



UNIVERSITI PUTRA MALAYSIA

***ELECTROCHEMICAL DETECTION OF Zn(II) USING AN ELECTRODE
MODIFIED WITH CALIXARENE***

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By

NUR IZZAH BINTI ROSLAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Master of Science**

April 2016

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

ELECTROCHEMICAL DETECTION OF Zn(II) USING AN ELECTRODE MODIFIED WITH CALIXARENE

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April 2016

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This work demonstrates a simple approach of developing electrochemical heavy metal ions sensor by employing calix[4]arene on indium tin oxide (ITO) electrode. The method involves the formation of self-assembled monolayers (SAMs) of 3-aminotrimethoxysilane (APTMS) on ITO, acting as a template for calix[4]arene attachment in which the different formation time of APTMS was initially studied. Contact angle and atomic force microscopy (AFM) characterizations were performed to study the surface wettability, roughness and topography. With the increasing immersion time, the values of contact angle and roughness increased. The values continue to increase after modifying the surface with calixarene. The surface modification with APTMS and calix[4]arene was confirmed using X-ray photoelectron spectroscopy (XPS) by analyzing the nitrogen and carbon regions. Cyclic voltammetry was used to monitor the blocking properties of films formed on ITO. It showed that the blocking properties modified with APTMS were improved by the modification of calix[4]arene on amine terminated ITO surfaces. Subsequent step was, the introduction of common heavy metal ions (Zn(II), Cu(II), and Fe(II)) towards the modify electrode. The electrochemical study was done by using differential pulse voltammetry (DPV) analysis by comparing the current produced for concentration of Zn(II), Cu(II) and Fe(II); the linear range of 1×10^{-2} M to 1×10^{-10} M, detection limit of 1.51×10^{-13} M for Zn(II); while with the linear range of 6×10^{-5} M to 2×10^{-6} M, detection limit of 1.31×10^{-7} M for Cu(II); and with the linear range of 1×10^{-2} M to 1×10^{-7} M, detection limit of 2.06×10^{-8} M for Fe(II). The effect of simultaneous ions was studied by comparing which ion interfere the most at the same concentration of analytes. The interference study also was done by using interfere ions such as Cu(II), Fe(II), Pb(II), Cd(II), and Ni(II) towards up to 1000-fold concentration of Zn(II). The sensitive and selective determination of Zn(II) make calix[4]arene a promising candidate for practical application in the field of detecting heavy metal ions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENGESANAN ION Zn(II) SECARA ELECKTROKIMIA MENGGUNAKAN PENGUBAHSUAIAN ELEKTROD DENGAN KALIKSARENA

Oleh

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April 2016

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Kajian ini menunjukkan satu pendekatan mudah untuk membangunkan sensor ion logam berat secara elektrokimia dengan menggunakan kaliks[4]arena di atas timah oksida indium (ITO). Kaedah ini melibatkan pembentukan ekalapisan dipasang sendiri (SAMs) 3-aminopropiltrimethoxysilana (APTMS) di atas ITO, yang bertindak sebagai templat untuk melekatkan kaliks[4]arena di mana perbezaan masa pembentukan APTMS telah dikaji terlebih dahulu. Karakteristik sudut sentuh dan daya mikroskop atom (AFM) telah dilakukan untuk mengkaji kebolehasahan, ketidakrataan dan topografi permukaan. Dengan peningkatan masa rendaman, nilai sudut sentuh dan ketidakrataan meningkat. Nilai tersebut terus meningkat selepas mengubahsuai permukaan dengan kaliks[4]arena. Permukaan yang diubahsuai dengan APTMS dan kaliks[4]arena disahkan menggunakan spektroskopi fotoelektron sinar-X (XPS) dengan menganalisis kawasan nitrogen dan karbon. Voltametri siklik digunakan untuk memerhatikan sifat penyekatan lapisan yang terbentuk di atas ITO. Ia menunjukkan sifat penyekatan bertambah baik dengan pengubahsuaian APTMS dengan mengubahsuai kaliks[4]arena di atas permukaan ITO yang diakhiri oleh amina. Seterusnya, pengenalan kepada logam (Zn(II), Cu(II), dan Fe(II)) kepada elektrod yang diubahsuai. Kajian elektrokimia telah dijalankan dengan menggunakan analisis voltametri getaran kebezaan (DPV) dengan membezakan arus yang terhasil untuk setiap kepekatan yang dikaji di antara 1×10^{-2} M hingga 1×10^{-10} M untuk Zn(II) dengan had pengesanan pada 1.51×10^{-13} M; sementara untuk Cu(II) di antara 6×10^{-5} M hingga 2×10^{-6} M dengan had pengesanan pada 1.31×10^{-7} M; dan untuk Fe(II) di antara 1×10^{-2} M hingga 1×10^{-7} M dengan had pengesanan pada 2.06×10^{-8} M. Kesan ion gangguan telah dikaji dengan membandingkan ion yang mana paling mengganggu pada kepekatan analit yang sama. Kesan ion gangguan luar juga dikaji dengan menggunakan ion seperti Cu(II), Fe(II), Pb(II), Cd(II), and Ni(II) terhadap sehingga 1000 kali kepekatan Zn(II). Penentuan Zn(II) yang sensitif dan selektif menjadikan kaliks[4]arena sebagai calon yang sesuai bagi aplikasi yang praktikal di dalam bidang menentukan ion logam berat.

