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SYNTHESIS AND CHARACTERIZATION OF TRANSPARENT SUPERHYDROPHOBIC FLUORINATED GRAPHENE OXIDE AND SILICA BASED SOL GEL COATING FILMS

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By

MOHD HAMZAH BIN HARUN

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

September 2020

DEDICATION

To my parents, Hajah Zarah binti Taib, Haji Harun bin Abdul Ghani, my wife, Dr. Norfazlinayati Othman, my lovely children, family, in-laws, supervisors and the lecturers, colleagues, relatives, friends and who have given me all supports, loves and patience.

Thank you very much.

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

SYNTHESIS AND CHARACTERIZATION OF TRANSPARENT SUPERHYDROPHOBIC FLUORINATED GRAPHENE OXIDE AND SILICA BASED SOL GEL COATING FILMS

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Chairperson : Professor Zainal Abidin Talib, PhD
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Transparent water repellent organosilica based coating containing tetraorthosilicate (precursor), fluoroalkylsilane (hydrophobic agent) and nanofillers (roughness agent) were prepared by sol-gel method. The coating was prepared by modification of silica (SiO_2) or graphene oxide (GO) nanofillers with siloxane having long chain fluoroalkylsilane that allow for reducing surface energy. Four different samples were prepared namely, tetraorthosilicate sol (TEOS sol), tetraorthosilicate-fluoroalkylsilane (TEOS-FAS), tetraorthosilicate-fluoroalkylsilane-silica (TEOS-FAS-SiO_2) and tetraorthosilicate-fluoroalkylsilane-graphene oxide (TEOS-FAS-GO). The hydrophobic coating solutions were prepared at different concentration percentages of silica and GO ranging from 0.04 pph - 0.20 pph respectively. The water contact angle, transmittance degree, surface morphology and topography, chemical composition and surface analysis were characterized by Attension Tensiometer, UV-Visible Spectrophotometer, Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscope (AFM), Fourier Transform Infrared Spectroscope (FTIR), and X-Ray Photoelectron Spectroscopy (XPS).

The contact angle for TEOS sol formulation at different concentrations of tetraorthosilicate showed a hydrophilic behavior in which the contact angle measured was lower than 90^o whereas for TEOS-FAS formulation, hydrophobic behavior was obtained in which the measured contact angles were between 90^o and 115^o. For TEOS-FAS-SiO_2 and TEOS-FAS-GO, the contact angles obtained were in the range of pre-superhydrophobic and superhydrophobic range (120^o - 168^o). Such behavior can be explained by the presence of hydrophobic agents which were fluoroalkylsilane and nanosize fillers which were SiO_2 and GO. To

investigate the durability of hydrophobicity value, the contact angle after peeling test using Scotch tape was measured. It showed that the TEOS-FAS-GO is more durable as the drop of contact angle value is more gradual as compared with other samples.

The transmittance for all samples showed that they were transparent and the range obtained was between 70% - 95%. FESEM images confirmed the presence of silica and GO in the samples in which for TEOS-FAS-SiO_2, uniform structure was obtained whereas for TEOS-FAS-GO, it showed that the silica from TEOS grew onto the graphene flakes. FTIR showed that the most important peak at 1036-1055 cm^{-1} has been obtained which confirmed the covalent attachment of FAS with silanol particles within tetraorthosilicate matrix in TEOS-FAS-GO and TEOS-FAS-SiO_2 formulation. AFM demonstrated that the roughness increased with the addition of silica and GO fillers with TEOS-FAS-GO gave relatively greater roughness than TEOS-FAS-SiO_2 samples. XPS analysis showed that FAS and TEOS molecules were successfully grafted on the SiO_2 and GO surfaces with hydroxyl and carboxyl groups were involved as well as silica nanoparticles from TEOS sol for TEOS-FAS-GO and silica nanoparticles itself for TEOS-FAS-SiO_2.

The introduction of SiO_2 and GO in the formulation of transparent TEOS sol formulation containing long chain fluoroalkylsilane enhance the surface roughness and thus induces the hydrophobicity in which the water contact angle obtained in the range of hydrophobicity and superhydrophobicity (120^o - 169^o). This indicates that the surface roughness plays an important role in enhancing hydrophobicity and lowering the surface free energy. Although the transmittance degrees obtained were slightly lower than TEOS sol and TEOS-FAS formulation which were around 70-95%, the transmittance is still within the accepted level since the hydrophobic coatings obtained were visible.

