

# FABRICATION OF ZINC OXIDE/GRAPHENE OXIDE NANOCOMPOSITE FOR ULTRAVIOLET PHOTOCONDUCTIVE SENSOR AND PHOTOCATALYTIC APPLICATION

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**UNIVERSITI PENDIDIKAN SULTAN IDRIS**

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**FABRICATION OF ZINC OXIDE/GRAPHENE OXIDE NANOCOMPOSITE FOR  
ULTRAVIOLET PHOTOCONDUCTIVE SENSOR AND PHOTOCATALYTIC  
APPLICATIONS**

**ALI ABDUL AMEER MOHAMMED**

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## ABSTRACT

The aim of this study was to fabricate zinc oxide (ZnO) and aluminium (Al) doped ZnO nanorods (NRs) nanowires (NWs) graphene oxide (GO) and reduced GO (rGO) for ultraviolet (UV) photoconductive sensor and photocatalytic applications. The method used to synthesize GO was electrochemical exfoliation assisted by custom-made triple-tails sodium 1, 4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1, 4-dioxobutane-2-sulphonate (TC14) and commercially available single-tail sodium dodecyl sulphate (SDS) surfactants. Then, to produce rGO the exfoliated GO was reduced via reduction process by adding hydrazine hydrate. The ZnO and AlZnO NRs and NWs were synthesized via sol-gel immersion method. The hybridized ZnO and AlZnO NRs and NWs samples with SDS-GO, SDS-rGO, TC14-GO and TC14-rGO were done by spray coating method. The ZnO/GO-based samples were characterized using scanning electron microscopy, energy dispersive X-ray, high resolution transmission electron microscopy, X-ray diffraction, micro-Raman, UV-visible (UV-Vis) spectroscopy and four-point probes measurement. The UV photocurrent measurement system and UV-Vis spectroscopy were then used to analyse the UV photoconductive sensor and photocatalytic performances respectively. The findings show that the highest sensitivity and responsivity of UV photoconductive sensor at around 47.3 and 345.7 mA/W were observed in AlZnO NWs/TC14-GO (24 hours) sample. Meanwhile 90 g of sand/ZnO NRs/TC14-GO with reaction time of 48 hours exhibited the highest photocatalytic efficiency of 100% removal of 5ppm of methylene blue (MB). The improvement of both UV photoconductive sensor and photocatalytic performances were believed due to the existence of GO that help to lower the recombination rate of electrons-holes by trapping the electron within the GO sheets. In conclusion, the AlZnO NWs/TC14-GO (24 hours) nanocomposites demonstrate a good material for UV photoconductive sensor application. The sand/ZnO NRs/TC14-GO is a great potential material for photocatalytic application. The implication of this study is a novel, green and economical approach for UV photoconductive sensor and photocatalytic application by using AlZnO NWs/TC14-GO (24 hours) and sand/ZnO NRs/TC14-GO, respectively.





## FABRIKASI NANOKOMPOSIT ZINK OKSIDA / GRAFIN OKSIDA MELALUI KAEDAH SEMBURAN UNTUK SENSOR FOTOKONDUKTIF ULTRAVIOLET DAN APLIKASI FOTOKATALITIK

