



**UNIVERSITI PUTRA MALAYSIA**

***FABRICATION OF CALIXARENE-BASED GRAPHENE-MODIFIED  
SCREEN-PRINTED CARBON ELECTRODES FOR SELECTIVE  
DETECTION OF ANTHRACENE***

**PUTRI NUR SYAFIEQAH BINTI ZAINAL**

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By

**PUTRI NUR SYAFIEQAH BINTI ZAINAL**

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

**March 2021**

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

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**March 2021**

**Chair : Associate Professor Shahrul Ainliah Alang Ahmad, PhD**  
**Faculty : Science**

Anthracene is one of the most widespread polycyclic aromatic hydrocarbons (PAHs) that consists of three fused benzene rings. To date, numerous approaches have been reported for electrochemical detection of anthracene based on various materials. Nevertheless, the critical issues in designing electrochemical sensors are the strategy to enhance the selectivity, sensitivity, and stability of the detection in environmental samples. Therefore, in this research work, different calix[4]arene-based materials such as tert-butyl-calix[4]arene (C4), thiolated-calix[4]arene (TC4) and, calix[4]arene-based metal-organic framework (C4TCA@MOF) were used as a receptor and incorporated with coupling materials, which are electrochemically reduced graphene oxide (ERGO) and gold nanoparticles (AuNPs) to develop different strategies of electrochemical sensor for the determination of anthracene. In brief, the first sensor was constructed based on C4 deposited on ERGO/SPCE (C4/ERGO-SPCE). The next sensor was proposed with a coupling material, AuNPs that was prepared through the synthetic route of Turkevich-Frens method and functionalized with TC4 to form TC4/AuNPs/ERGO-SPCE. Next, the third sensor was constructed by synthesizing a C4TCA@MOF through solvothermal method as a new receptor and deposited on AuNPs/ERGO (C4TCA@MOF/AuNPs/ERGO-SPCE). Under the optimal conditions, the C4/ERGO-SPCE exhibited a good linearity towards anthracene with concentration range from 2-8  $\mu\text{M}$  and limit of detection (LOD) 0.02637  $\mu\text{M}$ , while the performance of TC4/AuNPs/ERGO-SPCE increase comprehensively due to the presence of AuNPs with a linear concentration range from 1-7  $\mu\text{M}$  and LOD 0.00649  $\mu\text{M}$ . After the modification of C4 into C4TCA@MOF, the proposed sensor (C4TCA@MOF/AuNPs/ERGO-SPCE) revealed highest sensitivity and selectivity and demonstrated wide linear concentration range from 0.01-30  $\mu\text{M}$  with LOD 0.00521  $\mu\text{M}$ . The proposed sensor also was tested towards anthracene using portable potentiostat that was able to demonstrate a

satisfactory recoveries (90-93%) and statistical analysis of relative error (2.27-4.60%). With these proven advantages, the proposed sensors have a huge potential as an alternative analysis of anthracene in near future.



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

**FABRIKASI ELEKTROD BERASASKAN KALIKS[4]ARINA DAN GRAFIN  
KE ATAS ELEKTROD SKRIN BERCETAK KARBON UNTUK  
PENGESANAN SELEKTIF ANTRASIN**

