SENSITIVITY OPTIMISATION OF CALIXARENE-REDUCED GRAPHENE OXIDE THIN FILMS VIA LANGMUIR, OPTICAL, STRUCTURAL AND ELECTRICAL CHARACTERISATIONS

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SULTAN IDRIS EDUCATION UNIVERSITY

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Darvina Lim Choo Kheng

2020

ABSTRACT

The study aimed to investigate the characteristics of calixarene, reduced graphene oxide (rGO) and their composite in order to optimise the sensitivity of the composite. The calixarenes (calix[4]arene, calix[6]arene and calix[8]arene) and rGO were prepared in solution to form a Langmuir film by using Langmuir-Blodgett (LB) trough. The values of 30 mN/m and 15 mN/m were selected for calixarenes and rGO respectively for the thin film deposition. The surface potential (ΔV) and effective dipole moment ($\mu_{\perp}$) of calixarenes were also investigated. The optical properties of calixarene in solution and thin film were studied using UV-Visible (UV-Vis) spectroscopy and compared to ensure the stability of the thin film. Meanwhile, the rGO thin film was characterised with UV-Vis spectroscopy for the optical property, Raman spectroscopy for the crystallinity and four-point probe for the electrical property to obtain current-voltage (I-V) characteristics, resistivity, and conductivity. Field Emission Scanning Electron Microscopy (FESEM) was used to observe the surface morphology of calixarene and rGO thin films. Then, both the materials were fabricated into various types of calixarenes-rGO composites using the LB technique. Same characterisation procedures were applied to the newly formed composites using UV-Vis spectroscopy, Raman spectroscopy, four-point probe, and FESEM. Results showed that the addition of rGO in the fabrication of calixarene thin-film has improved the electrical property of the composite as calixarene is a non-conductive material. The structural and optical properties investigation also showed good structural and stable thin film formed from both materials. Calix[8]arene-rGO composited with 6 layers of rGO is the best-fabricated composite, as shown from the characterization process. As a conclusion, this study implies that rGO plays a significant role in improving the conductivity performance of calixarene, thus give rise to the further potential of calixarene in sensing application.

PENGOPTIMUNAN KEPEKAAN DALAM FILEM NIPIS LANGMUIR-BLODGETT KALIXAREN-GRAFIN OKSIDA TERTURUN HIBRID DENGAN PENCIRIAN LANGMUIR, OPTIK, STRUKTUR DAN KEELEKTRIKAN

ABSTRAK

Kajian ini bertujuan untuk menyiasat ciri-ciri kalixaren, grafin oksida terturun (rGO) dan komposit kedua-dua bahan ini untuk mengoptimunkan kepekaan komposit. Kalixaren (kalix[4]aren, kalix[6]aren dan kalix[8]aren) dan rGO telah disediakan dalam keadaan larutan untuk membentuk filem Langmuir dengan menggunakan tangki Langmuir-Blodgett (LB). Nilai 30 mN/m dan 15 mN/m telah dipIlih untuk pembentukan filem nipis kalixaren dan rGO. Keupayaan permukaan (ΔV) dan momen dwikutub berkesan ($\mu_{\perp}$) bagi kalixaren juga telah dikajikan. Sifat optik kalixaren dalam bentuk larutan dan filem nipis dikaji menggunakan spektroskop ultraungu-nampak (UV-Vis) dan dibandingkan untuk menjamin kestabilan filem nipis. Manakala, rGO pula dikaji dengan spektroskop UV-Vis untuk ciri optik, spektroskop Raman untuk ciri kehabluran dan pengesan arus empat titik untuk ciri keelektrikan seperti pencirian arus-voltan (I-V), resistiviti dan kekonduksian. Mikroskop elektron imbasan medan pancaran (FESEM) telah digunakan untuk pencirian permukaan filem nipis kalixaren dan rGO. Seterusnya, kedua-dua bahan ini digabungkan menjadi pelbagai komposit filem nipis kalixaren-rGO menggunakan kaedah LB. Pencirian yang sama dijalankan ke atas komposit filem nipis yang baru dibentukkan menggunakan spektroskop UV-Vis, spektroskop Raman, pengesan arus empat titik dan FESEM. Hasil kajian mendapati pertambahan rGO dalam penghasilan filem nipis kalixaren meningkatkan sifat keelektrikan komposit ini memandangkan kalixaren ialah bahan penebat. Kajian dari segi keoptikan dan penstrukturan juga menunjukkan pembentukan struktur filem nipis yang stabil dapat dibentuk daripada kedua-dua bahan ini. Kalix[8]aren-rGO yang mempunyai enam lapisan rGO ialah komposit yang paling baik antara semua komposit yang lain seperti yang ditunjukkan daripada hasil proses pencirian. Sebagai kesimpulannya, kajian ini memberi implikasi bahawa rGO penting dalam memainkan peranan meningkatkan kekonduksian kalixaren, seterusnya membuka potensi kalixaren dalam aplikasi pengesanan.