### ABSTRAK

Tujuan kajian ini adalah untuk memfabrikasi zink oksida (ZnO)/bahan berasaskan-grafin oksida (GO) untuk sensor fotokonduktif ultraviolet (UV) dan aplikasi fotokatalitik. Kaedah yang digunakan untuk mensintesis GO adalah pengelupasan elektrokimia yang dibantu oleh surfaktan buatan rangkaian bercabang tiga sodium 1, 4-bis (neopentiloksi) -3- (neopentioksikarbonil) -1, 4-dioksobutana-2-sulfonat (TC14) dan komersial rangkaian tunggal sodium dodesil sulfat (SDS). Kemudian, untuk menghasilkan penurunan GO (pGO), GO yang terkelupas diturunkan melalui proses pengurangan dengan menambahkan hidrazin hidrat. ZnO dan aluminium zink oksida (AlZnO) rod nano (NRs) dan wayarnano (NWs) disintesis melalui kaedah perendaman sol-gel. Sampel-sampel ZnO dan AlZnO NRs dan NWs dihibridisasi dengan SDS-GO, SDS-rGO, TC14-GO dan TC14-rGO menggunakan kaedah penyemburan. Sampel berasaskan ZnO/GO dicirikan dengan menggunakan mikroskop elektron, penyerakan tenaga sinar-X, mikroskop elektron penghantaran resolusi tinggi, pembelauan sinar-X, mikro-Raman, cahaya nampak UV-Vis dan pengukuran prob empat titik arus-voltan. Pengukuran fotoarus UV dan cahaya nampak UV-Vis kemudiannya digunakan untuk menganalisis tahap prestasi sensor fotokonduktif UV dan fotokatalitik. Hasil kajian mendapati bahawa sensitiviti dan responsif tertinggi untuk sensor fotokonduktif UV pada sekitar 47.3 dan 345.7 mA/W adalah terdapat di dalam sampel AlZnO NWs/TC14-GO (24 jam). Sementara itu 90 g pasir/ZnO NRs/TC14-GO dengan masa tindak balas 48 jam mempamerkan tahap kecekapan fotokatalitik yang paling tinggi dalam menyingkirkan 100% 5 ppm biru metilena. Penambahbaikan prestasi sensor fotokonduktif UV dan fotokatalitik yang ditunjukkan dipercayai adalah kerana adanya GO yang membantu menurunkan kadar rekombinasi elektron-lubang dengan memerangkap elektron di dalam helaian GO. Kesimpulannya, nanokomposit AlZnO NWs/TC14-GO (24 jam) merupakan bahan yang terbaik untuk diaplikasikan sebagai sensor fotokonduktif UV. Pasir/ZnO NRs/TC14-GO adalah bahan yang sangat berpotensi untuk digunakan di dalam aplikasi fotokatalitik. Implikasi kajian ini adalah pendekatan baharu, hijau dan ekonomik untuk sensor fotokonduktif UV dengan menggunakan AlZnO NWs/TC14-GO (24 jam) dan aplikasi fotokatalitik dengan menggunakan pasir/ZnO NRs/TC14-GO.



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## LIST OF ABBREVIATIONS

Al	Aluminium
$(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$	Aluminium Nitrate Nonahydrate
AlZnO	Aluminum Zinc Oxide
Ag	Silver
AOT4	Double-Tails Sodium Bis (3,5,5-Trimethyl-1-Hexyl) Sulfosuccinate
Ar	Argon
Au	Gold
Cr	Chromium
$^{\circ}\text{C}$	Degree Celsius
$\text{CO}_3\text{O}_4$	Cobalt oxide
cm	Centimeter
CNTs	Carbon Nanotubes
CVD	Chemical Vapour Deposition
$\text{C}_2\text{H}_7\text{NO}$	Mono-Ethanolamine
$\text{C}_3\text{H}_8\text{O}_2$	2-Methoxyethanol
D	Defect and Disorder-Peak
DI-water	De-Ionized Water
e	Electron
EDX	Energy Dispersive X-Ray
e-h	Electron-holes

eV	Electron Volt
Fe	Iron
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
G	Crystalline Graphite-Peak
GaN	Gallium Nitride
GE	Graphene
GO	Graphene Oxide
HCL	Hydrochloric Acid
HRTEM	High Resolution Transmission Electron Microscopy
HMT	Hexamethylenetetramine
Hz	Hertz
$\text{KMnO}_4$	Potassium Permanganate
I	Current
$I_{ph}$	Photocurrent
$I_d$	Darkcurrent
$P_{op}$	Optical power
ITO	Indium Tin Oxide
$I_D/I_G$	Intensity of D and G peak
I-V	Current-Voltage
M	Molar
meV	Mili Electron Volt
MB	Methylene Blue Dye
MOCVD	Metal Organic Chemical Vapour Deposition