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I certify that a Thesis Examination Committee has met on 22 April 2016 to conduct the final examination of Nur Izzah binti Roslan on her thesis entitled "Electrochemical Detection of Zn(II) using an Electrode Modified with Calixarene" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
APTMS	3-aminopropyltrimethoxysilane
BE	Binding energy
CA	Contact angle
CV	Cyclic voltammetry
DI	Deionized
DPV	Differential pulse voltammetry
EIS	Electrochemical Impedance Spectroscopy
GPES	General-Purpose-Electrochemical-System
ITO	Indium tin oxide
LOD	Limit of detection
NaCl	Sodium chloride
RMS	Root-mean square
SAMs	Self-assembled monolayers
XPS	X-ray photoelectron spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Heavy Metal Pollution

The water contamination by heavy metals in our environment is dangerous due to their toxicity that cause to long term side effects. The heavy metals such as cadmium, lead, zinc, nickel, copper, chromium and their components are often used in industries for metal finishing, mining and chemical industries (Shi et al., 2008) that lead to natural water contamination. This phenomenon becomes a major problem all over the world as the metals presence in excessive quantity will affect the quality in water consumption. Thus, the accumulation of heavy metal in human body will lead to kidney injury, respiratory failure, central nervous system disorder and if severe can cause death (Mohammed et al., 2011). Due to those problems, an exploration in developing a method to simple, sensitive and accurate heavy metal detection needs to be studied.

There are various sensitive and accurate techniques available for tracing heavy metals for example atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS), and inductively coupled plasma atomic spectroscopy (ICP-AES). However, these instruments are expensive and require high cost of maintenance, and highly trained personnel (Fei et al., 2014; Shi et al., 2008; Zhang et al., 2013). Thus, this limit the use of these techniques for demands in various types of heavy metal trace fields applications.

1.2 Calixarene

1.2.1 History

Calixarene can be defined as a macrocycle or cyclic oligomer compound that made up from hydroxyl alkylation of phenols and aldehydes. The first calixarene was synthesized by Adolph von Baeyer in year 1872 using formaldehyde heated with phenol by producing a resinous yield. Then, the study was ignored until 1905-1909 where Leo Baekland invented a procedure using phenol-formaldehyde reaction to produce the strong resin that get well-known with vast commercial success and marketed as Bakelite (Grady et al., 1996). After a long time, in 1944, Alois Zinke and Erich Ziegler at University of Graz in Austria described the synthesis of p-tert-butylcalix[4]arene compound that made from p-tert-butylphenol and aqueous formaldehyde with sodium hydroxide. The formation of this cyclic tetrameric structure was called as "mehrkernmethylenphenolvorbindingen" (Jose and Menon, 2007). David Gutsche in

year 1975 presented his results regarding synthesis of five cyclic tetramers in two symposia. The name of calixarene was then being invented. The name was suggested based on the design similarity of cyclic tetramer with ancient Greek vases named ‘calyx krater’, the aromatic macrocycles is ‘arene’ (Sharma and Cragg, 2011) (See Figure 1.1). In addition, the paper published by Gutsche summarized that “The products obtained from the base-catalyzed condensation of formaldehyde with several para-substituted phenols have been shown to be mixtures of two or more components which appear to be cyclic oligomers with five or more aromatic units in the cyclic array”. After that, the modern period of calixarene chemistry began (Kappe, 1994).



