UNIVERSITI PUTRA MALAYSIA

GRAPHENE AND GRAPHENE/ CARBON BLACK COMPOSITE-BASED COUNTER ELECTRODES FOR PLATINUM-FREE DYE-SENSITIZED SOLAR CELL

ALI KHALIFA ABDGALIL

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By

ALI KHALIFA ABDGALIL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

I dedicate this research to my great parents (Haji Khalifa and Haji Mesaada) who have been the source of my strength. I also dedicate this work to my beloved wife; Suad who has encouraged me all the way and her continuous encouragement took this work to completion. This work is also devoted to my brothers and sisters for their financial and moral support. I would not forget to dedicate my success to my sons (Al-rayan and Asser) who give me the meaning of life and the source of happiness all the time. Without your loving and support, I would never have completed this research.

May almighty Allah bless all of you with happiness, success and whatever is best

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman : Associate Professor Suhaidi Shafie, PhD
Faculty : Engineering

The role of the counter electrode in the dye-sensitized solar cell (DSSC) mechanism is to collect the electrons received from the external circuit, and mainly to catalyse the reduction of tri-iodide ions in the electrolyte system. The faster tri-iodide reduction, the faster oxidized dye molecules are regenerated, and thus better DSSC performance.

Typically, a platinum catalyst layer is used as a counter electrode in DSSC due to its high conductivity, stability and electrocatalytic activity. However, platinum is a rare and expensive material which prohibit its application for mass production of DSSC. It also corrodes when exposed to the iodine-based electrolyte, which therefore affect the long-term stability of the cell. For the aim of DSSC commercialization, extensive researches have been conducted to reduce the cost of DSSC by introducing effective and low-cost alternative materials. Carbon-based materials DSSC counter electrodes have attracted great interest as alternatives for Pt due to their low-cost, conductivity, catalytic activity, and chemical stability. Recently, owing to its superior electrical conductivity and high crystallinity, graphene was studied as DSSC counter electrode. Though, its catalytic activity for tri-iodide reduction is still considered low. The carbon black also exhibits high electrical conductivity, but with high electrocatalytic activity for tri-iodide reduction due to its higher surface area. Thus, it is expected that Graphene/ Carbon black composites would show higher catalytic activity and better performance as DSSC counter electrode and being promising alternative to replace the expensive platinum in DSSCs.

This research started with optimization of the single-layer screen-printed TiO_2 photoanode, and then is intended to investigate the application of low-cost and effective Graphene and Graphene/Carbon black (G/Cb) composites counter electrodes for DSSC.

Graphene counter electrodes were prepared by drop-casting the diluted graphene dispersion on FTO-coated glass substrates. The study focused on the effect of heat treatment of the graphene-based counter electrode on the DSSC performance.

Moreover, to enhance the electrocatalytic activity of the graphene electrodes, six different G/Cb composites-based counter electrodes were screen-printed on FTO-coated glass using six different pastes composing of varied graphene to carbon black powders ratios. For comparison, screen-printed Solaronix carbon paste and platinized-FTO were used as reference counter electrodes.

Different characterizations and measurements were undertaken to investigate the applicability of the proposed graphene and G/Cb electrodes to serve as counter electrodes in DSSCs. The graphene film with a thickness of ca. 25 µm and heated at 300^0 C possesses good adhesion and low sheet resistance 18.3 Ω/□ which was a promising value compared to other electrodes (as-deposited, 100^0 C, and 200^0 C). Hence, the DSSC used graphene electrode heated at 300^0 C shows power conversion efficiency of 3.32%, comparable to 4.48% obtained from Pt-based DSSC. The obtained power conversion efficiency was attributed to the high electrical conductivity of the graphene electrodes although they possess low electrocatalytic activity for tri-iodide reduction.