MgO	Magnesium Oxide
Mg(NO <sub>3</sub> ) <sub>2</sub>	Magnesium Nitrate
MWCNTs	Multi-Walled Carbon Nanotubes
NaNO <sub>3</sub>	Sodium Nitrate
NaOH	Sodium Hydroxide
Nb <sub>2</sub> O <sub>5</sub>	Niobium Pentaoxide
nm	Nanometer
NFs	Nanoflowers
NRs	Nanorods
NTs	Nanotubes
NWs	Nanowires
O	Oxygen
OH	Hydroxide
O II	Orange II dye
PH	Potential of Hydrogen
PLD	Pulsed Laser Deposition
PSS	Single-Tail Poly (Sodium 4-Styrenesulfonate)
PZT	Lead Zirconate Titanate
rGO	Reduced Graphene Oxide
RhB	Rhodamine B Dye
rpm	Radians Per Minute
S	Sensitivity
s	Second
SDBS	Sodium Dodecyl Benzene Sulphonate

SDS	Sodium Dodecyl Sulphate
H <sub>2</sub> SO <sub>4</sub>	Sulphuric Acid
SiC	Silicon Carbide
SiO <sub>2</sub>	Silicon Dioxide
SnO <sub>2</sub>	Tin Oxide
SrTiO <sub>3</sub>	Strontium Titanate
T	Temperature
TC14	Sodium 1, 4-Bis (Neopentyloxy)-3-(Neopentyloxycarbonyl)- 1, 4-Dioxobutane-2-Silphonate
TiO <sub>2</sub>	Titanium Dioxide
UV	Ultraviolet
UV-Vis	Ultraviolet Visible
V	Voltage
VS	Vapour-Solid
W	Watt
VLS	Vapour Liquid Solid
XRD	X-ray Diffraction
$\theta$	Angle between Incident and Diffracted Rays
$\mu\text{A}$	Microampere
$\mu\text{m}$	Micrometer
$\rho$	Electrical Resistivity
$\sigma$	Electrical Conductivity
Å	Angstrom
ZnO	Zinc Oxide
Zn (CH <sub>3</sub> COO) <sub>2</sub> . 2H <sub>2</sub> O	Zinc Acetate Dehydrate

$Zn(NO_3)_2$                       Zinc Nitrate Hexahydrate

$Zn_2SnO_4$                       Zinc Stannate

0-D                                Zero-Dimensional

1-D                                One-Dimensional

2-D                                Two-Dimensional

3-D                                Three-Dimensional

## LIST OF APPENDICES

- A Journal of IOP Publishing (2018)
- B Journal of IOP Publishing (2019)
- C International Postgraduate Conference on Science & Mathematics 2017
- D International Postgraduate Conference on Science & Mathematics 2018

## CHAPTER 1

### INTRODUCTION

This chapter discusses the research background of zinc oxide (ZnO) aluminium oxide (Al) based on ultraviolet (UV) photoconductive sensor application. The graphene oxide (GO) and reduced GO (rGO) assisted by commercially single tail sodium dodecyl sulphate (SDS) and custom made triple tails sodium 1, 4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1, 4-dioxobutane-2-silphonate (TC14) surfactants. The ZnO and composite ZnO with SDS- and TC14-GO based were also utilized for photocatalysis applications. Next, the research problems statement, objectives, scope and limitations of the research and the thesis organization are then described at the end of this chapter.



## 1.2 Research Background

UV photoconductive sensor are used in many different applications, including environmental monitoring, pharmaceuticals, optical communications, automobiles, space research, chemical and printing industry as well as robotics, hence it has emerge as a profound field of research (Monroy, Omns & Calle, 2003). A high performance UV photoconductive sensor should satisfy the following requirements in terms of high sensitivity ( $I_{photo}/I_{dark}$ ) and responsivity: the photocurrent through the device per unit power of irradiation per active area (M.H.Mamat, Khusaimi, Musa, M.F.Malek & Rusop, 2011).

