# การปรับปรุงขั้วไฟฟ้าทำงานสำหรับตรวจวัดสารประกอบกลุ่มไนโตรอะโรมาติก โดยเทคนิคไฟฟ้าเคมี

# WORKING ELECTRODE MODIFICATION FOR NITROAROMATIC COMPOUND DETECTION VIA ELECTROCHEMICAL TECHNIQUE

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โครงงานพิเศษนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรวิศวกรรมศาสตรบัณฑิต
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สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
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# WORKING ELECTRODE MODIFICATION FOR NITROAROMATIC COMPOUND DETECTION VIA ELECTROCHEMICAL TECHNIQUE

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ภาควิชานาโนวิทยาและนาโนเทคโนโลยี
วิทยาลัยนาโนเทคโนโลยีพระจอมเกล้าลาดกระบัง
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โครงงานพิเศษ

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## ABSTRACT

This research aims to study the electrochemical detection using cyclic voltammetric technique of nitromatric compound, nitro ($-NO_2$) group attached to the benzene. The three-electrode measurement was used to investigate the reduction behavior of nitro functional group. Gold, glassy carbon commercial electrodes were used to studied the effect of electrolyte. Among three eletrolytes, which are potassium chloride in phosphate, sodium chloride in phosphate and Ethylene glycol and ethanol in KCl in 30% water, Ethylene glycol and ethanol in KCl in 30% water provides the clearest reduction peak. As the results, cyclic voltammogram presented the reduction current peak of nitro group around -0.5 to -0.6 V. After that gold and carbon printed circuit board were used as working electrode, due to their easier modification method and lower cost, to studied the effect of electrode using the same electrolyte resulting to better reduction voltammogram. Furthermore, to improve the detection sensitivity printed circuit boards of gold and carbon were modified to improve reduction current peak detection using carbon nanotube(CNT), titanium dioxide nanoparticles and polyacrylic acid. In the result of CNT modified on gold Printed Screen Board provided higher sensitivity.



**Keywords:** Nitroaromatic compound, Cyclic voltammetry, Reduction current

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| **โครงงานพิเศษเรื่อง** | การปรับปรุงขั้วไฟฟ้าทำงานสำหรับตรวจวัดสารประกอบกลุ่มไนโตรอะโรมาติกโดยเทคนิคไฟฟ้าเคมี |
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**บทคัดย่อ**

ในงานวิจัยนี้ได้ศึกษาการตรวจวัดหมู่ฟังก์ชันไนโตรในสารประกอบไนโตรอะโรมาติก โดยใช้การตรวจวัดทางไฟฟ้าเทคนิคไซคลิกโวลแทมเมทรีแบบสามขั้วไฟฟ้า จ่ายความต่างศักดิ์ในช่วง -1.0 ถึง -0.6 โวลต์เป็นช่วงที่มีการเกิดรีดักชันของกลุ่มไนโตร โดยทั้งนี้ได้มีการศึกษาผลของสารละลายอิเล็กโตรไลต์ที่ใช้ในการวัดโดยใช้ขั้วทองและขั้วกลาสซี่คาร์บอน โดยศึกษาจากสารละลายสามชนิด ซึ่งประกอบด้วยโพแทสเซียมเฟอโรไซด์ยาไนด์ในสารละลายฟอสเฟส, โซเดียมคลอไรด์ในสารละลายฟอสเฟส และ เอทานอลผสมกับเอทิลีนไกลคอลในสารละลายโพแทสเซียมคลอไรด์ พบว่าสารละลายอิเล็กโตรไลต์ของเอทานอลผสมกับเอทิลีนไกลคอลในสารละลายโพแทสเซียมคลอไรด์ให้การตอบสนองของกระแสรีดักชันของหมู่ไนโตรได้ดีที่สุด หลังจากนั้นขั้วทองเคลือบบนแผงวงจรพิมพ์และขั้วคาร์บอนเคลือบบนแผงวงจรพิมพ์ได้ถูกนำมาทดสอบการตอบสนองในอิเล็กโตรไลต์เอทานอลผสมกับเอทิลีนไกลคอลในสารละลายโพแทสเซียมคลอไรด์เนื่องจากแผงวงจรพิมพ์มีราคาถูกกว่าและง่ายต่อการปรับปรุงขั้วมากกว่า ผลที่ได้คือขั้วทองเคลือบบนแผงวงจรพิมพ์สามารถตรวจวัดสารกลุ่มไนโตรอะโรมาติกได้ดี และเมื่อทำการปรับปรุงขั้วด้วย อนุภาคนาโนไทเทเนียมไดออกไซด์, ท่อคาร์บอนนาโน และ พอลิอะคริลิค แอซิด พบว่าการใช้ท่อนาโนคาร์บอนในการปรับปรุงขั้วไฟฟ้าทำงานสามารถให้การตอบสนองที่ดีขึ้น



**คำสำคัญ:** สารประกอบไนโตรอะโรมาติก; เทคนิคไซคลิกโวลแทมเมทรี; กระแสรีดักชัน

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Nichakorn Pansailom

May, 2017

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# CHAPTER 1

# INTRODUCTION

## 1.1 Statement and Significance of the problems

Nitroaromatic compound is regarded as one of volatile organic compound (VOC) which composed of several components such as nitrobenzene (NB), dinitrobenzene (DNB), trinitrobenzene (TNB), trinitrophenol (TNP) and trinitrotoluene (TNT). Among of them, the TNT is widely used as an explosive substance for military, mine industry and terrorist activity. However, the TNT exhibits high extreme toxicity on human and environment, i.e. it rapidly stimulates reproductive and lung cancer in human [1]. The TNT can be totally absorbed by plant and accumulated in mesophyll [2]. Therefore, detection of TNT in environments are in serious situation. The TNT in the environment is able to be detected throughout numerous methods like mass spectrometry (MS) [3-4], fluorescence spectrophotometry [5], raman spectrometry [6], high performance liquid chromatography (HPLC) [7], gas chromatography (GC) [1] and electrochemistry, respectively. Owing to a simplicity, low cost, fast response and portable system [8], the electrochemical technique gains a tremendous interesting for nitroaromatic detection. To detect nitroaromatic compound via electrochemical system, surface modification and surface functionalization of working electrode (detecting electrode) is necessary. For example, Boris Filanovsky *et.al.* demonstrates modification of $TiO_2$/Metal nanoparticles (NPs) on carbon based paper electrode to examine trinitrotoluene (TNT). They found that, by using $TiO_2$/Pt-NPs, the enhancement of drastic reduction current is significantly occurred. In 2014, Faheng Zang *et.al* reports on modifying Tobacco mosaic (TM) virus-like particle (VLP) as free-floating binding agent in bulk solution to improve the detection performance toward to TNT [9]. They also demonstrate that the diffusion coefficient of TNT in solution of VLP-bp-TNT, binding peptide (bp), is higher than 4 times as compared with the unmodified one. In 2015, Suparat Cotchim *et.al.* provide new strategy for investigating TNT in saline solution based on electrochemical measurement using poly(melamine)/graphene oxide modified on glassy carbon electrode. The detection limit as low as 0.34 $\mu g/dm^3$ was obtained [10]. In this research, we focus on TNT detection through three-electrode electrochemistry. The

working electrodes were modified with various material as polyacrylic acid (PAA), carbon nanotubes (CNT) and titanium dioxide ($TiO_2$). Moreover, electrolyte solutions, potassium ferrocyanide ($K_3Fe(CN_6)$) in phosphate buffer and ethylene glycol (EG)-ethanol-potassium chloride (KCl) mixed solution, were also studies. As a result, gold (Au) electrode modified with PAA illustrates low detection limit of 1 ppm.

## 1.2 Objectives

1.2.1. To study the modification techniques of the electrode
1.2.2. To modify the electrode using different materials
1.2.3. To study the responsibility of modified electrode in different electrolyte

## 1.3 Process of the study

This research studied the modification of electrode which can improve the sensitivity towards nitroaromatic explosive detection. The processes in this research were divided in to 3 parts:

1.3.1 Studying theory of modification technique on the working electrode and electrochemical detection technique.

1.3.2 Fabricating the membrane using various materials on gold coated electrode and carbon coated electrode which prepared by drop-casting and solvent evaporation technique.

1.3.3 Characterizing the property and sensitivity towards nitroaromatic compound.

## 1.4 Scope of research

This research intends to modified the working electrode as a sensor to detect the existed TNT in solution. The materials that used to modified the working electrode in this research were multiwallcarbon nanotube(MWCNT), polyacrylic acid(PAA), $TiO_2$. All those materials were drop-cast on to the electrode on the printed circuit board. The modified electrodes were examined via electrochemical characterization in various concentrationsx0. Then, they have been evaluated their properties such as the sensitivity and repeatability.

# CHAPTER 2

# GENERAL BACKGROUND

## 2.1. Nitroaromatic materials

Nitroaromatic compounds have nitro ($-NO_2$) moiety attached to the aromatic ring. The nitro group on the benzene ring changes the properties of the aromatic system. The two electron-withdrawing oxygen atoms on the $-NO_2$, together with the smaller electron-density demand by the electronegativity of nitrogen, pull the electron density towards them, depleting the ring slightly from its electron cloud. For this reason, when a nitrobenzene reacts with an electrophile (positively charged), it requires stronger conditions than benzene and the nitrobenzene that have become deactivated. Additionally, the electron density remaining on the ring has localized areas of slightly higher electron-density ($\delta^-$), alternating with slightly depleted areas ($\delta^+$), giving rise to preferred sites of attack for an incoming electrophile which by its nature is either electron-deficient or positive charged. Nitrobenzene can be found in many forms for example, dinitrobenzene (DNB) which $-NO_2$ attached to 2 sides of the benzene chain, and trinitrotoluene (TNT) which $-NO_2$ attached to 3 sides of the toluene. The derivative of nitrobenzene widely used in the most dangerous way is 2,4,6-trinitrotoluene(TNT) which is used as the main component in explosive found in military terrorist and mining industry [11-12].

