FABRICATION OF GRAPHENE OXIDE/TITANIUM DIOXIDE HYBRID MATERIAL FOR SOLAR CELL AND MEMBRANE APPLICATION

MUQOYYANAH

UNIVERSITI PENDIDIKAN SULTAN IDRIS

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FABRICATION OF GRAPHENE OXIDE/TITANIUM DIOXIDE HYBRID MATERIAL FOR SOLAR CELL AND MEMBRANE APPLICATION

MUQOYYANAH

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ABSTRACT

This study aimed to fabricate graphene oxide (GO)/titanium dioxide (TiO_2) hybrid-based material for dye-sensitized solar cells (DSSCs) and membrane separation applications. The electrochemical exfoliation assisted by customized triple-tail sodium 1, 4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1, 4-dioxobutane-2-sulphonate (TC14) and commercially available single-tail sodium dodecyl sulphate (SDS) surfactants were used to synthesize GO with water-based electrolyte and N, N-dimethylacetamide (DMAc) as solvents. The chemical reduction process utilizing hydrazine hydrate was then performed to produce reduced GO (rGO) which further hybridized with multi-walled carbon nanotubes (MWCNTs). The fabrication of DSSCs counter electrode (CE) was done by spraying deposition method on fluorine-doped tin oxide (FTO) as substrate and also coated by thin platinum (Pt). Meanwhile, different variety of TiO_2 nanostructures as DSSCs photoanode were synthesized by hydrothermal growth and squeegee methods with different recepi and synthesis time. On the other hand, the DMAc-based GO was used to fabricate nanofiltration (NF) membrane utilizing polyvinylidene fluoride (PVDF) as the main polymer material by using phase inversion method. The DSSCs and NF membrane samples were characterized using solar simulator and dye rejection test, respectively. The DSSCs finding showed that the highest energy conversion efficiency (1.559%) was achieved by TiO_2 NRs-NFs/TC14-rGO/TiO_2 NPs as photoanode and TC14-rGO_MWCNTs/Pt as CE with the value of open circuit voltage, short circuit density, and fill factor were 0.747 V, 3.275 mA/cm^2, and 53.5, respectively. Meanwhile, the NF membrane finding showed that PVDF/SDS-GO/TiO_2 presents the highest dye flux (10.148 L/m^{2}h) and high dye rejection efficiency (~92.76%). In conclusion, the synthesized GO showed a potential to be applied as electrode thin films and also membrane materials. Implication of this study is a novel, simpler, low-cost, and less harsh chemical for the GO synthesis to fabricate CE and photoanode film for DSSCs and also NF membrane.

FABRIKASI BAHAN HIBRID GRAFIN OKSIDA/TITANIUM DIOKSIDA UNTUK APLIKASI SEL SURIA DAN MEMBRAN

ABSTRAK

Kajian ini bertujuan memfabrikasi bahan hibrid berdasar kepada grafin oksida (GO)/titanium dioksida (TiO_2) untuk aplikasi sel suria terpeka warna (SSTW) dan membran pemisahan. Pengelupasan elektrokimia yang dibantu oleh surfaktan buatan rantaian bercabang tiga sodium 1, 4-bis (neopentiloksi)-3-(neopentiloksikarbonil)-1, 4-dioksobutana-2-sulfonat (TC14) dan komersial rantaian tunggal sodium dodesil sulfat (SDS) digunakan untuk mensintesiskan GO dengan elektrolit berasaskan air dan N, N-dimetilasetamida (DMAs) sebagai pelarut. Proses pengurangan kimia menggunakan hidrazin hidrat kemudiannya dilakukan untuk menghasilkan penurunan GO (pGO) yang selanjutnya dihibrid dengan nanotiub karbon berbilang dinding (NTK). Fabrikasi elektrod kaunter (EK) SSTW dilakukan menggunakan kaedah pemendapan semburan di atas timah oksida didop fluorin sebagai substrat dan juga disalut menggunakan platinum (Pt) tipis. Sementara itu, pelbagai TiO_2 struktur nano yang berbeza sebagai fotoanod SSTW disintesis menggunakan penumbuhan hidroterma dan kaedah *squeegee* dengan pelbagai resepi dan waktu sintesis. Selain itu, GO berdasar DMAs digunakan untuk memfabrikasi membran penapisannano (PN) menggunakan polivinilidin florida (PVDF) sebagai bahan polimer utama dengan menggunakan kaedah fasa penyongsangan. Sampel-sampel SSTW dan membran PN masing-masing dicirikan menggunakan solar simulator dan percubaan penyingkiran warna. Hasil kajian SSTW menunjukkan bahawa kecekapan penukaran tenaga yang paling tinggi (1.559%) dihasilkan dengan TiO_2 BtN-BgN/TC14-pGO/TiO_2 PtN sebagai fotoanod dan TC14-pGO_NTK/Pt sebagai EK dengan nilai dari voltan litar terbuka, kepadatan litar pintas, dan faktor pengisi masing-masing adalah 0.747 V, 3.275 mA/cm^2 dan 53.5. Sementara itu, dapatan kajian membran PN menunjukkan bahawa PVDF/SDS-GO/TiO_2 menunjukkan fluks warna yang paling tinggi (10.1478 L/m^{2}h) dan kecekapan penyingkiran warna yang tinggi (~92.76%). Kesimpulannya, GO yang telah disintesis menunjukkan potensi untuk diterapkan sebagai elektrod filem tipis dan juga bahan membran. Implikasi kajian ini adalah sebuah pendekatan baharu, lebih mudah, kos rendah, dan kurangnya bahan kimia untuk sintesis GO untuk hasilkan filem EK dan fotoanod untuk SSTW dan juga membran PN.