Further, the results showed that the DSSC based on CB40 composite exhibited maximum power conversion efficiency of 4.58% and fill factor of 0.56 with higher electrocatalytic activity than the graphene electrode. The achieved result is comparable to those shown by DSSCs using Pt and Solaronix carbon paste of 5.19 and 3.67 with fill factors 0.66 and 0.61, respectively. The low-cost, high conductivity and the porous structures of the introduced graphene and graphene/Carbon black counter electrodes make them potential candidates to replace the expensive platinum counter electrode.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

ELEKTROD BALAS BERASASKAN GRAFIN DAN KOMPOSIT GRAFIN/KARBON HITAM UNTUK SEL SURIA PEKA PEWARNA BEBAS PLATINUM

Oleh

ALI KHALIFA ABDGALIL

Jun 2021

Pengerusi : Professor Madya Suhaidi Shafie, PhD
Fakulti : Kejuruteraan

Elektrod kaunter memainkan peranan penting di dalam mekanisma Sel Pemeka Suria (DSSC). Selain peranannya dalam mengumpulkan elektron dari litar luar, ia juga berfungsi sebagai katalis pengurangan ion tri-iodida dalam elektrolit. Apabila pengurangan elektrolit berlaku dengan cepat, molekul pewarna teroksida akan dijana semula dengan cepat dan dengan itu meningkatkan prestasi sel. Biasanya, lapisan pemangkin platinum digunakan sebagai elektrod penghitung DSSC kerana kekonduksian yang tinggi, aktiviti elektro-katalitik, dan kadar tembus cahaya. Walau bagaimanapun, platinum adalah bahan yang mahal serta ia terhakis apabila terkena elektrolit redoks iodin/tri-iodida, dan oleh itu menghalang kestabilan jangka panjang sel. Untuk mencapai sasaran pengkomersialan DSSC, penyelidikan yang luas telah dilakukan untuk mengurangkan kos DSSC dengan memperkenalkan bahan yang efektif dan murah. Baru-baru ini, elektrod kaunter DSSC berasaskan bahan karbon menarik minat kerana kos rendah, kekonduksian tinggi, aktiviti katalitik, dan kestabilan kimia, yang menjadikan ianya alternatif yang berpotensi kepada platinum yang mahal untuk pengeluaran DSSC berskala besar. Penyelidikan ini dimulakan dengan pengoptimuman fotoanod TiO_2 yang dicetak secara *print-screen* dengan satu lapisan, dan kemudian bertujuan untuk mengkaji aplikasi praktikal elektrod kaunter grafena dan grafena / karbon hitam (G/Cb) yang murah dan berkesan untuk DSSC. Elektrod kaunter grafena disediakan hanya dengan meletakkan grafena yang telah diubahsuai ke atas substrat kaca bersalut fluorin timah oksida (FTO). Pelbagai pencirian dan analisis telah dilakukan untuk menyelidik kebolehlaksanaan filem grafena yang dicadangkan. Kajian ini memfokuskan kepada kesan panas terhadap prestasi filem grafena sebagai elektrod kaunter DSSC. Filem grafena dengan ketebalan kira-kira 25 µm yang dipanaskan pada suhu 300^0 C mempunyai lekatan yang baik dan kekonduksian elektrik yang tinggi dengan rintangan keping serendah 18.3 Ω / □ yang merupakan nilai yang amat meyakinkan berbanding dengan elektrod lain (seperti yang disimpan, 100^0 C, dan 200^0 C). Oleh itu, elektrod grafena yang dipanaskan pada suhu 300^0 C menunjukkan kecekapan penukaran foto ke elektrik 3.32% yang setanding dengan DSSC berasaskan

Pt sebanyak 4.48%. Kecekapan penukaran yang diperolehi disebabkan oleh kekonduksian elektrik yang tinggi dan struktur pori pada elektrod yang menyediakan tempat yang lebih berkesan untuk aktiviti elektro-katalitik. untuk berfungsi sebagai elektrod kaunter DSSC. Selain itu, enam elektrod kaunter komposit G/Cb berjaya dihasilkan dengan menggunakan enam pes berbeza yang dijadikandari serbuk grafena dan serbuk karbon berpelbagai. Pes dicetak pada kaca bersalut FTO dan kemudian dibakar di dalam tungku pada suhu 300^0 C. Sebagai perbandingan, pes karbon Solaronix yang telah di *screen-print* dan FTO-platinum digunakan sebagai rujukan elektrod kaunter. Pencirian dan pengukuran yang berbeza telah dikaji untuk setiap elektrod. Hasil kajian menunjukkan bahawa DSSC berdasarkan CB40 komposit menunjukkan kecekapan penukaran daya maksimum sebanyak 4.58% dan FF 0.56 dengan aktiviti elektro-katalitik yang baik. Hasil yang dicapai setanding dengan yang ditunjukkan oleh DSSC menggunakan Pt dan Solaronix pes karbon 5.19 dan 3.67 dengan faktor pengisian masing-masing 0.66 dan 0.61. Kos yang rendah, kekonduksian tinggi dan struktur berpori dari elektrod grafena dan grafena / karbon hitam yang diperkenalkan menjadikan ia calon yang berpotensi untuk menggantikan elektrod kaunter platinum yang mahal.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Suhaidi Shafie, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Janet Lim Hong Ngee, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Wan Zuha Wan Hassan, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Nowshad Amin, PhD
Professor
Faculty of Engineering
Universiti Kebangsaan Malaysia
(Member)