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LIST OF ABBREVIATIONS

CCD	Charge coupled device
C4	25, 26, 27, 28-tetrahydrocalix[4]arene
C6	Calix[6]arene-37, 38, 39, 40, 41, 42-hexol
C8	49, 50, 51, 52, 53, 54, 55, 56-octahydroxycalix[8]arene
C4-rGO-6	Calix[4]arene-6 layers of reduced graphene oxide
C6-rGO-6	Calix[6]arene-6 layers of reduced graphene oxide
C8-rGO-6	Calix[8]arene-6 layers of reduced graphene oxide
FESEM	Field emission scanning electron microscopy
G	Gas
GO	Graphene oxide
HMDS	1,1,1,3,3,3-Hexamethyldisilazane
L	Liquid
LB	Langmuir-blodgett
LS	Langmuir-schaefer
L1	Liquid-expanded
L2	Liquid-condensed
PMT	Photomultiplier tube
PVC	Poly(vinyl chloride)
rGO	Reduced graphene oxide
rGO-2	2 layer of reduced graphene oxide
rGO-4	4 layer of reduced graphene oxide
rGO-6	6 layer of reduced graphene oxide
S	Solid
UV-Vis	Ultraviolet-visible

LIST OF SYMBOLS

Ar	Argon
$CHCl_3$	Chloroform
cm	Centimeter
D	Debye unit (3.33564×10^{-30} C m)
D peak	Disorder peak
G peak	Graphite peak
g/mol	Molecular weight
Hg	Mercury
H_2	Hydrogen
I	Current
Ir	Infrared
I_D/I_G	Ratio of disorder / graphite
I-V	Current-Voltage
k	×1000
kHz	Kilo hertz
kV	Kilovolt
mg/ml	Milligram/milliliter
mm	Millimeter
mm/min	Millimeter / minute
mN/m	Milli Newton/meter
mol L^{-1}	Mol per liter
MΩ/cm	Megaohm/centimeter
mV	Millivolt
$NaBH_4$	Sodium borohydride
nm	Nanometer

nm^2	Nanometer square
OH	Hydroxyl
R_s	Sheet resistivity
r	Radius
V	Voltage / volt
Å	Angstrom
°C	Degree Celsius
Ω/□	Ohms per square
$\Omega^{-1}\ m^{-1}$	$Ohm^{-1}\ meter^{-1}$
Sm^{-1}	Siemens $meter^{-1}$
ΔV	Surface potential
μl	Microliter
∏	Surface pressure
Π-A	Surface pressure-Area
ΔV-A	Surface potential-area
γ	Surface pressure of water
$\gamma_{\circ}$	Surface pressure of water with the presence of research material
σ	Electrical conductivity
%	Percent
π	Constant of circle, 3.142
$\mu_{\perp}$	Average effective dipole
$\mu_{\perp}$-A	Effective dipole moment-area
ε	Molar absorptivity
ε_0	Vacuum permittivity ($8.854 \times 10^{-12}\ C^2N^{-1}m^{-2}$)
ε_r	Relative permittivity