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A	Area
Al_2O_3	Aluminium Oxide
AOT4	Sodium bis (3,5,5-trimethyl-1-hexyl)-2-sulfosuccinate
Ar	Argon
atm	Atmosfer
C	Carbon
CB	Conduction Band
CdS	Cadmium Sulfide
CdTe	Cadmium Telluride
CE	Counter Electrode
CIGS	Copper Indium Gallium Selenide
CVD	Chemical Vapor Deposition
D	Defect and Disorder Raman Peak
D-ann	Directly Annealed
DI	Deionize
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMPII	Dimethyl-propyl-benzimidiazole Iodide
DMSO	Dimethylsulfoxide
DSA	Drop Shape Analysis
DSSCs	Dye-sensitized Solar Cells

EDX	Energy Dispersive X-ray
E_g	Band Gap Energy
EIS	Electrochemical Impedance Spectra
F	Fluorine
Fe_3O_4	Black Iron Oxide
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTO	Fluorine-doped Tin Oxide
FWHM	Full Width at Half Maximum
G	Crystalline Graphitic Raman Peak
G-ann	Gradually Annealed
GO	Graphene Oxide
HCl	Hydrochloric Acid
H_2O_2	Hydrogen Peroxide
HRTEM	High Resolution Transmission Electron Microscopy
I	Integral or Current
I_D/I_G	Ratio of Raman's D- and G-Peak Intensity
IPCE	Incident Photon to Current Conversion Efficiency
ITO	Indium-doped Tin Oxide
I-V	Current-voltage
J_{sc}	Short Circuit Current Density
MB	Methylene Blue
MWCNTs	Multi-walled Carbon Nanotubes
N3	Cis-bis(isothiocyanato) bis(2,2′bipyridyl4,4′dicarboxylato) ruthenium(II)

N719	Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)
N749	Black Dye
NCFs	Nanocauliflowers
NF	Nanofiltration
NFs	Nanoflowers
NMP	N-methylpyrrolidone
Non-ann	Non-annealed
NPs	Nanoparticles
NRL	Natural Rubber Latex
NRs	Nanorods
NTs	Nanotrees
NWs	Nanowires
O	Oxygen
PAN	Polyacrylonitrile
PANI	Polyaniline
PEG	Poly(Ethylene Glycol)
PEI	Polyethyleneimine
PES	Polyethersulfone
PET	Polyethylene Terephthalate
PFDTES	Perfluorodecyltriethoxysilane
PMMA	Polymethylmethacrylate
ppm	Parts Per Million
PSf	Polysulfone
PSS	Polystyrenesulfonate

Pt	Platinum
PVDF	Polyvinylidene Fluoride
PVP	Polyvinylpyrrolidone
R	Dye Rejection Efficiency
RBM	Radial Breathing Mode
R_{ct}	Charge Transfer Resistance
rGO	Reduced Graphene Oxide
RO	Reverse Osmosis
R_s	Series Resistance
SDBS	Sodium Dodecyl Benzene Sulphonate
SDS	Sodium Dodecyl Sulphate
SiC	Silicon Carbide
Sn	Stannum
SnO_2	Stannic Oxide
$SrTiO_3$	Strontium Titanate
SWCNTs	Single-walled Carbon Nanotubes
t	Time
T	Transmittance
TBOT	Titanium (IV) Butoxide
TC14	Sodium 1 ,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1 ,4-dioxobutane-2sulphonate
TCVD	Thermal Chemical Vapor Deposition
THF	Tetrahydrofuran
Ti	Titanium
$TiCl_4$	Titanium Tetrachloride

TiO_2	Titanium Dioxide
TTIP	Titanium (IV) Isopropoxide
UV	Ultraviolet
UV-Vis	Ultraviolet Visible
V	Voltage
V_{oc}	Open-circuit Voltage
WCPO	Waste Cooking Palm Oil
wt%	Weight Percentage
XRD	X-ray Diffraction
ZnO	Zinc Oxide
Zn_2SnO_4	Zinc Stannate
ZrO_2	Zirconium Oxide
2D	Raman Signature of Graphitic Material
ε	Membrane Porosity
η	DSSCs Energy Conversion Efficiency
ρ	Density
θ	Angle
τ_n	Electron Lifetime
ω_G	G-band Raman Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Introduction

In this chapter, the research background of graphene oxide (GO)-based thin film and titanium dioxide (TiO_2) nanostructures with their hybridization as counter electrode (CE) and photoanode films for dye-sensitized solar cells (DSSCs) application are explained. In addition, the utilization of GO in the fabrication of nanofiltration (NF) membrane for membrane separation application (dye rejection) is also described clearly. Research problem, objectives, scope and limitations of this study are also presented in this chapter and ended by the thesis organization.

1.2 Research Background

Two of major problems faced by the world nowadays are high demand of electricity and lack of clean water. These become a crucial problems to be solved due to the rare and non-renewable plant or animal fossils as the major source of coal and oil for electricity. In addition, the rapid industrial factory growth caused another big problem such as polluted air and water from its waste product. These are mainly caused by high amount of dangerous heavy metal and dye waste which dissolved in the air and water, respectively.

The first major problem of high electricity demand which leads to the dependency on the non-renewable power source, such as coal, oil, and gas for electricity can be reduced by the effort of utilizing solar energy. The basic principle of solar energy is converting the sunlight into electricity. The development of that solar cell technology has gained a lot of interest since the invention of first generation silicon wafers solar cells in the 20th century by Russell Ohl and the next second generation solar cells based on amorphous silicon, copper indium gallium selenide (CIGS), and cadmium telluride (CdTe) (Bokalič & Topič, 2015). Good performance and high efficiency (η) of around 20% (Green, Emery, Hishikawa, Warta, & Dunlop, 2014) was achieved and became a potential candidate for reducing and slowly replacing the usage of the non-renewable power source. However, the scarcity of source element, high vacuum processes, and high temperature treatment induced high production costs, thereby limiting the fabrication of such solar cells at industrial scales (Bokalič & Topič, 2015).