Among various semiconducting materials, ZnO has been greatly accounted as favourable materials for UV photoconductive sensor due to the following properties including high electron mobility, wide direct band gap of 3.37 eV, high exciton binding energy of 60 meV, good transparency, ease and low cost of manufacturing (Lajvardi et al. 2018; Karak, 2017; Khamkhom et al. 2017). Various morphology structures of successfully synthesized ZnO nanostructures were produced including nanorods (NRs) (R. Ahmad, Ahn & Hahn, 2017) nanowires (NWs) (Hullavarad, S. S, Hullavarad, N. V, Karulkar, P. C, Luykx, A & Valdivia, 2007), nanotubes (NTs) (Yijun Zhang et al. 2015), nanotetrapods (Gedamu et al. 2014) and nanosheets (X. H. Huang et al. 2011). For great and promising UV photoconductive sensor materials, the one-dimensional (1-D) ZnO NRs and NWs are commonly used and have received the most attention. This is due to its large surface area and good electron transport, offering low charge recombination thus improved UV photoconductive sensor performance (M.F. Malek, Mohd Zainizan Sahdan, et al. 2013; M.F. Malek,





M.H.Mamat, et al. 2013). To obtain high-quality ZnO nanostructures, several methods, such as sol–gel immersion (Bahadur et al. 2008), hydrothermal (Xian et al. 2017), chemical bath deposition (Terasako et al. 2015) and chemical vapour deposition (CVD) (Jih-jen Wu & Liu, 2012), have been developed. Sol–gel immersion method is one of the most promising fabrication techniques for preparing ZnO thin film due to its facile, economic and simple fabrication with low reaction temperature and easy to control the ZnO growth as well as suitable to be applied in mass ZnO production (A.A.Ameer, Suriani, A.R.Jabur, N. Hashim, Fatiatun & K.Zaid, 2019).

However pristine ZnO demonstrated low operating sensitivity with weak photoresponsivity as a practical UV photoconductive sensor. The pristine ZnO thin films has shown low responsivity of only 34 mA/W under incident 365 nm wavelength at 10 V operating bias (D. Liu et al. 2018) which is unfavourable to be utilized in practical UV photoconductive sensor application. Doping small amount of active metals and carbonaceous allotropes to pristine ZnO seem to improve the performance of ZnO UV photoconductive sensing properties. The metallic such as iron (Fe) (Khayatian, Asgari, Ramazani, Akhtarianfar, Kashi, et al. 2017), Chromium (Cr) (S. Safa et al. 2018) and Al (Zi-QiangXu, HongDeng & JuanXie, 2006). Among all the Al doped-ZnO nanostructure was preferable due to its capability to increase the conductivity without weaken the optical transmission and also suggested to be easily incorporation into ZnO lattice (Jin, Hamberg & Granqvist, 1988). The non-metallic additives such as carbon nanotubes (CNTs), graphene, GO and rGO shown to be effective in separating of the photogenerated exciton via electrical field formation of the charge space around hetero-interfaces (M. Z. S. Safa & Mokhtari, 2017). The



composited of non-metallic to ZnO nanostructures also improves the photochemical stability which then assist to elevate ZnO UV photoconductive sensor sensitivity.

Meanwhile, for the use of ZnO for photocatalytic application, it has shown a great removal efficiency of organics and heavy metal pollutions in the water due to it become a serious issue (Y. Chang, 2015). There are many type of dye used in industrial such as methylene blue (MB), Rhodamine B (RhB) (K. Huang et al. 2014), Orange II( O II) (P. K. Chen et al. 2013) and so on. The MB were one of the dye used commonly in medicine (Jinbin Liu et al. 2013), textile industry (K. Singh & Arora, 2011), sensors (Nishiyabu et al. 2014). However, most of the water pollutions escape from traditional treatment due to high stability against light, chemicals and temperature (Gupta & Suhas, 2009). Meanwhile, in 1972 Honda and Fujishima discovered the first photocatalytic activity in titanium dioxide ( $\text{TiO}_2$ ) electrodes (Fujishima & Honda, 1972). The photocatalysis have been opened new door of elimination and degradation of organic dye pollutions in wastewater (J. Hou et al. 2011). The ZnO one of the promising material for the photocatalytic applications (Di et al. 2016; Becker et al. 2011). Among all the structures ZnO NRs was mostly utilized in water cleaning using photocatalysis process due to its high surface area to volume ratio.

Moreover, the efficiency of photocatalysis still very low due to fast recombination of electron-hole (e-h) rate (B. Li et al. 2012) wich estimated with nanosecond (Liang et al. 2016). The photocatalysis performance were show enhancement by doping and loading with metal (X. Hou et al. 2015), multi wall carbon nanotubes (MWCNTs) (Saleh, Gondal & Drmosh, 2010) GO .(B. Li et al.