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nanotechnology field is emerging rapidly as one of the most promising and outstanding potential areas to contribute more significant benefit to humankind from various life aspects, for instance, in medical (Boisseau & Loubaton, 2011), electronics and electrical (J. Lu et al., 2016; W. Lu & Lieber, 2007), instrument and building construction (Pacheco-Torgal & Jalali, 2011; Šesták, Moravcová, & Kahle, 2015), sensing technology (Keyser, 2016), cosmetic (Morganti, 2010), healthcare (Raffa, Vittorio, Riggio, & Cuschieri, 2010), industrial (Fakoya & Shah, 2017) and countless other fields (Duncan, 2011; Mukhopadhyay, 2014; Rashidi & Khosravi-Darani, 2011).

This field continuously presented discovery and invention for real-life application and advanced humankind to a whole new level in this millennium.

The development of methods and instruments to probe and manipulate matter from the smallest atomic size to the macro-molecular sized indeed give vast advantages to nanomaterial and nanotechnology research. Richard P. Feynman has foreseen the unimaginable greatness that assured by this field in his far-sighted 1959 lecture entitled “There’s Plenty of Room at the Bottom” at Caltech. Nobel laureate Dr Richard Feynman has vibrantly described the possibility to create small and more delicate tools to manipulate even small and more sensitive devices that can be utilised to create and modify objects at the nano or even lower than nanoscale (Feynman, 1992). The method proposed by Dr Feynman is known as a top-down approach in the new nanotechnology method, a complementary approach to recent year more popular method known as bottom-up approach (Figure 1.1).

For the bottom-up approach, the process required one starts with the atoms or molecules that continuous build-up to develop larger structures. On the other hand, the top-down approach takes place in the form of an idea where the macro-sized materials are being scaled down from the macroscopic scale to the nanometric level and build up again in the required nano form (Ashby, Ferreira, & Schodek, 2009). Several examples of these two approaches that generally associated with nanotechnology are self-assembly, biomineralisation, and chemical synthesis technique for the bottom-up approach, while photolithography and attrition for the top-down approach (Gu et al., 2010; Iqbal, Preece, & Mendes, 2012)

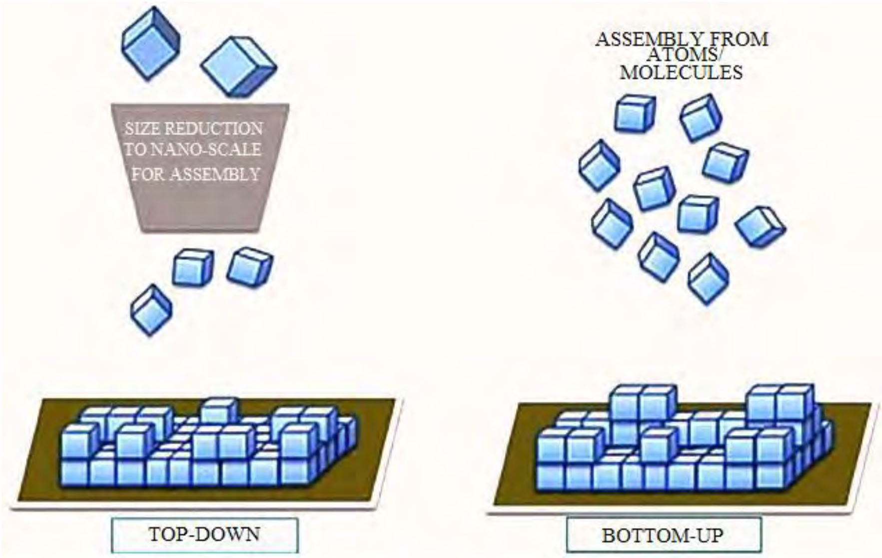

Figure 1.1. Top-down and bottom-up approaches in nanotechnology. Adapted from Handbook of Research on Diverse Applications of Nanotechnology in Biomedicine, Chemistry, and Engineering (pg 625), by Barbhuiya, S. and Qureshi, M., 2015, Hershey PA: Engineering Science Reference. Copyright 2015 by the IGI Global.