Figure 1.1: Calix crater (Jose and Menon, 2007).

1.2.2 Structural Characteristic of Calixarenes

Calixarenes, the receptor family received much interest for research purposes due to their unique characteristics as a receptor for molecules recognition (Yilmaz and Erdemir, 2013). Calixarenes is referred to a macrocyclic oligomers that linked the phenolic units via methylene bridging groups at positions (Zhang and Srinivasan., 2004). These macrocyclic molecules possess the hydrophobic upper rim and hydrophilic lower rim that can be modified depending on the needed and surrounded by a hollow cavity and exist in a ‘cup’ like shape with many dimensions dependent on phenolic units incorporated (Lo and Wong, 2008) (See Figure 1.2). The nomenclature for calixarene used a bracketed number that place in between calix and arene, that gives as “calix[n]arene”, where n denoted the number of aryl groups. For that reason, a cyclic tetramer was called “calix[4]arene”, a cyclic hexamer was called “calix[6]arene” and a cyclic octamer was called “calix[8]arene”.

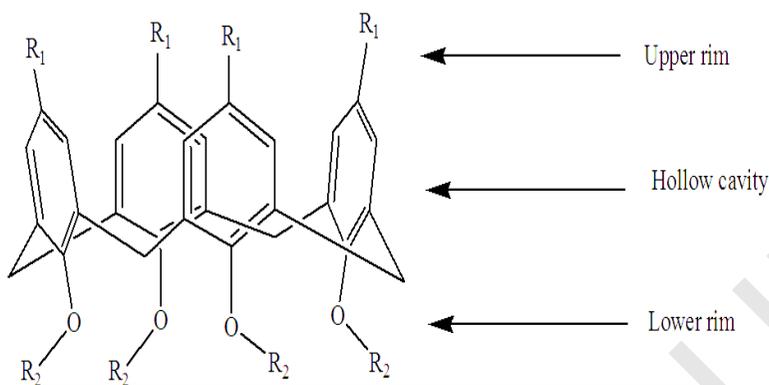


Figure 1.2: Schematic representation of typical cone conformation of calix[4]arene.

1.3 Applications of Calixarene and Its Derivatives

Calixarenes and its derivatives have been explored their extension ranging from optical and electrochemical sensors, extractant and stationary phases for more than past four decades. The availability and readily of calixarene to undergo chemical alteration make it suitable platforms to assemble various functional groups (Mikulásek et al., 2006). This fact enables calixarene to be used in biosensor (Perret et al., 2006) and chemical gas sensor (Cao et al., 2007; Tabakci et al., 2005). The recognition and formation of complexes with ions or molecules are obviously fascinating applications for derivatized calixarenes.

The complexation ability of calixarenes with ionic and neutral species paid a growing attention among researchers. The complexation of calixarene and metal ions draw a huge interest especially for environmental preservation. The applications include nuclear waste treatment especially uranium (Becker et al., 2008), strontium (Casnati et al., 2001) and cesium (Mohapatra et al., 2006). The removal of metal complexation involving alkali metal ions, alkaline earth metal ions (Zhang et al., 2004), and transition metal ions (Ak et al., 2008). This causes the calixarenes and its derivatives have widely been used for detection of heavy metal ions in aqueous solution including iron metals removal (Zareh et al., 2014), strontium, silver, mercury and copper (Benounis, 2012), chromium (Qiao et al., 2011), mercury (Bingol et al., 2010; Mahajan et al., 2008) cobalt, nickel, copper and cadmium (Ghaedi et al., 2009), lead (Honeychurch et al., 2001; Parsa et al., 2007).