Mohamad Rusop, PhD
Professor
Nano SciTech Centre
Universiti Teknologi MARA
(Member)

Md Akhtaruzzaman, PhD
Associate Professor
Faculty of Engineering
Universiti Kebangsaan Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Signature: ______________________________
Name of Chairman of Supervisory Committee: Professor Dr. Suhaidi Shafie

Signature: ______________________________
Name of Member of Supervisory Committee: Professor Dr. Janet Lim Hong Ngee

Signature: ______________________________
Name of Member of Supervisory Committee: Professor Dr. Wan Zuha Wan Hassan

Signature: ______________________________
Name of Member of Supervisory Committee: Professor Dr. Nowshad Amin

Signature: ______________________________
Name of Member of Supervisory Committee: Professor Dr. Mohamad Rusop

Signature: ______________________________
Name of Member of Supervisory Committee: Associate Professor Dr. Md Akhtaruzzaman

TABLE OF CONTENTS

		Page
ABSTRACT		i
ABSTRAK		iii
ACKNOWLEDGEMENTS		v
APPROVAL		vi
DECLARATION		viii
LIST OF TABLES		xiii
LIST OF FIGURES		xiv
LIST OF ABBREVIATIONS		xvii

CHAPTER

1	**INTRODUCTION**		1
	1.1	Background	1
	1.2	Statement of the problems	2
	1.3	Objectives of the study	4
	1.4	Scope and limitations	4
	1.5	Thesis Organization	5
2	**LITERATURE REVIEW**		6
	2.1	Introduction	6
	2.2	Solar Energy and Developments of Photovoltaics	6
	2.3	DSSC's Structure and Working Principles	9
	2.4	DSSC applications	11
	2.5	Measurements and Parameters of DSSCs	11
	2.6	Development of DSSC components and structure	13
		2.6.1 Transparent conductive oxides (TCO-Substrates)	13
		2.6.2 Photoanode	14
		2.6.3 Sensitizing Dye	15
		2.6.4 Electrolytes	17
	2.7	Developments in DSSC Counter Electrode	20
		2.7.1 Conductive Polymers Counter Electrode	23
		2.7.2 Transition Metals Compounds (TMCs) Counter Electrodes	26
		2.7.3 Nanocomposites based DSSC Counter Electrode	30
		2.7.4 Carbonaceous materials based DSSC Counter Electrode	34
	2.8	DSSC Sealing	47
	2.9	Summary	47
3	**MATERIALS AND EXPERIMENTAL WORK**		49
	3.1	Introduction	49
	3.2	Materials and Chemicals	51
	3.3	Substrates Preparation	53
	3.4	Substrates Oxygen Plasma Treatment	54

3.5 TiO_2 Paste Synthesis 54
3.6 Photoanode $TiCl_4$ Blocking Layers 56
3.7 Photoanode Preparation 56
3.8 Dye Solution Preparation 57
3.9 Electrolyte Solution Preparation 57
3.10 Counter Electrodes Preparation 58
3.10.1 Platinum Counter Electrode 58
3.10.2 Graphene-based Counter Electrode 58
3.10.3 Graphene/Carbon black Composite-based Counter Electrode 59
3.10.4 Solaronix Carbon Paste-based Counter Electrode 60
3.11 DSSCs Assembly Procedure 61
3.12 Characterizations and Measurements of Counter Electrodes 61
3.12.1 Raman Spectroscopy 61
3.12.2 FESEM and (EDS) Characterizations 62
3.12.3 Atomic Force Microscopy AFM 62
3.12.4 UV-VIS-NIR Spectrophotometer 62
3.12.5 Fourier Transform Infrared Spectroscopy (FTIR) 63
3.12.6 Determination of Dye Loading 64
3.12.7 Thickness Measurement 64
3.12.8 Sheet Resistance Measurement 65
3.13 DSSC Performance Evaluation 66
3.13.1 Solar Simulator and the Solar Spectrum AM1.5G 66
3.13.2 Incident Photon to Current Conversion Efficiency (IPCE) 66
3.13.3 Electrochemical Impedance Spectroscopy (EIS) 67
3.13.4 Cyclic Voltammetry Measurement (CV) 68
3.14 Summary 68