Both approaches have their pros and cons. The top-down approach, specifical photolithography, has been used in the industries for years to manufacture computer chips (Ashby et al., 2009). However, the top-down approach has its limitation and distress, typically from the slow process speed, expensive cost, and imperfection of the surface structure. The surface imperfection will have a severe impact on the physical and surface properties of the nanostructure as the surface over volume ratio for nanostructure is large (Cao & Wang, 2011). Meanwhile, the bottom-up approach is more preferred among researchers as it is generally more practical that involve specific chemical reaction among the atoms or molecules and take place due to the intermolecular interaction between them (Johal & Johnson, 2018). This approach can create nanostructure with few defects and contamination as compared to the top-down approach, thus build required nanostructure with a much more stable thermodynamics equilibrium state (Goyal, 2018).

One of the bottom-up approaches that can fabricate well defined layered structures with the precision up to molecular level is known as the Langmuir-Blodgett technique. Langmuir-Blodgett (LB) assembly is considered as a two-dimensional bottom-up layer-by-layer approach that exhibits characteristics such as fast, robust and facile, with more advantages from the aspect of precise control over the settlement and arrangement of the nanomaterials for functional devices such as nanosensors. By using LB assembly, the high orderly and uniform arrangement of two-dimensional molecules can be developed onto a substrate, generally through vertically dipping of the substrate into the water and draw the substrate out under monitored constant surface pressure (Pelton & Bryant, 2013). This technique is an easy yet elegant method for the nanomaterial bottom-up approach primarily used to fabricate nanosensor materials for real-life applications.

The motivation for sensor miniaturisation is very clear for decades. Hence, as the nanomaterials and nanotechnology method emerges like LB assembly, the prospect of building nanosensor has become a new interest among researchers for sensor development. According to Khanna (2012), nanosensor can be generally be defined as any sensor that developed from the nanotechnology technique; in another term fulfil one of the following properties:

- The sensor exists in nano size.
- The sensitivity of the sensor reaches nanoscale.
- Nanometers in spatial distance between the sensor and the object.

Sensor miniaturisation can achieve numerous benefits. Some of the benefits included high selectivity especially in using nanomaterials, small portable devices that can be carried anywhere, fast response time with the increasing sensitivity, low cost of sensor construction, various analytes detection in one time and less sample preparation or pretreatment process. Hence, building a nanosensor that makes up of nanomaterial through a bottom-up approach like the LB technique, thus can produce a well oriented, small and uniformly arranged sensor.

1.2 Research Background

Calixarenes are cyclic cavity-shape macromolecules that made up of phenol units bridged by the alkylidene groups among them. They are referred to as the third generation of supramolecule after cyclodextrin and crown-ester (Shinkai, 1993). The research fields that are surrounding this unique architecture macromolecule have established the “calixarene chemistry” (Jacques Vicens & Böhmer, 1991), ranging from the aspect of synthesis, hybrid or compose with other materials and potential application research into real-life application.

Calixarene has been proven tremendous time for their potential to work as the nanomaterials in the nanosensor development due to their ability and selectivity toward each respective type of ions, molecules or other substances (Becker, Tobias, Porat, & Mandler, 2008; Chester et al., 2014; Ma, Song, Boussouar, Tian, & Li, 2015).

By modifying the upper rims and the lower rims of the calixarenes, selective calixarene for specific target guest can be achieved through the host-guest interaction either using the lower/upper rims or the cavity itself (Legnani, Compostella, Sansone, & Toma, 2015; Murphy, McKinlay, Dalgarno, & Paterson, 2015). Besides that, by increasing or decreasing the phenolic unit number also has some effect on the selectivity (Zhou, Chen, & Diao, 2013). Therefore, calixarene also being described as the supramolecule with nearly infinite potentials waiting for explore.