In the family of calixarene, calix[4]arene is the most favored due to the rigid structures and its vase-like structure ideally make them complex with neutral molecules or ionic molecules. The designation of synthetic receptors by using calix[4]arene as molecular scaffold also was due to its stability and unique three-dimensional structure (Lo and

Wong, 2008). The parent calix[4]arene structure is easily to be modified either at lower rims or upper rims or both, with an increase solubility in organic solvent and improves the binding ability and selectivity for molecules or ions recognition (Zhou et al., 2005).

One interesting fact about calix[4]arenes is that they can form in 4 different conformations due to the flexibility in rotation of Ar-CH₂-Ar bonds; cone, partial cone, 1,2-alternate and 1,3-alternate conformation (Jose and Menon, 2007). The proper modified calix[4]arenes can act as host for various types of metal ions, also a perfect site for platforms to build up receptor for molecular recognition in the incorporation of suitable sensor system (Zhang et al. 2004). The different conformation of derivatized calix[4]arene had been applied as metals ions determination, for example; determination of Pb²⁺ ions by modified partial-cone conformation calix[4]arene (Buie et al., 2008), the synthesized derivative cone and 1,2-alternate calix[4]arene for Pb²⁺ and Hg²⁺ ion extraction (Zhang et al., 2007), the synthesis of novel proton di-ionizable p-tert-butylcalix[4]arene-crown-6 compounds were modified in cone, partial-cone and 1,3-alternate conformations for (Zhou et al., 2005). Other than that, the novel calix[4]arene-derivatized receptor with cone and 1,3-alternate conformation were synthesized for fluoride and chloride anions binding (Kim et al., 2015). The novel calix[4]arene-based glycoclusters were made to form the cone and 1,3-alternate structure for binding of galectin-3, a carbohydrate-binding proteins (Bernardi et al., 2014).

1.4 Self-assembled monolayer (SAMs)

1.4.1 History

The studies on self-assembled monolayers (SAMs) were performed as early 1950 s by Zisman, and Blackman and Dewar. The SAM method is the one of a branch in organic thin films other than Langmuir films, Langmuir-Blodgett (LB) films, and Organic molecular beam deposition (OMBE) and organic molecular beam epitaxy (OMBE) (Schreiber, 2000). The SAMs formation on surface was first reported in 1980s on adsorption of thiols and disulfides on gold; due to strong affinity of S- Au, multiple bonds with surface metal clusters of the transition metal surfaces were formed (Nuzzo and Allara, 1983).

1.4.2 Structural Characteristics and Applications

The SAM is more or less like a simple alkane on surface. SAM is formed from spontaneous chemisorption of a molecule onto a surface to form a stable and uniform layer of packing. SAMs consist of organic hydrocarbon molecules that bound to a surface and formed ordered monolayers due to Van der Waal's interactions between the molecules. The ideal SAMs structure can be divided into three parts: end group (act as terminal surface), alkyl chain and head group (molecules attached to surface of substrates) with substrates consist of hydroxylated surface (Figure 1.3). Two of the most

widely studied systems of SAMs are gold-alkylthiolate monolayers and alkylsilanemonolayers (Biddle, 2001).

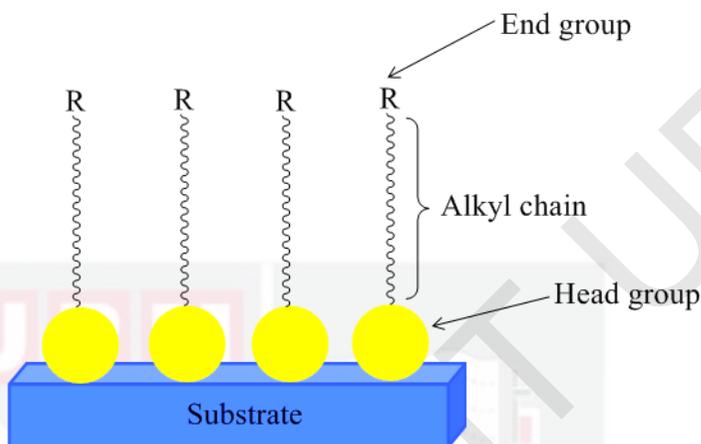


Figure 1.3: Basic structure of SAM.