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

SINTESIS DAN PENCIRIAN FILEM SALUTAN SUPERHIDROFOBIA LUTSINAR SOL GEL BERASASKAN SILIKA DAN GRAFIN OKSIDA TERFLUORIN

Oleh

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Pengerusi : Profesor Zainal Abidin Talib, PhD
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Salutan kalis air lutsinar berasaskan organosilika yang mengandungi tetraortosilikat (prekursor), fluoroalkilsilana (agen hidrofobik) dan pengisi nano (agen kekasaran) telah disediakan menggunakan kaedah sol-gel. Salutan tersebut telah disediakan dengan modifikasi pengisi nano silika atau grafin dengan siloksana yang mempunyai rantaian panjang fluoroalkilsilana yang membolehkan ia menurunkan tenaga permukaan. Empat sampel berbeza telah disediakan iaitu sol tetraorthosilikat (sol TEOS), sol tetraorthosilikat fluoroalkilsilana (TEOS-FAS), tetraorthosilikat-fluoroalkilsilana-silika (TEOS-FAS-SiO_2) dan tetraorthosilikat fluoroalkilsilana-grafin oksida (TEOS-FAS-GO). Larutan salutan hidrofobik telah disediakan pada purata kepekatan berbeza iaitu dari 0.04 pph hingga 0.20. Sudut sentuh air, darjah kepancaran, morfologi dan topografi permukaan, komposisi kimia dan analisa permukaan dicirikan dengan alat Attension Tensiometer, Meter Spektro UV-Tampak, Mikroskop Elektron Imbasan Medan Pancaran (FESEM), Mikroskop Daya Atom (AFM) Infra-Merah Transformasi Fourier (FTIR) dan Spektroskopi X-Ray.

Sudut sentuh untuk formulasi sol TEOS pada kepekatan berbeza tetraorthosilikat menunjukkan yang ia mempunyai sifat hidrofilik yang mana sudut sentuh yang diukur adalah lebih rendah daripada 90^o berbanding dengan formulasi TEOS-FAS, sifat hidrofobik diperoleh dengan sudut sentuh diukur adalah di antara 90^o dan 115^o. Sudut sentuh yang berbeza diperoleh bagi TEOS-FAS-SiO_2 dan TEOS-FAS-GO yang mana sudut sentuh diperolehnya dalam julat prasuperhidrofobik dan superhidrofobik (120^o - 168^o). Sifat sebegini boleh dijelaskan dengan kehadiran agen hidrofobik iaitu fluoroalkilsilana dan pengisi bersaiz nano iaitu SiO_2 and GO. Untuk menyiasat ketahanan nilai hidrofobik, sudut sentuh selepas ujian kupasan menggunakan pita Scotch telah diukur. Ia menunjukkan yang TEOS-FAS-GO lebih tahan memandangkan penurunan nilai

sudut sentuh lebih seragam berbanding sampel-sampel lain. Darjah transmisi untuk kesemua sampel menunjukkan yang setiap darinya lut sinar dan julat diperoleh ialah 70% - 95%. Imej FESEM mengesahkan kehadiran silika dan GO pada sampel yang mana struktur uniform bagi TEOS-FAS-SiO_2 didapati manakala bagi TEOS-FAS-GO, ia menunjukkan silika yang terhasil daripada TEOS tumbuh pada empingan grafin. FTIR menunjukkan yang puncak penting adalah pada 1036-1055 cm^{-1} s yang mengesahkan berlakunya sangkutan kovalen oleh FAS terhadap partikel silanol dalam matriks tetraorthosilikat bagi formulasi TEOS-FAS-GO dan TEOS-FAS-SiO_2. AFM menunjukkan yang kekasaran meningkat dengan penambahan pengisi silika dan GO dan TEOS-FAS-GO memberikan nilai kekasaran yang sangat tinggi. Analisis XPS menunjukkan molekul TEOS dan FAS tercangkuk pada permukaan SiO_2 dan GO dengan kumpulan berfungsi hidroksil dan karboksil terlibat dan juga partikel nano silika daripada sol TEOS untuk TEOS-FAS-GO dan partikel nano silika unuk TEOS-FAS-SiO_2.