Oleh

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Antrasin adalah salah satu polisiklik aromatik hidrokarbon (PAHs) yang ditemui secara meluas, terdiri daripada 3 gelang benzena terlakur. Sehingga kini, banyak pendekatan telah dilaporkan untuk pengesanan elektrokimia antrasin berdasarkan pelbagai bahan. Walau bagaimanapun, masalah kritikal dalam merangka sensor elektrokimia adalah strategi untuk meningkatkan selektiviti, kepekatan dan kestabilan pengesanan dalam sampel persekitaran. Justeru, dalam kerja penyelidikan ini, bahan berasaskan kaliks[4]arina yang berbeza seperti tert-butil-kaliks[4]arina (C4), kaliks[4]arina tiolat (TC4) dan struktur logam organik berasaskan kaliks[4]arina (C4TCA@MOF) digunakan sebagai reseptor dan digabungkan dengan bahan gandingan yang merupakan grafin oksida elektrokimia terturun (ERGO) dan nanopartikel emas (AuNPs) untuk membangunkan strategi sensor elektrokimia yang berbeza untuk penentuan antrasin. Secara ringkasnya, sensor pertama dibina berdasarkan pemendapan C4 ke atas ERGO/SPCE. Sensor seterusnya diusulkan dengan bahan gandingan, AuNPs yang disediakan melalui laluan sintetik *Turkevich-Frens* dan difungsikan dengan TC4 untuk membentuk TC4/AuNPs/ERGO-SPCE. Seterusnya, sensor ketiga dibina dengan mensintesis C4TCA@MOF melalui kaedah solvotermal sebagai reseptor dan dimendapkan ke atas AuNPs/ERGO (C4TCA@MOF/AuNPs/ERGO-SPCE). Di bawah keadaan optimum, C4/ERGO menunjukkan kelinearan yang baik terhadap antrasin dalam julat kepekatan dari 2-8  $\mu\text{M}$  dengan had pengesanan (LOD) 0.02637  $\mu\text{M}$ , sementara itu prestasi TC4/AuNPs/ERGO-SPCE meningkat secara komprehensif disebabkan oleh kehadiran AuNPs dengan kepekatan linear dari 1-7  $\mu\text{M}$  dan LOD 0.00649  $\mu\text{M}$ . Selepas pengubahsuaian C4 menjadi C4TCA@MOF, sensor yang dicadangkan C4TCA@MOF/AuNPs/ERGO-SPCE telah menunjukkan menunjukkan kepekatan dan selektiviti yang tertinggi dan menunjukkan julat kepekatan linear yang ketara dari 0.01-30  $\mu\text{M}$  dengan LOD 0.00521  $\mu\text{M}$ . Sensor yang dicadangkan juga diuji dengan menggunakan potentiostat mudah alih terhadap antrasin yang dapat menunjukkan perolehan semula yang memuaskan

sebanyak 90-93 % dan analisis statistik ralat relatif 2.27-4.60 %. Dengan terbuktinya kelebihan ini, sensor yang dicadangkan mempunyai potensi yang besar sebagai analisis alternatif antrasin dalam masa terdekat.



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I dedicate this thesis to all of them.

**DR. PUTRI NUR SYAFIEQAH ZAINAL**



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

AuNPs	Gold Nanoparticles
CV	Cyclic Voltammetry
C4	4-tertbutylcalix[4]arene
TC4	Thiolated Calix[4]arene
C4TCA	Calix[4]arene Tetracarboxylic Acid
DPV	Differential Pulse Voltammetry
ERGO	Electrochemically Reduced Graphene Oxide
MOF	Metal-Organic Framework
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
HPLC	High Performance Liquid Chromatography
HRTEM	High-Resolution Transmission Electron Microscopy
LOD	Limit of Detection
PAHs	Polycyclic Aromatic Hydrocarbons
SPCE	Screen Printed Carbon Electrode
TC4	Thiolated-Calix[4]arene
USEPA	United States Environmental Protection Agency
UV-VIS	Ultraviolet Visible
PXRD	Powder X-Ray Diffraction
EIS	Electrochemical Impedance Spectroscopy
USEPA	United States of Environment Protection Agency
SPR	Surface Plasmon Resonance
S/N	Signal/Noise



LLE	Liquid-liquid Extraction
Rct	Charge transfer resistance
Cdl	Double-layer capacitance



## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of research

Polycyclic aromatic hydrocarbons (PAHs) are comprised of two or more aromatic rings fused together in a linear, angular or cluster arrangement (Broniatowski *et al.*, 2017; Arey & Atkinson, 2003). They are considered as carcinogenic, mutagenic and teratogenic compounds which can cause long-term health effects such as cancer (Armstrong *et al.*, 2004), suppress the immune function (Burchiel & Luster, 2001) and induce genotoxic damage (Gamboa *et al.*, 2008; Brookes & Lawley, 1964). Naturogenic sources such as forest fire, organic matter diagenesis, and volcanic activity can cause PAHs to be released into environmental matrices. However, in the majority cases, the origination of PAHs is corresponded to the chemicals associated with petroleum-related activities. PAHs have polluted both marine and freshwater reservoir over the years via oil and gas operations, including the discharge of petroleum-incorporated substances (Yu *et al.*, 2019; Sun *et al.*, 2018). The worst-case scenario, due to their physicochemical properties, PAHs are deemed to be highly mobile in the environment which facilitate them to experience long-range dispersion, triggering global pollution issues (Dat & Chang, 2017). Due to the harmful properties, 16 major PAHs have been classified as the most impacted pollutants that are governed by the United States Environmental Protection Agency (USEPA) and the European Union (EU) (Andersson & Achten, 2015).