Once a SAM is formed on a substrate, the surface is completely filled with organic molecules. The presence of SAMs on the surface will alter the surface physical and chemical properties compared to the bare substrate. The most widely studied SAMs are alkylsiloxane (Sagiv, 1980) and alkanethiol (Folkers et al., 1992) formed on hydroxyl surfaces and metallic surfaces, respectively.

Basically, the formation of alkylsiloxane SAMs can be divided into 3 steps. Firstly, the alkoxy group (OX-Si) where X = alkyl group, of the head group undergoes hydrolysis in presence of absorbed water on a surface to form silanol containing species. Next, the silanol groups undergo condensation with the hydroxyl groups on the substrate. Finally, they will self-order themselves by forming hydrogen bond and covalently bonded. This covalent bond stabilizes the monolayer and as a preparation for further chemical modification (Pujari et al., 2014). The silane SAMs formation can be produced by using aminosilanes, chlorosilanes, alkoxy silanes, alkyl chainsilanes and others on silicon oxide (Kulkarni et al., 2006; Zhang and Srinivasan, 2004) and ITO surfaces (Chong et al., 2007).

As many types of SAMs, organosilane with terminated amine group molecules on hydroxyl groups bearing surfaces has grown a great interest. Many research applications were done using amine-terminated SAMs in biosensors development. The amine terminated group is reactive in immobilization of enzymes (Ulman, 1996) and antibodies, DNA (Sugimura and Nakagiri, 1997), metal ion sensing (Crego-Calama and Reinhoudt, 2001), modification of electrodes and adhesion promotion (Lee et al., 2007). As an example; 3-aminopropyltriethoxysilane (APTES) (Liu et al., 2005) was used to

gain the amine-terminated group for promoting protein adhesion and cell growth on biological implant.

1.5 Indium Tin Oxide (ITO)

Indium tin oxide (ITO) is a transparent semiconductor that widely used for attachment of organic molecules onto the surface by means of formation of thin films. ITO has many advantages including the availability and its transparency toward visible light where it has been broadly used as transparent electrodes in spectroelectrochemical studies (King et al., 2006). Other than that, the optical properties of ITO are more efficient for signal transduction for applications in visible and near infrared regions (Garten et al., 1996; Sheng et al., 2006) and besides the low electrical resistivity. Many studies show that ITO can be used as an ideal electrode for electrochemical study of biomolecules (King et al., 2006) and a suitable surface for immobilization of phosphonic acids, carboxylic acids and amines for electron transport study at the interface (Oh et al., 1999). The chemisorption of phosphonic acid onto hydroxyl surface of ITO had been done for self-assembled monolayer (SAMs) formation or spin-cast multilayer formation by chemical reaction (Cui et al., 2002; Huang et al., 2005).

Other than that, ITO is also very sensitive upon hydrogen peroxide (H_2O_2) treatment in basic condition in which produce hydrophilic groups on surface. The surface modification of ITO is same as other types of surface as it also needs a pre-treatment before any chemical modification to be done. The used of H_2O_2 treatment in liquid ammonia and water is to offer a good adhesion between the SAM and the ITO surfaces through an introduction of hydroxyl and oxygen upon the treatment (Jee et al., 2006).