An explosive is chemical substance which self-spread widely decomposition after initiation. Upon the decomposition, the stable compounds are formed which a pressure and heat are released. When detonated, it will be fast and high exothermic reaction. Explosives can be fundamentally classified into 2 different types based on the velocity of detonation. High explosives detonate very fast with give both shocks, which break the rock, and force. Low explosives just burn, and detonate slowly [13-14].

TNT represents the most important explosive ingredient for blasting charge of all weapons because of its stable and neutral. The TNT has been applied as an ingredient for mostly commercial detonators. The TNT classified as high explosive and will explode

violently compare to the low explosive. The reactions shown in eq. 2.1 and 2.2 are the examples of TNT occurring when explode and likely to occur a combination [15].

$$2C_7H_5N_3O_6 \longrightarrow 3N_2+5H_2+12CO+2C \quad .....2.1$$

or

$$2C_7H_5N_3O_6 \longrightarrow 3N_2+H_2+2CH_4+12CO \quad .....2.2$$

The TNT can be contaminated in water after exploded or wasted from industries and seeps into soil resulting in accumulate in organisms. When TNT entered to human's body it leads to many harmful effects such as anemia and abnormal liver function [16].

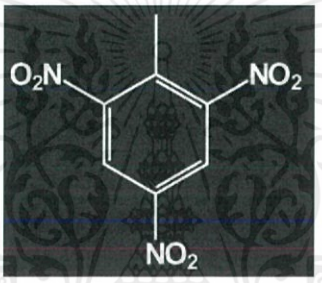


**Figure 2.1** TNT structure

Normally, the most popular technique that use to detect explosive is sniffing dog. Due to the excellent smell detection capability of dogs which they can detect even small amount of odor and detect many different kinds of substances. They have been successfully use dog for explosives detection. But there are still some problems, like dogs require rigorous training, testing and validation with different types of explosives. Dogs react to all kind of explosives because they smell the component of the explosive not the compound. There is a research that studying about the olfactory system of dogs, and presented that the limit of detection of Dogs is 1.14 ppt which is very low[17]. But there are still lots of drawbacks using dog as explosives detector. The first reason is that they need an extensive training not only for dog but for the handlers too. The second reason is dog can get tired while working for 1-2 h. so it is need to has 2-3 dogs in each position. The third reason is their work is up to their moods, it is not every times that they are willing to do their work, and animal's behavior is different from human, we are not able to control all the time. According to the given reasons above using dog as explosive detector spend so much money. There are many researchers try to figure out the

technique that could replace the sniffing dog, lead to low cost and 24 h working [15,18-19].

At present, explosives detection received many attentions of researcher all over the world. There are many of techniques measuring the explosives to replace the dog detection techniques. Such as infra-red (IR) spectroscopy [22], ion mobility spectroscopy [21-22], mass spectroscopy [23], nuclear magnetic resonance spectroscopy [24], and raman spectroscopy[6,25] which all these techniques have proved to be an accurate and reliable method for detecting explosive. But all these techniques have to use analytical instruments and shared the same advantages, which are the cost of the equipment, maintenance, complicated sampling and prepared sample, regarding all these reasons made them disable to continuous monitoring.

2.1.1 Health effects after exposure to TNT [26-27]

2.2.1.1. Inhalation Exposure:

Historically, in world war I, numerous worker in the work plant were cause by the adverse effect of TNT on liver. Initial symptoms are nausea, vomiting, fatigue, dizziness, petechiae and jaundice and then lead to death.

1.1 The effect after human has been exposure to TNT

**Table 2.1** Represent the human systemic effect after exposure toward TNT

| Systemic effects | Human |
|---|---|
| Respiratory effects | Can cause respiratory difficulties |
| Hematological effects | Anemia AND Fatal aplastic anemia brings to death |
| Hepatic Effects | many cases of toxic hepatitis were fatal |
| Immunological and Lymphoreticular Effects | No studies were located regarding immunological or lymphoreticular effects in humans |
| Reproductive Effects | 50% of workers in TNT production had incidence of sperm malefaction. |
| Genotoxic Effects | the urine of workers in explosives production found the highest level of mutagenic activity |
| Cancer | Can develop the primary cancer |

No studies were located regarding cardiovascular, gastrointestinal, musculoskeletal, or renal effects in humans or animals after inhalation exposure to TNT.

2.1.1.2. Oral exposure

The acute exposure has been tested to animals and the investigated results are shown below:

**Table 2.2** Represent the health effect of animal after animals have been exposure to TNT

| Exposure | Rat | Mouse | Dog(Beagle) |
|---|---|---|---|
| Acute exposure | Leading to death when lethal Dose over 660 mg/kg (mg of substance per kilogram of body weight) or become convulsion and tremors. | Leading to death when lethal Dose over 660 mg/kg (mg of substance per kilogram of body weight) or become convulsion and tremors | |
| Intermediate | Moderate anemia and leokoccytosis<br>Cholesterol increased.<br>Body weight decreased 15-20%<br>Decreased food intake<br>Liver and spleen weight increased significantly<br>Accumulation of yellow-brown pigmentation in the cortex<br>Decreased red blood cell and hematocrit<br>Increased yellow-brown pigment in tubular epithelial cells of renal cortex<br>Moderate diarrhea<br>Inflammation of small intestine | Increased spleen weight | 30% of dog died after 1 month of experiment.<br>Slight ataxia<br>Slight lethalargy<br>Increased spleen weight |

| | | | |
|---|---|---|---|
| Chronic exposure | Bone narrow fibrosis<br>Cholesterol increased<br>22% female got Cancer<br>95% Papilloma of urinary bladder | 28% Leukemia<br>Mild anemia<br>Reduce hemoglobin | |

## 2.2. Explosives detection techniques

### 2.2.1 Infra-red (IR) spectroscopy

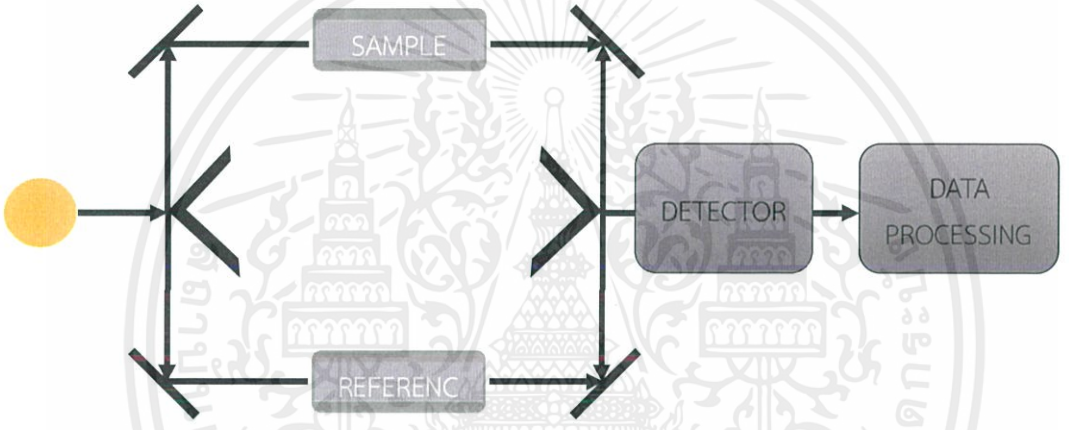


**Figure 2.2** Simplified schematic of infrared spectrometer

Infra-red (IR) spectroscopy use the IR region ($10^{-3}$-$10^{-6}$ m) of electromagnetic spectrum to identify the substance with their characteristic bonds and functional groups. The electromagnetic waves travel through these bond or functional group and vibrate matches to the transition electromagnetic waves with specific frequency and will absorb light with same frequency due to resonance. This technique enabled analysis of samples in normal atmosphere rather than within the spectrometer various samples chamber [21,28-29].

### 2.2.2 Ion mobility spectroscopy

Ion mobility spectroscopy (IMS) is the most widely used instrument for the detection of low concentration explosives. $^{26}$Ni or $^{241}$Am is usually used as the ionization injected electrically into the drift region. Under the applied electric field (approximately 200V/cm),

ions move toward the detector, mostly use a faraday plate, and create signal such as current. The drift times are related to the mass of the ions. It is possible to identify components within the sample through the comparison by determine the ratio of mass and charge with the known standard. Explosives substance such as TNT has been widely studied using this technique. The properties of TNT

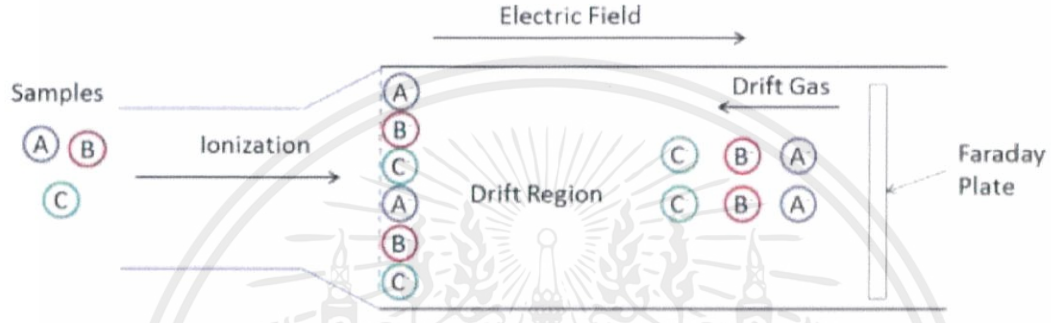


**Figure 2.3** Simplified schematic of mass spectroscopy [8, 20]

and its ions behavior present very good response in IMS compare to other explosives. Because the chemical in gaseous of TNT produces ions with good thermal and chemical stability. The mobility spectrum could be affected by the type of gas flow in the chamber and the sensitivity was increased when flow the oxygen. An advantage of this method is the speed, which takes in few second, but disadvantage is its selectivity. Researchers attend to increase the selectivity and accuracy of this technology. There is research report that coated the hot plate with polymer can decrease the limit of detection. Besides enhance the sensitivity some researcher interesting in miniaturize the IMS apparatus for hand held system [22-23].