Penampilan SiO_2 dan GO dalam formulasi sol TEOS lutsinar yang mengandungi fluoroalkilsilana rantai panjang meningkatkan kekasaran permukaan dan tahap hidrofobik di mana sudut sentuh air diperoleh dalam julat hidrofobik dan superhidrofobik. Ini menunjukkan yang kekasaran permukaan memainkan peranan penting dalam meningkatkan tahap hidrofobik dan menurunkan tenaga permukaan bebas. Walaupun darjah transmisi yang didapati sedikit rendah bagi TEOS-FAS-SiO_2 dan TEOS-FAS-GO daripada formulasi sol TEOS dan TEOS-FAS iaitu sekitar 70-95%, transmisi diperoleh masih pada tahap boleh diterima memandangkan salutan hidrofobik yang didapati adalah boleh tampak.

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

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
APTEOS	Aminopropyltriethoxysilane
ASTM	American Standard Testing Method
ATR	Attenuated Total Reflectance
CNT	Carbon nanotube
Co_3O_4	Cobalt oxide
CVD	Chemical vapor deposition
DSA	Drop shape analysis
DTG	Derivative Thermogravimetry
EDX	Energy Dispersive X-Ray
EQS	Equation of State
Eu	Europium complex
f_A	Surface fraction of air
FAS	Fluoroalkylsilane
FESEM	Field Emission Scanning Electron Microscopy
FG	Fluorographene
f_S	Surface fraction of solid
FTIR	Fourier Transform Infra-Red
G	Graphene
GO	Graphene oxide
H_2O	Water
HCl	Hydrochloric acid
HDMS	Hexamethyldisilazane
HDMSO	Hexamethyldisiloxane
HDPE	High density polyethylene
ITO	Indium tin oxide
LA	Liquid air interface
LBL	Layer by layer assembly
LS	Liquid solid interface
LV	Liquid vapor interface
MMT	Montmorillonite clay
MTMS	Methyltrimethoxysilane
N.A.	Not Available
PDMS	Polydimethylsiloxane
PDVB	Polydivinylbenzene
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PFTS	Perfluorooctyl trichlorosilane
PMMA	Polymethyl methacrylate
pph	Parts per hundred
PQ	Performance qualification
PS	Polystyrene
PU	Polyurethane
r	Surface roughness factor
rms	Root mean square
R_a	Roughness average
R_p	Maximum profile peak height

R_q	rms Roughness
R_t	Maximum height of the profile
R_v	Maximum profile valley depth
SEM	Scanning Electron Microscopy
SFE	Surface free energy
SiO_2	Silica
T	Transmittance
T_{max}	Maximum temperature
Ta_2O_5	Tantalum pentoxide
TEOS	Tetraorthosilicate
TGA	Thermogravimetric Analysis
TiO_2	Titania
UV	Ultraviolet
UV-Visible	Ultraviolet-Visible Spectroscopy
W_A	Work of adhesion
WCA	Water Contact Angle
XPS	X-Ray Photoelectron Spectroscopy
Z_{max}	Highest peak
Z_{min}	Lowest valley
$Z(M)$	Maximum peak
$Z(R)$	Average profile
ZnO	Zinc oxide
θ_*	Contact angle in Marmur mode
θ_o and θ_Y	Contact angle in Young's mode
θ_T	Threshold contact angle between Wenzel and Cassie & Baxter mode
γ_{AB}	Interfacial tension for vapor for A and B phase
γ_{AV}	Surface tension for vapor for A phase
γ_{BV}	Surface tension for vapor for B phase
γ_{LV}	Surface energy of liquid against vapor
γ_{SL}	Surface energy of surface against liquid
γ_{SV}	Surface energy of surface against vapor
θ	Contact angle
θ_A	Contact angle of air
θ_{CB}	Contact angle in Cassie & Baxter mode
θ_S	Contact angle of solid
θW	Contact angle on a rough surface
γ_{SV}^{h}	Surface tension of hydrogen
γ_{SV}^{ab}	Surface tension of dispersion acid base
γ_{SV}^{d}	Surface tension of dispersion
γ_{SV}^{o}	Surface tension of all interaction
γ_{SV}^{p}	Surface tension of polar

CHAPTER 1

INTRODUCTION

1.1 Overview of Transparent Water Repellent Coating

Water repellent coating refers to a coating that contains surface water contact angle *(θ)*, (Figure 1.1) (WCA) greater than 90°. If the WCA obtained is less than 90°, the coating is addressed as hydrophilic. And if it is higher than that, it is called hydrophobic and if it is greater than 150°, the coating is called as water superrepellent or superhydrophobic (Das et al., 2018).

