

ENHANCEMENT OF TITANIUM DIOXIDE (TiO<sub>2</sub>) DYE-SENSITIZED SOLAR  
CELLS (DSSCs) PERFORMANCE WITH INCORPORATION OF REDUCED  
GRAPHENE OXIDE (rGO)

AZMAN BIN TALIB

A thesis submitted in  
fulfillment of the requirement for the award of the  
Doctor of Philosophy in Electrical Engineering

Faculty of Electrical and Electronic Engineering  
Universiti Tun Hussein Onn Malaysia

MARCH 2022

Special dedication to

My lovely wife and precious children;

Norazlina Binti Ahmad

Muhammad Syamil Adha Bin Azman

Nurul Syuhaidah Binti Azman

Nur Syazwani Binti Azman

Muhammad Syafiq Azri Bin Azman

Nurul Ain Syahira Binti Azman



PTTA UTHM  
PERPUSTAKAAN TUNKU TUN AMINAH

## ACKNOWLEDGEMENT

I would like to express my gratitude to Allah with His permission I can finish my project successfully. Alhamdulillah, His Willingness has made it possible for me as the author to accomplish my research.

Special thanks dedicated to my supervisor Assoc. Prof. Dr. Mohd. Khairul Bin Ahmad for guiding this research at every stage with clarity, spending much time to discuss and help with this research, and that priceless gift of getting done by sharing his valuable ideas as well as his knowledge. Also thank you so much to my co-supervisor Assoc. Prof. Dr. Fariza Binti Mohamad for her guidance and discussion that really helped me in completing this research.

I am very greatly indebted to the Microelectronics and Nanotechnology - Shamsudin Research Centre (MiNT-SRC) family members and Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia for providing excellent lab facilities that make this work possible. Not forgotten to the expert in-charged person especially Miss Faezahana Binti Mohkhter, Mr. Ahmad Nasrul Bin Mohamed and Mr. Mohd. Azwadi Bin Omar that really helped my research runs smoothly.

I also want to show my gratefulness to the Ministry of High Education on the financial support through the scholarship and privileges provided in Hadiah Latihan Persekutuan (HLP) programme in furthering my study in the doctorate level.

To my wife and lovely children, thank you for your love, time, supporting and understanding throughout the duration on completing this research. Also thanks to my colleagues for their support and encouragement me to make this research successful.

## ABSTRACT

The purpose of this thesis is to investigate the structural, optical and electrical properties of titanium dioxide ( $\text{TiO}_2$ ) dye-sensitized solar cells (DSSCs) with the incorporation of reduced graphene oxide (rGO). In this experiment, rGO from electrochemical exfoliation, was deposited onto few fluorine-doped tin-oxide (FTO) substrat through spray pyrolysis deposition (SPD) method with different rGO volumes. Then, all the fabricated FTOs went through rutile-phase  $\text{TiO}_2$  (r- $\text{TiO}_2$ ) with hydrothermal synthesis. From DSSCs analysis, 0.50 mL of rGO volume exhibited the best photovoltaic (PV) performance with the efficiency of 2.61% and open-circuit voltage of 0.70 V. The successful synthesis of rGO, incorporated with  $\text{TiO}_2$  was confirmed using Raman spectroscopy. The analysis of the samples was done using X-ray diffraction, field emission scanning electron microscopy, ultraviolet-visible spectrophotometry, and incident photon-to-carrier conversion efficiency spectra. Then, another rGO which was produced through Hummers method, was incorporated into anatase-phase  $\text{TiO}_2$  (a- $\text{TiO}_2$ ) as nanocomposite (NC) mixture. After that, through SPD method, the NC mixture was deposited onto few FTOs. The a- $\text{TiO}_2$  was produced by adding TKC-302 into  $\text{TiO}_2$  P25 powder. The NC mixture samples significantly contributed towards the improvement of efficiency, when compared with samples without rGO. When 2 mL of rGO was added into a- $\text{TiO}_2$ , PV performance achieved the highest efficiency of 3.15% and current density of 5.98  $\text{mA}/\text{cm}^2$ . Finally, the combination of rGO and a- $\text{TiO}_2$  NC mixture, was overlayers onto r- $\text{TiO}_2$ . The 2 mL of rGO/a- $\text{TiO}_2$  NC mixture which was deposited through SPD onto r- $\text{TiO}_2$ , exhibited the best PV performance with the highest efficiency of 5.72% and the current density of 10.37  $\text{mA}/\text{cm}^2$ . The rGO acted as an important material, to maximise the photogenerated electrons of photo-induced charge carriers. The photogenerated electrons from dyes transferred through r- $\text{TiO}_2$ , effectively traveled out to the circuit load, which underwent recombination with holes in the solar cells with enhancement of rGO functions.

## ABSTRAK

Kandungan tesis ini adalah bagi menyiasat ciri-ciri struktur, optikal dan elektrik bagi titanium dioksida ( $TiO_2$ ) dye-sensitized solar cells (DSSCs) dengan gabungan reduced graphene oxide (rGO). Dalam eksperimen ini, rGO hasil dari pengelupasan elektrokimia, disebarkan ke atas beberapa keping fluorine-doped tin-oxide (FTO) dengan kaedah semburan dengan isipadu rGO yang berlainan. Kemudian, kesemua FTO tersebut akan melalui proses sintesis hidrotermal fasa-rutil titanium dioksida ( $r-TiO_2$ ). Dari analisis DSSCs, sampel rGO dengan 0.50 mL menunjukkan prestasi fotovoltai (PV) terbaik dengan kecekapan 2.61% dan voltan litar-terbuka 0.70 V. Kejayaan mensintesis rGO, dan digabungkan bersama dengan  $TiO_2$  ditentukan menggunakan spektroskopi Raman. Analisis ke atas sampel pula menggunakan difraksi sinar-X (XRD), mikroskop elektron pengimbas pelepasan medan (FE-SEM), sinar ultraungu (UV-Vis) spektrofotometri, dan spektrum kecekapan penukaran foton ke pembawa kejadian (IPCE). Kemudian, rGO lain yang disintesis melalui kaedah Hummers, digabungkan ke dalam larutan fasa-anates  $TiO_2$  ( $a-TiO_2$ ) sebagai campuran nanokomposit (NC), dan disebarkan ke atas beberapa keping FTO. Larutan  $a-TiO_2$  tersebut dihasilkan daripada serbuk  $TiO_2$  P25 yang dicampurkan dengan TKC-302. Campuran NC tersebut memberikan kesan peningkatan pada kecekapan PV sel, berbanding tanpa menggunakan rGO. Isipadu 2 mL rGO yang ditambahkan kepada  $a-TiO_2$ , menghasilkan kecekapan PV tertinggi iaitu 3.15% dan ketumpatan arus 5.98 mA/cm<sup>2</sup>. Dan akhir sekali, kombinasi campuran rGO dan  $a-TiO_2$  NC, yang disebarkan ke atas struktur  $r-TiO_2$  NS. Isipadu 2 mL campuran rGO/ $a-TiO_2$  NC, disebarkan ke atas struktur  $r-TiO_2$ , menghasilkan prestasi fotovoltai terbaik dengan kecekapan penukaran tertinggi 5.72% dan ketumpatan arus 10.37 mA/cm<sup>2</sup>. rGO bertindak sebagai bahan gabungan ke dalam  $a-TiO_2$ , memaksimumkan bilangan elektron pembawa cas. Membolehkan elektron dari dye dipindahkan melalui  $r-TiO_2$  NS, bergerak secara efektif ke beban, dengan menghalang penggabungan semula dengan lubang di sel suria dengan meningkatnya fungsi rGO.

## CONTENTS

<b>TITLE</b>	<b>i</b>
<b>DECLARATION</b>	<b>ii</b>
<b>DEDICATION</b>	<b>iii</b>
<b>ACKNOWLEDGEMENT</b>	<b>iv</b>
<b>ABSTRACT</b>	<b>v</b>
<b>ABSTRAK</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>xii</b>
<b>LIST OF FIGURES</b>	<b>xiv</b>
<b>LIST OF SYMBOLS AND ABBREVIATIONS</b>	<b>xx</b>
<b>LIST OF APPENDICES</b>	<b>xxiii</b>
<b>CHAPTER 1 INTRODUCTION</b>	<b>1</b>
1.1 Introduction	1
1.2 Research background	3
1.3 Problem statement	5
1.4 Objectives of the research	7
1.5 Scope of the research	7
1.6 Contribution of the research	8
1.7 Thesis outline	8

<b>CHAPTER 2</b>	<b>LITERATURE REVIEW</b>	<b>10</b>
2.1	Introduction	10
2.2	Fluorine-doped tin oxide glass substrate	10
2.3	Titanium dioxide	12
2.4	Hydrothermal synthesis	14
2.5	Spray Pyrolysis Deposition	16
2.6	Dyes	17
2.7	Electrolyte	20
2.8	Counter electrode	21
2.9	Dye-sensitized solar cells (DSSCs)	22
2.10	Reduced graphene oxide (rGO)	24
2.11	Research gap	26
<b>CHAPTER 3</b>	<b>METHODOLOGY</b>	<b>28</b>
3.1	Introduction	28
3.1.1	FTO substrate cleaning	28
3.1.2	The common fabrication process of r-TiO <sub>2</sub> NRs/NFs thin film on FTO substrate using hydrothermal synthesis method	30
3.1.3	Sample characterization	32
3.1.4	Solar simulator measurement	33
3.1.5	Properties characterization	34
3.2	Hydrothermal synthesis of r-TiO <sub>2</sub> NRs/NFs with various TBOT precursor volume	35
3.2.1	Preparation for the hydrothermal synthesis	35
3.3	Hydrothermal synthesis of r-TiO <sub>2</sub> NRs/NFs with various reaction time	37
3.3.1	Preparation for the hydrothermal synthesis	38

3.3.2 Solar simulator measurement	39
3.4 Hydrothermal synthesis of r-TiO <sub>2</sub> NS direct growth on FTO/rGO thin film	40
3.4.1 Preparation of rGO by using electrochemical exfoliation method and reducing process	40
3.4.2 Deposition of rGO layer onto FTO/rGO thin film	42
3.4.3 Preparation for the hydrothermal synthesis	43
3.4.4 Solar simulator measurement	44
3.5 Effect of various rGO/a-TiO <sub>2</sub> NC mixture volume, SPD onto FTO substrate	45
3.5.1 Preparation of rGO via improved Hummers method and reducing process	46
3.5.2 Preparation of a-TiO <sub>2</sub> NPs solution	47
3.5.3 Preparation of NC mixture of rGO incorporated into a-TiO <sub>2</sub> NPs solution	47
3.5.4 Deposition of pure a-TiO <sub>2</sub> and rGO/a-TiO <sub>2</sub> NC mixture, SPD onto FTO substrate	47
3.5.5 Solar simulator measurement	49
3.6 Effect of deposition various a-TiO <sub>2</sub> NPs volume, overlayers onto r-TiO <sub>2</sub> NS	49
3.6.1 Preparation for the hydrothermal synthesis	50
3.6.2 Preparation of a-TiO <sub>2</sub> NPs solution	50
3.6.3 Deposition of various a-TiO <sub>2</sub> NPs volume, overlayers onto r-TiO <sub>2</sub> NS	51
3.6.4 Solar simulator measurement	52
3.7 Effect of various rGO volume incorporate into a-TiO <sub>2</sub> NPs, overlayers onto r-TiO <sub>2</sub> NS	53
3.7.1 Preparation for hydrothermal synthesis	54
3.7.2 Preparation of rGO	54