### 2.2.3 Mass spectroscopy

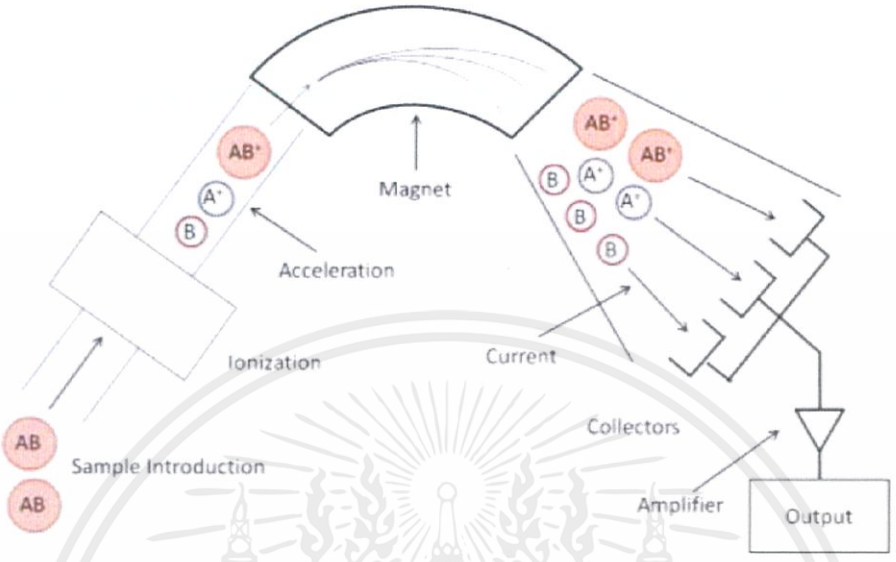


**Figure 2.4** Simplified schematic of mass spectroscopy [8, 20]

Mass spectrometry (MS) has been widely used in explosive detection due to its excellent specificity in identifying in both quantity and quality of substances. The principle is when sample move through the analyzer, the speed and direction of ionized molecules and their fragment of the samples are change because of electric and magnetic field. The magnitude of deflection of the moving ion's path is determined by its mass-to-charge ratio, thus the chemical composition of substance can be separated and analyzed. Using this technology is limited in identifying molecule that produce similar fragmented ions. Adaptation has been used to enhance the mass resolving capability of mass spectrometry in identifying hydrocarbon compound [3-4,15,30].

## 2.3 Electroanalytical technique

Electrochemical analysis is a technique relate to the relationship between electrical signal and electrical reaction, which study the interest material by measuring the potential (volts) and/or current (amperes) in an electrolyte containing interest material. Each electroanalytical technique, for instance, cyclic voltammetry (CV) has certain characteristic

potentials, which can be derived from the measured curves. All the characteristic peaks are related to its electrochemical properties.

2.3.1 Cyclic voltammetry

The hysteresis graph of cyclic voltammetry is the characteristic of 'reversible' voltammetric current responses that is controlled by mass transport/diffusion processes in the solution phase. In order to understand the origin of cyclic voltammogram shape, it may be helpful to think of the observed current response at each potential as being composed of two simpler current responses based on:

(i) the conventional 'transient' or potential step technique (chronoamperometry), in which the decay of the current at a given potential is monitored as a function of time

(ii) the conventional 'steady-state' technique (polarography, hydrodynamic or micro electrode methods) in which the current is independent of time.

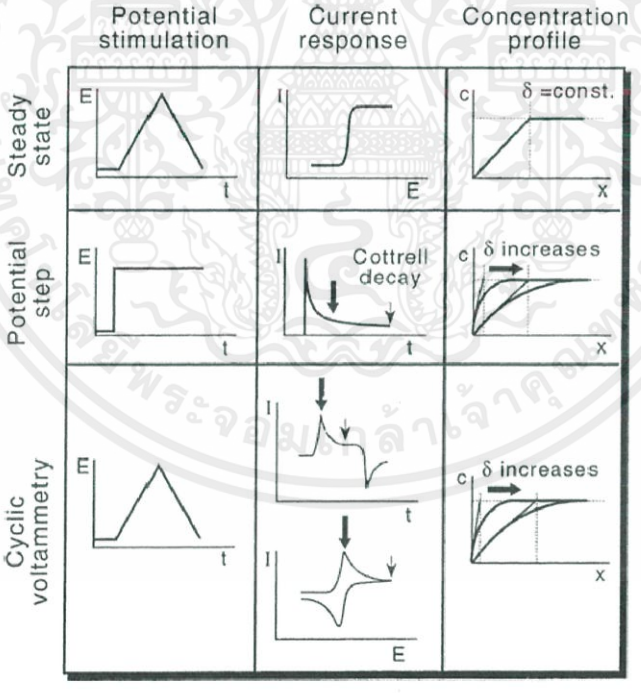


**Figure 2.5** Steady-state, chronoamperometric, and Cyclic voltammetric simulation plots

Figure.2.5 compares the characteristic of (a) a steady-state process, (b) a potential step experiment, and (c) a cyclic voltammogram. The steady-state experiment is

independent of time and gives a sigmoidally shaped response. Most important is the extent to which the concentration profile penetrates into the solution phase. For a steady-state process, there is no time dependence and the diffusion layer thickness(δ) remains constant. In a chronoamperometric or potential step experiment, the diffusion layer thickness continuously moves into the solution phase. During the initial course of a cyclic voltammetric experiment, the diffusion layer also moves into the solution phase. However, this is certainly followed by a second change in concentration generated after

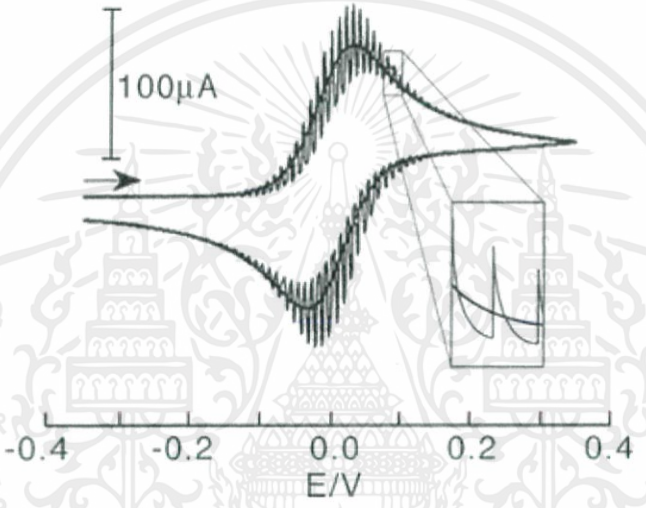


**Figure 2.6** Sampling and averaging is used in staircase voltammetry to give conventional voltammogram for sufficiently small potential steps.

the reversal of the scan direction. The close relationship between the different applied potential techniques in electrochemistry can be understood by considering cyclic staircase voltammetry as shown in Figure 2.6. Most commercial computerised instrumentation relies on digital electronics, and, instead of applying an analogue potential ramp, a staircase potential is applied. Measurements are taken in the last part of the step interval. The current response from the staircase voltammogram can be seen to oscillate above and below the current expected for a conventional cyclic voltammogram. By choosing sufficiently small interval times and potential steps, current responses essentially identical to those obtained by analogue instrumental forms of cyclic voltammetry are obtained. However, the distortion of voltammetric signals caused by the use of large steps has to be considered and, indeed, may even be usefully applied for particular purposes. If

staircase voltammetry is applied uncritically, considerable errors, e.g. in the determination of the charge under a peak by integration, will possible[31-32].

Applications of cyclic voltammetry are extensive and include the analysis of solids [33] as well as solutions, media with/without added supporting electrolyte, emulsions and suspensions [34], frozen solutions [35], polymers [36], membrane and liquid/liquid systems [37], and biological systems such as enzymes or cultures of bacteria [38]. Common experimental configuration for cyclic voltammograms consists of an electrochemical cell that has three electrodes and all are immersed in a liquid and connected to a potentiostat. The Electrodes are used in cyclic voltammetry are:

- Reference electrode: Ag/AgCl is the commonly used which can obtained commercial or prepare easily in laboratory.
- Counter electrode: most stable material non-reactive material, platinum is the commonly used.
- Working electrode: Pt, gold, Glassy carbon and other inlaid disc electrode. This electrode is usually modified to improve or develop the ability of the analyzation.

The potentiostat allows the potential difference between the reference and working electrode to be controlled with minimal interference from IR (ohmic) drop. In this configuration, the current flowing through the reference electrode also can be minimised therefore avoiding polarisation of the reference electrode and keeping the applied potential distribution between the working and reference electrode stable.

For the solution with sufficient supporting electrolyte, the electrical double layer at working electrode occupies a distance about 1 nm from the electrode surface. In figure 2.7 shown that there consist of compact layer and diffuse layer. The diffuse layer extends into the solution phase depend on electrolyte's concentration and the double layer also can affect on the kinetics of electrochemical processes.

2.3.2 Potentiometric measurement

In potentiometry, the potential of a suitable indicator electrode is measured versus a reference electrode. Whereas the indicator electrode is indirect contact with the analyte solution, usually salt bridge in various forms is used to separate the reference electrode from the analyte solution. The electrode potential of the indicator electrode is normally

directly proportional to the exponential function of the analyte activity in the solution. Potentiometric methods have been and still are popular due to the attractive features of potentiometry that the equipment is inexpensive and simple.