DSSCs as third generation solar cells becomes a remarkable and promising subject since its invention by O'Regan and Grätzel in 1991 to replace both previous generation solar cells by adopting photosynthesis effect of plant leaves (O'Regan & Grätzel, 1991). DSSCs offers a simple fabrication, flexibility and design opportunities, low-cost material, light weight, and relatively high η (Bokalič & Topič, 2015; Demir, Sen, & Sen, 2017; O'Regan & Grätzel, 1991; Qin et al., 2015; M. Zhu, Li, Liu, & Cui, 2014). Basically, DSSCs consists of four parts; an anode electrode (photoanode) coated of semiconductor layer, a photo sensitizer (dye), an electrolyte containing redox couple, and cathode electrode (CE). Although up to 14.7% efficiency was achieved by Kakiage et al. (2015) and presents a possibility to chase the CIGS and CdTe solar cells, the investigation of DSSCs performance improvement are still wide open such as the improvement of photoanode and CE, and the replacement of dye or electrolyte.

CE has an important role in DSSCs for facilitating electron transfer from photoanode to complete the current cycle. Platinum (Pt) nanoparticles (NPs) is a common material used as CE due to its high electrocatalytic activity and electrical conductivity (Mehmood, Malaibari, et al., 2016; Popoola, Gondal, Alghamdi, & Qahtan, 2018; M. Y. Song et al., 2012). High η of 13.8% was achieved by using Pt material as CE (Kakiage et al., 2015). As an expensive due to its scarcity and easily corroded material, the utilization of Pt as CE need to be reduced and finally replaced by other materials with high transparency, low-cost and high conductivity (Cruz, Pacheco, & Mendes, 2012; Kong, 2013; Wan, Zhang, et al., 2015).

Several carbon-based material such as activated carbon, single- or multi-walled carbon nanotubes (S- or MWCNTs) (Chang et al., 2013; Ramasamy, Lee, Lee, & Song, 2008; Yun et al., 2018), and graphene (Bi et al., 2013) were investigated to reduce and slowly replace Pt due to its low-cost, relatively good electrocatalytic activity, and resistant to the corrosion (Cruz et al., 2012). As high conductive material, MWCNTs CE film fabricated by spin and spray coating methods yield high η of 5.97% (Dobrzański et al., 2017) and 7.59% (Ramasamy et al., 2008), respectively.

Graphene, a 2-D new carbon nanomaterial built of sp^2 carbon arranged in honeycomb lattice, becomes another promising alternative replacement for Pt (Kavan, Yum, & Grätzel, 2011; Kavan, Yum, Nazeeruddin, & Grätzel, 2011; Z.-Y. Li, Akhtar, Kuk, Kong, & Yang, 2012) due to its outstanding electrical and optical properties (Gee et al., 2013; Pan, Hou, Yang, & Liu, 2015; L.-J. Wang et al., 2014; Y. Zhang, Xu, Sun, Li, & Pan, 2011). Chemical vapor deposition (CVD) is the most popular method to produce high purity and controllable thickness of produced graphene. Unfortunately, this method involves an explosive precursor with high synthesis temperature of approximately 1000°C (Mikhailov, 2011).

GO as a graphene derivative becomes an alternative approach and can be chemically synthesized based on Hummers' method. High-quality GO is also produced by using this method, but the utilization of strong acid, poisonous chemicals, and the complex synthesis procedures restrict and make this method complicated (Kang et al., 2016). The transfer process to fabricate thin film is also a challenge due to the powder form of produced graphene and GO based on both methods (CVD and Hummers'). A dispersing agent, such as tetrahydrofuran (THF) (T.-T. Wu & Ting, 2013), alcohol (K. Xu et al., 2016), carbonated water (J. Kim et al., 2010), N-methylpyrrolidone (NMP) (Ekanayaka, Hong, Shen, & Song, 2017; N. Liu et al., 2008), and N,N-dimethylformamide (DMF) (Ambrosi & Pumera, 2016), iso-propanol (Nagavolu et al., 2016), and also water (Johra, Lee, & Jung, 2014) is strongly required to disperse GO powder into the solution form, thereby making it easily transferrable.

A simple and low-cost method known as electrochemical exfoliation can be a promising method to produce GO in the solution form, which can be easily transferred onto desired substrate. Furthermore, electrochemical exfoliation offers a considerable potential in large-scale production due to the high volume of produced solution from a single-synthesis process (Yu, Lowe, Simon, & Zhong, 2015). Various solvents usually used as electrolytes in the electrochemical process include acetonitrile, DMF, dimethylsulfoxide (DMSO), propylene carbonate, nitric and sulfuric acid (Ambrosi & Pumera, 2016; J. Liu, Poh, et al., 2013; Parvez, Li, et al., 2013; M. Zhou et al., 2013). Water-based exfoliation, which utilizes surfactant, offers a more environment-friendly approach compared to the chemical, acid, or sulfuric electrolytes.

The hydrophobic nature of surfactant chains attached to the carbon (C) bonds and hydrophilic heads of the surfactant stabilize the GO dispersion in the solution. Therefore, the surfactant chain (tail) number is important in the exfoliation process because it determines the quality of the synthesized GO. The intercalation process during electrochemical exfoliation can be increased by increasing the number of surfactant tail groups. Mohamed et al. (2015, 2014, 2016) investigated the single-, double- and triple-tail surfactants and showed that the customized triple-tail surfactant, namely sodium 1 ,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1 ,4-dioxobutane-2-sulphonate (TC14), improves the MWCNTs dispersion in latex nanocomposites.