3.7.3 Preparation of a-TiO <sub>2</sub> NPs solution	54
3.7.4 Preparation of rGO incorporated into a-TiO <sub>2</sub> NPs solution	54
3.7.5 Deposition of rGO/a-TiO <sub>2</sub> NC mixture onto r-TiO <sub>2</sub> NS	54
3.7.6 Solar simulator measurement	56
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>	<b>58</b>
4.1 Introduction	58
4.2 Hydrothermal synthesis of r-TiO <sub>2</sub> NRs/NFs with various TBOT precursor volume	58
4.2.1 Structural analysis	58
4.2.2 Surface morphology	61
4.2.3 Optical properties	64
4.2.4 Electrical properties	67
4.3 Hydrothermal synthesis of r-TiO <sub>2</sub> NRs/NFs with various reaction time	68
4.3.1 Structural analysis	68
4.3.2 Surface morphology	70
4.3.3 Optical properties	76
4.3.4 Electrical properties	78
4.4 Hydrothermal synthesis of r-TiO <sub>2</sub> NS direct growth on FTO/rGO thin film	82
4.4.1 Structural analysis	82
4.4.2 Surface morphology	84
4.4.3 Optical properties	86
4.4.4 Electrical properties	87
4.5 Effect of various rGO/a-TiO <sub>2</sub> NC mixture volume, SPD onto FTO substrates	90
4.5.1 Structural analysis	90
4.5.2 Surface morphology	97



4.5.3 Optical properties	100
4.5.4 Electrical properties	103
4.6 Effect of deposition various a-TiO <sub>2</sub> NPs volume, overlayered onto r-TiO <sub>2</sub> NS thin film	107
4.6.1 Structural analysis	107
4.6.2 Surface morphology	109
4.6.3 Optical properties	110
4.6.4 Electrical properties	111
4.7 Effect of various rGO volume incorporate into a-TiO <sub>2</sub> NPs, overlayered onto r-TiO <sub>2</sub> NS	114
4.7.1 Structural analysis	114
4.7.2 Surface morphology	117
4.7.3 Optical properties	118
4.7.4 Electrical properties	119
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATIONS</b>	<b>122</b>
5.1 Introduction	122
5.2 Conclusion	122
5.3 Recommendation	124
<b>REFERENCES</b>	<b>125</b>
<b>APPENDICES</b>	<b>146</b>



PTTA UTHM  
PERPUSTAKAAN TUN AMINAH

## LIST OF TABLES

2.1	The efficiency of morphology combination in solar cells fabrication.	16
2.2	I-V measurement of DSSCs based on various types of natural dyes [102].	20
2.3	The DSSCs efficiency of TiO <sub>2</sub> phases with rGO incorporation fabrication.	27
3.1	Hydrothermal synthesis with various TBOT precursor volume.	36
3.2	The label of the prepared samples under various TBOT volume.	36
3.3	Hydrothermal synthesis with various reaction time.	38
3.4	Label of the prepared samples at various reaction time.	38
3.5	Label of r-TiO <sub>2</sub> NS samples direct growth on FTO/rGO substrate.	43
3.6	Label of pure a-TiO <sub>2</sub> and rGO/a-TiO <sub>2</sub> NC mixture samples on the FTO substrate.	48
3.7	Label of a-TiO <sub>2</sub> NPs volume samples, overlayered onto r-TiO <sub>2</sub> NS.	52
3.8	Label of rGO/a-TiO <sub>2</sub> NC mixture samples onto r-TiO <sub>2</sub> NS.	55
4.1	Predominant crystallite size variant under different TBOT volume.	61
4.2	The size of r-TiO <sub>2</sub> NRs/NFs growth using various TBOT volume.	64
4.3	Values of the energy bandgap of samples (a) TB3 (b) TB4 (c) TB5 and (d) TB6.	66
4.4	Electrical properties of samples for various TBOT volume.	67
4.5	Full-width Half-Maximum and crystallite size of sample fabricated with different reaction time.	70
4.6	The size of TiO <sub>2</sub> growth under various hydrothermal reaction time.	71
4.7	The EDX data for samples prepared at various reaction time.	76
4.8	Values of the energy bandgap of RT5, RT10, RT15, RT20 and RT25 prepared samples.	77

4.9	Electrical properties of prepared samples at various reaction time.	79
4.10	Photovoltaic parameters of DSSCs with different TiO <sub>2</sub> reaction time.	80
4.11	Structural parameters calculated from XRD patterns for r-TiO <sub>2</sub> NS direct growth on FTO/rGO.	84
4.12	EDX data for prepared samples at different rGO volume for r-TiO <sub>2</sub> NS direct growth on FTO/rGO.	86
4.13	Photovoltaic parameters of DSSCs with different rGO volume of r-TiO <sub>2</sub> NS direct growth on FTO/rGO.	88
4.14	Values of the energy bandgap of various rGO/a-TiO <sub>2</sub> NC mixture.	103
4.15	Photovoltaic parameters DSSCs various rGO/a-TiO <sub>2</sub> NC mixture volume.	104
4.16	Photovoltaic parameters DSSCs of highest efficiency sample without rGO, and with rGO incorporation.	107
4.17	Photovoltaic parameters of DSSCs of various a-TiO <sub>2</sub> NPs volume overlayers onto r-TiO <sub>2</sub> NS thin film.	111
4.18	Photovoltaic parameters of DSSCs of various rGO volume incorporated into a-TiO <sub>2</sub> NPs, overlayers onto r-TiO <sub>2</sub> NS.	119



## LIST OF FIGURES

1.1	Generations of solar cells technology [5].	2
2.1	Ball and stick of the structure of SnO <sub>2</sub> [48].	11
2.2	The schematic drawing of the SnO <sub>2</sub> film at an early stage formed by the SPD process [51].	12
2.3	Unit cells of the TiO <sub>2</sub> modifications rutile, brookite and anatase (from left to right) [56].	13
2.4	Spray pyrolysis deposition method [90].	17
2.5	Molecular structure of several metal-complex dye with efficiency [97].	18
2.6	Working mechanism of metal-free organic dye. Do and Acc are denoting donor and acceptor, respectively [98].	19
2.7	Structure and the viscosity of several ionic liquids [104].	21
2.8	Layers of DSSCs components [115].	23
2.9	A schematic diagram of a DSSCs showing the principles of operation [71].	24
2.1	Fullerene (0D), nanotube (1D), graphene (2D), and graphite (3D) (from left to right) [120], [121].	26
2.11	The derivatives of graphene.	26
3.1	Process for experiments synthesis and characterization.	29
3.2	FTO substrate cleaning procedure.	30
3.3	Teflon-lined stainless steel autoclave.	31
3.4	Illustration of the FTO substrate leans against the container wall.	32
3.5	Photoanode immersed in N719 dye.	33
3.6	Pt CE and photoanode clamped for efficiency measurement under solar simulator tester.	34
3.7	Chart of various TBOT precursor volume.	35

3.8	Hydrothermal synthesis with various TBOT precursor volume.	37
3.9	Chart of various reaction time.	37
3.1	Hydrothermal synthesis with various reaction time.	39
3.11	Illustration of r-TiO <sub>2</sub> NRs/NFs test circuit measurement.	39
3.12	Chart for hydrothermal synthesis of r-TiO <sub>2</sub> NS direct growth on FTO/rGO substrate.	40
3.13	Electrochemical exfoliation process.	41
3.14	GO reducing process to rGO by hydrazine hydrate.	42
3.15	Hydrothermal synthesis of r-TiO <sub>2</sub> NS direct growth on FTO/rGO substrate.	44
3.16	Illustration of r-TiO <sub>2</sub> NS direct growth on FTO/rGO test circuit measurement.	45
3.17	Chart of various rGO/a-TiO <sub>2</sub> NC mixture volume, onto the FTO substrate.	46
3.18	Various rGO/a-TiO <sub>2</sub> NC mixture volume, SPD onto FTO substrate.	48
3.19	Illustration of rGO/a-TiO <sub>2</sub> NC test circuit measurement.	49
3.2	Chart of various a-TiO <sub>2</sub> NPs volume, overlayered onto r-TiO <sub>2</sub> NS.	50
3.21	Various a-TiO <sub>2</sub> NPs volume, overlayered onto r-TiO <sub>2</sub> NS.	51
3.22	Illustration of a-TiO <sub>2</sub> NPs overlayered onto r-TiO <sub>2</sub> NS test circuit measurement.	52
3.23	Chart of various rGO volume incorporated into a-TiO <sub>2</sub> NPs, overlayered on r-TiO <sub>2</sub> NS.	53
3.24	Various rGO/a-TiO <sub>2</sub> NC mixture volume, overlayered onto r-TiO <sub>2</sub> NS.	55
3.25	Illustration of rGO/a-TiO <sub>2</sub> NC overlayered onto r-TiO <sub>2</sub> NS solar simulator circuit.	56
3.26	Schematic diagram of rGO/a-TiO <sub>2</sub> NC overlayered onto r-TiO <sub>2</sub> NS DSSCs.	57
4.1	XRD peak patterns of r-TiO <sub>2</sub> NRs/NFs prepared using (a) TB3 (b) TB4 (c) TB5 and (d) TB6 of TBOT volume.	59
4.2	FE-SEM images of TB3 under (a) 5,000x (b) 50,000x magnification (c) cross-section view, and (d) EDX spectrum.	62

4.3	FE-SEM images of TB4 under (a) 5,000x (b) 50,000x magnification (c) cross-section view, and (d) EDX spectrum.	63
4.4	FE-SEM images of TB5 under (a) 5,000x (b) 30,000x magnification (c) cross-section view, and (d) EDX spectrum.	63
4.5	FE-SEM images of TB6 under (a) 5,000x (b) 50,000x magnification (c) cross-section view, and (d) EDX spectrum.	64
4.6	UV-Vis spectra of r-TiO <sub>2</sub> samples (a) TB3 (b) TB4 (c) TB5 and (d) TB6.	65
4.7	Bandgap estimation of (a) TB3, (b) TB4, (c) TB5, and (d) TB6 prepared samples.	66
4.8	XRD patterns of the as-synthesis samples (a) RT5 (b) RT10 (c) RT15 (d) RT20 and (e) RT25 at 150 °C, respectively.	69
4.9	FE-SEM images of r-TiO <sub>2</sub> NRs/NFs synthesis at 5 hours under (a) 5,000x (b) 30,000x magnification (c) cross-section view, and (d) EDX spectrum.	73
4.10	FE-SEM images of r-TiO <sub>2</sub> NRs/NFs synthesis at 10 hours under (a) 5,000x (b) 30,000x magnifications (c) cross-section view, and (d) EDX spectrum.	73
4.11	FE-SEM images of r-TiO <sub>2</sub> NRs/NFs synthesis at 15 hours under (a) 5,000x (b) 30,000x magnification (c) cross-section view, and (d) EDX spectrum.	74
4.12	FE-SEM images of r-TiO <sub>2</sub> NRs/NFs synthesis at 20 hours under (a) 5,000x (b) 30,000x magnification (c) cross-section view, and (d) EDX spectrum.	74
4.13	FE-SEM images of r-TiO <sub>2</sub> NRs/NFs synthesis at 25 hours under (a) 5,000x (b) 30,000x magnification (c) cross-section view, and (d) EDX spectrum.	75
4.14	UV-Vis spectra of (a) RT5 (b) RT10 (c) RT15 (d) RT20 and (e) RT25 of r-TiO <sub>2</sub> thin film.	76
4.15	Bandgap estimation of (a) RT5, (b) RT10, RT15, RT20 and RT25 prepared samples.	78
4.16	J-V characteristics of the DSSCs made with TiO <sub>2</sub> photoanodes of different reaction time.	80