Out of 16 PAHs reported, 2- to 3-ring PAHs such as naphthalene and anthracene are comparatively more crucial and environmentally harmful due to their higher emission percentage and greater water solubility (Andersson *et al.*, 2005). In fact, they are prevalent micropollutants in the atmosphere and environmental water. As a result, anthracene with 3-fused benzene rings serve as representative role in the environmental matrices and need to be regularly monitored for controlling purposes due to its properties that are persistent, bioaccumulative and toxic to human health and environment (Zhang *et al.*, 2011; Zhuang & Zhou, 2009). Thus far, numerous traditional approaches have been examined using chromatographic techniques such as HPLC (Toriba *et al.*, 2003), GC (Zhang *et al.*, 2010; Paputa-Peck *et al.*, 1983), and LC-MS (Wolkenstein, 2019; Itoh *et al.*, 2006) to classify anthracene and its family members of PAHs. Despite of their high sensitivity and selectivity, these methods suffer from intricate sample pre-treatment steps and involve the employment of expensive and huge instruments that are impractical for routine control assessment. In recent years, the miniaturization of the chromatographic system has received remarkable attention which involves a small sample and reagents volume (Yuan

& Oleschuk, 2018). Nonetheless, a major consideration associated with the portable chromatographic devices is the difficulty in stationary phase coating where the  $\mu$ -column used in the system is relatively too short for adequate separation of complex samples such as PAHs. Furthermore, the introduction of small-scale working pressure to the cylinder pressure of the gas used can reduced the sensitivity significantly due to the constant interruption of the analysis to refill the mobile phase reservoir, thus affect the flow rates of the mobile phase. In addition, the miniaturization process also reduced the injection volumes, hence reduced the sensitivity due to the limited number of compounds with fluorescence and absorbance properties (Nazario *et al.*, 2015). These challenges have evolved the research's interest in developing advanced analysis technologies with the simplest integrated system without compromising the sensitivity. Recently, the electrochemical method has taken centre stage as an alternative way to conventional chromatographic techniques for the determination of PAHs due to their properties that are easy to prepare and construct, inexpensive, sensitive, environmental friendly and applicable for on-site detection (Zhu *et al.*, 2014). Electrochemical sensors represent the most remarkable device in analytical chemistry that enable to provide any information regarding the composition of a system in real-time by coupling an electrochemical transducer to a chemically selective layer (receptor-recognition element) through redox reaction. The selective interaction between the recognition element and chemical species (target analyte) is transformed into a detectable signal, where the signal generated is proportional to the concentration of the analyte. Therefore, the exploration of a simplified integrated system based on the electrochemical approach will bring a new evolution as a decentralized analysis with favourable features in the near future.

## 1.2 Problem statements and research motivation

As comparative analysis to mass, optical and thermal sensors, the electrochemical sensors have been receiving tremendous consideration over traditional techniques such as chromatography and spectroscopy in a vast range of important applications in the field of clinical, industrial, environmental, and agricultural analysis. Nevertheless, the critical issues in designing electrochemical sensors are the strategy to enhance the selectivity, sensitivity, and stability for the detection of the environmental samples. Therefore, it is necessary to explore further the performance and efficiency of the electrode by introducing a variety of receptors for chemically modified electrodes (CMEs) to address the challenges. Over the past decades, the field of CMEs have experienced a period of rapid growth to exert more direct control over the chemical nature of an electrode surface. The capability of CMEs to deliberately control and manipulate the surface properties actively can meet the needs of sensing problems, leading to a variety of desirable outcomes; improve selectivity and sensitivity, increase stability, offer wider potential window, and enhance fouling resistance. Thus far, numerous researches have been conducted on determination of anthracene in real water samples. Despite of their promising analysis at a very low concentration, the developed CMEs had the adsorption

capacity to some PAHs interferent up to 20% due to the unspecific active material used for the electrode modification.

Recently, macrocycles, known as calix[n]arenes which belong to the cyclic oligomer subclass have been highlighted in numerous precedent studies as perceptible recognition elements for cations, anions, and neutral target molecules. The incorporations of a central cavity in the cone conformation are capable to form stable host-guest complexes by possessing supramolecular ability with various guests (Kang *et al.*, 2000; Kim *et al.*, 1999). Furthermore, the versatility of these macrocycles that able to vary in size, shape and functional groups have driven these macrocycles as highly selective receptor since they have different binding affinities towards various molecules depending on the purposes. However, despite their promising synergistic properties in a sensing application, the employment of calix[n]arenes as a chemiresistive sensor remain reasonably unexplored due to the poor conductivity. Therefore, in this work, different integration strategies were outlined by utilizing the coupling materials; electrochemically reduced graphene oxide (ERGO) and gold nanoparticles (AuNPs) to explore the performance of the developed sensors with regards to electrochemical properties, sensitivity and selectivity for the detection of anthracene.