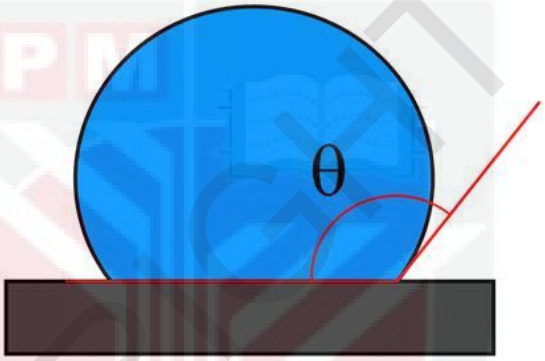

Figure 1.1: The water contact angle (θ) – the angle that is taken from the angle occurred between the plane of a surface and the tangent from which the water droplet in contact with the surface.

Water repellent surface can be observed in nature. It varies between hydrophobic and superhydrophobic. The Lotus effect (a name given after the Lotus plant, *Nelumbo nucifera*) is the name that describes self-cleaning phenomenon of some leaf surfaces (Figure 1.2). When the leaf distinguishes high water repellency, water shall form close-spherical droplets that reel across the surface instead of sliding. The reeling phenomenon collects foreign body dirt and debris and thereby clean the surface naturally. The greater self-cleaning phenomena can be observed for rougher surface. The plant leaves which possess waxy coatings but poor rough microstructure is not so efficient at self-cleaning. Contrary with the leaves that possess both characteristics namely waxy coatings and rough surface, the self-cleaning is more efficient (Neinhuis & Barthlott, 1997).

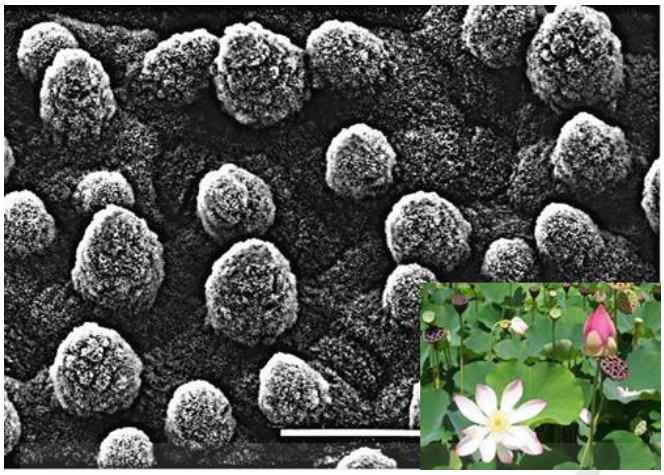

Figure 1.2: SEM image of Nelumbo nucifera leaf distinguishing high roughness surface. A scale bar shown is 50 μm. An inset shows the original image of the leaf (Neinhuis & Barthlott, 1997)**.**

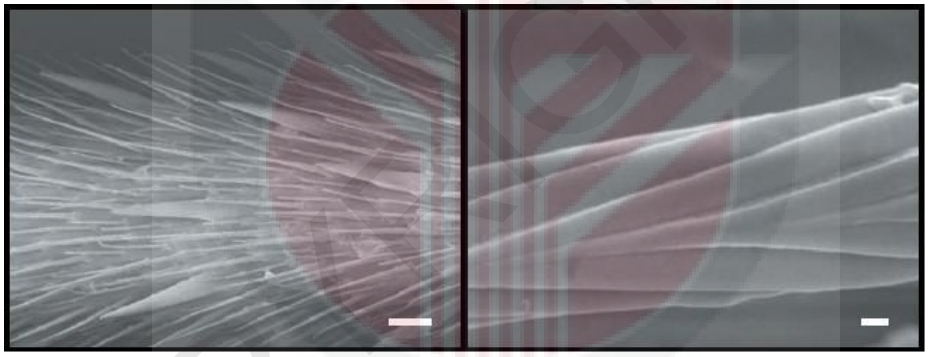

Figure 1.3: SEM image of water striders leg. Spindle-like structures emanating off the leg contain nanosize grooved structure, contributed to dual-scale roughness to the leg. A secreted wax acts to repel water. (Scale bar – left = 20 μm and right = 200 nm)(Yan et al., 2011)