4 RESULTS AND DISCUSSIONS 69
4.1 Introduction 69
4.2 Photoanode Optimization 69
4.2.1 FESEM and EDX Microstructure Characterizations 69
4.2.2 AFM Morphological Study 71
4.2.3 Determination of Dye Loading 72
4.2.4 Energy Band-gap of TiO2 Photoanode 77
4.2.5 TiO_2 Film Thickness Optimization 78
4.3 Graphene-based DSSC Counter Electrode 81
4.3.1 Graphene Electrodes Conductivity Measurement 81
4.3.2 Raman Spectroscopy of Graphene Counter Electrode 83
4.3.3 Atomic Force Microscopy Imaging for Graphene Counter Electrode 85
4.3.4 FESEM and EDX Analysis for Graphene Counter Electrode 86
4.3.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis 88
4.3.6 Cyclic Voltammetry Measurements for Graphene Counter Electrode 89

		4.3.7 EIS Characteristics for Graphene Counter Electrode	91
		4.3.8 Photovoltaic Performance of Graphene-CE Based DSSCs	92
	4.4	Graphene/Carbon Black Composites Counter Electrodes for DSSC	94
		4.4.1 G/Cb Composite Films Conductivity Measurement	95
		4.4.2 Raman Spectroscopy of G/Cb Composite Counter Electrodes	96
		4.4.3 FESEM and EDX for G/Cb Composite Counter Electrodes	97
		4.4.4 AFM Topological Study for G/Cb Composite Counter Electrodes	98
		4.4.5 Cyclic Voltammetry for G/Cb Composite Counter Electrodes	99
		4.4.6 EIS Characterization for G/Cb Composite Counter Electrodes	101
		4.4.7 Electrodes Performance Evaluation of DSSCs based on G/Cb Composite Counter	102
	4.5	Summary	105
5	**CONCLUSION AND FUTURE WORKS**		106
	5.1	Conclusion	106
	5.2	Future Works	107
REFERENCES			108
APPENDICES			128
BIODATA OF STUDENT			137
LIST OF PUBLICATIONS			138

LIST OF TABLES

Table		Page
2.1	Comparison in DSSC performance with different photoanode materials	14
2.2	The photovoltaic characteristics of the DSSCs constructed using counter electrodes of carbon materials -reported in related literature tested under one sun condition 100 $mW/cm2$	43
2.3	States of the art of efficiency records of different DSSCs from literature, tested under standard one sun condition at 100$mW/cm2$	48
3.1	List of chemicals and materials used in this research	52
3.2	Ingredients distribution of the composite pastes	60
4.1	Elemental distribution of the TiO_2 obtained from EDS analysis	71
4.2	N719 Dye concentrations and their absorption at wavelength 516 nm	75
4.3	Dye concentrations and their absorption at wavelength peak around 516 nm	76
4.4	J-V characteristics for DSSC using TiO_2 photoanodes of different thicknesses and Pt-based CE	78
4.5	Records for the thickness measurement and average thickness of the dried graphene films deposited on glass substrates	81
4.6	Sheet resistance (Rs) recoded values, resistivity, and conductivity corresponding values for as deposited and heated graphene films on glass substrates	82
4.7	Summary of Raman intensity ratios for the graphene films	85
4.8	Photovoltaic performance parameters of DSSCs fabricated with graphene-based counter electrodes	93
4.9	Recorded thickness measurements for the films deposited using G/Cb composites and Solaronix carbon pastes	95
4.10	Recorded sheet resistance measurements for G/Cb composites and Solaronix C-paste films deposited on glass substrates	95
4.11	EIS resultant parameters for DSSCs with different counter electrodes	101
4.12	Photovoltaic performance parameters of DSSCs fabricated with G/Cb composites, Solaronix carbon paste, and Pt counter electrodes	103