4.17	The IPCE spectra of DSSCs made with TiO <sub>2</sub> thin film of different reaction time.	81
4.18	Raman spectra of rGO.	82
4.19	XRD patterns of FTO/rGO/TiO <sub>2</sub> thin film synthesis (a) bare FTO substrate (b) FT_Ref (c) FRT_0.25 (d) FRT_0.50 (e) FRT_0.75 and (f) FRT_1.00.	83
4.20	FE-SEM pictures of the samples prepared (a) FRT_0.25 (b) FRT_0.50 (c) FRT_0.75 and (d) FRT_1.00 (e) FT_Ref	85
4.21	UV-Vis spectra of the (a) FT_Ref (b) FRT_0.25 (c) FRT_0.50 (d) FRT_0.75 and (e) FRT_1.00.	87
4.22	J-V characteristics of the DSSCs (a) FT_Ref (b) FRT_0.25 (c) FRT_0.50 (d) FRT_0.75 and (e) FRT_1.00.	88
4.23	The IPCE spectra of DSSCs (a) FRT_0.25 (b) FRT_0.50 (c) FRT_0.75 (d) FRT_1.00 and (e) FT_Ref.	90
4.24	Raman spectra of (a) a-T_1, (b) a-T_2, (c) a-T_3 and (d) a-T_4.	91
4.25	Raman intensity of the first Eg(1) mode of (a) a-T_1, (b) a-T_2, (c) a-T_3, and (d) a-T_4.	92
4.26	Raman spectra of Raman shift (100-800 cm <sup>-1</sup> ) (a) R/a-T_1, (b) R/a-T_2, (c) R/a-T_3, and (d) R/a-T_4.	93
4.27	Raman spectra of Raman shift (1000-3000 cm <sup>-1</sup> ) (a) R/a-T_1, (b) R/a-T_2, (c) R/a-T_3, and (d) R/a-T_4.	94
4.28	Raman intensity of the first Eg mode of (a) R/a-T_1, (b) R/a-T_2, (c) R/a-T_3, and (d) R/a-T_4.	95
4.29	ID/IG ratio and IG/I2D ratio of a-T and R/a-T samples respectively versus volume spray.	96
4.30	XRD patterns of (a) a-T_1, (b) a-T_2, (c) a-T_3, (d) a-T_4, (e) R/a-T_1, (f) R/a-T_2, (g) R/a-T_3, and (h) R/a-T_4.	97
4.31	FE-SEM images of cross-section view of (a) a-T_1, (b) a-T_2, (e) R/a-T_1, and (f) R/a-T_2 under 15,000x magnification, (c) a-T_3 and (g) R/a-T_3 under 10,000x magnification, (d) a-T_4, and (h) R/a-T_4 under 7,000x magnification.	99



4.32	UV-Vis spectra of the N719-loaded (a) a-T <sub>1</sub> , (b) a-T <sub>2</sub> , (c) a-T <sub>3</sub> , (d) a-T <sub>4</sub> , (e) R/a-T <sub>1</sub> , (f) R/a-T <sub>2</sub> , (g) R/a-T <sub>3</sub> , and (h) R/a-T <sub>4</sub> .	100
4.33	Bandgap estimation of the N719-loaded (a) a-T <sub>1</sub> , (b) a-T <sub>2</sub> , (c) a-T <sub>3</sub> , (d) a-T <sub>4</sub> , (e) R/a-T <sub>1</sub> , (f) R/a-T <sub>2</sub> , (g) R/a-T <sub>3</sub> , and (h) R/a-T <sub>4</sub> .	102
4.34	J-V characteristics of the DSSCs (a) a-T <sub>1</sub> , (b) a-T <sub>2</sub> , (c) a-T <sub>3</sub> , (d) a-T <sub>4</sub> (e) R/a-T <sub>1</sub> , (f) R/a-T <sub>2</sub> , (g) R/a-T <sub>3</sub> and (h) R/a-T <sub>4</sub> .	103
4.35	The IPCE spectra of DSSCs (a) a-T <sub>1</sub> , (b) a-T <sub>2</sub> , (c) a-T <sub>3</sub> , (d) a-T <sub>4</sub> , (e) R/a-T <sub>1</sub> , (f) R/a-T <sub>2</sub> , (g) R/a-T <sub>3</sub> , and (h) R/a-T <sub>4</sub> .	106
4.36	J-V characteristics of highest efficiency sample without rGO (a) a-T <sub>4</sub> , and with rGO incorporation (b) R/a-T <sub>4</sub> .	106
4.37	XRD patterns of thin film synthesis (a) a-r-T <sub>4</sub> , (b) a-r-T <sub>3</sub> , (c) a-r-T <sub>2</sub> , (d) a-r-T <sub>1</sub> , (e) FT_Ref and (f) a-TiO <sub>2</sub> NPs on FTO.	108
4.38	FE-SEM images of cross-section view of (a) a-r-T <sub>1</sub> , (b) a-r-T <sub>2</sub> , (c) a-r-T <sub>3</sub> , and (d) a-r-T <sub>4</sub> under 3,000x magnifications.	109
4.39	UV-Vis spectra of the N719-loaded (a) a-r-T <sub>4</sub> , (b) a-r-T <sub>3</sub> , (c) a-r-T <sub>2</sub> , (d) a-r-T <sub>1</sub> and (e) FT_Ref.	110
4.40	J-V characteristics of the DSSCs (a) a-r-T <sub>1</sub> , (b) a-r-T <sub>2</sub> , (c) a-r-T <sub>3</sub> , (d) a-r-T <sub>4</sub> and (e) FT_Ref.	112
4.41	The IPCE spectra of DSSCs (a) a-r-T <sub>1</sub> , (b) a-r-T <sub>2</sub> , (c) a-r-T <sub>3</sub> , (d) a-r-T <sub>4</sub> and (e) FT_Ref.	113
4.42	Raman spectra of (a) RT <sub>1</sub> , (b) RT <sub>2</sub> , (c) RT <sub>3</sub> , (d) RT <sub>4</sub> and (e) FT_Ref.	114
4.43	XRD patterns of thin film synthesis (a) RT <sub>4</sub> , (b) RT <sub>3</sub> , (c) RT <sub>2</sub> , (d) RT <sub>1</sub> and (e) FT_Ref.	116
4.44	FE-SEM images of cross-section view of (a) RT <sub>1</sub> , (b) RT <sub>2</sub> , (c) RT <sub>3</sub> , and (d) RT <sub>4</sub> under 3,300x magnifications.	117
4.45	UV-Vis spectra of the N719-loaded (a) RT <sub>1</sub> , (b) RT <sub>2</sub> , (c) RT <sub>3</sub> , (d) RT <sub>4</sub> and (e) FT_Ref.	118
4.46	J-V characteristics of the DSSCs (a) RT <sub>1</sub> , (b) RT <sub>2</sub> , (c) RT <sub>3</sub> , (d) RT <sub>4</sub> and (e) FT_Ref.	120

- 4.47 The IPCE spectra of DSSCs (a) RT\_4, (b) RT\_3, (c) RT\_2, 121  
(d) RT\_1 and (e) FT\_Ref.



### LIST OF SYMBOLS AND ABBREVIATIONS

$\theta$	-	angle
$\lambda$	-	wavelength
$^{\circ}\text{C}$	-	degree celsius
$\beta$	-	Full Width Half Maximum (FWHM)
$l$	-	length
$w$	-	width
$t$	-	thickness of the films
$h$	-	hour
$\eta$	-	efficiency
$D$	-	crystallite size
$K$	-	Scherrer constant
$E$	-	applied potential (V)
$i$	-	current response (A)
$v$	-	scan rate ( $\text{mV}\cdot\text{s}^{-1}$ )
$\rho$	-	resistivity of the films
$R_s$	-	sheet resistance
$\alpha$	-	absorption coefficient
$E_g$	-	energy bandgap
$R$	-	resistivity
$\hbar\nu$	-	photon energy
$0D$	-	zero-dimensional
$1D$	-	one-dimensional
$2D$	-	two-dimensional
$3D$	-	three-dimensional
$\mu\text{m}$	-	micrometre
$Abs$	-	absorbance

<i>CE</i>	-	counter electrode
<i>Cl</i>	-	chloride
<i>CO<sub>2</sub></i>	-	carbon dioxide
<i>C</i>	-	carbon
<i>DSSCs</i>	-	dye-sensitized solar cells
<i>FE-SEM</i>	-	Field Emission – Scanning Electron Microscope
<i>FF</i>	-	fill factor
<i>FTO</i>	-	fluorine doped tin-oxide
<i>FWHM</i>	-	full width half maximum
<i>GW</i>	-	giga watt
<i>H</i>	-	hydrogen
<i>HCl</i>	-	hydrochloric acid
<i>IR</i>	-	infrared
<i>I</i>	-	current (A)
<i>V</i>	-	voltage (V)
<i>ITO</i>	-	indium doped tin-oxide
<i>J<sub>sc</sub></i>	-	short-circuit current density (mA/cm <sup>2</sup> )
<i>MΩ</i>	-	mega ohm
<i>MW</i>	-	mega watt
<i>Na</i>	-	sodium
<i>NC</i>	-	nanocomposite
<i>NFs</i>	-	nanoflowers
<i>nm</i>	-	nanometre
<i>NPs</i>	-	nanoparticles
<i>NRs</i>	-	nanorods
<i>O</i>	-	oxygen
<i>OH</i>	-	hydroxide
<i>p</i>	-	positive
<i>Pt</i>	-	platinum
<i>PCE</i>	-	power energy conversion efficiency
<i>PV</i>	-	photovoltaic
<i>RE</i>	-	renewable energy
<i>RMS</i>	-	root mean square

<i>Si</i>	-	silicone
<i>SnO<sub>2</sub></i>	-	tin oxide
<i>Sn</i>	-	tin
<i>T</i>	-	transmittance
<i>TBOT</i>	-	titanium butoxide
<i>TCO</i>	-	transparent conducting oxide
<i>Ti</i>	-	titanium
<i>TiO<sub>2</sub></i>	-	titanium dioxide
<i>a-TiO<sub>2</sub></i>	-	anatase-phase of titanium dioxide
<i>r-TiO<sub>2</sub></i>	-	rutile-phase of titanium dioxide
<i>DI</i>	-	de-ionized
<i>EDX</i>	-	energy dispersive x-ray
<i>CVD</i>	-	chemical vapour deposition
<i>EIS</i>	-	electrochemical impedance spectroscopy
<i>GO</i>	-	graphene oxide
<i>rGO</i>	-	reduced graphene oxide
<i>H<sub>2</sub>O<sub>2</sub></i>	-	hydrogen peroxide
<i>H<sub>2</sub>SO<sub>4</sub></i>	-	sulphuric acid
<i>H<sub>3</sub>PO<sub>4</sub></i>	-	phosphoric acid
<i>KMnO<sub>4</sub></i>	-	potassium permanganate
<i>mL</i>	-	mili litre
<i>SPD</i>	-	spray pyrolysis deposition
<i>SDS</i>	-	sodium dodecyl sulfate
<i>TBP</i>	-	4- <i>ter</i> -butylpyridine
<i>UV</i>	-	ultraviolet
<i>UV-Vis</i>	-	ultraviolet-visible
<i>V<sub>oc</sub></i>	-	open-circuit voltage (V)
<i>XRD</i>	-	x-ray diffraction
<i>atm</i>	-	atmosphere
<i>RF</i>	-	radio frequency
<i>Ru</i>	-	ruthenium
<i>I<sup>-</sup>/I<sub>3</sub><sup>-</sup></i>	-	iodide/triiodide
<i>ZnO</i>	-	zinc oxide

**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	List of Publications	146
B	VITA	149



**PTTA UTHM**  
PERPUSTAKAAN TUNKU TUN AMINAH

## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

The energy produced by fossil fuels has become today's primary driver in the growth of civilization. The produced energy will affect industrial and agricultural development of any country. Therefore, the survival of a country relies on the continuous conservation of resources. The high availability of fossil fuels will add to a nation's economic richness and materials standards. The intensive use of fossil fuels could affect the atmosphere and ecology [1]. With the demand for electricity, several countries are searching for environmentally sustainable, green and non-conventional alternatives [2]. Solar power is one of the possible forms of green electricity. Solar energy becomes an effective energy source and a critical energy resource since it is one of the renewables that may be utilized when other supplies including fossil fuels have been exhausted. With the high promotion of solar panels, there have been developments in the number of innovations that utilize solar cells in solar energy science.

