the ID/IG ratio for GNPs type 2 powders. The thermal stability of sintered GNPs type 2 powders was investigated by TGA which showed that GNPs type 2 is stable up to 500 °C. Electrical conductivity

study reveals that addition of GNPs type 2 into TiO_2 film increased the electrical conductivity from $1.43 \times 10^{-4} \text{ S/m}$ (pure TiO_2 film) to $2.20 \times 10^{-4} \text{ S/m}$ (with 0.6 wt % of GNPs) $4.41 \times 10^{-4} \text{ S/m}$ (with 5 wt% of GNPs). The morphology of GNPs type 2 plus TiO_2 composite film/WE was studied by SEM which showed that GNPs types 2 were well dispersed in TiO_2 composite film. In overall, we believe that this is a simple, fast, and low-cost fabrication method to enhance the power conversion efficiency of DSSC by incorporation of electrically conductive GNPs type 2 into the TiO_2 film/WE-DSSC. It is expected that the power conversion efficiency could further enhance through optimization of the WE and overall DSSC device.

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Electrodes for DSSCs

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Chapter 8: Conclusions and Future Work

8.1 Conclusion

In this work a series of various nanocomposite materials have been prepared and investigated for the development of potentially inexpensive, stable and efficient DSSCs. We believe that this work has successfully demonstrated the possibility of the use of different nanomaterials in various parts of DSSCs.

One of our main aims was to enhance the photovoltaic and stability properties of IL based electrolytes by the addition of various carbon based nanomaterials. In this work we have successfully developed the preparation of IL (PMII) based quasi solid state electrolytes by the addition of various carbon based nanoparticles with very low to very high weight %. It was found that 1-15 weight % of graphene has almost no visible effect on flow of PMII but they can only make a gel like material and 20-40 wt % resulting in quasi solid state electrolyte. 1 to 10 wt % of graphene based quasi solid state electrolyte showed a very little increase in the power conversion efficiency (up to 0.2 %). However, the power conversion efficiencies of DSSCs increased sharply (up to 2.10%) when 30 wt % of graphene was added into PMII. We believe that at low concentrations the graphene flakes were apart from each other and did not provide sufficient charge transfer. As the concentration increased the graphene flakes moved closer to each other and as a result there was a fast electron transfer from the Pt of the CE toward WE, hence viscous quasi solid state electrolytes showed higher power conversion efficiency. When the amount of graphene was increased up to 35 to 40 weight %, the power conversion efficiencies decreased to 0.59 % and 0.48 % respectively. This reduced power conversion efficiencies were most likely due to the reason that at 35 to 40 wt % graphene cannot be properly dispersed in PMII and thus homogeneity of composite electrolyte decreased and could not provide enough PMII penetration into the sensitized porous TiO_2 layer and inhibits the diffusion of I^- and I_3^- ions in electrolyte. The power conversion efficiencies of DSSCs increased from 0.16% (pure PMII) to 1.43% with addition of SWCNTs (7wt %) into PMII. These results showed that The 2D graphene could potentially make a better contact with TiO_2 of working electrode (WE) as well as to Pt of the counter electrode (CE) compared to curved CNTs and as a result more efficient electrons would transfer from the CE to the WE, resulting in higher power conversion efficiency than 1D SWCNTs based quasi

solid state electrolyte/DSSC. The power conversion efficiency was further improved to 2.50 % with hybrid quasi solid state electrolyte which contained SWCNTs (3 wt %) and graphene (12 wt %) in PMII. It was previously reported that electrical conductivity of graphite/graphene composite can be increased by the addition of small quantities of SWCNTs [1]. This might be the reason in our case as well. Furthermore, it was also demonstrated that DSSC can be fabricated without any Pt with a moderate efficiency (1.18%) as graphene and SWCNTs can act as an electrocatalyst in hybrid quasi solid state electrolytes based DSSCs. Our results demonstrated that the incorporation of carbon based nanomaterial into IL has enhanced the DSSC power conversion efficiency because carbon nanomaterials can serve simultaneously both as charge transporter in the ILs and as electrocatalysts for the reduction of I_3^- [2-4]. The stability study has also shown that these quasi solid state based DSSCs possess the higher efficiencies than pure PMII based DSSCs under the same condition. TGA studies have demonstrated that these electrolytes have high thermal stability up to 300 °C.