Since ITO is a conducting material, it is mainly used as a substrate for electrochemical analysis. The studies made by Zehner et al. showed that the dipolar moments form a SAM on gold, and with that the SAM can be used to control the function. As a matter of fact, this hypothesized that a SAM have the ability to increase the work function of ITO and improve its performance (Robert W. Zehner et al., 1999). Basically, there are various chemical modifications of self-assembled monolayer (SAMs) on ITO that can increase the work function of an ITO without changing the transmittance. This has been studied by Jee et al. where they formed various types of SAMs on ITO surface. This includes 4-chlorophenyl trichlorosilane (4-CPTS), chloromethyltrichlorosilane (CMTS), 4-chlorophenyl phosphonic acid (4-CPPA), 3-nitrophenyl phosphonic acid (3-NPPA), and 2-chloroethyl phosphonic acid (2-CEPA) SAMs on ITO that increased ITO work function. The CMTS SAM on ITO produced a highest work function (5.695 eV) in which this is the highest work function of ITO with a SAM. This is due to the increment of bonding energy of oxygen in ITO with CMTS SAM generated, thus increased the work function of ITO with SAM. This happened when the interface layer between the organic layer (SAM) and the ITO electrode showed a possible ohmic contact to occur, as the work function of ITO with SAM increase, thus removed the energy barrier between the interfaces. The energy barrier removal will improve the performance and efficiency of the organic devices. The increment of work function of ITO caused

by the increase of bonding energy of oxygen atoms with combination of indium and tin atoms in ITO modified with SAMs (Jee et al., 2006).

1.6 Electrochemical Measurement

The electrochemical techniques can be divided into two categories; voltammetric and polarography techniques. The voltammetry techniques had been chosen as the most preferable method for chemical and biochemical research.

Voltammetry is defined as the measurement of current in an electrochemical cell under complete concentration polarization condition where the rate of oxidation and reduction of the analyte is limited by the rate of mass transfer of the analyte to the electrode surface. This method was developed from polarography method that was discovered by Czechoslovakian chemist Jaroslav Heyrovsky in early 1920s. The polarography method uses dropping mercury electrode (DME) that differs it from other types of voltammetry.

Voltammetry is widely applied for electron transfer studies at chemically modified electrode surfaces (Muthurasu and Ganesh, 2012), adsorption processes on surfaces (Park et al., 2001), and oxidation and reduction processes at interfaces (Chong et al., 2007; Lukkari et al., 1998).

The electrochemical cell consists of, a working electrode, a reference electrode, and a counter electrode (Figure 1.4). All the reaction or transfer of interest happened on working electrode surface. The reduction or oxidation of the substance occurs on modified working electrode surface at certain applied potential. This result in the mass transport of a new material to the electrode surface and produced a current.

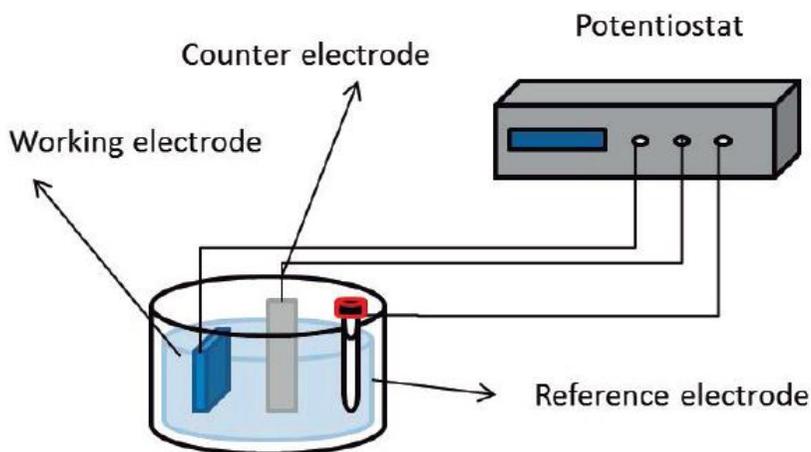


Figure 1.4: Cell setup for electrochemical analysis using potentiostat
(Culebras et al., 2014).

The electrochemical heavy metal detection offers high sensitivity and selectivity with low operational cost, simple instrumentation, along with fewer samples requires. As studied by Thompson and co-workers, the used of voltammetry technique such as cyclic voltammetry (CV) analysis was performed along with ICP-MS/AES technique for determination of uranium cation (UO_2^{2+}) by using gold electrode modified with calix[4]arene (Evans-thompson et al., 2002). Other than that, Zhang and co-workers also synthesized calix[4]arene derivative and growth a SAMs on gold surface for Ba^{2+} and Ca^{2+} ions detection. The detection was done using cyclic voltammetry and impedance spectroscopy (Zhang et al., 2004). The work done by Park and co-workers which also successfully detected their Ca^{2+} ions using self-assembly of quinone-functionalized calix[4]arene on silver electrode by cyclic voltammetry and square wave voltammetry (SWV) analysis (Park et al., 2001).