The galvanic potential difference of a single electrode is not directly measurable, because it is not possible to connect the two phases of an electrode with a measuring system without creating new phase boundaries with additional electrochemical equilibria and thus additional. Galvanic cells consist of electrically connected electrodes. The cell reaction is the sum of the single electrode reactions, and the cell voltage E is the sum of

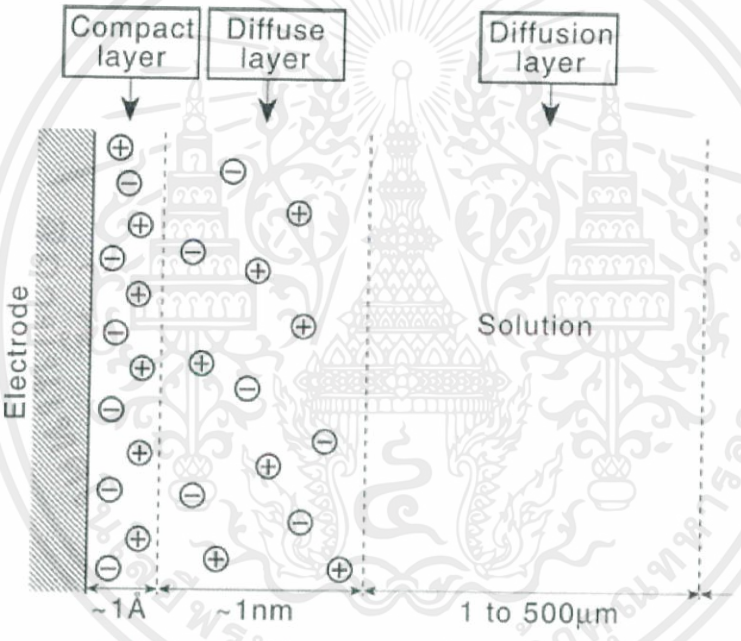


**Figure 2.7** Representation of the solution phase in the electrode surface (not in scale)

the overall potential drops at the phase boundaries and within the phases. The key element for potentiometric is the indicator electrode which will be described below.

1. The glass electrode is the most frequently used ion-selective electrode. It is applied in almost all laboratories for the determination of pH values.

2. Redox electrode is used when both the oxidation and the reduction reaction are formed in a solution, an inert metal can attain a potential, which only depends on the ratio of the activities of these two species.

3. Metal electrode contains the cations of metal. In contrast to redox electrodes, ions as charged particles are exchanged across the phase boundary. An example of this

electrode is the silver electrode, a silver wire in a silver-ion-containing solution (Figure2.8). that the reaction can be monitored as seen in equation 2.1

$$Ag^0 \rightleftharpoons Ag^+ + e^- \quad (2.1)$$

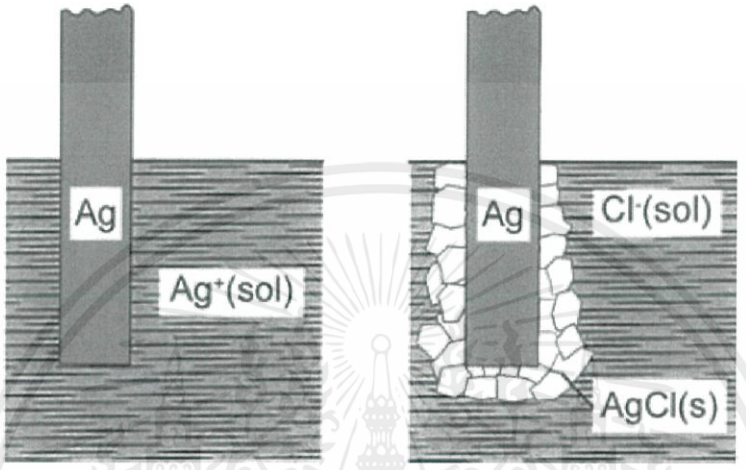


**Figure 2.8** (a) Schematic description of the Ag electrode

When ions are transferred between two phases (between solution and membrane) this Galvanic potential difference is increased. The term membrane denotes a thin plate separating two liquid phases. Membranes are divided into three groups:

1. Large meshed membranes. Rapid mixing of different electrolyte solutions is delayed, and a diffusion potential arises due to the different diffusion coefficients of solution.

2. Close meshed membranes. Only ions or molecules up to a certain size can pass the membrane.

3. Thick membranes. Two Galvanic potential differences can occur at the two interfaces, and diffusion potentials may build up in the membrane. Among the thick membranes, those of glass are most important.

## 2.4 Literatures review

Up to present sniffing dogs are still be the extensive way for explosive detection. They can locate the hidden explosive and also can smell the target even there is a very low concentration[40]. Michael Krausa[41] had published his work about vapor explosive detection and said that sniffing dog is the most effective way to detect explosive in large

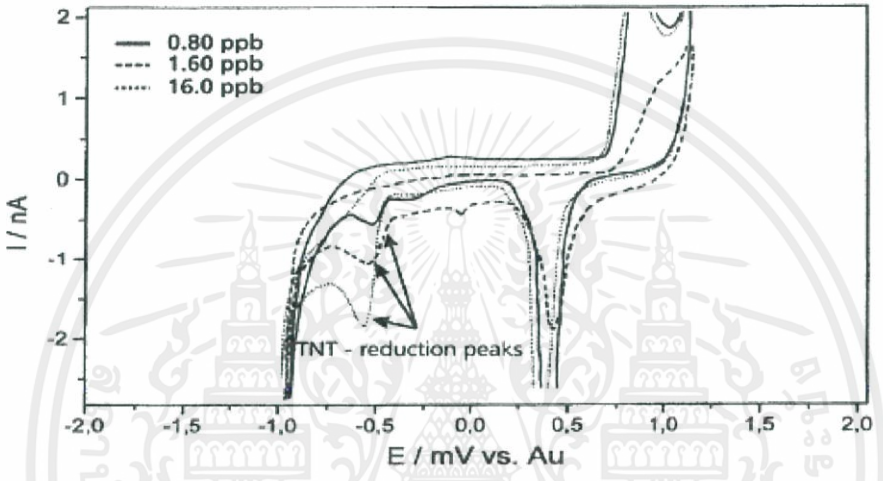


Figure 2.9 Cyclic voltammogramms of different vapor TNT concentration using gold microelectrode, v=100mV/s [26]

area. However, the problem is a training a dog costs a lots to overcome that the explosive sensors are developed[42]. There are many techniques and sensors used in explosives

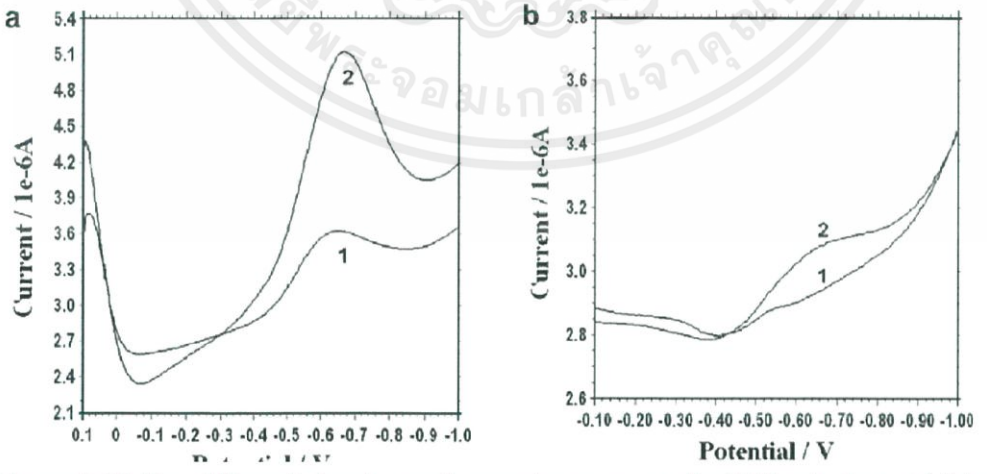


Figure 2.10 The differential pulse voltammetry response for TNB solution at (a) bare electrode (b) MSU/PDDA with various layer[45]

detection. Gas sensor has been promoted to detect explosives but the main challenges of explosive detection using gas sensor are the small vapor pressure in normal environment (of explosives and will decreasing with the increasing in distance from the source) and operation temperature. For decades, many researchers try to overcome the detection techniques limitations. In this research is aim to study the explosives detection with electrochemical technique which considered as the most suitable way due to it is easy operation, fast response, low detection limit, high sensitivity and viable options for miniaturization but still has drawback which is non selectivity.[43]. The Fraunhofer Institute publish another electrochemical detection for explosive using chemical sensor and gold used as working electrode[44]. The cyclic voltammogramms of different vapor TNT concentration using gold microelectrode were studied. The voltammetric sensors is

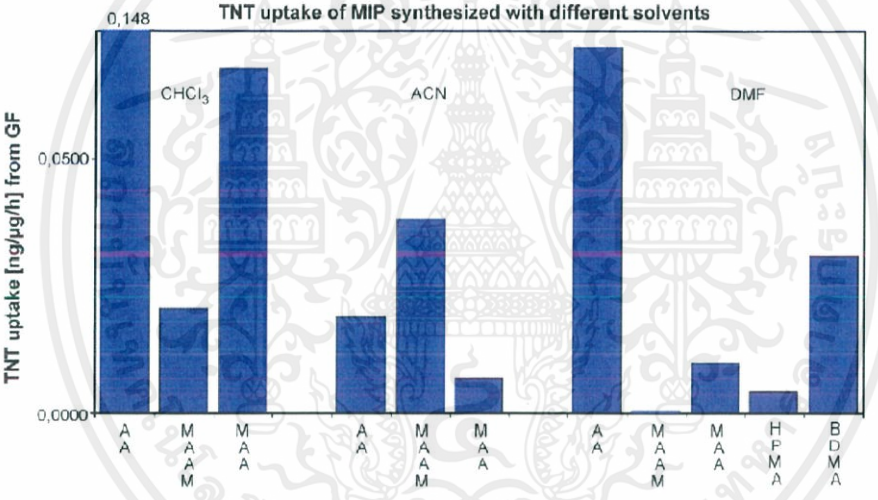


**Figure 2.11** Comparison of TNT uptake of different imprinted polymer types synthesis with different solvents[47]

conditional to the electron transfers reaction (reduction) of the nitro group in TNT and the reduction current is measured. Due to TNT is the nitroaromatic group which classified as an easily-reductive group (excellent electron accepter). Working electrode for detect nitro-explosive can be carbon or gold. The intentional modification of electrode can develop the enhanced detection. Carbon structure also commonly used in field of sensor especially the well-known carbon nanotube(CNT). Modified electrode based on CNT coating is very useful to increase the sensitivity due to its good electric conductivity and good absorptivity. In addition, there are many works that use graphene for detecting explosives due to its unique characteristics, such as electrical conductivity, large surface-area-to-volume ratio and very good in absorptivity. The atom in graphene is contact to

the environment, lead to the highly sensitive to electrical and chemical perturbation. Another usually used is graphene oxide (GO). Robinsin *et al.*[46] fabricated sensor using reduced graphene oxide (RGO) as a sensing materials and could detect explosive at the levels of parts-per-billion (ppb). Furthermore Huang *et al.*[47] also used sulfonate/RGO