The so-called solar cells is a photovoltaic structure used primarily to transform solar radiation to electricity dependent on sunlight photosynthesis. The solar cells is an efficient and useful system because of its electricity production capabilities that have been explored extensively in a variety of recent reports [3], [4]. As summarized in Figure 1.1, the solar cells are categorized into three generations based on the time period in which it was discovered. Initially, thin silicon wafer was used to manufacture most of the solar cells. They are also known as the first-generation solar cells. Then, the third generation solar cells are the most advanced cells. They have multijunction

and hot carrier cells, consist of nanomaterials and polymers and are able to exhibit the optimum features compared to earlier generations. They are more efficient, less expensive and adopt the up-conversion, down-conversion, and solar thermal technologies [5].

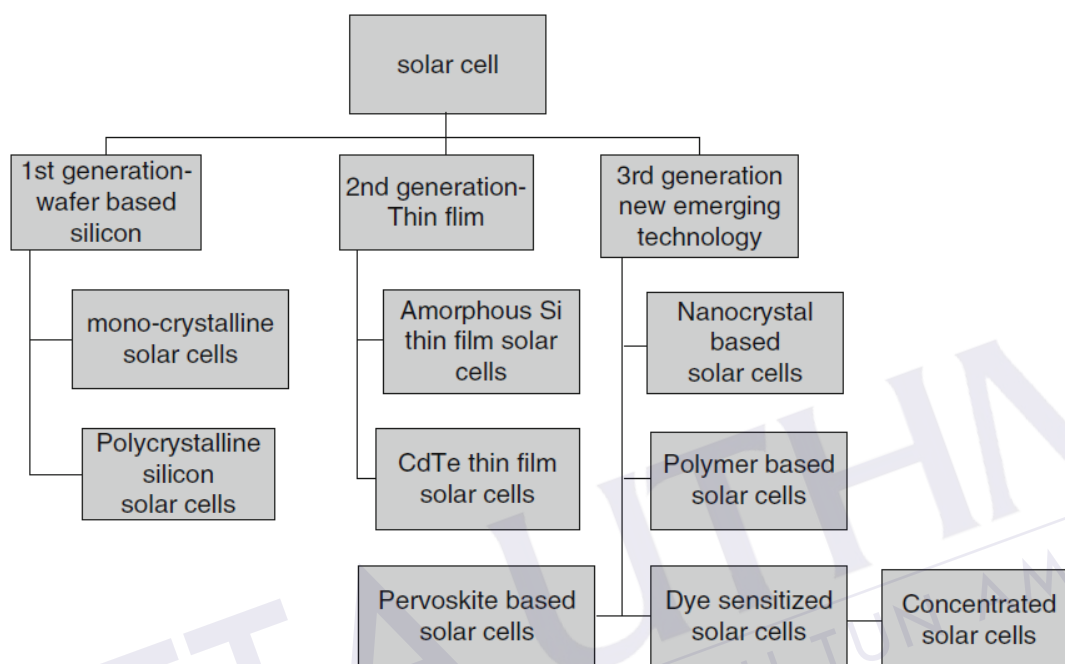


Figure 1.1: Generations of solar cells technology [5].

Dye-sensitized solar cells (DSSCs) is the third generation solar technology which provides effective charge separation that allows electricity to be generated even in low light condition. The first DSSCs was invented in 1991 based on artificial photosynthesis system to generate electricity [6]. Currently, DSSCs are still in the research phase to enhance its efficiency. The average efficiency of this new type of solar cells is 15% [7], [8]. Overall, DSSCs device manufacturing is considered as a low cost, simple and promising technique to provide high performance of electrical generation efficiency. DSSCs are currently in the testing stage to increase their performance. There are five components of a DSSCs. They are translucent fluoride-doped tin oxide (FTO) glass substrate, semiconductors material, dye sensitizer adsorber on the surface of the semiconductors, electrolytes, and counter electrodes (CE) [7].



## REFERENCES

1. M. H. Bender, "Potential conservation of biomass in the production of synthetic organics," *Resources, Conservation and Recycling*, vol. 30, no. 1, pp. 49–58, 2000.
2. K. H. Solangi, M. R. Islam, R. Saidur, N. A. Rahim, and H. Fayaz, "A review on global solar energy policy," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 4, pp. 2149–2163, 2011.
3. R. W. Miles, "Photovoltaic solar cells: Choice of materials and production methods," *Vacuum*, vol. 80, no. 10, pp. 1090–1097, 2006.
4. A. Jäger-Waldau, "Photovoltaics and renewable energies in Europe," *Renewable and Sustainable Energy Reviews*, vol. 11, no. 7, pp. 1414–1437, 2007.
5. C. M. Bhadra, P. G. Tharushi Perera, V. K. Truong, O. N. Ponamoreva, R. J. Crawford, and E. P. Ivanova, "Renewable bio-anodes for microbial fuel cells," *Handbook of Ecomaterials*, vol. 2, pp. 1167–1182, 2019.
6. B. and M. G. O'regan, "A low-cost, high-efficiency solar cell based on dye-sensitized," *Nature*, vol. 354, pp. 56–58, 1991.
7. M. K. Nazeeruddin, E. Baranoff, and M. Grätzel, "Dye-sensitized solar cells: A brief overview," *Solar Energy*, vol. 85, no. 6, pp. 1172–1178, 2011.
8. B. Li, L. Wang, B. Kang, P. Wang, and Y. Qiu, "Review of recent progress in solid-state dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 90, no. 5, pp. 549–573, 2006.
9. A. Goetzberger, J. Luther, and G. Willeke, "Solar cells: Past, present, future," *Solar Energy Materials and Solar Cells*, vol. 74, no. 1–4, pp. 1–11, 2002.
10. P. V. A. Baum, "The conversion of solar energy into electricity," *Solar Energy*, vol. 7, no. 4, pp. 180–187, 1963.

11. R. R. King, D. C. Law, K. M. Edmondson, C. M. Fetzer, G. S. Kinsey, H. Yoon, R. A. Sherif, and N. H. Karam, "40% efficient metamorphic GaInPGaInAsGe multijunction solar cells," *Applied Physics Letters*, vol. 90, no. 18, pp. 90–93, 2007.
12. H. Gerischer, M. E. Michel-Beyerle, F. Reberstrost, and H. Tributsch, "Sensitization of charge injection into semiconductors with large band gap," *Electrochimica Acta*, vol. 13, no. 6, pp. 1509–1515, 1968.
13. P. Wang, S. M. Zakeeruddin, R. Humphry-Baker, J. E. Moser, and M. Grätzel, "Molecular-Scale Interface Engineering of TiO<sub>2</sub> Nanocrystals: Improving the Efficiency and Stability of Dye-Sensitized Solar Cells," *Advanced Materials*, vol. 15, no. 24, pp. 2101–2104, 2003.
14. M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin, and Z. Lin, "Recent advances in dye-sensitized solar cells: From photoanodes, sensitizers and electrolytes to counter electrodes," *Materials Today*, vol. 18, no. 3, pp. 155–162, 2015.
15. A. Chiappone, F. Bella, J. R. Nair, G. Meligrana, R. Bongiovanni, and C. Gerbaldi, "Structure-Performance Correlation of Nanocellulose-Based Polymer Electrolytes for Efficient Quasi-solid DSSCs," *ChemElectroChem*, vol. 1, no. 8, pp. 1350–1358, 2014.
16. E. I. Radeva, I. N. Martev, D. A. Dechev, N. Ivanov, V. N. Tsaneva, and Z. H. Barber, "Sensitivity to humidity of TiO<sub>2</sub> thin films obtained by reactive magnetron sputtering," *Surface and Coatings Technology*, vol. 201, no. 6, pp. 2226–2229, 2006.
17. Y. O. Ken-ichiro Iuchi and A. F. Tetsu Tatsuma, "Cathode-Separated TiO<sub>2</sub> Photocatalysts Applicable to a Photochromic Device Responsive to Backside Illumination," vol. 16, no. 7, pp. 10–12, 2004.
18. S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, "Efficient photochemical water splitting by a chemically modified n-TiO<sub>2</sub>," *Science*, vol. 297, no. 5590, pp. 2243–2245, 2002.
19. X. Z. Li and F. B. Li, "Study of Au/Au<sup>3+</sup>-TiO<sub>2</sub> photocatalysts toward visible photooxidation for water and wastewater treatment," *Environmental Science and Technology*, vol. 35, no. 11, pp. 2381–2387, 2001.
20. E. Reck and S. Seymour, "The effect of TiO<sub>2</sub> pigment on the performance of

- paratoluene sulphonic acid catalysed paint systems,” *Journal of Chemical Information and Modeling*, vol. 53, no. 9, pp. 1689–1699, 2019.
21. J. J. Wu, G. R. Chen, H. H. Yang, C. H. Ku, and J. Y. Lai, “Effects of dye adsorption on the electron transport properties in ZnO-nanowire dye-sensitized solar cells,” *Applied Physics Letters*, vol. 90, no. 21, pp. 2–5, 2007.
  22. Y. Wang, L. Zhang, K. Deng, X. Chen, and Z. Zou, “Low temperature synthesis and photocatalytic activity of rutile TiO<sub>2</sub> nanorod superstructures,” *Journal of Physical Chemistry C*, vol. 111, no. 6, pp. 2709–2714, 2007.
  23. B. Liu and E. S. Aydil, “Growth of oriented single-crystalline rutile TiO<sub>2</sub> nanorods on transparent conducting substrates for dye-sensitized solar cells,” *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 3985–3990, 2009.
  24. K. Zhu, N. R. Neale, A. Miedaner, and A. J. Frank, “Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO<sub>2</sub> nanotubes arrays,” *Nano Letters*, vol. 7, no. 1, pp. 69–74, 2007.
  25. B. Tan and Y. Wu, “Dye-sensitized solar cells based on anatase TiO<sub>2</sub> nanoparticle/nanowire composites,” *Journal of Physical Chemistry B*, vol. 110, no. 32, pp. 15932–15938, 2006.
  26. A. T. Smith, A. M. LaChance, S. Zeng, B. Liu, and L. Sun, “Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites,” *Nano Materials Science*, vol. 1, no. 1, pp. 31–47, 2019.
  27. N. A. F. Al-Rawashdeh, B. A. Albiss, and M. H. I. Yousef, “Graphene-Based Transparent Electrodes for Dye Sensitized Solar Cells,” *IOP Conference Series: Materials Science and Engineering*, vol. 305, no. 1, 2018.
  28. Y. Chen, G. C. Egan, J. Wan, S. Zhu, R. J. Jacob, W. Zhou, J. Dai, Y. Wang, V. A. Danner, Y. Yao, K. Fu, Y. Wang, W. Bao, T. Li, M. R. Zachariah, and L. Hu, “Ultra-fast self-assembly and stabilization of reactive nanoparticles in reduced graphene oxide films,” *Nature Communications*, vol. 7, pp. 1–9, 2016.
  29. E. Nouri, M. R. Mohammadi, and P. Lianos, “Impact of preparation method of TiO<sub>2</sub>-RGO nanocomposite photoanodes on the performance of dye-sensitized solar cells,” *Electrochimica Acta*, vol. 219, pp. 38–48, 2016.
  30. R. Zhao, Q. Geng, L. Chang, P. Wei, Y. Luo, X. Shi, A. M. Asiri, S. Lu, Z. Wang, and X. Sun, “Cu<sub>3</sub>P nanoparticle-reduced graphene oxide hybrid: An