1.6.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) has been widely used in electroanalytical studies in chemistry. This technique is based on varying the potential at a working electrode in both forward and reverse directions at some scan rate while observing the current.

The advantage of CV technique is that it offers on half-reactions occurring at the working electrode, providing information regarding the chemical or physical phenomena happened to the studied electrochemical reaction.

The important parameters in cyclic voltammogram are the peak currents (i_{pa} , i_{pc}) of anodic and cathodic peak current, and peak potentials (E_{pa} , E_{pc}). The electron transfer

process is said to be fast is when the reaction is electrochemically reversible where the peak separation is determined by:

$$\Delta E_p = |E_{pa} - E_{pc}| = 2.303 RT/nF$$

For a reversible redox process at 25°C with n electrons ΔE_p should be 0.0592/n V or about 60 mV for one electron. But, in reality this value is difficult to obtain due to many reasons such as cell resistance. Irreversible reaction is caused by slow electron transfer rate results in $\Delta E_p > \frac{0.0592}{n} V$ or greater than 70 mV for one electron (Kounaves, 1997).

Cyclic voltammetry was discovered to be a significant method as an analysis tool that gives information about the mechanisms of oxidation or reduction reactions under various conditions.

1.6.2 Differential Pulse Voltammetry (DPV)

The innovation of pulse voltammetric technique is due to the fact that by adjusting the potential, the current measured in a pulsed method, a considerable discrimination of the charging (non-faradic) current can be attained. Differential pulse voltammetry is one of the types of pulse methods where the speed and sensitivity were improved from over the years.

DPV is an electrochemical method with the addition of a pulse of constant amplitude at the end of each potential step. The current is sampled before and at the end of pulse. This sampling point permits the decay of the non-faradic (charging) current. The difference in current is recorded as the result with presence of peaks for observation. The difference between current measurements is plotted against the base potential. The discrimination opposes to the charging current resulting to lower detection limits (as compared with linear sweep technique), thus causes DPV technique is well-suited for quantitative analysis (Kounaves, 1997). This ability makes this pulse technique is more sensitive to faradaic currents (reduction or oxidation currents) than conventional voltammetry.

DPV however produces peaks for faradic currents rather than sigmoidal waveform obtained from normal pulse techniques. Due to that, this results in improvement of resolution for multiple analyte systems and various quantitation ("Application Note S-7," 1982). Other reason is the current measured is also known as differential pulse voltammogram (Refer Figure 1.5), in which the difference measurement between currents for each single pulse enables increase of sensitivity of DPV and normal pulse voltammetry (NPV) (Gulaboski and Pereira, 2008).

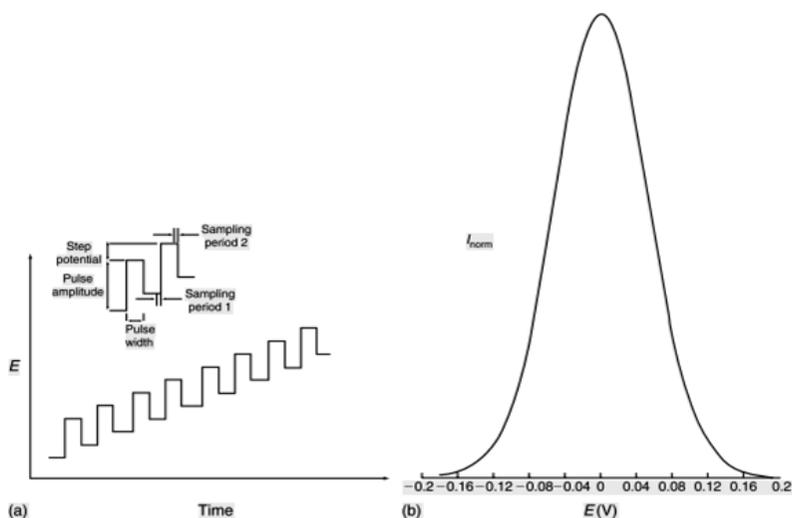


Figure 1.5: a) Potential form, b) resulting simulated voltammogram in DPV (Gulaboski, 2008).