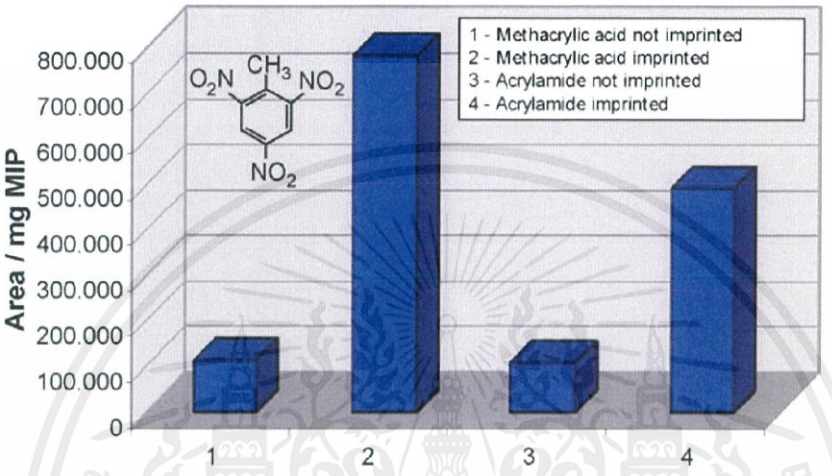


**Figure 2.12** TNT response of imprinted and non-imprinted MIP synthesized with MAA and AA as measured by SPME-GC-MSD peak areas per mg MIP[47]

doped silver nanoparticles (Ag NPs) printed on the polyimide which can promote the higher sensitivity and ability to response at room temperature.

Guoyue Shi *et al.*[35] reported the electrochemical detection for nitroaromatic explosive by mesoporous-silica/diallyl-dimethyl ammonium chloride (MSU/PPDA) layer by-layer modified electrode. In figure 2.10 shown the comparison electrochemical response of trinitrobenzebe (TNB) for 1.0 μM and 14 nM using bare electrode and (MSU/PPDA) layer-by-layer modified electrode. Both bare and modified electrode represented single voltammetry peak. It seems that modified electrode displays higher response than the bare electrode for both concentrations even though at 14 nM hardly to distinguish these both concentrations of TNB.

In 2007 fraunhofer Institute in Germany reported[48] the technique to detect TNT by molecularly imprinted polymers using quart crystal microbalance technology which aim to test the performance of sensor using different polymer binding with explosive. The performance tested of the resulting TNT imprinted and non-imprinted were carried via commercial gaslab21 with fundamental frequency 100 MHz. When the mass is increase the frequency will decrease. This research encountered the traditional polymerization can break the cavity sites, to avoid this problem this study prepares by suspension polymerization. For TNT possible to approach with non-covalent binding. Work of Baitinger *et al.*[36] shown the fact that nitroaromatic components are weak hydrogen bond accepter. This work synthesized MIP using different functional group of acrylates to find

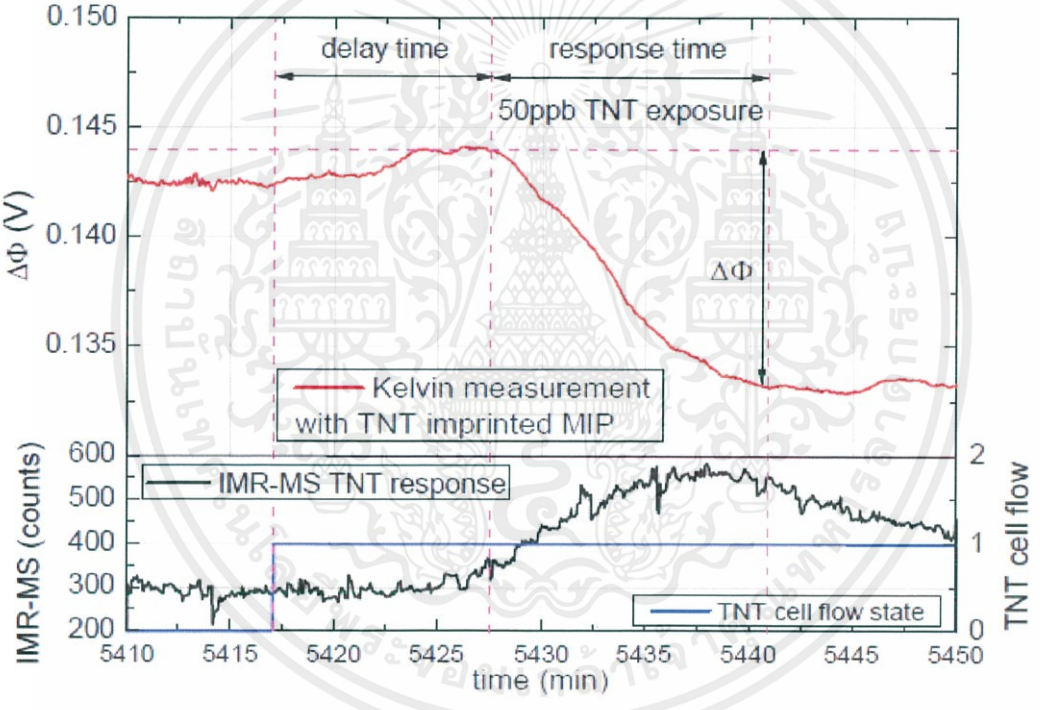


**Figure 2.13** Kelvin Probe measurement: transient response of a TNT-MIP sample exposure to 50 ppb TNT vapor. [37]

the best interaction. In figure 2.11 presented TNT-imprinted polymers methacrylic acid and the acrylamide monomer that have a good response to TNT. If compare to the non-imprinted polymers, the imprinted MIPs show a higher tendency to adsorb or detect TNT. In figure 2.12 shown comparison of various polymers used with different solvents resulting in different responds performance.

In 2012 Fraunhofer Institute, Pohle *et al.*[49] published their research about work function read-out molecularly imprinted polymer explosive detector with Siemens AG Corporate Company. This research use kelvin probe measurement performed in nitrogen gas flow, using hybrid suspended gate field effect devices (HSGFET) as a sensor for MIP based on methacrylamide (MAAM) as monomer which prepared on the gold electrode. The concentrations of TNT have analyzed by gas sampling on TENAX tube and gas

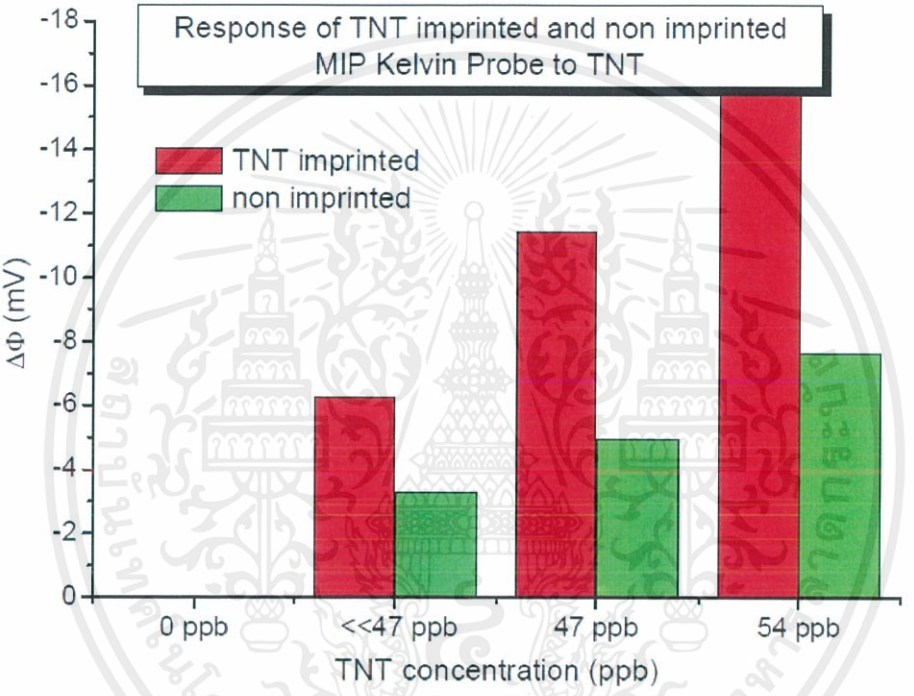


**Figure 2.14** Comparison of the work function response of a non -imprinted and a TNT-MIP sample to TNT vapor [38]

chromatography mass spectroscopy (GC-MS) analysis. Transient concentration of TNT can be monitoring via Ion molecule reaction mass spectrometry. In figure 2.13 shown the transient of TNT flowed during exposure to approx. 50 ppb. The delay time is related to the flow of TNT from TNT cell to detected position, kelvin probe, then the clear response is observing when TNT vapor reach the kelvin probe region. This work reported that work function of TNT represented the stronger response and concentration dependent response compare to non-imprinted (figure 2.14). This technique not only has good sensitivity but also great selectivity to TNT while the other high concentrations familiar gas flew the response of the sensor still toward to TNT. This demonstrate that this techniques outstanding selectivity to TNT.