LIST OF FIGURES

Figure		Page
2.1	Chart of the highest confirmed conversion efficiencies obtained from solar cells of different photovoltaic technologies	8
2.2	Typical DSSC structure using Pt-based counter electrode	9
2.3	Schematic demonstration for DSSC working mechanism	10
2.4	Typical J-V characteristics curve of DSSC [34]	12
2.5	Chemical Structures of dye Materials: N3, N719 and Black Dye [122]	16
3.1	Sequential chart of DSSC device fabrication Process	50
3.2	(a) Schematic configuration for G/Cb composite- based DSSC, (b) photograph of fabricated DSSC with different views	51
3.3	Flowchart of substrates preparation	54
3.4	Schematic flowchart illustrating the process for $TiO2$ paste preparation	55
3.5	Fabricated $TiO2$ photoanode with 1 $cm2$ area on FTO substrates	57
3.6	Drop- casting of graphene films	59
3.7	Photograph for the G/Cb composite pastes	60
3.8	(a) Thickness profilometer with sample (b) Processing and display unit (c) Pictorial illustration for scans directions (d) Record display for TiO_2 film thickness	65
3.9	IPCE spectra obtained from N719 sensitized and Pt-based DSSC	67
4.1	(a) FESEM image of $TiO2$ film deposited on FTO (b) cross-sectional view	70
4.2	EDX result for the $TiO2$ photoanode	70
4.3	(a) 3D AFM topographic images of TiO_2 film annealed at 450^0C, and (b) 2D view AFM image of the same TiO_2 film	71
4.4	AFM image roughness measurements record for the TiO_2 annealed at 450^0C	72

4.5 Absorption spectra for the N719 dye-loaded $TiO2$films at different times 73

4.6 Absorption spectra of desorbed dye solutions from $TiO2$ films loaded at different times 74

4.7 Absorption spectra of diluted N719 dye solutions at different concentrations 75

4.8 N719 dye concentrations calibration curve (Red) with the fitted curve (Blue) 76

4.9 Tauc plot of bare TiO_2 photoanode annealed at 450^0C 77

4.10 Photovoltaic characteristics for DSSCs using TiO_2 photoanode with different thicknesses and Pt counter electrode, at (AM1.5G, 100 mW/cm^2) conditions 78

4.11 DSSC J-V characteristics as a function of TiO_2 photoanode thickness 80

4.12 The relationship between the heating temperature and the sheet resistance for the graphene films 83

4.13 Raman spectra for graphene fabricated films 84

4.14 AFM topological image of graphene film deposited on FTO-substrate 86

4.15 The morphological FESEM images for the graphene films 87

4.16 EDX Elemental distribution 88

4.17 FTIR spectra for multilayer graphene powder 89

4.18 The obtained CV voltograms of Pt/FTO and graphene CEs recorded in ($I-/I3-$) electrolyte in acetonitrile at scan rate of 20 mVs^{-1} 90

4.19 Nyquist plots of the symmetrical cells using Pt/FTO and graphene counter electrode heated at 300; inset is the equivalent fitting circuit 91

4.20 (a) J-V Characteristics for DSSCs using as-deposited and heated at (100, 200, and 300) ^{0}C graphene-CEs, compared with the DSSC using the standard Pt-CE, (b) the corresponding Dark J-V characteristics for the respective DSSCs 92

4.21 IPCE spectra for DSSCs fabricated using graphene counter electrode heated at 300 ^{0}C and Pt counter electrode 94

4.22 Staked Raman spectra (bottom to top) for the pure graphene (G100) and G/Cb composites CB20, CB40, CB60, and CB80 and pure carbon black CB100 counter electrodes 96

4.23 FESEM images for the pure graphene (G100), the G/Cb composites CB20, CB40, CB60, and CB80 and pure carbon black (CB100) counter electrodes 98

4.24 AFM micrographs (a–f) showing the surface topology and roughness of the pure graphene (G100), the G/Cb composites CB20, CB40, CB60, and CB80 and pure carbon black (CB100) counter electrodes, respectively 99