High water repellency in nature can also be observed in animal for example water strider legs. Its legs contain greatly defined microstructure as well as layered with secreted wax (Figure 1.3). Some insect wings also possess water repellent properties attributed to surface microstructure and its composition. These include dragon fly, butterfly wings, as well as penguin skin.

These surface properties and their usefulness in nature as described above have provided inspiration to the scientific communities to design artificial water repellent surface that has great potentials in self-cleaning coatings, anti-microbial, automotive windows, and anti-corrosion.

As of 2015, the hydrophobic coating in the world market size was USD 1.34 billion and it is expected that there will be witnessed a significant growth in the future owing to its high demand in automotive, aerospace and construction industry (https://www.grandviewresearch.com/industry-analysis/hydrophobic-coating-market). In addition, the innovations to employ the nanoparticles in hydrophobic coatings that provide the high surface area and improved performance has opened new avenues for the industry growth over the expected period.

1.2 Problem Statement

Nowadays, to produce durable and transparent water repellent coating is a great challenge. There are several inorganic nanoparticles and transparent polymers that can be employed to synthesize transparent water repellent coating but the water repellency of this artificial coating always suffer degradation due to robust outdoor environment that lessens the water repellency characteristic. In natural lotus leaves, the continuous water repellency is attributed to the continuous metabolism of their surface wax layer and thus maintain the water repellency during their life time.

The scientists and researchers very often do not report the degree of transparency of the water repellent coatings. The main reason which can be presumed is the water repellent coating is normally optically translucent. It is in our knowledge that water repellency is contributed by high surface roughness and hydrophobic chemical composition. The limited report obtained for the transparency of water repellent coating is because both characteristics are in competition with each other. By enhancing surface roughness, it shall increase the surface water repellency but simultaneously enhance the scattered light falls on a surface which is addressed as Mie scattering. This scattering occurs when the diameter of the scattering particles is near to the incident light wavelength and thus is identified as the main factor in reducing the optical transparency of water repellent surface (Mie, 1908; Yu et al., 2015).

There are several methods to synthesize transparent water repellent coating include plasma processing, electrospinning, chemical and physical deposition but those methods require high voltage of electricity, high content of chemical residues and environmental unfriendly (Celia et al.,2013). Sol gel technique is found the best method to overcome these problems (Gu et al., 2017; Das et al., 2018). In addition, there are several approaches to control optical transparency of water repellent coating include chemical vapor deposition and solution immersion method. However, spray coating which was used in this study appears as the most practical, low cost, scalable and well adapted technique to coat small to large substrate with various geometries. The transparent characteristic can be controlled by spray-coating process whereas water repellency can be regulated by adjusting the loading amount of long chain fluoroalkylsilane as well as the amount GO and Silica.(Yang et al., 2009; Mahadik et al., 2016)

1.3 Scope of Study

The aim of this study is to synthesize transparent water repellent coating comprises of tetraorthosilicate, TEOS that will act as precursor, fluoroalkylsilane; FAS which works as hydrophobic agent and graphene oxide, GO and silica respectively that work as nanofiller that is possible in enhancing the roughness of the coating surface. Silica is one of the conventional nanofillers that are usually applied in hydrophobic study. However, the durability of silica incorporated water repellent coating becomes a concern among scientist. Thus, the employment of GO in this study is to investigate its potential in this field as well as to look at the durability of GO incorporated water repellent coating. Sol gel method is used because of ease to synthesis, cheap and feasible(Mahadik et al., 2017; Tadanaga et al., 1997) while the spraying technique is proposed to deposit the coating formulation onto the surface of glass microslide substrate because as compared to other techniques, such as dipping, brushing and spin coating, it promises adaptability and controlled thickness (Yang et al., 2009).