In 2016, Andreu *et al*[50] report the principle component analysis (PCA) use for electronic tongue (E-tongue) for explosives detection. All explosives solutions used in this

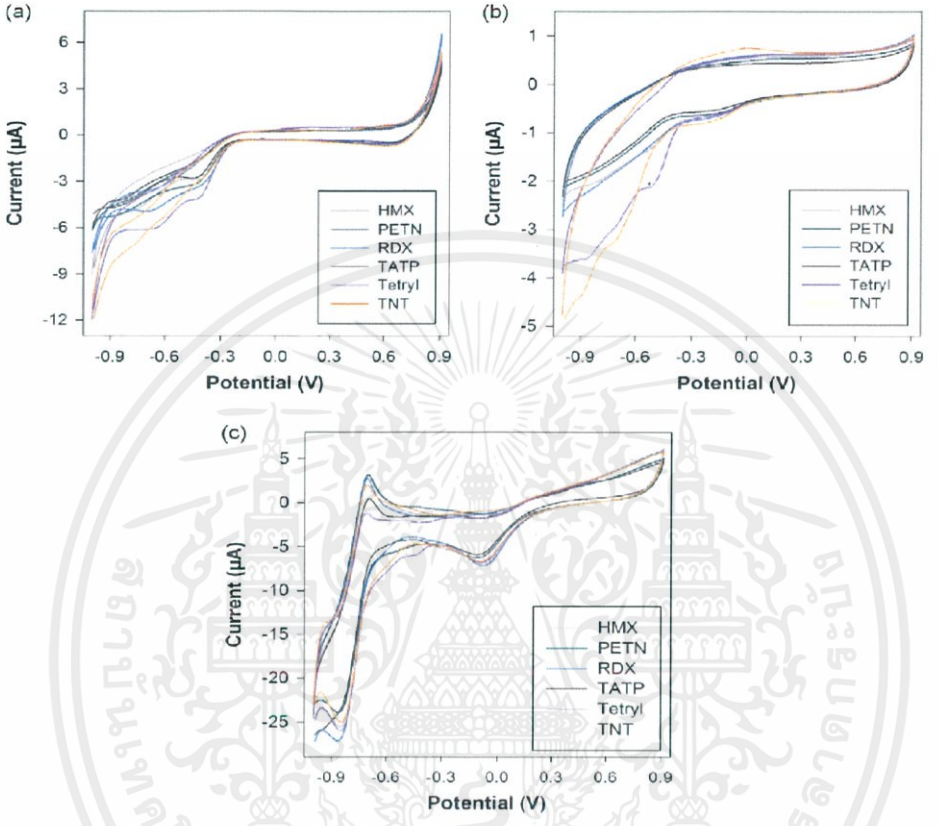


**Figure 2.15** Example of different voltammograms obtained from (a) epoxy graphite electrode, (b) gold electrode and (c) Pt electrode measuring in 100 mg/mL solution [38]

process dissolved in acetonitrile. Samples used in this experiment are 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritoltetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), N-methyl-N,2,4,6-tetranitroaniline (Tetryl) and andtriacetonetriperoxide (TATP). These explosives will be measured and recorded the signal by using three different electrode materials. All the explosives were dissolved in the acetonitrile. The cyclic voltammetry measurement used to characterize those explosives. As seen the cyclic voltammetry results in figure 2.15, complex and highly overlapped signal are obtained for all electrode. As these results give information of signal that obtained from different electrode and ability to distinguish the signal from different solution using PCA in figure.2.16.

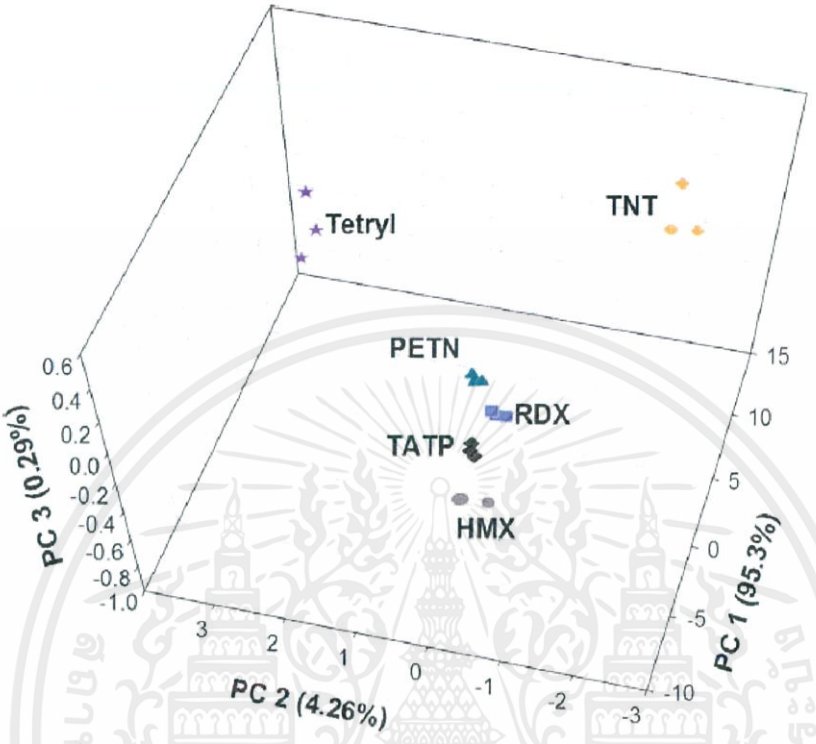


**Figure 2.16** Score plot of the first three components obtained after PCA analysis.

Recentky, Linjuan Guo *et al.*[51] presented that nitro-explosive vapor can detected using ZnO/rGO core shell micro-shottky junction as low as 9 ppm of TNT with anti-interfering properties. Because of very low shottky-junction, it can lead to the huge change in electric signal, when the TNT is absorbed on the surface. It will trap electron from the shottky-junction leading to the change of the barrier. In figure 2.17 shown the high sensitivity, selectivity and repeatable with real time detection of the ZnO/rGO core shell micro-shottky junction. Additionally, this sensor has an anti-interfering ability which tested with other vapor that can be found in normal environment.

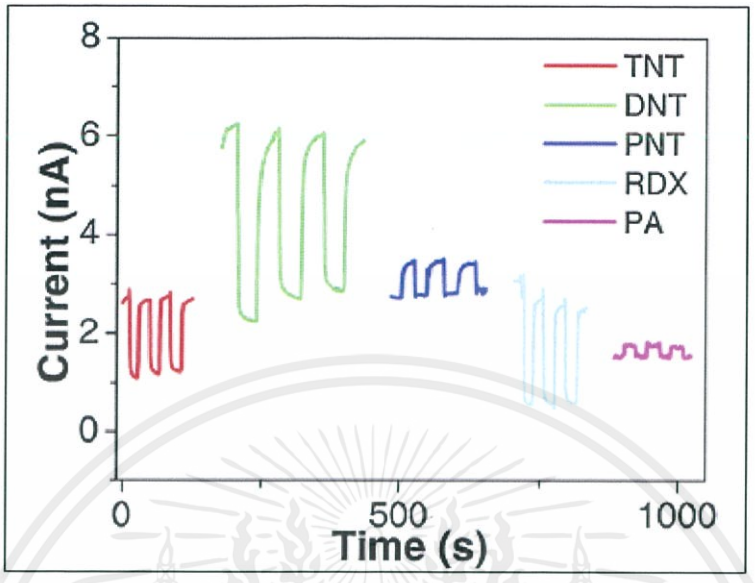


Figure 2.17 Current changes of rGO/ZnO shottky junction[40]

# CHAPTER 3

# MATERIALS AND METHODS

This research aims to study the ability to detect nitro-aromatic explosive which focuses on 3 parameters.

1. The effect of electrolyte used in electrochemical processes which effect on the appearance of reduction peak of nitro group in nitroaromatic explosives.

2. The effect of electrode material which pay a significant role in ability to investigate the electrochemical detection of nitroaromatic compound.

3. The effect of membrane modified on the electrode which could help to absorb the nitroaromatic molecule toward the electrode. This membrane expected to improve the ability of nitroaromatic detection.

The details of experiment will be finely described below in each topic.

## 3.1 Chemicals

3.1.1 Deionized Water (DI water)

3.1.2 Acetonitrile (ACN, $C_2H_4N$) was purchased from Carlo Erba

3.1.3 Potassium ferrocyanide ($K_4Fe(CN)_4$) was purchased from Carlo Erba

3.1.4 Disodium hydrogen phosphate ($Na_2H(CN)_4$) was purchased from Univar

3.1.5 Sodium dihydrogen phosphate ($NaH_2(CN)_4$) was purchased from Univar

3.1.6 Sodium chloride (NaCl) was purchased from Carlo Erba

3.1.7 Ethanol (EtOH, $CH_2OH$) was purchased from Carlo Erba

3.1.8 Potassium Chloride (KCl) was purchased from Carlo Erba

3.1.9. Ethylene Glycol (EG, $(CH_2OH)_2$) was purchased from Sigma Aldrich

3.1.10 Polyacrylic acid (PAA) was purchased from Signa Aldrich

3.1.11 Chitosan

3.1.12 Polymethylmathacrylate (PMMA) was purchased from Signa Aldrich

3.1.13 Carbonnanotube (CNT)

3.1.14 Titanium dioxide nanoparticles ($TiO_2$ NPs)

3.1.15 Piranha solution

## 3.2 Apparatus

3.2.1 Gold Printed Circuit Boards were purchased from Microline curcuit

3.2.2 Gold Electrode was purchased from Metrohm

3.2.3 Glassy Carbon Electrode was purchased from Metrohm

3.2.4 Carbon Printed Circuit Boards were purchased from Dropsense

3.2.5 Ag/AgCl Reference Electrode was purchased from Metrohm

3.2.6 Platinum Counter Electrode was purchased from Metrohm

3.2.7 Potentiostat Galvanostat (PGSTAT 302N)

## 3.3 Experimental

Experiment section 1: The study of various electrolyte effected on nitroaromatic detection

This experiment is the study of effect of electrolyte toward the reduction current of nitro group in TNT. Glassy Carbon was used in this experiment because it is gas-impermeable, highly resistant to chemical attack, electrically conductive, and obtainable in a relatively pure state. Moreover, it inert to strong acids and oxidizing agents. And gold electrode also used in this experiment. Three electrolytes were used in this experiment including 0.5 mM $K_4Fe(CN)_6$ in 0.1 M phosphate, EtOH+EG (1:1) in 0.1 M KCl 30% water and 0.1M NaCl in 0.1M phosphate buffer. All the experimental details will be discussed below:

1. GC electrode preparation:

Clean the electrode using polishing set including aluminium oxide power and polishing cloth. Take a small amount of alumina powder on the cloth provided in the kit, then add 2-3 drops of DI water and clean the electrode gently.