- efficient electrocatalyst to realize N<sub>2</sub>-to-NH<sub>3</sub> conversion under ambient conditions,” *Chemical Communications*, vol. 56, no. 65, pp. 9328–9331, 2020.
31. M. Szindler, W. Matysiak, M. Libera, P. Jarka, and M. Szindler, “Study of dye sensitized solar cells photoelectrodes consisting of nanostructures,” *Applied Surface Science*, vol. 491, pp. 807–813, 2019.
  32. V. Naresh and N. Lee, “A review on biosensors and recent development of nanostructured materials-enabled biosensors,” *Sensors (Switzerland)*, vol. 21, no. 4, pp. 1–35, 2021.
  33. M. Aftabuzzaman, C. Lu, and H. K. Kim, “Recent progress on nanostructured carbon-based counter/back electrodes for high-performance dye-sensitized and perovskite solar cells,” *Nanoscale*, vol. 12, no. 34, pp. 17590–17648, 2020.
  34. Y. Gu, T. Wang, Y. N. Dong, H. Zhang, D. Wu, and W. Chen, “Ferroelectric polyoxometalate-modified nano semiconductor TiO<sub>2</sub> for increasing electron lifetime and inhibiting electron recombination in dye-sensitized solar cells,” *Inorganic Chemistry Frontiers*, vol. 7, no. 17, pp. 3072–3080, 2020.
  35. F. Babar, U. Mehmood, H. Asghar, M. H. Mehdi, A. U. H. Khan, H. Khalid, N. ul Huda, and Z. Fatima, “Nanostructured photoanode materials and their deposition methods for efficient and economical third generation dye-sensitized solar cells: A comprehensive review,” *Renewable and Sustainable Energy Reviews*, vol. 129, no. May, 2020.
  36. A. Omar, M. S. Ali, and N. Abd Rahim, “Electron transport properties analysis of titanium dioxide dye-sensitized solar cells (TiO<sub>2</sub>-DSSCs) based natural dyes using electrochemical impedance spectroscopy concept: A review,” *Solar Energy*, vol. 207, no. July, pp. 1088–1121, 2020.
  37. S. Ni, D. Wang, F. Guo, S. Jiao, Y. Zhang, B. Wang, L. Yuan, L. Zhang, L. Zhao, D. Wang, F. Guo, S. Jiao, Y. Zhang, J. Wang, B. Wang, L. Yuan, L. Zhang, and L. Zhao, “Accepted Manuscript,” 2018.
  38. G. A. M. Ali, M. M. Yusoff, H. Algarni, and K. F. Chong, “One-step electrosynthesis of MnO<sub>2</sub>/rGO nanocomposite and its enhanced electrochemical performance,” *Ceramics International*, vol. 44, no. 7, pp. 7799–7807, 2018.
  39. M. Mohandoss, S. Sen Gupta, A. Nelleri, T. Pradeep, and S. M. Maliyekkal, “Solar mediated reduction of graphene oxide,” *RSC Advances*, vol. 7, no. 2, pp. 957–963, 2017.

40. M. Fathy, A. Gomaa, F. A. Taher, M. M. El-Fass, and A. E. H. B. Kashyout, "Optimizing the preparation parameters of GO and rGO for large-scale production," *Journal of Materials Science*, vol. 51, no. 12, pp. 5664–5675, 2016.
41. T. F. Emiru and D. W. Ayele, "Controlled synthesis, characterization and reduction of graphene oxide: A convenient method for large scale production," *Egyptian Journal of Basic and Applied Sciences*, vol. 4, no. 1, pp. 74–79, 2017.
42. K. Surana, S. Konwar, P. K. Singh, and B. Bhattacharya, "Utilizing reduced graphene oxide for achieving better efficient dye sensitized solar cells," *Journal of Alloys and Compounds*, vol. 788, pp. 672–676, 2019.
43. J. Chen, B. Yao, C. Li, and G. Shi, "An improved Hummers method for eco-friendly synthesis of graphene oxide," *Carbon*, vol. 64, no. 1, pp. 225–229, 2013.
44. W. Liu, K. Yin, F. He, Q. Ru, S. Zuo, and C. Yao, "A highly efficient reduced graphene oxide/SnO<sub>2</sub>/TiO<sub>2</sub> composite as photoanode for photocathodic protection of 304 stainless steel," *Materials Research Bulletin*, vol. 113, no. December 2018, pp. 6–13, 2019.
45. F. I. Chowdhury, T. Blaine, and A. B. Gougam, "Optical transmission enhancement of fluorine doped tin oxide (FTO) on glass for thin film photovoltaic applications," *Energy Procedia*, vol. 42, pp. 660–669, 2013.
46. Z. and J. M. Jarzebski, "Physical properties of SnO<sub>2</sub> materials II. Electrical properties," 1976.
47. A. L. Dawar and J. C. Joshi, "Semiconducting transparent thin films: their properties and applications," *Journal of Materials Science*, vol. 19, no. 1, pp. 1–23, 1984.
48. L. Mahdavian, "Thermodynamic study of alcohol on SnO<sub>2</sub> (100)-based gas nano-sensor," *Physics and Chemistry of Liquids*, vol. 49, no. 5, pp. 626–638, 2011.
49. A. V. Moholkar, S. M. Pawar, K. Y. Rajpure, C. H. Bhosale, and J. H. Kim, "Effect of fluorine doping on highly transparent conductive spray deposited nanocrystalline tin oxide thin films," *Applied Surface Science*, vol. 255, no. 23, pp. 9358–9364, 2009.
50. B. Zhang, Y. Tian, J. X. Zhang, and W. Cai, "The role of oxygen vacancy in

- fluorine-doped SnO<sub>2</sub> films,” *Physica B: Condensed Matter*, vol. 406, no. 9, pp. 1822–1826, 2011.
51. K. Murakami, K. Nakajima, and S. Kaneko, “Initial growth of SnO<sub>2</sub> thin film on the glass substrate deposited by the spray pyrolysis technique,” *Thin Solid Films*, vol. 515, no. 24 SPEC. ISS., pp. 8632–8636, 2007.
  52. A. Fahmi, C. Minot, B. Silvi, and M. Causá, “Theoretical analysis of the structures of titanium dioxide crystals,” *Physical Review B*, vol. 47, no. 18, pp. 11717–11724, 1993.
  53. S. K. Simakov, “Nano- and micron-sized diamond genesis in nature: An overview,” *Geoscience Frontiers*, vol. 9, no. 6, pp. 1849–1858, 2018.
  54. X. D. and X. Liu, “Correlation between anatase-to-rutile transformation and grain growth in nanocrystalline titania powders,” *Science*, vol. 235, no. 4784, p. 9, 1998.
  55. D. Reyes-Coronado, G. Rodríguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. De Coss, and G. Oskam, “Phase-pure TiO<sub>2</sub> nanoparticles: Anatase, brookite and rutile,” *Nanotechnology*, vol. 19, no. 14, 2008.
  56. J. Moellmann, S. Ehrlich, R. Tonner, and S. Grimme, “A DFT-D study of structural and energetic properties of TiO<sub>2</sub> modifications,” *Journal of Physics Condensed Matter*, vol. 24, no. 42, 2012.
  57. M. Xu, Y. Gao, E. M. Moreno, M. Kunst, M. Muhler, Y. Wang, H. Idriss, and C. Wöll, “Photocatalytic activity of bulk TiO<sub>2</sub> anatase and rutile single crystals using infrared absorption spectroscopy,” *Physical Review Letters*, vol. 106, no. 13, pp. 1–4, 2011.
  58. D. Cahen, G. Hodes, M. Grätzel, J. F. Guillemoles, and I. Riess, “Nature of Photovoltaic Action in Dye-Sensitized Solar Cells,” *Journal of Physical Chemistry B*, vol. 104, no. 9, pp. 2053–2059, 2000.
  59. Z. Lin, A. Orlov, R. M. Lambert, and M. C. Payne, “New insights into the origin of visible light photocatalytic activity of nitrogen-doped and oxygen-deficient anatase TiO<sub>2</sub>,” *Journal of Physical Chemistry B*, vol. 109, no. 44, pp. 20948–20952, 2005.
  60. Y. Qiu, W. Chen, and S. Yang, “Double-layered photoanodes from variable-size anatase TiO<sub>2</sub> nanospindles: A candidate for high-efficiency dye-sensitized solar cells,” *Angewandte Chemie - International Edition*, vol. 49, no. 21, pp.



- 3675–3679, 2010.
61. D. A. H. Hanaor and C. C. Sorrell, “Review of the anatase to rutile phase transformation,” *Journal of Materials Science*, vol. 46, no. 4, pp. 855–874, 2011.
  62. M. Langlet, M. Burgos, C. Coutier, C. Jimenez, C. Morant, and M. Manso, “Low temperature preparation of high refractive index and mechanically resistant sol-gel TiO<sub>2</sub> films for multilayer antireflective coating applications,” *Journal of Sol-Gel Science and Technology*, vol. 22, no. 1–2, pp. 139–150, 2001.
  63. S. Das, S. Kar, and S. Chaudhuri, “Optical properties of SnO<sub>2</sub> nanoparticles and nanorods synthesized by solvothermal process,” *Journal of Applied Physics*, vol. 99, no. 11, 2006.
  64. H. Bin Wu, H. H. Hng, and X. W. D. Lou, “Direct synthesis of anatase TiO<sub>2</sub> nanowires with enhanced photocatalytic activity,” *Advanced Materials*, vol. 24, no. 19, pp. 2567–2571, 2012.
  65. R. C. Xie and J. K. Shang, “Morphological control in solvothermal synthesis of titanium oxide,” *Journal of Materials Science*, vol. 42, no. 16, pp. 6583–6589, 2007.
  66. H. G. Yang, G. Liu, S. Z. Qiao, C. H. Sun, Y. G. Jin, S. C. Smith, J. Zou, H. M. Cheng, and G. Q. Lu, “Solvothermal synthesis and photoreactivity of anatase TiO<sub>2</sub> nanosheets with dominant {001} facets,” *Journal of the American Chemical Society*, vol. 131, no. 11, pp. 4078–4083, 2009.
  67. H. Park, W. R. Kim, H. T. Jeong, J. J. Lee, H. G. Kim, and W. Y. Choi, “Fabrication of dye-sensitized solar cells by transplanting highly ordered TiO<sub>2</sub> nanotube arrays,” *Solar Energy Materials and Solar Cells*, vol. 95, no. 1, pp. 184–189, 2011.
  68. X. Liu, P. K. Chu, and C. Ding, “Surface modification of titanium, titanium alloys, and related materials for biomedical applications,” *Materials Science and Engineering R: Reports*, vol. 47, no. 3–4, pp. 49–121, 2004.
  69. M. T. SARODE, P. N. SHELKE, S. D. GUNJAL, Y. B. KHOLLAM, M. G. TAKWALE, S. R. JADKAR, B. B. KALE, K. C. MOHITE, and P. KOINKAR, “Effect of Annealing Temperature on Optical Properties of Titanium Dioxide Thin Films Prepared By Sol-Gel Method,” *International Journal of Modern*