2012) and rGO (Y. Zhao et al. 2017). Which the loading and doping material on ZnO nanostructure slow the recombination e-h rate. But, the problems with metallic element are poor in transparency which can dramatically affect the photocatalysis efficiency. The hybrid of GO with ZnO nanostructure show enhancement in the photocatalysis efficiency. This enhancement was believed due to lowering the recombination e-h rate (Opoku et al. 2017). In the meantime the UV absorption of the ZnO nanostructures were found to increase with the existence of CNTs, GO and rGO. Nevertheless, the tubular structure of CNTs limits the active surface area to be accessible for ZnO nanostructures. The presence of GO and rGO also assist to decrease the recombination rate of produced exciton and provide ultra-fast carrier transportation between electrodes via conductive GO and rGO network (Ding et al. 2013; C. Chen, 2018).

Graphene, a single layer form of carbon with a two-dimensional (2-D) hexagonal lattice, has shown many outstanding properties, including high mobility of charge carriers (Y. Chen & Ma, 2010; Shahil & Balandin, 2012), unique transport performance (W. Hong et al. 2008), high mechanical strength (Papageorgiou, Kinloch & Young, 2017) thermal conductivity (Colonna et al. 2016), stretchable and almost transparent. Due to this graphene is suitable for many technological applications such as graphene-based nanoelectronics, nanocomposite materials, photocatalytics, energy storage and conversion, molecular gas sensors and transparent conductive film. All of these engineering applications need massive production of excellent quality graphene materials. However, pristine graphene cannot directly be used because of its high production cost and lack of functional groups especially for nanocomposite interfacial bonding.



Therefore, other derivatives of graphene such as GO has been used as a starting precursor because of its (1) functional groups that increase GO hydrophilicity in aqueous solutions, (2) readily scalable materials and (3) versatile handling for chemical functionalization. GO was defined as  $sp^2$ -hybridized planar carbon sheets that are highly oxidized by oxygen functional groups, is widely used in electronics applications. Various methods for GO production have been reported elsewhere. Among them is Hummer's method, which has been widely used for GO production due to its easy scale-up. However, it involves strong acids and hazardous chemicals that would be detrimental to the environment if implemented industrially at a large scale. At present, the electrochemical exfoliation method is greener, simpler and more convincing methods for producing high-quality GO in large quantity. This was due to the lower chemical utilization by this method and its ability to be easily carried out in a water-based medium (Ambrosi & Pumera, 2016; Cooper & Kinloch, 2015).

Nonetheless, the agglomeration GO and interfacial control between ZnO nanostructures and GO is the major drawback in the development of homogenous ZnO/GO hybrid nanocomposites films, thus it is necessary to prevent GO substances from agglomeration. Its unique properties can only be achieved when it is only associated with individual sheet, therefore keeping them well separated is highly required. Hence, the used of surfactant compounds for better dispersion of GO is needed. To date, the most effective surfactant for GO dispersion is limited on single and long chain characteristics (SDS, SDBS, PSS, etc.) (Suriani, Fatiatun, et al. 2018; Suriani, Muqoyyanah, et al. 2018; Ali A A Mohammed. Suriani & Akram R Jabur, 2018). In contrast to custom made hyper branched tri-chain surfactant namely sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate





(TC14), it is believed to provide extra chain to interconnect between GO and ZnO nanostructures (NRs and NWs). It then resulted in better dispersion and homogeneity of GO based nanocomposites films that later offer excellent solutions pertinent to ZnO UV photoconductive sensor performance. The TC14 surfactant have shown better option compared to the single-chain SDS surfactant in dispersing CNTs throughout the latex matrix via latex technology then resulted in better electrical conductivity. Surfactants have been recognized as the third component in the enhancement of the interfacial interaction between GO/rGO and other type of hybrids materials (Suriani, M.D Nurha, et al. 2015; Suriani, Nurhafizah, et al. 2017). Therefore, an appropriate selection of surfactant may facilitate the formation of conductive nanocomposites between GO/rGO and ZnO nanostructure. Careful selection and systematic study of surfactant architecture, particularly the tail group toward GO dispersion into nanocomposites, are important.