Additionally, different surfactant tail groups in one-step electrochemical exfoliation intermixed with natural rubber latex (NRL) nanocomposite are successfully utilized by Suriani, Nurhafizah, Mohamed, Zainol, & Masrom (2015). The fabricated electrode utilizing TC14 surfactant also yields higher conductivity and capacitance value as compared to the commercially available single-tail sodium dodecyl sulphate (SDS) surfactant used in supercapacitor application. The high interaction of GO/NRL due to the triple interactions of TC14 surfactant results in wrinkled and crumpled tissue-like sheets with low agglomeration (Suriani, Nurhafizah, Mohamed, Masrom, Sahajwala, et al., 2016). The further reduction process of the synthesized GO assisted with customized triple-tail TC14 surfactant and subsequently mixed with the radiation vulcanization NRL provides higher conductivity and capacitance values compared to the pristine GO (Suriani, Nurhafizah, Mohamed, Masrom, Mamat, et al., 2017).

Overall, the usage of GO and reduced GO (rGO) as CE material either by Hummers' or exfoliation method were also presents relatively high η (Z.-Y. Li et al., 2012; Qiu, Zhang, Wang, Chen, & Wang, 2014; Suriani, Nurhafizah, Mohamed, Mamat, et al., 2017). Recently, η of 4.72% was achieved by using rGO as CE (K. Xu et al., 2016), while GO exhibits lower η (1.59%) (Z.-Y. Li et al., 2012) due to its higher oxygen-functional groups which resulted higher electron transfer resistance and decreased DSSCs performance. However, the DSSCs η based on GO or rGO CE thin films was found relatively lower as compared to the utilization of Pt as CE. In order to improve its performance, the hybridization between carbon-based materials were widely investigated such as GO- or rGO-MWCNTs. By hybridizing them, higher η (6.91%) was achieved as compared to the pristine rGO or MWCNTs film due to the larger surface area and higher electrical conductivity (Yeh et al., 2014). Nonetheless, its η was still lower as compared to the conventional Pt CE film (13.8%) (Kakiage et al., 2015).

On the other hand, several Pt improvement such as fabrication method, materials modification, and hybridization with other materials were also done in order to achieve higher DSSCs efficiency (Demir, Savk, Sen, & Sen, 2017; Demir, Sen, et al., 2017). M. Y. Song et al. (2012) combined urea in the Pt fabrication using homogeneous deposition method followed by reduction using ethylene glycol and achieved 9.34% DSSCs η. They also found that smaller Pt particles was better to increase catalytic activity due to the larger surface area (M. Y. Song et al., 2012). Meanwhile, Bajpai et al., (2011) showed that ~27% Pt loading combined with graphene yields higher efficiency (2.91%) as compared to ~34% Pt loading (~2.79%). Therefore, less Pt loading results in increased DSSCs performance when it is hybridized with GO or rGO. The hybridization of Pt with carbon-based material is still an object of investigation to obtain higher η.

In this present work, both customized triple-tail TC14 and commercially available single-tail SDS surfactants are used in the water-based electrolyte preparation to assist the exfoliation process and investigate their effects on GO production. Chemical reduction process is carried out to produce rGO due to a water-based solution that requires low temperature during reduction. Among several reducing agents, such as chemicals, plant extracts, microorganisms, proteins and hormones, hydrazine hydrate was selected due to its effectiveness in thin and fine rGO production (Chua & Pumera, 2014). The spraying deposition method is chosen among various transfer methods, such as chemical etching, roll-to-roll process, drop casting, and spin and dip coating to transfer GO and rGO solutions. This method is used due to its simple process, easy control, potential for large-scale production and suitability for various substrates (Pham et al., 2010). Fluorine-doped tin oxide (FTO) is selected as a substrate with better performance as compared to indium-doped tin oxide (ITO). ITO displayed thermal instability and two times higher sheet resistance compared to FTO after sintering process. In addition, higher η was achieved by using FTO thus this substrate is recommended for DSSC application (Sima, Grigoriu, & Antohe, 2010).

Furthermore, the hybridization of rGO and MWCNTs which then coated by thin Pt NPs (10 nm) are also done in this work in order to investigate its performance as compared to the pristine rGO, MWCNTs, and Pt NPs CE thin films. In addition, its also done to improve the rGO conductivity and catalytic activity. The MWCNTs was produced from waste cooking palm oil (WCPO) as precursor by modified thermal CVD (TCVD) method (Azmina, Suriani, Falina, Salina, Rosly, et al., 2012; Azmina, Suriani, Falina, Salina, & Rusop, 2012; Suriani, Muhamad, et al., 2011; Suriani, Nor, & Rusop, 2010). To the best of our knowledge, this is the first report which utilized MWCNTs from WCPO and its hybridization with TC14-rGO before coating with thin Pt NPs as CE thin film and combined it with TiO_2 as photoanode for DSSCs application.

The morphology structure of photoanode material also plays a key role in the DSSCs photovoltaic performance. This is due to their role on providing surface area for dye molecules adsorption, light absorption, and also transferring the excited electrons to the substrate. Several semiconductor oxide layers that have been used as photoanodes for DSSCs are zinc oxide (ZnO) (Jiang, Sun, Lo, Kwong, & Wang, 2007; D. Wang et al., 2017; Xie et al., 2018), stannic oxide (SnO_2) (Kavan, Yum, & Grätzel, 2011;

Ramasamy et al., 2008), zinc stannate (Zn_2SnO_4) (J. Gong, Liang, & Sumathy, 2012), strontium titanate ($SrTiO_3$) (C. W. Kim, Suh, Choi, Kang, & Kang, 2013) and TiO_2 (M. K. Ahmad, Mohan, & Murakami, 2015; M. K. Ahmad, Mokhtar, et al., 2016; M. K. Ahmad, Soon, et al., 2016; Fazli et al., 2017; Ullattil & Periyat, 2017; Ullattil, Thelappurath, et al., 2017; J.-F. Wang, Zhang, & He, 2018; D. Zhang, Yoshida, Oekermann, Furuta, & Minoura, 2006). Among all, ZnO and TiO_2 are the most popular semiconductor materials investigated in the DSSCs application. This is due to their nontoxicity, wide band gap energy, and good carrier mobility (Y. J. Hwang, Hahn, Liu, & Yang, 2012; Lei, Li, Zhang, & Anpo, 2016; Qin et al., 2015; Tamilselvan, Yuvaraj, Kumar, & Rao, 2012).