- Physics: Conference Series*, vol. 06, pp. 13–18, 2012.
70. C.-P. Lin, H. Chen, A. Nakaruk, P. Koshy, and C. C. Sorrell, “Effect of Annealing Temperature on the Photocatalytic Activity of TiO<sub>2</sub> Thin Films,” *Energy Procedia*, vol. 34, pp. 627–636, 2013.
  71. M. M. Hasan, A. S. M. A. Haseeb, R. Saidur, and H. H. Masjuki, “Effects of annealing treatment on optical properties of anatase TiO<sub>2</sub> thin films,” *World Academy of Science, Engineering and Technology*, vol. 40, pp. 221–225, 2009.
  72. T. Peng, X. Xiao, F. Ren, J. Xu, X. Zhou, F. Mei, and C. Jiang, “Influence of annealing temperature on the properties of TiO<sub>2</sub> films annealed by ex situ and in situ TEM,” *Journal Wuhan University of Technology, Materials Science Edition*, vol. 27, no. 6, pp. 1014–1019, 2012.
  73. M. K. Ahmad, “Low temperature and normal pressure growth of rutile-phased TiO<sub>2</sub> nanorods/nanoflowers for DSC application prepared by hydrothermal method,” *Journal of Advanced Research in Physics*, vol. 3, no. 2, pp. 2011–2013, 2012.
  74. K. Byrappa and T. Adschiri, “Hydrothermal technology for nanotechnology,” *Progress in Crystal Growth and Characterization of Materials*, vol. 53, no. 2, pp. 117–166, 2007.
  75. R. S. Mohar, S. Iwan, D. Djuhana, C. Imawan, A. Harmoko, and V. Fauzia, “Post-annealing effect on optical absorbance of hydrothermally grown zinc oxide nanorods,” *AIP Conference Proceedings*, vol. 1729, 2016.
  76. J. Zhang and L. Gao, “Synthesis and characterization of antimony-doped tin oxide (ATO) nanoparticles by a new hydrothermal method,” *Materials Chemistry and Physics*, vol. 87, no. 1, pp. 10–13, 2004.
  77. J. Gong, L. Luo, S. H. Yu, H. Qian, and L. Fei, “Synthesis of copper/cross-linked poly (vinyl alcohol) (PVA) nanocables via a simple hydrothermal route,” *Journal of Materials Chemistry*, vol. 16, no. 1, pp. 101–105, 2006.
  78. G. W. Morey and P. Niggli, “The hydrothermal formation of silicates, a review,” vol. 0, no. 1, p. 6, 1913.
  79. L. M. Dem’yanets and A. N. Lobachev, “Some Problems of Hydrothermal Crystallization,” *Crystallization Processes under Hydrothermal Conditions*, pp. 1–26, 1973.
  80. K. Byrappa, N. Keerthiraj, and S. M. Byrappa, *Crystals — Design and*



*Processing*. 2015.

81. G. Rajamanickam, S. Narendhiran, S. P. Muthu, S. Mukhopadhyay, and R. Perumalsamy, "Hydrothermally derived nanoporous titanium dioxide nanorods/nanoparticles and their influence in dye-sensitized solar cell as a photoanode," *Chemical Physics Letters*, vol. 689, pp. 19–25, 2017.
82. M. Marandi, Z. Goudarzi, and L. Moradi, "Synthesis of randomly directed inclined TiO<sub>2</sub> nanorods on the nanocrystalline TiO<sub>2</sub> layers and their optimized application in dye sensitized solar cells," *Journal of Alloys and Compounds*, vol. 711, pp. 603–610, 2017.
83. U. T. Pawar, S. A. Pawar, K. Jin-Hyeok, and P. S. Patil, "Dye sensitized solar cells based on hydrothermally grown TiO<sub>2</sub> nanostars over nanorods," *Ceramics International*, 2016.
84. S. M. Mokhtar, M. K. Ahmad, C. F. Soon, N. Nafarizal, A. B. Faridah, A. B. Suriani, M. H. Mamat, M. Shimomura, and K. Murakami, "Fabrication and characterization of rutile-phased titanium dioxide (TiO<sub>2</sub>) nanorods array with various reaction times using one step hydrothermal method," *Optik*, vol. 154, pp. 510–515, 2018.
85. W. Li, J. Yang, Q. Jiang, Y. Luo, Y. Hou, S. Zhou, and Z. Zhou, "Bi-layer of nanorods and three-dimensional hierarchical structure of TiO<sub>2</sub> for high efficiency dye-sensitized solar cells," *Journal of Power Sources*, vol. 284, pp. 428–434, 2015.
86. K. H. Park and M. Dhayal, "Simultaneous growth of rutile TiO<sub>2</sub> as 1D/3D nanorod/nanoflower on FTO in one-step process enhances electrochemical response of photoanode in DSSC," *Electrochemistry Communications*, vol. 49, pp. 47–50, 2015.
87. Y. Jiang, M. Li, D. Song, X. Li, and Y. Yu, "A novel 3D structure composed of strings of hierarchical TiO<sub>2</sub> spheres formed on TiO<sub>2</sub> nanobelts with high photocatalytic properties," *Journal of Solid State Chemistry*, vol. 211, pp. 90–94, 2014.
88. M. B. Tahir, M. Rafique, M. S. Rafique, T. Nawaz, M. Rizwan, and M. Tanveer, "Photocatalytic nanomaterials for degradation of organic pollutants and heavy metals," *Nanotechnology and Photocatalysis for Environmental Applications*, pp. 119–138, 2020.

89. L. F. Gorup, L. H. Amorin, E. R. Camargo, T. Sequinel, F. H. Cincotto, G. Biasotto, N. Ramesar, and F. de A. La Porta, "Methods for design and fabrication of nanosensors: the case of ZnO-based nanosensor," *Nanosensors for Smart Cities*, pp. 9–30, 2020.
90. S. S. Taib, M. K. Ahmad, M. Z. A. Rahman, F. Mohamad, N. Nafarizal, C. F. Soon, A. S. Ameruddin, A. B. Faridah, M. Shimomura, and K. Murakami, "TiO<sub>2</sub> based dye-sensitized solar cell prepared by Spray Pyrolysis Deposition (SPD) technique," *International Journal of Integrated Engineering*, vol. 10, no. 1, pp. 109–113, 2018.
91. O. A. Ileperuma, G. R. Asoka Kumara, H. S. Yang, and K. Murakami, "Quasi-solid electrolyte based on polyacrylonitrile for dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 217, no. 2–3, pp. 308–312, 2011.
92. G. R. A. Kumara, S. Kaneko, A. Konno, M. Okuya, K. Murakami, B. Onwona-agyeman, and K. Tennakone, "Large area dye-sensitized solar cells: Material aspects of fabrication," *Progress in Photovoltaics: Research and Applications*, vol. 14, no. 7, pp. 643–651, 2006.
93. K. Kalyanasundaram and M. Grätzel, "Efficient dye-sensitized solar cells for direct conversion of sunlight to electricity.," *Material Matters (Milwaukee, WI, United States)*, vol. 4, no. 4, pp. 88–91, 2009.
94. U. Mehmood, S. U. Rahman, K. Harrabi, I. A. Hussein, and B. V. S. Reddy, "Recent advances in dye sensitized solar cells," *Advances in Materials Science and Engineering*, vol. 2014, 2014.
95. M. Grätzel, "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, no. 1–3, pp. 3–14, 2004.
96. M. K. Nazeeruddin, R. Splivallo, P. Liska, P. Comte, and M. Grätzel, "A swift dye uptake procedure for dye sensitized solar cells," *Chemical Communications*, vol. 12, pp. 1456–1457, 2003.
97. A. Mishra, M. K. R. Fischer, and P. Büuerle, "Metal-Free organic dyes for dye-Sensitized solar cells: From structure: Property relationships to design rules," *Angewandte Chemie - International Edition*, vol. 48, no. 14, pp. 2474–2499, 2009.

98. H. Hug, M. Bader, P. Mair, and T. Glatzel, "Biophotovoltaics: Natural pigments in dye-sensitized solar cells," *Applied Energy*, vol. 115, pp. 216–225, 2014.
99. K. Hara, Z. S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-Oh, C. Kasada, A. Shinpo, and S. Suga, "Oligothiophene-containing coumarin dyes for efficient dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 109, no. 32, pp. 15476–15482, 2005.
100. K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, and H. Arakawa, "Dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells based on novel coumarin dyes," *Solar Energy Materials and Solar Cells*, vol. 77, no. 1, pp. 89–103, 2003.
101. M. R. Narayan, "Review: Dye sensitized solar cells based on natural photosensitizers," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 1, pp. 208–215, 2012.
102. G. Calogero, G. Di Marco, S. Cazzanti, S. Caramori, R. Argazzi, A. Di Carlo, and C. A. Bignozzi, "Efficient dye-sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits," *International Journal of Molecular Sciences*, vol. 11, no. 1, pp. 254–267, 2010.
103. J. Wu, Z. Lan, S. Hao, P. Li, J. Lin, M. Huang, L. Fang, and Y. Huang, "Progress on the electrolytes for dye-sensitized solar cells," *Pure and Applied Chemistry*, vol. 80, no. 11, pp. 2241–2258, 2008.
104. F. T. Kong, S. Y. Dai, and K. J. Wang, "Review of recent progress in dye-sensitized solar cells," *Advances in OptoElectronics*, vol. 2007, no. 1, pp. 1–13, 2007.
105. S. E. Koops, P. R. F. Barnes, B. C. O'Regan, and J. R. Durrant, "Kinetic competition in a coumarin dye-sensitized solar cell: Injection and recombination limitations upon device performance," *Journal of Physical Chemistry C*, vol. 114, no. 17, pp. 8054–8061, 2010.
106. C. T. Yip, X. Liu, Y. Hou, W. Xie, J. He, S. Schlücker, D. Y. Lei, and H. Huang, "Strong competition between electromagnetic enhancement and surface-energy-transfer induced quenching in plasmonic dye-sensitized solar cells: A generic yet controllable effect," *Nano Energy*, vol. 26, pp. 297–304, 2016.
107. Y. L. Lee, C. L. Chen, L. W. Chong, C. H. Chen, Y. F. Liu, and C. F. Chi, "A platinum counter electrode with high electrochemical activity and high

- transparency for dye-sensitized solar cells,” *Electrochemistry Communications*, vol. 12, no. 11, pp. 1662–1665, 2010.
108. X. Fang, T. Ma, G. Guan, M. Akiyama, T. Kida, and E. Abe, “Effect of the thickness of the Pt film coated on a counter electrode on the performance of a dye-sensitized solar cell,” *Journal of Electroanalytical Chemistry*, vol. 570, no. 2, pp. 257–263, 2004.
  109. C. Y. Lin, J. Y. Lin, C. C. Wan, and T. C. Wei, “High-performance and low platinum loading electrodeposited-Pt counter electrodes for dye-sensitized solar cells,” *Electrochimica Acta*, vol. 56, no. 5, pp. 1941–1946, 2011.
  110. S. Ali and P. M. J. Elrod, “Biomimicry in Solar Energy Conversion with Natural Dye-Sensitized Nanocrystalline Photovoltaic Cells,” in *Biochemistry*, 2007, pp. 1–22.
  111. S. S. Hegedus and A. Luque, “Status, Trends, Challenges and the Bright Future of Solar Electricity from Photovoltaics,” in *Handbook of Photovoltaic Science and Engineering*, 2003, pp. 1–43.
  112. M. Grätzel, “Solar energy conversion by dye-sensitized photovoltaic cells,” *Inorganic Chemistry*, vol. 44, no. 20, pp. 6841–6851, 2005.
  113. W. Guter, J. Schöne, S. P. Philipps, M. Steiner, G. Siefer, A. Wekkeli, E. Welsler, E. Oliva, A. W. Bett, and F. Dimroth, “Current-matched triple-junction solar cell reaching 41.1% conversion efficiency under concentrated sunlight,” *Applied Physics Letters*, vol. 94, no. 22, pp. 94–97, 2009.
  114. V. Baglio, M. Girolamo, V. Antonucci, and A. S. Aricò, “Influence of TiO<sub>2</sub> film thickness on the electrochemical behaviour of dye-sensitized solar cells,” *International Journal of Electrochemical Science*, vol. 6, no. 8, pp. 3375–3384, 2011.
  115. S. James and R. Contractor, “Study on Nature-inspired Fractal Design-based Flexible Counter Electrodes for Dye-Sensitized Solar Cells Fabricated using Additive Manufacturing,” *Scientific Reports*, vol. 8, no. 1, pp. 1–12, 2018.
  116. M. J. Jeng, Y. L. Wung, L. B. Chang, and L. Chow, “Particle size effects of TiO<sub>2</sub> layers on the solar efficiency of dye-sensitized solar cells,” *International Journal of Photoenergy*, vol. 2013, 2013.
  117. K. Lee, R. Kirchgeorg, and P. Schmuki, “Role of transparent electrodes for high efficiency TiO<sub>2</sub> nanotube based dye-sensitized solar cells,” *Journal of Physical*