On the other hands, reduced graphene oxide (rGO) that prepared through the reduction process of graphene oxide (GO), also arises as another prospective material for functional electronic nanosensors (G. Lu, Ocola, & Chen, 2009; Robinson, Perkins, Snow, Wei, & Sheehan, 2008; Zor, Saglam, Alpaydin, & Bingol, 2014). This is because when GO exists in its oxidation state, it is an electric insulator that unsuitable to be used for electronic nanosensors since one of the main factors that ensure an excellent sensor is the sensitivity that depends on the conductivity properties, which transfer the host-guest interaction to the required electrical signal. However, through chemical reduction process by hydrazine or sodium borohydride ($NaBH_4$) can eliminate some of the oxygen atoms that attached to the GO and recovers certain aromatic double-bonding in the carbon, thus result in a partially reduced GO that being named as rGO (G. Lu et al., 2009). The produced rGO exhibit enhanced conductivity property and chemically active defect sites that can readily prepared for interaction with other molecules (Robinson et al., 2008).

Several types of researches have been carried out through the hybridisation of these two nanomaterials in recent years, give rise to encouraging results for further study of these two nanomaterials such as demonstrated by Zhou et al. (2013). The first generation of supramolecule, cyclodextrin, after composes with rGO also displayed high supramolecular recognition and electrochemical response (Fu, Lai, & Yu, 2015; D. Lu et al., 2012; Zor et al., 2014). Besides that, the second generation of supramolecule, crown-ester also demonstrated the same effect after composited with rGO as reported in Wei, Xu, Ren, Xu, & Qu (2012), with the addition of carbon dots. Hence, the hybridization of these two nanomaterials, calixarene and rGO seem to be promising from the previous research and offers an exciting, new and waiting to be explored research field from the aspect of nanosensor for various uses.

1.3 Problem Statement

The sensor has been part of the crucial tools necessary in various daily life applications from the aspect of the automobile, healthy and medical applications, industries, household applications, space applications, wastewater, and pollution monitoring, plus disaster monitoring and robotic development. In short, sensors are needed for process monitoring, experimental modelling, product testing and qualification, fault prediction, detection and diagnosis, advisory or warning generation, surveillance and more (Silva, 2017). A sensor helps to input the data from real life and “learn” from the data to interact back to human or the system need.

As the modern-day require sophisticated, complex, long life span and lower or higher detection limit sensor as compared to the old days, nanomaterials and nanotechnology have been seen as a big leap for sensor development nowadays. Hence, the urges to create, fabricate and construct applicable real-life sensors have been increasing in demand as time goes by. The requirements for modern detectors moved towards characteristics that include fast responses time, portable, low detection limit and easily manipulate. Other features include long life span, or single-use depends on the condition, high sensitivity and selectivity, high stability, high reliability under extreme condition, low cost of synthesis and less cumbersome production process.

Therefore, nanomaterials from various forms like oxide-based (zinc oxide, cobalt oxide etc.), metal-based (gold, silver, platinum etc.), carbon-based (fullerenes, carbon nanotubes, graphene etc.), polymer-based and supramolecules (cyclodextrin, crown ether and calixarene) have been explored throughout these decades by researchers around the globe to fulfill the modern days sensor requirements. Among all these nanomaterials, calixarenes as one in the supramolecular families generate unneglectable interest for sensing applications in different fields like gas sensing and heavy metals pollution sensing (Eddaif, Shaban, & Telegdi, 2019; Kumar, Chawla, & Zou, 2017). Although the excellent host-guest interaction of this supramolecule and its derivatives have been well-known (Sharma & Cragg, 2011), the calixarenes still need to combine with other materials to enhance the sensitivity to give more reliable and amplified sensing signal. Hence, calixarene always combines with other potential materials for sensing purposes.