2. Measurement procedure

Firstly, the GC electrode was immersed in 50 mM $K_4Fe(CN)_6$ in phosphate buffer solution and TNT dissolved in ACN for cyclic voltammetric measurement. The CV characteristics was investigated in potential range of –1.0 to -0.2 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s.

Second, the GC electrode was immersed in the 0.1NaCl in 0.1M Phosphate buffer. containing TNT dissolved ACN in various concentration for cyclic voltammetric

measurement. The CV characteristics was investigated in potential range of −0.2 to +1.0 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s

Third, the GC electrode was immersed in the EtOH+EG(1:1) in 0.1 M KCl 30%water containing TNT in various concentration for cyclic voltammetric measurement. The CV characteristics was investigated in potential range of −0.2 to +1.0 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s

Finally, gold electrode was used to examine the effect of electrolyte in the same conditions as GC electrode.

Experiment section 2: The study of effect of printed circuit boards as electrode for nitroaromatic detection

1. Electrode preparation

Gold PCB: Firstly, bare PCBs were cleaned with EtOH followed by DI water in ultrasonic bath for 5 minutes. After that, the PCBs were cleaned by immersed in piranha solution for 2 minutes followed by pretreated in 0.5 mM $K_4Fe(CN)_6$ in phosphate buffer solution using cyclic voltammetry between -1 to +1 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s.

2. Experimental measurement

At first, the electrode was immersed in EtOH+EG(1:1) in 0.1 M KCl 30%water for cyclic voltammetric measurement. The CV characteristics was investigated in potential range of −0.2 to +1.0 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s.

Experimental section 3: Modified the electrode and studied the effect

In this section gold and Carbon PCBs were used as substrate with active area 0.03 and 0.1 $cm^2$ respectively. CNT, PAA and $TiO_2$ were used as modified material. PAA was a good candidate due to it has carboxyl

group (-COOH) which can bind the hydrogen bond with nitroaromatic compound. It was expected that it's would help to absorb more TNT molecule toward electrode and increase occurrence of the electrochemical reduction. $TiO_2$ expected to be an electron conductor which increase the reduction current of cyclic voltammetric measurement and increase the surface area of the active surface on working electrode. CNT expected to increase the electron carrier in system. Furthermore, due to the rich in electron CNT expected to absorb more nitroaromatic molecule toward working electrode. All the experimental details will be described below.

1. PAA modified electrode on gold PCB

1.1 Gold PCB was clean carefully same as in experiment section2 followed by oxygen plasma

1.2 PAA was dissolved in acetic acid 3% in with 10 %w/w of PAA

1.3 PAA solution was drop onto gold working electrode of PCB

1.4 PAA/gold-PCB was exposed by UV crosslinker

2. $TiO_2$ modified electrode on Carbon-PCB

2.1 Carbon-PCB was cleaned using DI water and then wipe the water off carefully

2.2 $TiO_2$ was dispersed in 2.5 %w/w EtOH in ultrasonic bath

2.3 $TiO_2$ was dropped onto the C PCB

3. TiO2 modified electrode on Gold-PCB

3.1 Gold-PCB was clean carefully same as in experiment section2 followed by oxygen plasma

3.2 $TiO_2$ was dispersed in 2.5 %w/w EtOH in ultrasonic bath

3.3 $TiO_2$ was dropped onto the gold-PCB

4. Electrochemical measurement

At first, the electrode was immersed in EtOH+EG(1:1) in 0.1 M KCl 30%water contained TNT for cyclic voltammetric measurement. The CV characteristics was investigated in potential range of –1.0 to -0.2 V (vs. Ag/AgCl) at the scan rate of 0.05 V/s.

# CHAPTER 4

# RESULTS AND DISCUSSIONS

This chapter is regarding to discuss the results of the three experiments which are:

Experiment section1: Studied of the effect of electrolyte of reduction current based on TNT detection

Experiment section2: Using selected electrolyte from experiment section1 and examine the printed circuit board

Experiment section3: Modifying the PCB improving nitroaromatic detection sensitivity

These three experiments were orderly affiliated . First is studied the effect of ion in electrolyte which provided the significantly different reduction current peak. After obtained electrolyte that provided the best reduction peak of nitro group, the electrolyte was then used to the PCB working electrode. After obtained voltammogram gold-PCB exhibited the reduction peak of TNT, then gold PCBs were modified and measured the electrochemical behavior of TNT.

To investigate the electrochemical behavior were achieved by potentiometry and to study the effect of reduction current of TNT appeared in voltammogram. which nitro group in TNT will show the unique reduction potential around -0.5 to -0.6 V.

The chemical formula declararion

1. 2-animo-4,6 dinitrotoluene (2-A-4,6-DNT)
2. 4-animo-2,6 dinitrotoluene (4-A-2,6-DNT)
3. 2,6-diamino-4-nitrotoluene (2,6-DA-4-NT)
4. 2,4-diamino-6-nitrotoluene (2,4-DA-6-NT)
5. 2,4,6-triaminotoluene (2,4,6-TAT)

## 4.1 The study of various electrolyte effected on nitroaromatic detection

Cyclic voltammetry was used to determine the reduction potential of nitro group in nitroaromatic compound. The CV characteristic graphs or cyclic voltammogram of GC electrode with the active area of 0.03 $cm^2$ were used to evaluate the ability to detect nitroaromatic compound, in this study was TNT. The electrolyte which studied in this

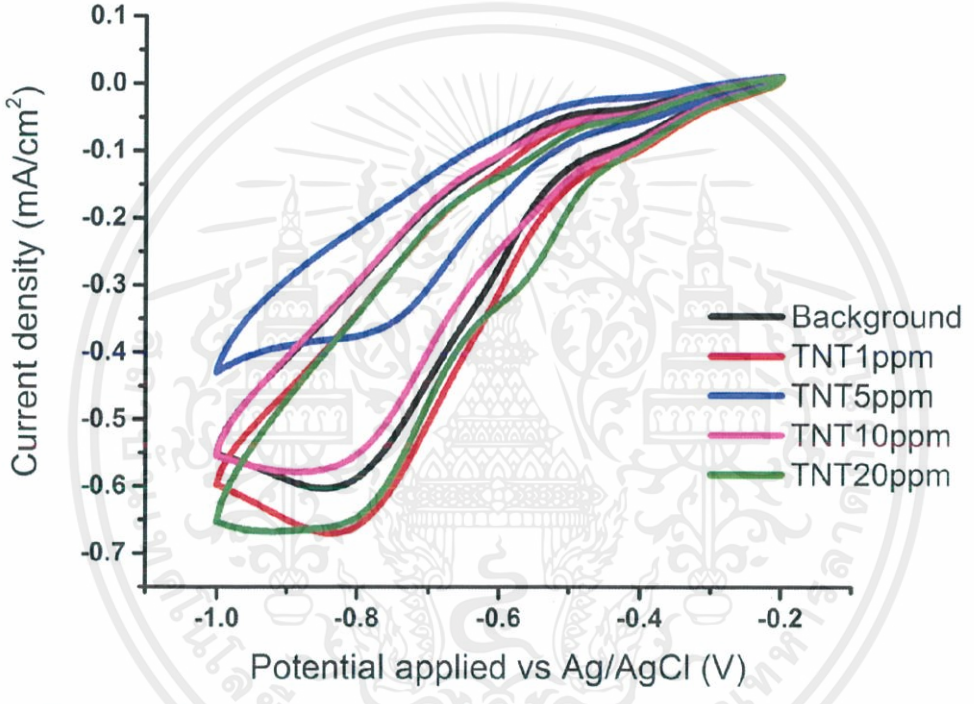


**Figure 4.1** Cyclic voltammogram of GC electrode immersed in $K_4Fe(CN)_6$

research are ($K_4Fe(CN)_6$) in phosphate, NaCl in phosphate and in EtOH+EG(1:1) in 0.1 M KCl 30%water. The GC electrode was immersed in solution during the electrochemical processes. First, ($K_4Fe(CN)_6$) was used and the result was shown in Figure 4.1. In figure4.1 demonstrated the appearance of reduction potential at -0.8 V to all TNT concentration and also the same in background solution, no existing of TNT. However, there is potential peak represented the reduction of $H_2O$ at potential of -0.8 V [52] and unclear peak around -0.5 V. that related to the reduction potential of nitro group in 20ppm of TNT which cannot be detected at 1, 5, 10 ppm. because of low concentration and the ability of GC electrode which is not procure the absorbability. Figure 4.2 shown the cyclic voltammogram of GC electrode that immersed in 0.1 M NaCl and 0.1 M phosphate electrolyte. All TNT

concentrations provided reduction peak at -0.78 V. which mentioned earlier that it was probably the reduction of $H_2O$. However, there is only one concentration of 20ppm of TNT can exhibit the reduction peak of nitro group at reduction potential of -0.5 V. This can be assumed that 1,5,10 ppm of TNT cannot be detected using bare GC electrode due to the low concentration. Figure 4.3 demonstrated the cyclic voltammogram of GC electrode immersed in EtOH+EG(1:1) in 0.1 M KCl 30%water. All TNT concentrations represent the nitro group reduction peak at -0.5 V. Furthermore, EtOH+EG(1:1) in 0.1 M KCl and 30% water electrolyte gave results with an excellent proportional between reduction current and concentration.