4.25 The obtained CV voltagrams of Pt/FTO compared with the pure graphene (G100), the G/Cb composites CB20, CB40, CB60, and CB80, pure carbon black (CB100) and Solaronix Carb-based counter electrodes, recorded in $(I-/I3-)$ electrolyte in acetonitrile at scan rate of 50 mVs^{-1} 99

4.26 Nyquist plots for the DSSCs fabricated using pure graphene (G100), the G/Cb composites CB20, CB40, CB60, and CB80, pure carbon black (CB100) and Solaronix C-based CEs compared with Pt-CE cell, Inset is the equivalent circuit 101

4.27 (a) J-V Characteristics for DSSCs using G/Cb Composites, compared with the DSSC using the Pt and Solaronix Carb CEs, (b) the corresponding Dark J-V characteristics for the respective DSSCs 102

4.28 IPCE spectra for DSSCs fabricated with G/Cb composites, Solaronix carbon paste, and Pt counter electrodes 104

LIST OF ABBREVIATIONS

AM	Air Mass
AFM	Atomic Force Microscopy
Cb	Carbon Black
CB	Conduction band
CE	Counter Electrode
CN	Carbon NanoTubes
CV	Cyclic Voltammetry
DSSC	Dye-Sensitized Solar Cell
FESEM	Field Emission Scanning Electron Microscope
FF	Fill Factor
EIS	Electrochemical Impedance Spectroscopy
EQE	External Quantum Efficiency
FTO	Fluorine doped Tin oxide
FWHM	Full Width at Half Maximum
G	Graphene
GNP	Graphene nanoplatelet
GO	Graphene Oxide
HOMO	Highest Occupied Molecular Orbital
HTMs	Hole- Transporting Materials
IPCE	Incident photon-to-current conversion efficiency
IQE	Internal Quantum Efficiency
ITO	Indium doped Tin Oxide
JSC	Short circuit current density

LH	Light Harvesting
LHE (λ)	Light harvesting efficiency at wavelength λ
LUMO	Lowest Unoccupied Molecular Orbital
MWCN	Multi-walled carbon nanotubes
PCE	Power Conversion Efficiency
PEDOT	Polypyrrole, poly(3,4-ethylenedioxythiophene)
PE	Polyethylene-terephthalate
Pt	Platinum
PV	Photovoltaics
rGO	reduced Graphene Oxide
SWCNT	Single-walled carbon nanotubes
tBA	tertiary Butyl Alcohol
TCO	Transparent Conducting Oxide
TW	Tera-Watt
UV-VIS-NIR	Ultraviolet-Visible-Near
VB	Valence Band
VOC	Open circuit potential
YW	Yotta Watts

CHAPTER 1

INTRODUCTION

1.1 Background

Since many decades, the World largely relies on traditional non-renewable energy sources the so-called fossil fuels in the forms of coal, oil and natural gas. Although, there are several problems related to fossil fuels sources like: depletion, increasing cost and environmental issues such as greenhouse gas emissions, pollution and their impact on weather and climate changes. These considerations have encouraged the researchers and industries for the development of sustainable, green, efficient and low-cost energy resources. There are different forms of renewable energy resources include nuclear energy, wind energy, hydroelectric energy, and solar energy. Although the nuclear power plants do not produce air pollution or have an impact on the global warming emissions and able to generate significant electricity, the probability of high risk is always last despite its tight safety regulations. Wind energy is usually used for operating turbines to generate electricity, but it requires widespread areal extent to produce significant amounts of energy. Furthermore, the unpredictable nature and the increase in maintenance cost of wind turbines hampers the wind energy to be the best solution for many counties. Nowadays, 16% of electrical power is obtained initially as converted energy from hydroelectric energy [1]. However, this might be not a real renewable source and is imperfect due to the high constructions cost and the probability of havoc and damages during natural disasters such as flooding and earthquakes.

The sun provides a constant and steady source of solar power over the year. Compared with all other renewable energy sources, solar energy is widely recognised as the most promising alternative for fossil energy sources due to its abundance and sustainability. Therefore, solar energy latches extensive attraction by researchers and industries.

Sunlight energy is converted directly into electricity using solar panels. Various types and generations of the solar cells were devolved during the years.