In the meantime, the reduction of GO to rGO was favourable due to the restoration of conjugation electronic structure from  $sp^3$  to the  $sp^2$  structure. RGO is also known to consist of several layers of graphite which has been reduced from the GO sheets through two processes which includes (i) chemical reduction such as hydrazine hydrate (Chua and Pumera 2014; Bo et al. 2014) and also thermal treatment such as microwave irradiation (S. N. Alam, Sharma & Kumar, 2017). These carbon materials have been chosen as multifunctional nanofillers in the nanocomposite field nowadays. The selection of rGO was particularly due to the presence of reactive sites along the structures which thus can improve the electrical, charge ion mobility, enhance the compatibility and increased the interaction to the ZnO nanostructure. In comparison to the thermal treatment, the used of hydrazine hydrate as a reducing agent





through the chemical reduction approach was more favourable as this approach were more controllable, ease and rapid method to produce a bulk quantity of rGO in a short time (Suriani, Mohamed, et al. 2018; Compton & Nguyen, 2010).

Meanwhile, among various methods for GO/rGO films fabrication, spraying method gained much attention due to its portable, easy and flexible on various large area substrates as compared to the sputtering and dip coating methods where these methods requires ultra-high vacuum facility thus give non cost-effective to the UV photoconductive sensor applications (Jiao, Zhang & Chen, 2014; Pham et al. 2010).

In term of interior mechanism namely the optimal amount of GO/rGO on the ZnO surface, the chemical and electronic interaction at the surface of GO/rGO and ZnO nanostructures, the interfacial hybrid heterostructure control during the fabrication of between GO/rGO-ZnO nanostructures and some other detail are yet not clear and need further investigation fundamentally (Y. Yang & Liu, 2011; K. Yang et al. 2011). The understanding of those mention phenomono lead to improving the UV photoconductive sensing and photocatalytic properties of ZnO nanostructures/GO/rGO nanocomposites in a more consistent manner. A novel and systematic study on the understanding of the role, effect and interaction of heterojunction ZnO nanostructures/GO and rGO hybrid nanocomposites to enhance UV photoconductive sensing and photocatalytic activity is necessary and important (Z. Li et al. 2013; Xuewen Fu et al. 2012). Herein, in this work ZnO and AlZnO NRs and NWs be fabricated via sol-gel immersion method before composited with both GO and rGO. The GO produced by using electrochemical exfoliation method with the assistance of custom made tri-chain hyper-branched TC14 surfactant. In this work as well, both





customized and commercially available surfactants used in the water-based electrolyte preparation to assist the exfoliation process and investigate their effects on GO production towards improving UV photoconductive sensing and photocatalytic properties of ZnO and AlZnO NRs and NWs. Chemical reduction process 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 selected due to its effectiveness in thin and fine rGO production (Ren et al. 2011). The spraying deposition and immersion methods chosen among various transfer methods to transfer GO and rGO solutions. This method used due to its simple process, easy control, potential for large-scale production and suitability for various substrates (Pham et al. 2010).



### 1.3 Problem Statement

Many researcher have been reported the ZnO is a promising candidate for UV photoconductive sensor and photocatalytics application (G. Huang, Zhang, & Bai 2019; Khun et al. 2015; Y. Liu et al. 2015). Among all the structure of ZnO the NRs and NWs have shown the best performance for UV photoconductive sensor and photocatalytic applications due to its large surface area and good electron transport. Among various synthesis method of ZnO nanostructures, sol-gel immersion is one of the most promising fabrication due to its facile, economic and simple fabrication with low reaction temperature and easy to control the ZnO growth as well as suitable for high volume ZnO production.