ZnO presents better carrier mobility, lower electron recombination, and flexible synthesis process as compared to TiO_2 (Quintana, Edvinsson, Hagfeldt, & Boschloo, 2007). Recently, high DSSCs η of 8.22% was achieved when ZnO was treated by 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES) hexane solution after dye immersion (Xie et al., 2018). However, less chemical stability of ZnO yields the precipitation after dye immersion thus resulted less dye loading, poor electron injection, and lower efficiency (Quintana et al., 2007). TiO_2 offers better chemical and physical stabilities (Lei et al., 2016; Qin et al., 2015; Tamilselvan et al., 2012), large surface area (Tamilselvan et al., 2012), and presents higher DSSCs efficiency as compared to ZnO thus suitable to be applied as a photoanode material (Quintana et al., 2007; Tiwana, Docampo, Johnston, Snaith, & Herz, 2011).

TiO_2 has three crystallite forms (phases) which are commonly known as anatase, rutile, and brookite. Brookite is not beneficial for several applications due to its unstable form at room temperature. Anatase is a metastable form which can transformed into rutile by high temperature, while rutile is the most stable form. Both anatase and rutile forms are commonly utilized for DSSCs application due to their high photocatalytic activity (Lei et al., 2016). However, the drawback of TiO_2 as compared to ZnO as photoanodeis its lower electron mobility and higher electron recombination thus requiring improvement (Quintana et al., 2007). It is known that TiO_2 morphology can critically affect the TiO_2 performance, thereby its improvement and modification (J.-Y. Liao, He, Xu, Kuang, & Su, 2012) were widely investigated to solve this problem. These include varying layer numbers (Z.-S. Wang, Yanagida, Sayama, & Sugihara, 2006), addition of different haze (Chiba, Islam, Komiya, Koide, & Han, 2006) and other metal oxide coatings or dopings (Dahlan, Md Saad, Berli, Bajili, & Umar, 2017; Kroon et al., 2007), utilization of other nanostructures and mixing the TiO_2 phase (Yasin, Guo, & Demopoulos, 2016; W. Zhou et al., 2011). Combination of the crystallinity phase may yield high photocatalytic activity and consequently improve the η value (Fazli et al., 2017; L.-J. Wang et al., 2014; J. Zhao, Wu, Zheng, Huo, & Tu, 2015).

The zero-dimensional (0-D) TiO_2 NPs provide a large specific area for effective dye adsorption, which may increase DSSCs η thus highly recommended. Recently, one-dimensional (1-D) TiO_2 nanostructures such as nanorods (NRs) (M. K. Ahmad, Soon, et al., 2016; Qin et al., 2015), nanotubes (J. Hu et al., 2016), and nanowires (NWs) (Faisal, 2015; W. Wu et al., 2012) gain a lot of interest to be applied as DSSCs photoanode due to its better light harvesting, less grain boundary, slow electron recombination, and faster electron transport (Sadhu & Poddar, 2014; W. Wu et al., 2012). The combination of both morphologies and phases was proven to give better DSSCs performance as compared to the pure phase. Hafez, Lan, Li, & Wu (2010) showed that the pure TiO_2 NRs and TiO_2 NPs give lower η (4.4 and 5.8%, respectively) as compared to the TiO_2 NRs/NPs bilayer photoanode (7.1%). Y. Cao et al. (2016) also achieved higher η of 7.39% by utilizing bilayered photoanode consisting of TiO_2 NRs and TiO_2 NPs as compared to pure film (0.54 and 4.63% of TiO_2 NRs and TiO_2 NPs, respectively). Moreover, W. Wu et al. (2012) also showed that two layers photoanode consists of TiO_2 NWs/NPs presents 7.92% efficiency as compared to the pure film. These results were also in a good agreement with several works done by utilizing both different morphologies and phases (M. K. Ahmad & Kenji, 2013; Rezvani, Parvazian, & Hosseini, 2016; J. Wang et al., 2014; W. Wu et al., 2012).

Post-treatment of TiO_2 nanostructures, such as annealing, also critically affects the optical and electrical properties of fabricated films. Ahn et al. (2011) showed that post-annealing of TiO_2 nanobarbed fibres resulted in higher crystallinity and higher conductivity as indicated by a lower band gap energy (E_g). Hasan, Haseeb, Saidur, & Masjuki (2008) reported that the TiO_2 morphology structure remains unchanged as the annealing temperature increases (300–600°C), while its transmittance decreases due to surface roughness. Meanwhile, D. Zhao et al. (2008) showed that the surface roughness factor for TiO_2 NPs increases with the annealing temperature (350–600°C). A low annealing temperature (350°C) yielded small-sized crystallites, while a higher temperature (600°C) improved the crystallinity, thus decreasing the internal surface area and impending the dye adsorption. Moreover, L. Meng, Li, and Santos (2011) found that the top ends of TiO_2 NRs sharpen as the annealing temperature increases (200–500°C). They also showed that higher DSSCs η was achieved by the annealed films as compared to the as-deposited films without annealing. This is also in a good agreement with results from M. K. Ahmad, Soon, et al. (2016), who obtained the highest dye adsorption and DSSCs η by annealing TiO_2 NRs at 450°C for 30 minutes.