1.4 Objectives of the Study

The general aim of this study is to prepare water repellent coatings either in hydrophobic or superhydrophobic range by mean of sol gel technique and to study the effect of fluorination of fluoroalkylsilane with GO and silica nanofillers respectively on the morphology and topography of the sample, water contact angle, transmittance degree, vibrational assignment of chemical molecules and surface chemistry. Thus, the objectives of the study are concluded as follows:

i. to develop a transparent water repellent formulation by sol gel method and subsequently produce the water repellent coating deposited on glass microslides by spraying technique.

ii. to identify the vibrational assignment of chemical molecules and surface chemistry of the water repellent coating at different concentrations of TEOS, FAS, GO and silica nanofillers respectively for determining the functional groups and elemental composition involved in the sol gel reaction of the coating formulations.

iii. to characterize the optical transparency, surface morphology and topography of the water repellent coating at different concentrations of TEOS, FAS, GO and silica nanofillers respectively for determining the surface roughness.

iv. to investigate the thermal and hydrophobic properties of the water repellent coating at different concentration of TEOS, FAS, GO and silica nanofillers respectively.

1.5 Significances of the Study

The research shall determine the potential of graphene derivative namely graphene oxide in the synthesis of water repellent coating. The characterizations that were carried out are compared with silica incorporated water repellent coating especially on the parameter of the water contact angle and the durability of the measured water repellency. Silica, being a nanofiller that enhance the surface roughness has been studied extensively in superhydrophobic coating area. The price of this material is also affordable which is good for commercialization.

However, it also contains hindrance which include issues on its durability and dispersibility (Shen et al., 2010) . This can be overcome by using graphene oxide in which graphene, a derivative from carbon materials is excellent in thermal, mechanical and environmental stability. Graphene alone is not suitable because it is very inert and difficult to be dissolved in common solvents (Yang et al., 2017). The incorporation of graphene oxide can also give additional characteristic such as the coating is more conductive which is good in optoelectronic device.

In addition, the utilization of graphene oxide as a nanofillers in the fabrication of superhydrophobic thin sol gel film in comparison with other materials such as silica (Kavale et al., 2011; Mahadik et al., 2016; Sun et al., 2017) and fluorinated polymers (Ma and Hill, 2006; Lin et al., 2010; Mundo, et al., 2008) is quite limited because the research on superhydrophobic graphene and its derivative are in its early stage. Besides that, how to manipulate the full use of superhydrophobic graphene and its derivatives. Despite water repellent ability, graphene possesses several other merits include mechanical strength, high surface area, flexibility and optical transparency (Potts et al., 2011; Artiles et al., 2011), It can be anticipated that the synergy between outstanding characteristics of graphene and its derivatives with water repellency can provide to novel applications in the field of optoelectronics, electronic devices and anti-microbial (Wang et al., 2015). An exciting future for superhydrophobic graphene shall be witnessed and it is all due to the contribution of multidisciplinary scientists and engineers in the designing of such surfaces.

1.6 Thesis Outlines

In **Chapter 1**, the overview of water repellent coating and problem statement in relation to the study is discussed. In addition, the scope of the research and the objectives are also reported. The significance of study is mentioned at the end of the chapter.

In **Chapter 2**, the first phase of this chapter reviews the basic theory in water repellency and the models reported by earlier scientists. Then the past and present methods in producing synthetic water repellent coating from different materials are reviewed thoroughly in the next phase of the chapter.

In **Chapter 3**, the methodology in synthesizing water repellent coating by sol gel technique is discussed. The first part consists of the preparation of (TEOS) sol, followed by tetraorthosilicate-fluoroalkylsilane (TEOS-FAS) and finally tetraorthosilicate-fluoroalkylsilane-silica formulation and tetraorthosilicate-fluoroalkylsilane-graphene oxide formulation.

In **Chapter 4**, the results and discussion pertaining to the samples prepared are reported. The water contact angle or WCA, UV-Visible, FESEM, AFM, FTIR and XPS were reported in order to characterize the hydrophobicity, transmittance degree, surface morphology and topography, vibrational assignment of molecules and surface elemental analysis of water repellent coatings.

In **Chapter 5**, a conclusion from the finding is presented. The way forward as a continuity of the present work is also being proposed.

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