Nevertheless the application of ZnO as UV photoconductive sensor and photocatalytic are limited due to low operating sensitivity, weak photoresponsivity and low removal efficiency. The pristine ZnO thin films has shown low responsivity of only 34 mA/W (D. Liu et al. 2018), and 51% removal percentage for UV photoconductive sensor and photocatalytic (M. Y. Guo et al. 2011), respectively which are unfavorable to be utilized as practical UV photoconductive sensor and photocatalytic application. However, the pristine ZnO have been composite with metallic such as Al and non-metallic such as GO and rGO in order to improve the efficiency of UV photoconductive and photocatalytic applications (Zi-QiangXu, Hong Deng, JuanXie, 2006; M. Z. S. Safa & Mokhtari, 2017). Meanwhile, common methods for GO production are Hummers and electrochemical exfoliation method. Hummer's method was unfavourable due to it used strong acids and hazardous chemicals that would be detrimental to the environment. The electrochemical exfoliation method was more convincing to synthesize GO solution due to its greener, simple preparation and economic (Jose, 2011). The chemical reduction process carried out to produce rGO via hydrazine hydrate due to its benefits of low operation temperature and capable to produce high quality rGO in a short time with high efficiency in the nanoelectronic applications due to the presence of reactive sites along the structures and efficient interaction between the oxygen containing functional groups with the electrolyte.

The major problem on the ZnO/GO hybrid films fabrication is the absence of high quality heterojunction interfacial of nanocomposites for efficient UV photoconductive sensing and photocatalytic properties (C. Xie et al. 2018; Suriani, Fatiatun, et al. 2018). The situation is worsen by the agglomeration of GO due to van der Waals force making interfacial control between ZnO nanostructures and GO more



complicated and causes the major drawback in the development of homogenous ZnO/GO nanocomposites films. Thus it is necessary to prevent GO substances from agglomeration as its unique properties can only be achieved when it is only associated with individual sheet, therefore keeping them well separated is highly required. Hence, the used of surfactant compounds for better dispersion of GO is needed. To date, the most effective surfactant for GO dispersion is limited to single and long chain characteristics (SDS, SDBS, PSS, etc.). In contrast to custom made hyper branched tri-chain surfactant namely sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate (TC14), it is believed to provide extra chain to interconnect between GO and ZnO nanostructures. It resulted in better dispersion, interfacial connectivity and homogeneity of ZnO/GO hybrid nanocomposites films that then offer excellent solutions pertinent to UV photoconductive sensing properties of ZnO. The TC14 surfactant have shown better option compared to the single-chain SDS surfactant in dispersing CNTs throughout the latex matrix via latex technology then resulted in better electrical conductivity.

Surfactants have been recognized as the third component in the enhancement of the interfacial interaction between GO/rGO and other type of hybrids materials (N. G. Sahoo et al. 2012; K. S. Kim et al. 2009; Jose, 2011). Therefore, an appropriate selection of surfactant may facilitate the formation of conductive nanocomposites between GO/rGO and ZnO nanostructure. Careful selection and systematic study of surfactant architecture, particularly the tail group toward GO/rGO dispersion into nanocomposites, are important. Hence, for the first time we introduce novel, facile, green and economic preparation of ZnO and AlZnO nanostructures/agglomerated free GO and rGO assisted with hyper branched surfactant for efficient UV photoconductive





sensing and photocatalytic properties. The spraying deposition and immersion methods chosen among various transfer methods to transfer SDS- and TC14-GO and rGO solutions. This method used due to its simple process, easy control, potential for large-scale production and suitability for various substrates. Various techniques used for physical characterizations, including FESEM, EDX, HRTEM, micro-Raman spectroscopy, XRD, UV-Vis spectroscopy and I-V measurement. UV photoresponse measurements of the ZnO nanostructures (NRs and NWs with aluminium and without aluminium doped)/GO and rGO fabricated UV photoconductive sensors performed by using the UV photocurrent measurement system (Keithley 2400) operated at 365 nm with a power density of  $750 \text{ m W/cm}^2$  and a bias voltage of 5 V.

The photocatalytic performance of sand/ZnO NRs and sand/ZnO NRs/GO samples were evaluated by the photodegradation of MB UV irradiation by UV light 365 nm with a power density of  $750 \text{ m W/cm}^2$ . The degradation of MB was obtained by UV-Vis spectroscopy absorbance at 665 nm. The UV photoconductive sensing and photocatalytic mechanism investigation on the role and effect of GO in improving the UV photoconductive sensing and photocatalytic properties of ZnO nanostructures/GO nanocomposites are discussed in detail. The novel systematically study on the understanding towards the role, effect and interaction of heterojunction ZnO nanostructures/GO hybrid nanocomposites to enhance UV photoconductive sensing and photocatalytic activity is necessary and important particular at fundamental level.