1.6.3 Electrochemical Impedance Spectroscopy (EIS)

EIS technique is an electrochemical technique that typically used to determine k_{ET} for redox-active SAMs. EIS measures the frequency response of a system by quantifying its impedance, Z . This is performed by putting on a small AC signal over a range of frequencies at a certain potential. Measuring impedances over a wide range of frequencies permits the value of each of individual element for electron transfer of redox species attach to a monolayer.

EIS was applied to determine the electron transfer reactions of the redox probes on SAM modified surfaces. The data were used to get the charge transfer resistance (R_{CT}) value, that give an information on blocking ability of the monolayer towards the redox species diffusion process (Ganesh, 2006).

EIS data commonly been plotted in two ways, a Bode plot or a Nyquist plot. For Bode plots, the log of impedance magnitude, $\log(Z)$, and the phase, ϕ are plotted splitly versus $\log(\text{frequency})$. For Nyquist plot, the ordinate denoted by the imaginary axis, Z_{Im} , and the abscissa is the real axis, Z_{Re} . Many data analysis are using Nyquist plots as compared with Bode plots.

For monolayer analysis, at high frequencies, the plot appeared in ellipse shape where no electron transfers to occur with R_{ct} become negligible. But, at low frequencies the

Nyquist plot ellipse never reach Z_{Re} , and the plot becomes a vertical line (Eckermann et al., 2010).

1.7 Problem Statement

Heavy metals such as Zn(II), Cu(II) and Fe(II) were basically natural constituents from the earth crust, but they are discharged to the environment due to natural phenomena and human actions. The pollution of natural waters by copper, zinc and ferum give a great concern among researchers. Cu(II) ions play an important role in physiological processes in human body, and known to be an essential element for human life. The amount of copper that required for normal metabolism is about $40 \mu\text{gL}^{-1}$, but if it was present in excessive amount, it will become toxic for the body. The presence of copper excessively can cause diseases to human body such as kidney problem and lung cancer (Hu et al., 2011). While the abundance of zinc ions in atmosphere causes it to be easily consumed by human and lead to many diseases such as pulmonary manifestations, fevers, chills and gastroenteritis (Yilmaz et al., 2009). Ferum is a second most abundant metal in earth's crust, and it also a crucial element in human nutrition. The presence of ferum (II) salts in drinking water supplies are unstable and appeared as precipitation as insoluble iron (III) that settles out as a rust-coloured silt (Iron in Drinking-water, 1996). There are various sources of zinc, copper and ferum contamination. They may come from industrial and household waste discharges, the leakage from sewage systems into water sources (Raj et al., 2013). The long-termed exposure from these types of heavy metals may result in slow progressing of physical and muscular, Parkinson's disease, and the long-term contact will cause cancer. So, this is how critical it was to detect these ions in real life.

Most of the traditional instruments that were used for metal ions detection such as ICP-MS, AAS and ICP-AES are high cost and bulky. They required a well-trained personnel and time consuming analyses.

In this work, by using electrochemical method, it offers a better alternative to detect metal ions such as Zn(II), Cu(II) and Fe(II) which are portable, ultrasensitive and selective.

1.8 Objectives of the studies

1.8.1 General Objective

The objective of this research is to develop electrochemical heavy metal ions sensor by employing calix[4]arene on self-assembled monolayer on indium tin oxide (ITO) electrode.

1.8.2 Specific Objectives

1. To modify electrode of 3-aminopropyltrimethoxysilane (APTMS) SAMs on ITO that act as template for calix[4]arene attachment.
2. To investigate the optimization of electrode based on the choosing of correct supporting electrolyte and deposition time.
3. To study the electrochemical detection of Zn(II), Cu(II) and Fe(II) based on modified calix[4]arene/APTMS/ITO Electrode

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PUBLICATIONS

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