Besides post-annealing treatment, the hybridization of TiO_2 nanostructures with carbonaceous material, such as CNTs, graphene, GO, or rGO was also done in order to improve the TiO_2 electrical properties (Ilyas, Gondal, Baig, Akhtar, & Yamani, 2016; S.-B. Kim et al., 2015; J. Liu, Fu, et al., 2015; L. Liu, Zhang, Zhang, & Feng, 2017; Mehmood, Malaibari, et al., 2016; J. Song et al., 2011; J. Wang et al., 2014; J. Zhao, Wu, et al., 2015). This is due to the high conductivity of the carbonaceous material, which increases the electron transfer through TiO_2, decreases the electron recombination, and yields higher short circuit current density (J_{sc}). Higher η of 7.52% was achieved by J. Zhao, Wu, et al. (2015) when utilizing TiO_2-rGO nanocomposite via one-step hydrothermal method as compared to pure TiO_2 NPs film (6.39%). Meanwhile, L. Liu et al. (2017) achieved 6.85% efficiency when immersing the prepared TiO_2 NPs in the GO solution and then reducing them via thermal reduction process. However, they also found that less dye adsorption occurred in the sample with excessive rGO amount. Therefore, high amount of rGO must be avoided.

The configuration of the photoanode film also gives different effects in DSSCs performance. J. Song et al. (2011) sprayed a rGO layer on TiO_2 NPs and achieved 6.06% efficiency. They also found that a thicker rGO layer was not beneficial for dye adsorption, which decreased η. In contrast, J. Liu, Fu, et al. (2015) deposited the rGO layer between TiO_2 NPs films by the electrospray method. By spraying 1 layer of rGO (40 nm) between two TiO_2 NPs films, a higher efficiency (7.8%) was obtained as compared to pure TiO_2 NPs films (7.1%) and thicker (120 nm) rGO layers (7.3%).

Furthermore, when they investigated multiple rGO layers between the TiO_2 NPs films, the highest η (8.9%) was achieved by three rGO layers as compared to five layers rGO (6.1%).

In this work, the novel combination of rutile 1-D TiO_2 nanostructures (NRs and NWs) synthesized by hydrothermal growth method (M. K. Ahmad, Mohan, et al., 2015; M. K. Ahmad & Murakami, 2015; Faisal, 2015) and anatase 0-D TiO_2 NPs applied by squeegee method (D. Zhang et al., 2006) are used as bottom and upper layer of photoanode layer, respectively. Both methods are chosen due to its low-cost with simple preparation and fabrication. The three-dimensional (3-D) TiO_2 nanoflowers (NFs), nanotrees (NTs), and nanocauliflowers (NCFs) are also produced during hydrothermal synthesis. In addition, the novel hybridization of TiO_2 NRs-NFs with rGO based on customized triple-tail TC14 surfactant (TC14-rGO) and TC14-rGO_MWCNTs hybrid solution are also done by the simple spraying deposition method before applying TiO_2 NPs. In addition, the post-annealing treatment of TiO_2 NRs-NFs after hydrothermal growth is also done in order to investigate its effect in the DSSCs performance.

The second major problem of clean water can comes from high amount of dangerous heavy metal and dye waste which dissolved in the air and water, respectively. This contamination results from the rapid industrial factory growth, such as textile industries, pharmaceuticals, metal plating, and printing industries which causes the lack of clean water. The difficulty in treating dye wastewater which contains toxic substances and are non-degradable substances, becomes an important issue that needs to be solved (Z. Zhu et al., 2017). Several methods that are generally used to remove dye from contaminated water are chemical and physical sorption, evaporation, biological degradation, chemical oxidation, flocculation-coagulation, photocatalytic system, electrodeposition, and membrane separation/filtration (Makertihartha, Rizki, Zunita, & Dharmawijaya, 2017; Z. Zhu et al., 2017). Among these methods, membrane filtration gains considerable interest due to its several advantages, such as simple operation, minimal chemical used, low energy, good separation, easy automation, low pollution, and high recovery rate (Méricq, Mendret, Brosillon, & Faur, 2015; Z. Zhu et al., 2017).

The pollutant filtration efficiency is strongly affected by the membrane type. The membrane can be divided into microfiltration, ultrafiltration, NF, and reverse osmosis (RO) based on its pore size (Shon, Phuntsho, Chaudhary, Vigneswaran, & Cho, 2013). NF membrane offers some advantages for textile wastewater, such as relatively high water flux and permeability compared with RO, low operating pressure, low energy consumption, small pore size (1–5 nm), and high efficiency to remove the dye (Safarpour, Vatanpour, Khataee, & Esmaeili, 2015; Shon et al., 2013; Z. Zhu et al., 2017). Several methods that are generally used to prepare the membrane include interfacial polymerization, stretching, sintering, track-etching, electrospinning, and phase inversion method (Lalia, Kochkodan, Hashaikeh, & Hilal, 2013).

Phase inversion method is commonly used due to its simple and easy preparation. Then, the morphology of the fabricated membrane is strongly affected by several factors, including polymer concentration, solvent (Madaeni & Taheri, 2011; Nasib, Hatim, Jullok, & Alamery, 2017), non-solvent (Thürmer, Poletto, Marcolin, Duarte, & Zeni, 2012), composition, coagulant temperature (X. Wang, Zhang, Sun, An,

& Chen, 2008), precipitation time, temperature and evaporation time before immersion, additive (N. M. Mokhtar, Lau, Ng, Ismail, & Veerasamy, 2015; Ngang, Ooi, Ahmad, & Lai, 2012), and casting thickness (Madaeni & Taheri, 2011). Various polymer materials that are generally used for membrane fabrication include polysulfone (PSf), polyacrylonitrile (PAN), polyaniline (PANI) (Yusoff et al., 2018), polystyrenesulfonate (PSS), polyethersulfone (PES) (Zinadini, Zinatizadeh, Rahimi, Vatanpour, & Zangeneh, 2014), polymethylmethacrylate (PMMA), polyethyleneimine (PEI), polyvinylpyrrolidone (PVP), and polyvinylidene fluoride (PVDF) (X. Cao, Ma, Shi, & Ren, 2006; Kumaran, Alagar, Kumar, Subramanian, & Dinakaran, 2015; Ngang et al., 2012; Z. Zhu et al., 2017). The formation of membrane pores with either finger- or sponge-like structure is also affected by the membrane solution viscosity (Nasib et al., 2017). These properties are strongly affected by the polymer material and solvent types. An extremely low polymer molecular weight results in exceedingly weak membrane, whereas an excessively high value makes the membrane difficult to process due to the highly viscous solution (J. F. Kim, Jung, Wang, Drioli, & Lee, 2017).