## 1.4 Research Objectives

- i. To fabricate ZnO and AlZnO NRs/NWs via sol-gel immersion methods and its hybridized with SDS and TC14-GO and rGO via spray coating method.
- ii. To fabricate sand/ZnO NRs via sol-gel immersion method and its hybridization with SDS and TC14-GO by immersion method.
- iii. To determine the potential application of ZnO and AlZnO NRs/NWs/SDS- and TC14-GO and rGO hybrid nanocomposites in UV photoconductive sensors and photocatalytic application.
- iv. To investigate the UV photoconductive sensing and photocatalytic mechanisms on the role and effect of GO on the ZnO nanostructure based on UV photoconductive sensor and photocatalytic performance

## 1.5 Scope and Limitation of Studies

This research focuses on fabricated (SDS-GO and TC14-GO) by electrochemical exfoliations method. Followed by producing (SDS-rGO and TC14-rGO) by using hydrazine hydrate as reducing agent based on reductions process. The synthesized SDS-GO, TC14-GO, SDS-rGO and TC14-rGO samples were characterized by FESEM, EDX, HRTEM, Raman spectroscopy, XRD, UV-Vis spectroscopy and I-V measurement in order to determine the morphological, structural, optical and electrical properties, respectively. Furthermore, the second part of this thesis was on UV photoconductive sensor applications. By fabrication pristine ZnO and AlZnO NRs (4 hours) at 95 °C and pristine ZnO and AlZnO NWs (12 and 24 hours) at 90 °C by using sol-gel immersion methods were grow on the MgZnO seed layers. Followed

by coating by SDS-GO, SDS-rGO, TC14-GO and TC14-rGO based on spray coating methods followed by annealing at 400 °C in argon ambient. The fabricated ZnO and AlZnO NRs and NWs (12 and 24 hours) samples were characterized by FESEM, EDX, HRTEM, Raman spectroscopy, XRD, UV-Vis spectroscopy and I-V measurement in order to determine the morphological, structural, optical and electrical properties, respectively. And analysis by UV photocurrent two probes measurement system (Keithley 2400) operated at 365 nm with a power density of 750 m W/cm<sup>2</sup> and a bias voltage of 5 V to obtain the responsivity and sensitivity of UV photoconductive sensor.

Meanwhile, the third part of this thesis was based on photocatalytic applications. Which the ZnO NRs (4 hours) were synthesized on sands particles at 95 °C by sol-gel immersion methods. Followed by immersion sand/ZnO NRs (4 hours) in SDS- and TC14-GO at 90 °C for 2 hours followed by annealing at 400 °C in argon ambient. The synthesized sand/ZnO NRs and sand/ZnO/SDS- and TC14-GO samples were characterized by FESEM, EDX, XRD and Raman spectroscopy in order to determine the morphological and structural properties. The UV-Vis spectroscopy was used to determine the removal MB percent.

## 1.6 Thesis Organization

This thesis involves of five chapters. Chapter 1 includes introduction, research background, research problem, research objectives, scope and limitation of studies. Chapter 2 presents deeper review that explains the synthesis method, structures and properties and of of ZnO properties, nanostructures, and synthesis method of ZnO nanostructures. Next, the properties of GO and rGO and the synthesis methods of GO and rGO. And focused on the pristine ZnO, doped ZnO and hybrid or composite with GO and rGO based on UV photoconductive sensor and photocatalysis applications. The chapter 3 which covers the synthesized GO and rGO, fabricated ZnO and AlZnO/NRs and NWs and hybrid with GO and rGO, characterizations and analysis technique are explained. The Chapter 4 were discussed the results in details and the mechanism on the role and effect of GO in improving the UV photoconductive sensor and photocatalysis applications of ZnO/GO nanocomposites. Finally, the Chapter 5 conclude the conclusion and suggestions for future work.