- Chemistry C*, vol. 118, no. 30, pp. 16562–16566, 2014.
118. X. Liu and M. C. Hersam, “Interface Characterization and Control of 2D Materials and Heterostructures,” *Advanced Materials*, vol. 30, no. 39, pp. 1–34, 2018.
  119. F. Iskandar, U. Hikmah, E. Stavila, and A. H. Aimon, “Microwave-assisted reduction method under nitrogen atmosphere for synthesis and electrical conductivity improvement of reduced graphene oxide (rGO),” *RSC Advances*, vol. 7, no. 83, pp. 52391–52397, 2017.
  120. S. Basu and P. Bhattacharyya, “Recent developments on graphene and graphene oxide based solid state gas sensors,” *Sensors and Actuators, B: Chemical*, vol. 173, pp. 1–21, 2012.
  121. A. S. Lemine, M. M. Zagho, T. M. Altahtamouni, and N. Bensalah, “Graphene a promising electrode material for supercapacitors—A review,” *International Journal of Energy Research*, vol. 42, no. 14, pp. 4284–4300, 2018.
  122. A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, “Superior thermal conductivity of single-layer graphene,” *Nano Letters*, vol. 8, no. 3, pp. 902–907, 2008.
  123. H. Zhang, D. Wang, J. Liu, H. Wei, F. Liu, J. Xu, S. Li, Z. Qin, J. Guo, R. Wang, H. Jia, J. Zhang, and Y. Liu, “Review on Thermal Conductivity of the Graphene Reinforced Resin Matrix Composites,” *IOP Conference Series: Materials Science and Engineering*, vol. 562, no. 1, 2019.
  124. I. V. G. and A. A. F. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, “Electric Field Effect in Atomically Thin Carbon Films,” vol. 306, no. 5696, pp. 666–669, 2016.
  125. C. Huang, S. Gupta, C. Lo, N. Tai, and S. Gupta, “Highly transparent and excellent electromagnetic interference shielding hybrid films composed of silver-grid/(silver nanowires and reduced graphene oxide),” *Materials Letters*, vol. 253, pp. 152–155, 2019.
  126. R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, “Fine structure constant defines visual transparency of graphene,” *Science*, vol. 320, no. 5881, p. 1308, 2008.
  127. M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, “Graphene-Based Ultracapacitors,” *Nano Letters*, vol. 8, no. 10, pp. 3498–3502, 2008.

128. M. F. Y. M. Hanappi, M. Deraman, M. Suleman, M. A. R. Othman, N. H. Basri, N. S. M. Nor, E. Hamdan, N. E. S. Sazali, and N. S. M. Tajuddin, "Preparation and characterization of graphene/turbostratic carbon derived from chitosan film for supercapacitor electrodes," *AIP Conference Proceedings*, vol. 1940, no. 1, pp. 1–8, 2018.
129. C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene," *Science*, vol. 321, no. 5887, pp. 385–388, 2008.
130. K. M. Wibowo, M. Z. Sahdan, N. I. Ramli, A. Muslihata, N. Rosni, V. H. Tsen, H. Saim, S. A. Ahmad, Y. Sari, and Z. Mansor, "Detection of Escherichia Coli Bacteria in Wastewater by using Graphene as a Sensing Material," *Journal of Physics: Conference Series*, vol. 995, no. 1, 2018.
131. M. Kalbacova, A. Broz, J. Kong, and M. Kalbac, "Graphene substrates promote adherence of human osteoblasts and mesenchymal stromal cells," *Carbon*, vol. 48, no. 15, pp. 4323–4329, 2010.
132. S. S. Varghese, S. Lonkar, K. K. Singh, S. Swaminathan, and A. Abdala, "Recent advances in graphene based gas sensors," *Sensors and Actuators, B: Chemical*, vol. 218, pp. 160–183, 2015.
133. F. Liu, X. Chu, Y. Dong, W. Zhang, W. Sun, and L. Shen, "Acetone gas sensors based on graphene-ZnFe<sub>2</sub>O<sub>4</sub> composite prepared by solvothermal method," *Sensors and Actuators, B: Chemical*, vol. 188, pp. 469–474, 2013.
134. K. Tadyszak, J. K. Wychowaniec, and J. Litowczenko, "Biomedical applications of graphene-based structures," *Nanomaterials*, vol. 8, no. 11, pp. 1–20, 2018.
135. G. S. Selopal, R. Milan, L. Ortolani, V. Morandi, R. Rizzoli, G. Sberveglieri, G. P. Veronese, A. Vomiero, and I. Concina, "Graphene as transparent front contact for dye sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 135, pp. 99–105, 2015.
136. C. D. Reddy, S. Rajendran, and K. M. Liew, "Equilibrium configuration and continuum elastic properties of finite sized graphene," *Nanotechnology*, vol. 17, no. 3, pp. 864–870, 2006.
137. S. Sajjad, S. A. Khan Leghari, and A. Iqbal, "Study of Graphene Oxide Structural Features for Catalytic, Antibacterial, Gas Sensing, and Metals



- Decontamination Environmental Applications,” *ACS Applied Materials and Interfaces*, vol. 9, no. 50, pp. 43393–43414, 2017.
138. U. A. Kanta, V. Thongpool, W. Sangkhun, N. Wongyao, and J. Wootthikanokkhan, “Preparations, characterizations, and a comparative study on photovoltaic performance of two different types of graphene/TiO<sub>2</sub> nanocomposites photoelectrodes,” *Journal of Nanomaterials*, vol. 2017, pp. 1–13, 2017.
139. D. Kumaresan, S. Jothi, J. D. Mcgettrick, T. M. Watson, D. Kumaresan, S. Jothi, J. D. Mcgettrick, T. M. Watson, and A. Surface, “Reduced graphene oxide wrapped hierarchical TiO<sub>2</sub> nanorod composites for improved charge collection efficiency and carrier lifetime in dye sensitized solar cells,” *Applied Surface Science*, vol. 428, pp. 439–447, 2018.
140. H. Cai, J. Li, X. Xu, H. Tang, J. Luo, K. Binnemans, D. E. De Vos, J. Li, X. Xu, H. Tang, J. Luo, K. Binnemans, J. Fransaeer, and D. E. De Vos, “Nanostructured composites of one-dimensional TiO<sub>2</sub> and reduced graphene oxide for efficient dye-sensitized solar cells,” *Journal of Alloys and Compounds*, vol. 697, pp. 132–137, 2016.
141. A. B. Suriani, Muqoyyanah, A. Mohamed, M. H. Mamat, M. H. D. Othman, M. K. Ahmad, H. P. S. Abdul Khalil, P. Marwoto, and M. D. Birowosuto, “Titanium dioxide/agglomerated-free reduced graphene oxide hybrid photoanode film for dye-sensitized solar cells photovoltaic performance improvement,” *Nano-Structures and Nano-Objects*, vol. 18, pp. 1–14, 2019.
142. M. K. Ahmad, C. F. Soon, N. Nafarizal, A. B. Suriani, A. Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, and K. Murakami, “Effect of heat treatment to the rutile based dye sensitized solar cell,” *Optik*, vol. 127, no. 8, pp. 4076–4079, 2016.
143. B. Viswanathan and K. J. A. Raj, “Effect of surface area, pore volume and particle size of P25 titania on the phase transformation of anatase to rutile,” *Indian Journal of Chemistry - Section A Inorganic, Physical, Theoretical and Analytical Chemistry*, vol. 48, no. 10, pp. 1378–1382, 2009.
144. J. Zhang, P. Zhou, J. Liu, and J. Yu, “New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO<sub>2</sub>,” *Physical Chemistry Chemical Physics*, vol. 16, no. 38, pp. 20382–20386, 2014.

145. P. Benjwal, B. De, and K. K. Kar, "1-D and 2-D morphology of metal cation co-doped (Zn, Mn) TiO<sub>2</sub> and investigation of their photocatalytic activity," *Applied Surface Science*, vol. 427, pp. 262–272, 2018.
146. A. B. Suriani, A. Mohamed, N. Hashim, M. S. Rosmi, M. H. Mamat, M. F. Malek, M. J. Salifairus, and H. P. S. A. Khalil, "Reduced graphene oxide/platinum hybrid counter electrode assisted by custom-made triple-tail surfactant and zinc oxide/titanium dioxide bilayer nanocomposite photoanode for enhancement of DSSCs photovoltaic performance," *Optik*, vol. 161, pp. 70–83, 2018.
147. A. B. Suriani, M. D. Nurhafizah, A. Mohamed, M. H. Mamat, M. F. Malek, M. K. Ahmad, A. Pandikumar, and N. M. Huang, "Enhanced photovoltaic performance using reduced graphene oxide assisted by triple-tail surfactant as an efficient and low-cost counter electrode for dye-sensitized solar cells," *Optik*, vol. 139, pp. 291–298, 2017.
148. F. I. M. Fazli, M. K. Ahmad, C. F. Soon, N. Nafarizal, A. B. Suriani, A. Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, and K. Murakami, "Dye-sensitized solar Cell using pure anatase TiO<sub>2</sub> annealed at different temperatures," *Optik*, vol. 140, pp. 1063–1068, 2017.
149. F. W. Low, C. W. Lai, S. Bee, and A. Hamid, "Facile Synthesis of High Quality Graphene Oxide from Graphite Flakes Using Improved Hummer ' s Technique," *Journal of Nanoscience and Nanotechnology*, vol. 15, no. 1, pp. 1–5, 2015.
150. Y. S. Lim, Y. P. Tan, H. N. Lim, W. T. Tan, M. A. Mahnaz, Z. A. Talib, N. M. Huang, A. Kassim, and M. A. Yarmo, "Polypyrrole/graphene composite films synthesized via potentiostatic deposition," *Journal of Applied Polymer Science*, vol. 128, no. 1, pp. 224–229, 2013.
151. M. Jithin, K. Saravanakumar, V. Ganesan, V. R. Reddy, P. M. Razad, M. M. Patidar, K. Jeyadheepan, G. Marimuthu, V. R. Sreelakshmi, and K. Mahalakshmi, "Growth, mechanism and properties of TiO<sub>2</sub>nanorods embedded nanopillar: Evidence of lattice orientation effect," *Superlattices and Microstructures*, vol. 109, pp. 145–153, 2017.
152. J. Lin, Y. U. Heo, A. Nattestad, Z. Sun, L. Wang, J. H. Kim, and S. X. Dou, "3D hierarchical rutile TiO<sub>2</sub> and metal-free organic sensitizer producing dye-