Additionally in this work various carbon based nanomaterial i.e. graphene, SWCNTs and mixture of graphene plus SWCNTs were incorporated in optimized binary ILs (EMISCN + PMII). The power conversion efficiencies were increased from 1.40% (optimized binary IL = EMISCN/PMII) to 2.04% , 2.24% and 3.07% with addition of SWCNTs, graphene and hybrid SWCNTs + graphene into binary IL based DSSCs respectively. We believe that power conversion efficiencies were increased due to fabrication of more homogeneous carbon based quasi solid state electrolytes in less viscous binary IL than pure PMII. It is also known that diffusion of rate redox couple also enhances in less viscous binary IL based quasi solid state electrolytes and also provides better penetration into TiO_2 film of the WE [4]. In addition the effect of incorporation of various concentrations of GuSCN into the best quasi solid state electrolytes i.e. hybrid of SWCNTs plus graphene into binary ILs was studied. It was found that the addition of 0.05M of GuSCN into the binary IL gave the best power conversion efficiency (3.60%). This might be explained by the more efficient surface passivation preventing electron recombination reactions at the TiO_2 /dye/electrolyte interface.

In our work we have also developed new Pt free CEs for DSSCs. We have successfully replaced Pt of the CE with hybrid composite of GNPs type 3 plus MWCNTs into PEDOT: PSS matrix. These various carbon based material were dispersed in conducting polymer PEDOT: PSS aqueous dispersion, via non-covalent approach that allowed the retention of their good electrical properties as in this case the

graphitic sp^2 structure in carbon ring does not change. These materials can be adsorbed onto the GNPs and CNTs surface, rendering the msoluble in aqueous or organic solvents [5]. These various kinds of composites CEs were deposited on FTO coated glass substrates i.e. 1) GNPs type 3, 2) MWCNTs and 3) a various combination of MWCNTs and GNPs type 3 into PEDOT: PSS matrix. However only hybrid C coated on FTO/glass substrate-CE, which was contained GNPs type 3 (22 wt %) and MWCNTs (44 wt %) into PEDOT: PSS film, demonstrated a higher power conversion efficiency of 4.10% compared to standard Pt coated FTO/CE–DSSC (3.90%). This study demonstrated that the addition of GNPs (22 wt %) to MWCNTs (44 wt %) composite result in increased electrical conductivity and reduced R_{ct} of the CE. As consequence hybrid C-CE demonstrated higher power conversion efficiency. Furthermore, the hybrid C-CEs were also tested in DSSCs with various type electrolytes system i.e. organic based electrolytes, ionic liquid electrolyte (PMII) and quasi solid state electrolyte. Hybrid-C-CE/DSSC with quasi solid state electrolyte and ionic liquid electrolyte demonstrated power conversion efficiencies of 1.88 % and 0.38 % respectively. This work showed that hybrid composite of GNPs and MWCNTs in PEDOT: PSS can be used as efficient catalysts in CE. The TGA study demonstrated that GNPs and MWCNTs samples are highly thermally stable either in powder form or in composite film. Thus, the hybrid C-CE can be used as effective metal-free CE to replace Pt in high-performance DSSC.

In this work we have also developed and investigated the Pt and FTO free CEs with various composite films which were prepared with addition of three different types of GNPs into PEDOT: PSS matrix. The PEDOT: PSS was also doped with NMP solvent, showing that electrical conductivity was increased with addition of NMP into PEDOT: PSS film. The power conversion efficiencies of DSSCs were increased by the addition of all three types of GNPs into NMP doped PEDOT: PSS matrix /glass-CE than pure NMP doped PEDOT: PSS film/glass-CE. However, the highest power conversion efficiency of 3.70 % was achieved with the GNPs type 2 plus NMP doped PEDOT: PSS composite film/glass-CE compared with the power conversion efficiencies of 1.35 % for NMP doped PEDOT: PSS film/glass-CE. The electrical conductivity studies of the composites revealed that all three types of GNPs increased the electrical conductivity of NMP doped PEDOT: PSS composite films/CEs but GNPs type 2 plus PEDOT: PSS composite film/CE showed the highest conductivity of 190 S/cm. These results suggest that electrical conductivity of GNPs plus NMP doped