Solar cells can be classified into three generations: The first generation cells is a conventional crystalline silicon wafer-based cells (polysilicon and monocrystalline) are the dominant commercial solar cells technology. Si-based solar cells exhibit a complicated fabrication procedures and expensive producing equipment [2]. The second generation cells use semiconductors thin films technologies such as amorphous silicon, CIGS (Copper-Indium-Gallium-Selenium), and CdTe (Cadmium Telluride) cells. CdTe cells can compete the crystalline silicon cells in cost/watt. However, these technologies still exhibit some problems; CIGS cells suffer the toxicity and humidity issues [3]; CdTe solar cells encounter low production due to rare of Tellurium and toxicity of Cadmium [4].

Third generation solar cells include a number of thin film technologies and are still in research development stage and have not industrialized yet. Perovskite and Dye-Sensitized Solar Cells are known as the third generation solar cells. Despite their relatively low conversion efficiencies and low stability issues, there are lots of researches invested in these technologies as they promise to achieve the aim of producing low-cost, high-efficiency solar cells.

1.2 Statement of the problems

In 1991, Dye-Sensitized Solar Cell (DSSC) was demonstrated by O'Regan and Grätzel1 as a promising alternative to silicon solar cells with the potential of high conversion efficiency [5]. A typical DSSC structure consists first of dye-adsorbed TiO_2 mesoporous film coated on a transparent conductive oxide (TCO) glass as the photoanode. Second, an electrolyte system containing Iodide/Tri-iodide (I^-/I_3^-) redox couple in a proper mediator. Third, a counter electrode to provide faster bath for the electrons coming from the external circuit and capable to catalyse the reduction of tri-iodide ions [6]. The counter-electrode (CE) is one of the most critical components in the DSSC. It plays an important role to determine the device efficiency. Its function is to reduce the electrolyte redox species which regenerating the sensitizing dye after excitation and electron injection, or collection of the holes from the hole conducting material in a solid-state DSSC [7]. Typically, the Platinum-coated fluorine-doped tin oxide (FTO) glass is used for DSSC counter electrode, because of the Platinum's high electrical conductivity, excellent stability, and excellent catalytic activity toward the reduction of the tri-iodide ions in electrolyte system. Besides, its light reflection feature is significantly utilized [8],[9],[10].

However, platinum is an expensive noble material, and it requires special high-cost equipment for conventional deposition [11]. Moreover, The Pt-coated FTO is usually prepared through high-temperature hydrolysis processes or thermal platinization that are incompatible with flexible conducting substrates which inhibit their usability in many different applications. Furthermore, Pt corrodes in iodide-based electrolytes and generate PtI_4 especially when it is in the form of thin layer [12],[13],[14].

Finding new alternative conductive and catalytic materials to replace the expensive platinum is considered one direction to minimize the overall cost for the DSSC fabrication.

To overcome the issues related to the use of platinum in DSSC, extensive research work have been conducted to explore new conductive and catalytic materials as counter electrode. Thus, development of efficient, low cost and Pt-free DSSC.

Many different types of abundant and Pt-free CE materials have been investigated as DSSC counter electrode. For instance, transition metal oxides [11], sulfides [15], conducting polymers such as PEDOT:PSS and its composites [16], carbon materials such as carbon black [17], mesoporous carbon [18], carbon nanotubes (CNTs) [19], and graphene-based materials and its composites [20],[10],[21].

According to Velten et al., 2012 and Lee et al., 2008, the carbonaceous materials are considered excellent potential candidates for replacing Pt counter electrode in DSSC because they exhibit low cost, corrosion resistant, and electrically conductive [26],[21]. Carbon black (Cb) is a conductive material with high specific surface area, hence, it possess excellent catalytic activity for the reduction of tri-iodide ions in the electrolyte. Carbon materials usually exhibit active catalytic sites at their edges. Carbon black with its high surface area has many edges, providing more active sites than that of the highly structured carbon materials, such as graphene and carbon nanotubes [23]. Besides, carbon black composites exhibit comparable performance to platinum [24],[25],[26].