PVDF presents excellent properties, including chemical, alkali, and corrosion resistance; thermal, chemical, and UV stability; good membrane-forming properties; high mechanical strength; and good solubility in many organic solvent, thereby making it applicable for water treatment (Ngang et al., 2012; Nikooe & Saljoughi, 2017; Z. Wang, Yu, et al., 2012; Z. Zhu et al., 2017). Meanwhile, the generally used organic solvents include NMP (Nasib et al., 2017; Thuyavan, Anantharaman, Arthanareeswaran, & Ismail, 2016), DMF (Thürmer et al., 2012), DMSO (Thuyavan et al., 2016), and N,N-dimethylacetamide (DMAc) (Madaeni & Taheri, 2011; Nasib et al., 2017; Thuyavan et al., 2016).

Madaeni and Taheri (2011) investigated the effect of polymer concentration, casting thickness, and solvent type on the morphology of the fabricated membrane. The result showed that 20 wt% of PVDF presents wider and longer finger-like pore morphology as compared to lower PVDF content. They also found that 200 μm casting thickness results in the highest flux and permeability. The utilization of DMAc in the membrane solution preparation results in high porosity and flux compared with NMP and DMF (Madaeni & Taheri, 2011; Nasib et al., 2017; Thuyavan et al., 2016; X. Wang, Zhang, et al., 2008). Meanwhile, Buonomenna, Macchi, Davoli, and Drioli (2007) showed that the direct immersion in the coagulant after casting process results in higher porosity as compared to the delayed immersion. Membrane solution heating during stirring process also resulted higher porosity membrane than the room temperature stirring process. Thürmer et al. (2012) also found that the use of pure water as coagulant results in an asymmetric pore membrane with higher hidrophilicity than ethanol, followed by a water coagulant.

However, PVDF is well-known as high hydrophobic material which reduces the flux and permeability, hence requiring modification, either through physical or chemical means (X. Cao et al., 2006). In improving PVDF hydrophilicity, hydrophilic inorganic NPs additive, such as aluminium oxide (Al_2O_3), black iron oxide (Fe_3O_4), cadmium sulfide (CdS), silica, carbon-based and semiconductor materials are clearly needed. Carbon nanotubes, graphene, GO, and rGO which are carbon-based materials are widely investigated for PVDF modification. Among these materials, GO gained considerable interest due to its large surface area and high amount of oxygen-functional groups (Z. Zhu et al., 2017). Z. Zhu et al. (2017) obtained higher hidrophilicity and water flux than pure PVDF membrane by adding GO. GO addition also alters the membrane morphology of the finger-like structure. Y. Zhao et al. (2013) showed that PVDF/GO blend membrane presents higher rejection as compared to pure PVDF membrane. This result also agreed with the findings of other studies (M. Hu & Mi, 2013; Z. Xu, Zhang, et al., 2014; P. Zhang et al., 2017).

Most studies reported the use of the powder form of GO that resulted from Hummers' method as additives in membrane solution preparation (M. Hu & Mi, 2013; Z. Wang, Yu, et al., 2012; Y. Zhao et al., 2013). As mentioned before, the synthesized GO by Hummers' or modified Hummers' methods produced good quality GO. However, it presents unsafe and inefficient synthesis method due to the usage of strong acid and highly toxic material and its complex synthesis steps, respectively (Kang et al., 2016). Electrochemical exfoliation method then becomes a promising solution due to its simple, low-cost, and low chemical consumption (Yu et al., 2015). On the other hand, several metal oxides such as ZnO, zirconium oxide (ZrO_2), and TiO_2 were widely developed as an additive due to their good properties such as stability, availability, antibacterial activity, and the presence of abundant hydroxyl groups. The abundance of hydroxyl groups improves the hydrophilicity of the material, thus increasing the flux and permeability (X. Cao et al., 2006). Ngang et al. (2012) shows that PVDF-TiO_2 mixed-matrix membrane enhances the water permeability and increases the methylene blue (MB) rejection.

Hence, in this work, the directly synthesized DMAc-based GO assisted by commercially available single-tail SDS surfactant is used as a solvent before mixing it with TiO_2 as an additive to fabricate modified PVDF-based NF membrane. TiO_2 is utilized to further improve the membrane's hydrophilicity. Then, pristine PVDF membrane fabricated by DMAc and also PVDF/SDS–GO fabricated using the directly synthesized DMAc-based GO are used for comparison. Afterward, the three fabricated membranes are used to investigate their effectiveness for MB rejection application. To the best of our knowledge, this work presents a novel and simple GO synthesis through electrochemical exfoliation assisted by SDS surfactant by utilizing DMAc as the solvent for PVDF-based membrane fabrication.

1.3 Problem Statement

Pristine Pt is known as an outstanding material utilized as CE film for DSSCs application. However, high cost of Pt due its scarcity increases the DSSCs production cost thus limits its application. The utilization of GO and rGO as a derivative of graphene material which offers a low-cost, relatively high electrical and physical properties is a promising method to reduce and further slowly replaced the utilization of Pt. The electrochemical exfoliation method presents simpler synthesis process of GO as compared to Hummers' method which utilizing strong acids and hazardous chemicals. The utilization of customized triple-tail TC14 surfactant as dispersing and stabilizing agent in the electrochemical exfoliation offers better exfoliation as compared to the commercially available single-tail SDS surfactant.