PEDOT: PSS composites films greatly depends on the diameter and surface area of GNPs. GNPs type 1 and type 2 have similar average diameter (up to 5 μm) but different surface area (GNPs 1 = 50 m^2/g and GNPs 2 = 100 m^2/g). Thus we can say that electrical conductivity of GNPs type 2 is greater than GNPs 1 due to its higher surface area. GNPs type 3 has a very high surface (600–750 m^2/g) but shows lower electrical conductivity (164 S/cm) than GNPs type 1 and GNPs type 2 plus NMP doped PEDOT: PSS composites films. This is thought to be due to the large contact resistance between small-size GNPs type 3 (diameter = 2 μm) which as a result shows a lower electrical conductivity than GNPs type 1 and GNPs type 2 based films. The power conversion efficiency was further improved to 4.29 % by optimizing the sintering temperature for GNPs type 2 plus NMP doped PEDOT: PSS composite film-CE which was optimal at 150 $^{\circ}\text{C}$. The Raman spectroscopy study demonstrated that some defects were present in GNPs type 2 composite films/CEs. Therefore we believe that the power conversion efficiency can be potentially further improved upon by sintering the initial GNPs powder at high temperature to prepare the CE.

Finally in our work various wt% of GO and sintered GNPs type 2 were incorporated into TiO_2 films using this new composite film as WEs in DSSCs. It was found that the power conversion efficiencies of DSSCs were decreased with addition of GO into TiO_2 films/WEs in all cases. These results demonstrated that the GO are not suitable material for the preparation of an efficient WE for DSSC. However, the power conversion efficiencies were increased with addition of sintered GNPs type 2 into TiO_2 films/WEs. The highest power conversion efficiency of 4.77 % was achieved with 0.6 wt% of GNPs into TiO_2 film/WE-DSSC compared to 3.75 % of pure TiO_2 film/WE-DSSC. Raman spectroscopy was done on as supplied GNP type 2 and sintered GNPs type 2 powders which show that the ID/IG was decreased from 0.34 to 0.06, this shows that sintering process removed the attached functional groups and thus decreased the ID/IG ratio for GNPs type 2 powders.

In overall we believe that this research should make a contribution to the development of various components of DSSCs with potentially low-cost fabrication and enhanced power conversion efficiency. However, some follow on research and development are necessary to further optimize our materials, technology and DCCS fabrication process for potential large scale production and commercialization.

8.2 Future work

To further increase the photovoltaic performances of the DSSCs with these alternative materials are required the optimization of the formulations and preparation processes of these new materials and corresponding DCCSs. It is important to notice that due to the absence of glovebox in our work all experiments have been performed at so-called “open cell”, where electrolytes were deposited on one of the electrodes at the ambient conditions (open air) before cell was sealed. As result the electrolyte and other parts of the cell are exposed to air and moisture which are detrimental to some of the materials resulting in lower efficiency of the cell in overall. Future work should expand the use of these materials and techniques for the “closed cell” fabrication approach, when the cell is initially assembled and sealed and then electrolyte is introduced into the cell under vacuum via a small hole, which then sealed with surlyn. We believe that this approach will enable us to achieve much better efficiencies due to the minimal exposure of electrolytes to air and moisture. Moreover we think that the preparation of quasi solid state electrolytes by introduction of various types graphene (e.g. with different surface area and diameter) into various types of IL and mixture of IL must be performed under anaerobic conditions (e.g. under argon) to prevent any oxidation or hydrolysis of the components. It is also necessary to improve the dispersion of graphene in quasi solid state electrolytes that should further improve the power conversion efficiency of DSSC. Furthermore, it is also important to optimize the various other parts of DSSC to increase the power conversion efficiency with these new alternative materials. The thickness and area of TiO_2 film is important parameters that greatly affect the power conversion efficiency of DSSC, therefore it is necessary to optimize these two parameters of TiO_2 film of the WE for quasi solid state electrolytes.

For all applications good quality CNTs or GNPs dispersion is vital. Therefore it would also be very interesting and important to carry out a systematic study of the pristine CNTs or GNPs or hybrid of these two nanomaterial dispersed into PEDOT: PSS dispersion and then diluted with various other low viscose organic solvents, for example chloroform or ethanol, etc. Thus, for future work we propose the preparation of stable and homogenous dispersion by incorporation of these various carbon based nanomaterial in PEDOT: PSS dispersion. It is expected that all these strategies would further improve the power conversion efficiency of the DSSC.

8.3 References

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