Very recently, various graphene and its composites have been materialized as potential catalysts for DSSC cathodes, due to graphene's high crystallinity, chemical, and thermal stability as well as the high electron mobility. So far, most of graphene CEs that have been used were fabricated primarily through reduction of graphene oxide, and they are mostly deposited on flexible substrates. This research is aimed to examine two different carbon materials as DSSC counter electrodes for the reduction of (I_3^-) species. First, examining the pure and high crystalline conductive graphene dispersion as counter electrode for DSSC. The high electrical conductivity and crystallinity facilitate a production of high current density and voltage. Furthermore, in order to enhance the catalytic activity of the graphene electrode, another investigation is to combine the high crystalline conductive graphene and carbon black materials in different G/Cb composites.

The proposed composites might provide high conductivity from both materials, especially from graphene, and also a good catalytic activity from carbon black. All proposed materials possess a range of fascinating properties in terms of conductivity, excellent adhesion and a range of electrochemical activity. The most interestingly, graphene dispersion and the G/Cb composites shows porous nanoplatelets microstructure.

This porous structure provide many catalytic reduction sites for reducing tri-iodide (I_3^-) as well as the deep penetration of electrolyte [8]. Easy casting techniques (drop casting and screen printing) are used to deposit the proposed materials on FTO-coated glass. In addition, the DSSC fabrication process should be optimized in order to achieve the aimed results.

1.3 Objectives of the study

The purpose of this study is to investigate two different carbon materials as candidates to replace the expensive platinum used for (I^-/I_3^-)-based DSSC counter electrodes. This study aims to introduce two different low-cost and effective carbon materials for DSSC counter electrode with retaining high power conversion efficiency. In this work, high crystallinity graphene dispersion, and other six (6) different Graphene/ Carbon black composites are investigated as counter electrodes in DSSCs. However, all introduced materials are compared with the standard Pt-coated FTO and the commercial Solaronix Carbon paste made counter electrodes. To accomplish the aim of this project, there are set of objectives which have to be resolved include:

1. To study the electrical properties of the films deposited using the high crystallinity graphene dispersion and G/Cb composites as conductive materials to be applicable for DSSC counter electrode.
2. To examine the electrocatalytic activity of the graphene dispersion-based electrode and G/Cb composites as DSSC counter electrode for the reduction of tri-iodide (I_3^-) ions in the redox couple.
3. To suggest the most effective fabrication procedure of the Iodine-mediated DSSCs using the graphene dispersion-based and the G/Cb composites as counter electrodes for high DSSC performance.

1.4 Scope and limitations

This research work does not seek to address the problems of graphene or carbon black synthesis methods. Due to limitation of screen-printing mesh size and for the purpose of easy-handling, the area for both photoanode and counter electrode of the DSSC devices was initially fabricated as 1 cm^2. After that, a black metal mask with aperture of 0.25 cm^2 was always placed onto each photoanode during the cell photovoltaic test to form the accurate active area and to avoid the light diffusion issues [27]. However, the solar simulator is calibrated before measurement. As there are different types of electrolytes, this research work focuses on the Iodine-mediated DSSC fabrication and characterization based on the standard platinum counter electrode and the proposed graphene and G/Cb composite-based counter electrodes. However, another, commercial (Solaronix carbon paste) counter electrode is used for comparison. This research concerns only the standard N719 sensitized-TiO_2 photoanode. In this research, although the photoanode fabrication procedure is optimized and characterized, all parameters related to the photoanode are still out of the research scope. Moreover, this research covers neither solid-state nor flexible dye-sensitized solar cells.

1.5 Thesis Organization

This project thesis is organized in five chapters as per the followings:

Chapter one is the introductory part that discusses the background of the energy resources and the photovoltaic devices focusing on the third generation DSSC technology. It also highlights the research problem statement. In addition to that, the general research aims and the specific objectives, research scope, and limitations, as well as the thesis outlines have been presented.

Chapter two introduces a background about energy demand and the photovoltaics technology developments. Also, it describes the structure and work principle of the dye-sensitized solar cells. Then, it reviews the previous studies related to development in dye-sensitized solar cell components. Mainly, it addresses the development in the counter electrode materials.

Chapter three initially introduces the materials and methods used in the dispersion modification and pastes synthesis. Furthermore, it demonstrates the DSSC components preparation processes, DSSC complete assembly. The characterization techniques and measurements methods used in the research are explained and discussed in this chapter.

Chapter four presents and discusses all the results achieved from the research study.

Chapter five briefly highlights the research conclusion and findings. It also presents a possible recommendation for future studies.

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