On the other hands, rGO after reduced from graphene oxide, being utilised in sensing field and plays a vital role in improving the sensor application from various aspect like the sensitivity, response time, range of response and conductivity (Bo et al., 2014; X. Li et al., 2016). In Zhang, Chang, Li, Liu, & Xue (2016), rGO hybrid with tin dioxide to form a nanocomposite film and this hybrid result in an ultrahigh sensitive and fast response humidity sensor. Meanwhile, Fritea, Tertiş, Cosnier, Cristea, & Săndulescu (2015) confirm that with the addition of rGO in their β-cyclodextrin/tyrosinase biosensor, the biosensor displayed enhanced sensitivity toward their target organic compound dopamine, a type of neurotransmitter.

Hence, these two nanomaterials, calixarene, and rGO seem to be exciting partners to be combined for further investigation to study the synergic effect that may occur from the hybridisation. According to Zhu & Fang (2014), selectivity and sensitivity play an essential role in a sensor, where the earlier one being contributed by the design of supramolecule exclusively for individual guests, while the latter property being contributed by the supramolecular binding affinity and the signal transduction from the host-guest interaction. For the first and second properties, calixarene can provide the necessary selectivity, while the rGO can assist in enhancing the sensitivity, resulting in better supramolecular nanosensor. Hence, calixarene with 4, 6 and 8 phenol units are chosen as the core substances in this research to combine with rGO to study the characteristics especially from the aspect of sensitivity. Calix[n]arenes (n = 4, 6, 8) are chosen due to their binding capabilities toward divalent cations and commercially available.

1.4 Research Objectives

i. To characterise the characteristics of calix[n]arene (n = 4, 6, 8) in Langmuir and Langmuir-Blodgett (LB) film using LB technique, surface potential (ΔV) probe, Ultraviolet-Visible (UV-Vis) spectroscopy and Field Emission Scanning Electron Microscopy (FESEM).

ii. To characterise the characteristics of reduced graphene oxide (rGO) thin-film developed through the LB technique using micro-Raman (Raman) spectroscopy, UV-Vis spectroscopy, FESEM, and four-point probe.

iii. To fabricate calixarene-rGO composite thin film through the Langmuir-Blodgett technique.

iv. To characterise calixarene-rGO composite and compare with calixarene and rGO using UV-Vis spectroscopy, Raman spectroscopy, FESEM, and four-point probe.

1.5 Significant of Research

The sensor development throughout the world still has enormous potentials to be developed, utilising all kinds of nanomaterials or macroscopic substances to achieve the desired result, then further incorporate the research findings into commercially available products that can benefit humankind. Hence, the suggestion of portable, easy use and remote sensor targeting on different specific purposes either for small scale purposes like household uses and industries uses to global scale purposes like earth pollution monitoring are needed.

Since the calixarene and rGO possess promising properties for the sensor, the hybrid of these two nanomaterials is thrilling research to be done. The field that involves composing these two nanomaterials together for sensing purpose still very less, as compared to the hybrid of cyclodextrin, the first supramolecule generation and rGO (Chen et al., 2013; Nag et al., 2014; Zor, Bingol, Ramanaviciene, Ramanavicius, & Ersoz, 2015). Hence, new research findings from this research can be contributed to the sensor field involving these two nanomaterials. Besides that, the characterisation of both materials thin film and their composite can provide an insight into the development of rGO and calixarene using the LB technique.

Besides, the characterisation process that carried onto the hybrid materials can reveal whether these two materials still possess their distinctive properties and enhance each other in the sensing part or not. Moreover, further research can employ the positive result in involving other novel synthesis calixarenes to obtain better selectivity and sensitivity supramolecular nanosensor.

1.6 Scope and Limitation

In this research, calix[n]arene (n = 4, 6, 8) is used as the sensing material for metal cations. The first part of this study focuses on the characterisation of calix[n]arene from the aspect of surface pressure-area isotherm, surface potential-area isotherm and effective dipole moment using Langmuir technique before the calixarene is being deposited onto the substrate using LB technique. The optimized parameters for this part are the concentration of calix[n]arene solution (0.2 mg/ml), type of solvent (chloroform-$CHCl_3$), pressure sensor (filter paper), temperature (22°C), deposition surface pressure (30 mN/m), barrier speed (12 mm/min), dipper speed (5 mm/min) and deionized water subphase (18.2 MΩ/cm). Then, the deposited calixarene thin film is going to be characterised and visualised using UV-Visible (UV-Vis) spectroscopy and Field Emission Scanning Electron Microscope (FESEM).