### 1.3 Research objectives

The general objective of this thesis is to present the findings of the research strategy in designing the electrochemical sensors based on different calix[4]arene-based for the detection of anthracene. The thesis will provide analytical and physicochemical data of the developed sensors. The following specific objectives targeted for this research:

- i. To modify, characterize and optimize different strategies in developing of calix[4]arene-based sensor [namely (C4/ERGO-SPCE, TC4/AuNPs/ERGO-SPCE and C4TCA@MOF/AuNPs/ERGO-SPCE)].
- ii. To examine the analytical performance of the developed calix[4]arene-based sensors for electrochemical analysis of anthracene.
- iii. To integrate the developed sensor C4TCA@MOF/AuNPs/ERGO-SPCE with portable potentiostat.
- iv. To evaluate the performance of the fabricated prototype towards real sample analysis.
- v. To validate the developed sensor and portable potentiostat towards the established technique (HPLC).

## 1.4 Novelty of research

To the best of our knowledge, the proposed sensors was the first attempt reported for anthracene determination with an advanced features such as highly efficient material, cost-effective and eco-friendly. Significantly, by utilizing calix[4]arenes-based material as a receptor for chemically modified electrode, an excellent selectivity performance was achieved due to the behavior of calix[4]arene cavity size that matches more efficiently with the molecular size of anthracene. By outclassing the problems arose from the established techniques such as time consuming and tedious sample preparation, the sensor reported in this work has a potential as a promising tools for monitoring the level of anthracene in environmental matrices which then can be used to make decision or warning to protect public health and environment.

## 1.5 Scope of the study

This study focuses mainly on developing electrochemical sensors by employing different calix[4]arene-based receptors for the detection of anthracene. Generally, calix[4]arenes have poor conductivity and stability which limit its application in the electrochemical assay. Hence, the integration of calix[4]arenes with supporting materials was further explored for sensor characteristic improvement. The first electrochemical sensor developed was fabricated by employing ERGO as an immobilization matrix to increase the active surface area for the deposition of calix[4]arene (C4/ERGO). In spite of the significant increase in the availability of calix[4]arene cavities, the developed sensor, however, suffers from current instability due to the poor conductivity properties. The next developed sensor was designed to introduce a conducting material by functionalizing the thiolated calix[4]arene (TC4) with AuNPs while retaining the ERGO as an immobilization matrix to stabilize the hybrid material (TC4/AuNPs/ERGO). Regrettably, the formation of a calix[4]arene monolayer is unsatisfactory to appoint a high concentration of target analyte due to the limited accessible cavities, meanwhile the multilayer formation of calix[4]arenes arrangement optimizes the the  $\pi$ -stacking interactions between the adjacent calix[4]arene through non-covalent interactions, hence block the diffusion of target analyte.

In response to this shortcoming, a possible strategy to defeat this issue is by synthesizing a new metal-organic framework with calix[4]arene-based ligands to form a new sensor (C4TCA@MOF/AuNPs/ERGO). The framework formation can elegantly serve the feasibility of forming hierarchically-porous materials with two levels of porosity; the ligand and the structural framework itself, thus significantly improve the analytical measurement caused by the limited accessible cavities of calix[4]arene. Finally, the scope of the study was wrapped up with the development of a portable customized electrochemical device based on the best outstanding performance of fabricated calix[4]arene-based sensor for the determination of anthracene in real water samples.

## 1.6 Thesis Structure

The thesis consists of 6 chapters and organized as follows. Chapter 1 is the introduction of the thesis which constitutes of research background, problem statements and research motivation, research objectives, novelty of research, and scope of the study. Chapter 2 reviews the relevant available literature on the sources and occurrence of PAHs in water, recent development of electrochemical sensors for electroanalysis of PAHs, challenges and future outlooks. Chapter 3 reports the surface modification of the screen-printed carbon electrode (SPCE) with calix[4]arene-functionalized electrochemically reduced graphene oxide (C4/ERGO) in the selective electrochemical detection of anthracene. Chapter 4 provides data on the development of electrochemical sensor based on thiolated calix[4]arene-functionalized gold nanoparticles with assisted of ERGO (TC4/AuNPs/ERGO) for the selective recognition of anthracene. Chapter 5 describes the fabrication and analytical data of electrochemical sensor based on metal-organic framework-calix[4]arene based ligand (C4TCA@MOF), AuNPs, and ERGO as a sensing platform for electrochemical detection of anthracene (C4TCA@MOF/AuNPs/ERGO). This chapter also presents the integration of portable customized potentiostat based on the best outstanding performance of fabricated calix[4]arene-based sensor for the determination of anthracene in real water samples. Chapter 6 discusses the concluding remarks from the research works, significant finding, and provide the directions for future research.

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