Further chemical reduction process utilizing hydrazine hydrate instead of several reducing agents resulted thin and fine rGO with low oxygen (O) content thus increase the films conductivity. The produced solution form from electrochemical exfoliation and chemical reduction process gives an advantage in the transfer process in order to fabricate thin film. More fabrication steps and the usage of solvent to disperse GO powder which absolutely needed in Hummers' method can be hindered. Spraying deposition method offers simpler and easier to control the film fabrication. In order to improve the electrical properties of CE film, the hybridization of TC14-rGO and MWCNTs from WCPO is carried out. Thin Pt coating is also carried out in order to increase the electrocatalytic activity of the fabricated CE thin film.

Meanwhile, the bilayered photoanode film consists of different TiO_2 nanostructures morphology and crystalline phases is also fabricated to achieve higher dye adsorption and faster electron transport. The hybridization of TiO_2 nanostructures with the produced TC14-rGO and TC14-rGO_MWCNTs are also carried out in order to achieve higher conductivity thus decrease the electron recombination during DSSCs process. Hydrothermal growth and squeegee method are selected for TiO_2 nanostructures synthesis method due to its simpler preparation and synthesis process. On the other hand, more fabrication steps of GO as the additive for membrane fabrication can be reduced by performing the direct electrochemical exfoliation. Direct DMAc-based GO in the solution form can be obtained from single step. The hazardous and complex step of Hummers' method can be avoided thus presents a simpler and safer synthesis method for membrane fabrication.

Therefore, in this work, GO-based material synthesized from the simple electrochemical exfoliation assisted by customized triple-tail TC14 and commercially available single-tail SDS surfactants are used for DSSCs and membrane application. The water-based GO is used to fabricate various CE thin films and also photoanode hybrid film for DSSCs. Meanwhile, DMAc-based GO is used to fabricate PVDF-based NF membrane for dye rejection application.

1.4 Research Objectives

The goals of this study are:

i. To improve the DSSCs photovoltaic performance by utilizing various kind of GO- and rGO-based CE thin films and its hybridization.

ii. To enhance the DSSCs photovoltaic performance by utilizing various kind of TiO_2 nanostructures and its hybridization as photoanode film.

iii. To investigate the novel direct DMAc-based GO synthesized from electrochemical exfoliation for membrane separation application.

iv. To improve the NF membrane performance by utilizing the synthesized DMAc-based GO and TiO_2 nanostructures.

1.5 Scope and Limitations of Study

The utilized surfactant in the synthesis of GO is limited to the customized triple-tail TC14 and commercially available single-tail SDS surfactants. Next, the production of rGO is carried out by chemical reduction process utilizing hydrazine hydrate instead of thermal reduction process due to the water-based solvent. Its hybridization to fabricate CE hybrid thin film is only focused with MWCNTs based on WCPO. The thin Pt NPs is only coated for TC14-rGO and TC14-rGO_MWCNTs film.

Meanwhile, 0-, 1-, and 3-D TiO_2 nanostructures are utilized as photoanode film instead of ZnO. The TiO_2 crystalline phase is only focused on rutile and mixed of anatase and rutile. The 0-D TiO_2 nanostructures is limited to TiO_2 NPs, while the 1-D nanostructures is limited to TiO_2 NRs and NWs. TiO_2 NFs, NTs, and NCFs are the 3-D TiO_2 nanostructures which simultaneously produced during hydrothermal method of 1-D TiO_2 NRs. The hybridization of photoanode film is done for only TiO_2 NRs-NFs film utilizing TC14-rGO and TC14-rGO_MWCNTs hybrid solutions. Meanwhile, the utilization of carbonaceous and semiconductor material as additive for the membrane fabrication are limited for the GO and TiO_2, respectively. In addition, the investigation of dye rejection application is limited for MB dye with low concentration (10 ppm).

The fabricated GO- and rGO-based CE thin films and its hybridization, and also the NF membrane are characterized using several instrumentations. FESEM and EDX are used to investigate the morphology and element compound of various fabricated photoanode, CE thin films, and NF membrane. Meanwhile, HRTEM, XRD, micro-Raman spectroscopy are used to investigate the structural properties. Diffrac.eva V4.0 software is used to determine the phase, crystallite size, and crystallite percentage from XRD data. The integral breadth (*I* breadth) measurement is preferred instead of full width at half maximum (FWHM) due to its accuracy. The optical and electrical properties of fabricated film are measured by UV-Vis, four-point probe equipment with Keithley as sourcemeter and Leios TMXpert software as data analysis. Moreover, UV-Vis is also used to measure the absorption of the treated water after dye rejection test was performed. The contact angle measurement is used to measure the hydrophilicity of fabricated NF membrane utilizing drop shape analysis. Solar simulator under 1M solar illumination is used for DSSCs efficiency measurement, while dead-end stirred cell is used for the flux and dye rejection measurement.

1.6 Thesis Organization

This work is focused on two applications based on GO- or rGO-based material. The improvement of DSSCs efficiency by utilizing various type of CE thin films and various type of TiO_2 nanostructures are done for DSSCs application. Meanwhile, the investigation of DMAc-based GO using NF membrane tested for MB is done for dye rejection application. This thesis consists of 5 chapters which presents the details work regarding DSSCs and dye rejection applications. Chapter 1 explains the research background, problem statement, research objectives, and scope and limitations of the study. The fundamental theories and previous studies related to DSSCs and NF membrane applications are intensively describes in Chapter 2. It is divided into two main parts, and each part of applications is explained clearly. The synthesis and fabrication process, and also characterization technique of various CE thin films, TiO_2 nanostructures, and NF membrane are clearly explained in Chapter 3. Next, Chapter 4 explains the results of each application including the morphology, structural, optical, electrical, and performance of fabricated CE and photoanode films and also NF membrane. The last chapter (Chapter 5) summarizes the results of both applications and cover the suggestion for the future work.