For the second part of the study, the characterisation process onto rGO thin film will be carried out after the rGO is being deposited onto the substrate using the LB technique. The optimization parameters for this part are the concentration of rGO (2 mg/ml), type of solvent (methanol or also known as CH_3OH), ultrasonication period (10 hours), pressure sensor (filter paper), temperature (22°C), deposition surface pressure (15 mN/m), barrier speed (5 mm/min), dipper speed (2 mm/min), deionized water subphase (18.2 MΩ/cm), drying period (8 hours) and drying temperature (80°C). The rGO thin film will be characterised by UV-Vis spectroscopy, four-point probe, FESEM, and Raman spectroscopy.

In the final part, the rGO will be deposited onto the substrate first, followed by the calixarene. Then, the composite will be studied through UV-Vis spectroscopy, FESEM, four-point probe, and Raman spectroscopy to understand the interaction and change in properties between both.

1.7 Thesis Overview

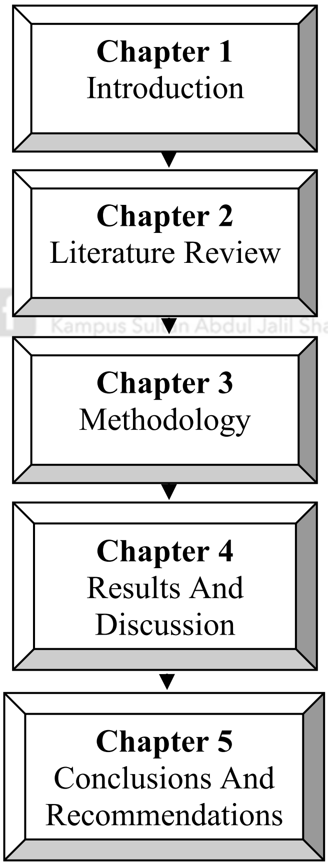

Figure 1.2. Flow chart of chapter 1

Chapter 1 focus on an introduction to nanotechnology, two methods that synonym to nanotechnology which is top-down approach and bottom-up approach, LB technique as one of a bottom-up approach that used in the study and properties of nanosensor. Then, the research background introduces the research materials, calixarene, and rGO plus their potential hybridisation; follow up with problem statement that stated the need for this research related to the sensor development. The research objectives, significant, scope, and limitation of research also listed in this chapter. Last, by not least, the overall thesis overview is displayed to ease the understanding of the whole structure of the study.

Chapter 2 highlights the background of the primary research materials, calixarene, and rGO. The research materials applications in the sensing area are emphasised. Then, the LB technique that acts as the primary technique to fabricate the research material is described together with the scientific instrument utilised in the characterisation process. Summary and research gaps are listed to provide rational and motivation for this study.

Chapter 3 emphasises the procedures for the preparation and characterisation of calixarene and rGO. The preparation and characterisation steps for calixarene Langmuir monolayer and thin film, rGO Langmuir monolayer, and thin-film were described in detail. Besides that, the fabrication process of calixarene-rGO composite, plus the characterisation also being described in this chapter. Scientific instruments and the parameter utilised also being listed.

Chapter 4 details the result from this study, start from the characterisation of calixarene in solution and film form from the aspect of surface pressure, surface potential, optical and surface morphology. Then, the properties of rGO also are detailed in terms of surface pressure, and the optical property includes Raman spectra, surface morphology, and electric property. Lastly, the characteristics of composite examined after the two materials combine and the result compared with the previous individual ones to give much more details about the new composite.

Chapter 5 concludes the study and gives some relevant future research gaps that can be continued from this study for more exploration of the combination of calixarene and rGO.