- sensitized solar cells 8.6% conversion efficiency,” *Scientific Reports*, vol. 4, pp. 1–8, 2014.
153. H. Z. Asl and S. M. Rozati, “High-quality spray-deposited fluorine-doped tin oxide: effect of film thickness on structural, morphological, electrical, and optical properties,” *Applied Physics A: Materials Science and Processing*, vol. 125, no. 10, pp. 1–8, 2019.
  154. L. H. Lalasari, T. Arini, L. Andriyah, F. Firdiyono, and A. H. Yuwono, “Electrical, optical and structural properties of FTO thin films fabricated by spray ultrasonic nebulizer technique from SnCl<sub>4</sub> precursor,” *AIP Conference Proceedings*, vol. 1964, no. May 2018, 2018.
  155. H. Sutiono, A. M. Tripathi, H. M. Chen, C. H. Chen, W. N. Su, L. Y. Chen, H. Dai, and B. J. Hwang, “Facile synthesis of [101]-oriented rutile TiO<sub>2</sub> nanorod array on FTO substrate with a tunable anatase-rutile heterojunction for efficient solar water splitting,” *ACS Sustainable Chemistry and Engineering*, vol. 4, no. 11, pp. 5963–5971, 2016.
  156. X. Kang, S. Liu, Z. Dai, Y. He, X. Song, and Z. Tan, “Titanium dioxide: From engineering to applications,” *Catalysts*, vol. 9, no. 2, pp. 1–32, 2019.
  157. M. Barthelemy, X. Castel, L. Le Gendre, J. Louis, M. Denis, and C. Pissavin, “Effect of Titanium Dioxide Film Thickness on Photocatalytic and Bactericidal Activities Against *Listeria monocytogenes*,” *Photochemistry and Photobiology*, vol. 95, no. 4, pp. 1035–1044, 2019.
  158. A. Talib, M. K. Ahmad, N. Ahmad, N. Nafarizal, F. Mohamad, C. F. Soon, A. B. Suriani, M. H. Mamat, K. Murakami, and M. Shimomura, “Performance of dye-sensitized solar cell using size-controlled synthesis of TiO<sub>2</sub> nanostructure,” *International Journal of Integrated Engineering*, vol. 12, no. 2, pp. 106–114, 2020.
  159. M. Imran, S. Riaz, and S. Naseem, “Synthesis and Characterization of Titania Nanoparticles by Sol-gel Technique,” *Materials Today: Proceedings*, vol. 2, no. 10, pp. 5455–5461, 2015.
  160. M. K. Ahmad, S. M. Mokhtar, C. F. Soon, N. Nafarizal, A. B. Suriani, A. Mohamed, M. H. Mamat, M. F. Malek, M. Shimomura, and K. Murakami, “Raman investigation of rutile-phased TiO<sub>2</sub> nanorods/nanoflowers with various reaction times using one step hydrothermal method,” *Journal of Materials*

- Science: Materials in Electronics*, vol. 27, no. 8, pp. 7920–7926, 2016.
161. S. Shalini, N. Prabavathy, R. Balasundaraprabhu, T. S. Kumar, D. Velauthapillai, P. Balraju, and S. Prasanna, “Studies on DSSC encompassing flower shaped assembly of Na-doped TiO<sub>2</sub> nanorods sensitized with extract from petals of *Kigelia Africana*,” *Optik*, vol. 155, pp. 334–343, 2018.
  162. V. V. Burungale, V. V. Satale, A. J. More, K. K. K. Sharma, A. S. Kamble, J. H. Kim, and P. S. Patil, “Studies on effect of temperature on synthesis of hierarchical TiO<sub>2</sub> nanostructures by surfactant free single step hydrothermal route and its photoelectrochemical characterizations,” *Journal of Colloid and Interface Science*, vol. 470, pp. 108–116, 2016.
  163. G. C. Collazzo, S. L. Jahn, N. L. V. Carreño, and E. L. Foletto, “Temperature and reaction time effects on the structural properties of titanium dioxide nanopowders obtained via the hydrothermal method,” *Brazilian Journal of Chemical Engineering*, vol. 28, no. 2, pp. 265–272, 2011.
  164. S. Shamsudin, M. K. Ahmad, N. Nafarizal, C. F. Soon, R. A. Rahim, D. A. L. Alakendram, M. Shimomura, and K. Murakami, “Fabrication of TiO<sub>2</sub> nanoflowers powder with various concentration of CTAB,” *International Journal of Integrated Engineering*, vol. 12, no. 2, pp. 197–205, 2020.
  165. S. B. Wategaonkar, R. P. Pawar, V. G. Parale, D. P. Nade, B. M. Sargar, and R. K. Mane, “Synthesis of rutile TiO<sub>2</sub> nanostructures by single step hydrothermal route and its characterization,” *Materials Today: Proceedings*, vol. 23, pp. 444–451, 2020.
  166. S. Livraghi, A. M. Czoska, M. C. Paganini, and E. Giamello, “Preparation and spectroscopic characterization of visible light sensitized N doped TiO<sub>2</sub> (rutile),” *Journal of Solid State Chemistry*, vol. 182, no. 1, pp. 160–164, 2009.
  167. M. R. D. Khaki, M. S. Shafeeyan, A. A. A. Raman, and W. M. A. W. Daud, “Application of doped photocatalysts for organic pollutant degradation - A review,” *Journal of Environmental Management*, vol. 198, pp. 78–94, 2017.
  168. N. Jiang, Y. Du, S. Liu, M. Du, Y. Feng, and Y. Liu, “Facile preparation of flake-like blue TiO<sub>2</sub> nanorod arrays for efficient visible light photocatalyst,” *Ceramics International*, no. January, pp. 1–7, 2019.
  169. F. W. Low, C. W. Lai, and S. B. A. Hamid, “One-step hydrothermal synthesis of titanium dioxide decorated on reduced graphene oxide for dye-sensitised

- solar cells application,” *International Journal of Nanotechnology*, vol. 15, no. 1/2/3, p. 78, 2018.
170. H. Zhang, Y. Lv, C. Yang, H. Chen, and X. Zhou, “One-Step Hydrothermal Fabrication of TiO<sub>2</sub>/Reduced Graphene Oxide for High-Efficiency Dye-Sensitized Solar Cells,” *Journal of Electronic Materials*, vol. 47, no. 2, pp. 1630–1637, 2018.
171. S. Z. Siddick, C. W. Lai, J. C. Juan, and S. B. Hamid, “Reduced Graphene Oxide - Titania Nanocomposite Film for Improving Dye-Sensitized Solar Cell (DSSCs) Performance,” *Current Nanoscience*, vol. 13, no. 5, 2017.
172. Y. Zhang, W. Wu, K. Zhang, C. Liu, A. Yu, M. Peng, and J. Zhai, “ Raman study of 2D anatase TiO<sub>2</sub> nanosheets ,” *Phys. Chem. Chem. Phys.*, vol. 18, no. 47, pp. 32178–32184, 2016.
173. R. Hazem, M. Izerrouken, A. Cheraitia, and A. Djehlane, “Raman study of ion beam irradiation damage on nanostructured TiO<sub>2</sub> thin film,” *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*, vol. 444, no. October 2018, pp. 62–67, 2019.
174. M. Tortello, S. Colonna, M. Bernal, J. Gomez, M. Pavese, C. Novara, F. Giorgis, M. Maggio, G. Guerra, G. Saracco, R. S. Gonnelli, and A. Fina, “Effect of thermal annealing on the heat transfer properties of reduced graphite oxide flakes: A nanoscale characterization via scanning thermal microscopy,” *Carbon*, vol. 109, pp. 390–401, 2016.
175. Y. J. Xu, Y. Zhuang, and X. Fu, “New insight for enhanced photocatalytic activity of TiO<sub>2</sub> by doping carbon nanotubes: A case study on degradation of benzene and methyl orange,” *Journal of Physical Chemistry C*, vol. 114, no. 6, pp. 2669–2676, 2010.
176. F. I. M. Fazli, N. Nayan, M. K. Ahmad, M. L. M. Napi, N. K. A. Hamed, and N. S. Khalid, “Effect of annealing temperatures on TiO<sub>2</sub> thin films prepared by spray pyrolysis deposition method,” *Sains Malaysiana*, vol. 45, no. 8, pp. 1197–1200, 2016.
177. V. Madurai Ramakrishnan, N. Muthukumarasamy, S. Pitchaiya, S. Agilan, A. Pugazhendhi, and D. Velauthapillai, “UV-aided graphene oxide reduction by TiO<sub>2</sub> towards TiO<sub>2</sub>/reduced graphene oxide composites for dye-sensitized solar cells,” *International Journal of Energy Research*, vol. 45, no. 12, pp. 17220–

- 17232, Oct. 2021.
178. K. A. Kumar, K. Subalakshmi, and J. Senthilselvan, "Effect of co-sensitization in solar exfoliated TiO<sub>2</sub> functionalized rGO photoanode for dye-sensitized solar cell applications," *Materials Science in Semiconductor Processing*, vol. 96, no. January, pp. 104–115, 2019.
  179. J. Ma, W. Ren, J. Zhao, and H. Yang, "Growth of TiO<sub>2</sub> nanoflowers photoanode for dye-sensitized solar cells," *Journal of Alloys and Compounds*, vol. 692, pp. 1004–1009, 2017.
  180. L. Gomathi Devi and M. Srinivas, "Hydrothermal synthesis of reduced graphene oxide-CoFe<sub>2</sub>O<sub>4</sub> heteroarchitecture for high visible light photocatalytic activity: Exploration of efficiency, stability and mechanistic pathways," *Journal of Environmental Chemical Engineering*, vol. 5, no. 4, pp. 3243–3255, 2017.
  181. M. A. Agam, N. N. Awal, S. A. Hassan, J. A. Yabagi, M. Q. Hamzah, and A. Talib, "Energy band gap investigation of polystyrene copper oxide nanocomposites bombarded with laser," *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, vol. 66, no. 2, pp. 125–135, 2020.
  182. A. Omar, M. S. Fakir, K. S. Hamdan, N. H. Rased, and N. A. Rahim, "Photovoltaic performances and lifetime analysis of TiO<sub>2</sub>/rGO DSSCs sensitized with Roselle and N719 dyes," *IOP Conference Series: Materials Science and Engineering*, vol. 1127, no. 1, p. 012041, 2021.
  183. M. Y. A. Rahman, A. S. Sulaiman, A. A. Umar, and M. M. Salleh, "Dye-sensitized solar cell (DSSC) utilizing reduced graphene oxide (RGO) films counter electrode: effect of graphene oxide (GO) content," *Journal of Materials Science: Materials in Electronics*, pp. 1674–1678, 2017.
  184. T. Supasai, N. Henjongchom, I. M. Tang, F. Deng, and N. Rujisamphan, "Compact nanostructured TiO<sub>2</sub> deposited by aerosol spray pyrolysis for the hole-blocking layer in a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cell," *Solar Energy*, vol. 136, pp. 515–524, 2016.
  185. A. B. Suriani, N. Nafarizal, M. K. Ahmad, M. Shimomura, M. H. Mamat, A. B. Faridah, C. F. Soon, K. Murakami, and S. M. Mokhtar, "Fabrication and characterization of rutile-phased titanium dioxide (TiO<sub>2</sub>) nanorods array with various reaction times using one step hydrothermal method," *Optik*, vol. 154,

pp. 510–515, 2017.

186. F. W. Low, C. W. Lai, K. M. Lee, and J. C. Juan, “Enhance of TiO<sub>2</sub> dopants incorporated reduced graphene oxide via RF magnetron sputtering for efficient dye-sensitised solar cells,” *Rare Metals*, vol. 37, no. 11, pp. 919–928, 2018.