In this experiment, we demonstrated the effect of electrolyte used in the processes and implied that EtOH+EG(1:1) in 0.1M KCl 30% water electrolyte provided a very good results. This electrolyte must be adjusted pH to 9 for release $OH^-$ ions in the solution which these ions were expected to increase a carrier in the solution. The reduction peak of nitro group in TNT are reference from the research of C. Chua *et al.*[53] which the nitro

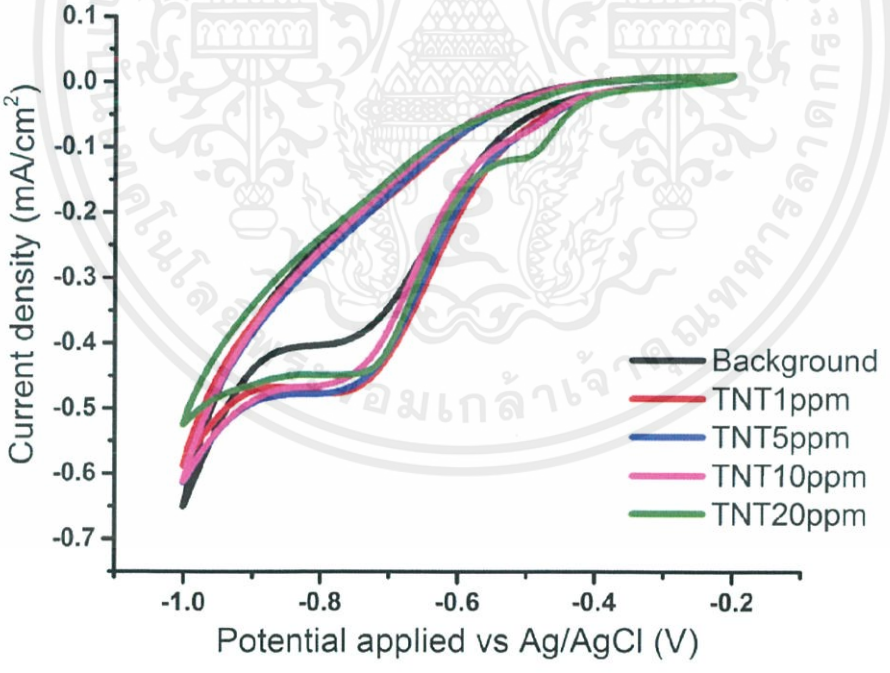


**Figure 4.2** Cyclic voltammogram of GC electrode immersed in NaCl in phosphate

group can be reduced in to amino group ($-NH_2$) at potential -0.45 to -0.55 V.

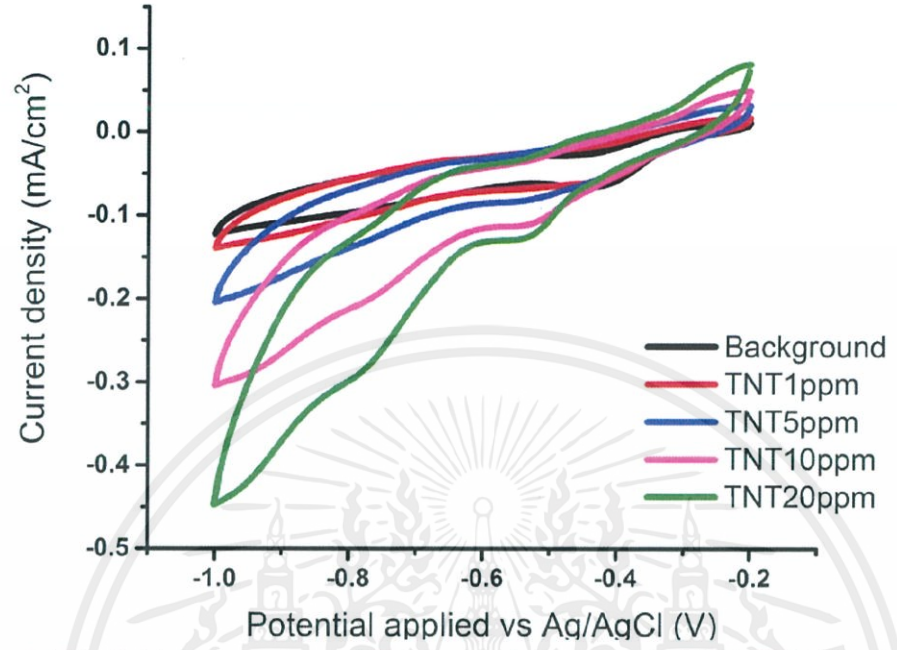


Figure 4.3 Cyclic Voltammogram of GC electrode immerse in EtOH+EG(1:1) in 0.1 M KCl 30%water

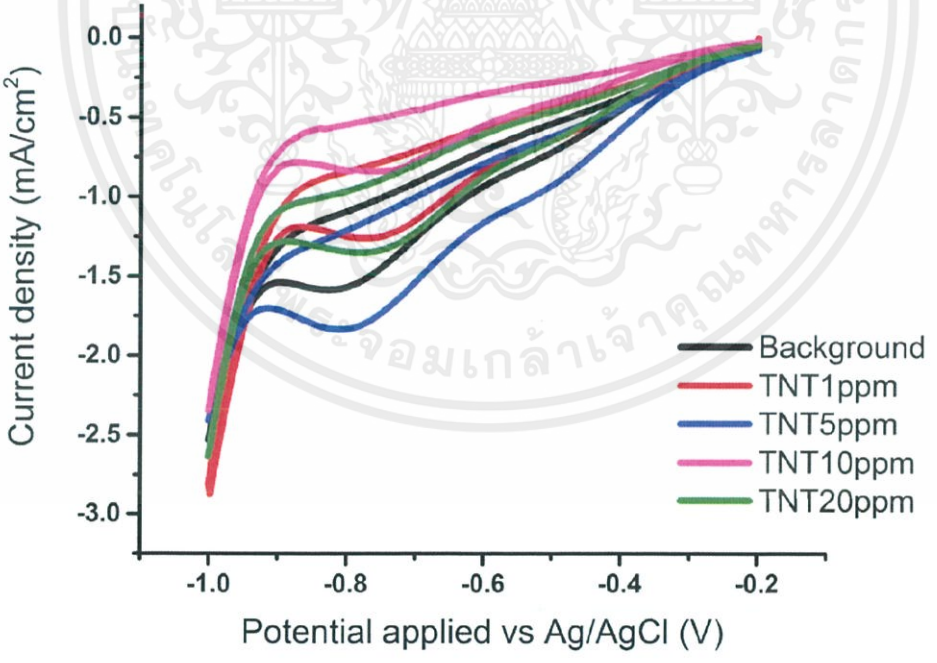


**figure 4.4** Cyclic voltammogram of gold electrode immersed in $K_4Fe(CN)_6$

However, the $K_4Fe(CN)_6$ is not suitable to use in this work because the reduction potential

of $Fe^{3+}$ to $Fe^{2+}$ is not in the measurement range.

Gold electrode also use to examine TNT detection using the same three electrolytes as GC electrode. In figure 4.4 demonstrated the CV graph of TNT detection obtained from gold electrode immersed in $K_4Fe(CN)_6$ represented the current peak around -0.7 to -0.8 V

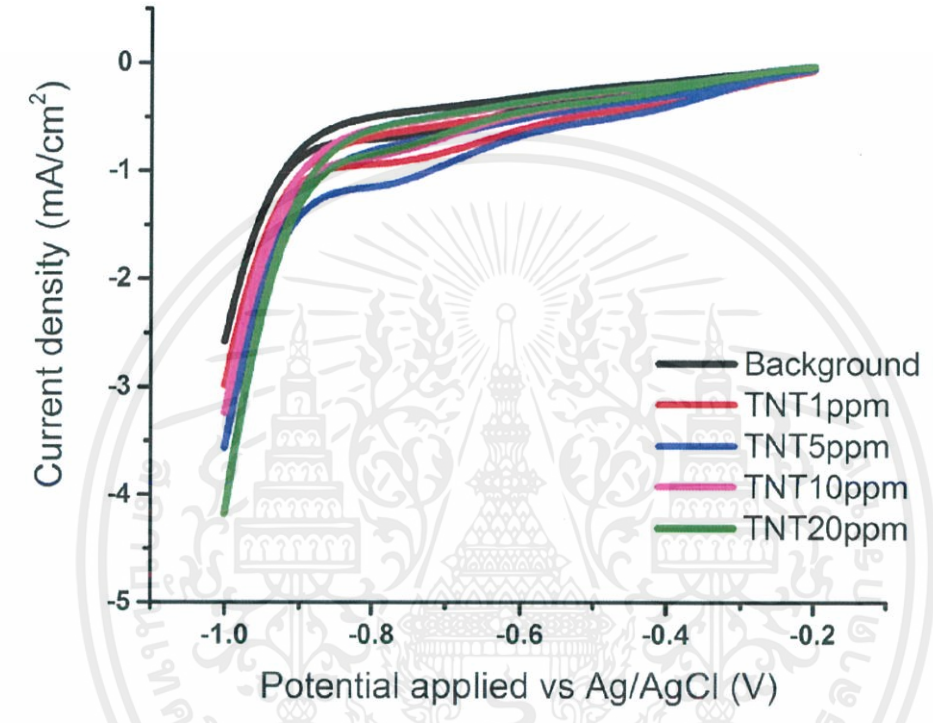


**Figure 4.5** Cyclic voltametry of gold electrode in NaCl in phosphate

which is the reduction potential of water. There is no reduction peak of nitro group in any concentration of TNT. Figure 4.5 exhibit the CV graph of gold electrode immersed in NaCl in phosphate represented no peak neither $H_2O$ nor nitro group. Figure 4.6 presented the CV graph of gold electrode immersed in EtOH+EG(1:1) in 0.1 M KCl 30%water indicated the reduction peak of nitro group around -0.5 V. In this experiment GC and gold electrode exhibited the reduction behavior of Nitro group in EtOH+EG(1:1) in 0.1M KCl 30%water and GC electrode provided the better CV graph compared to gold electrode.

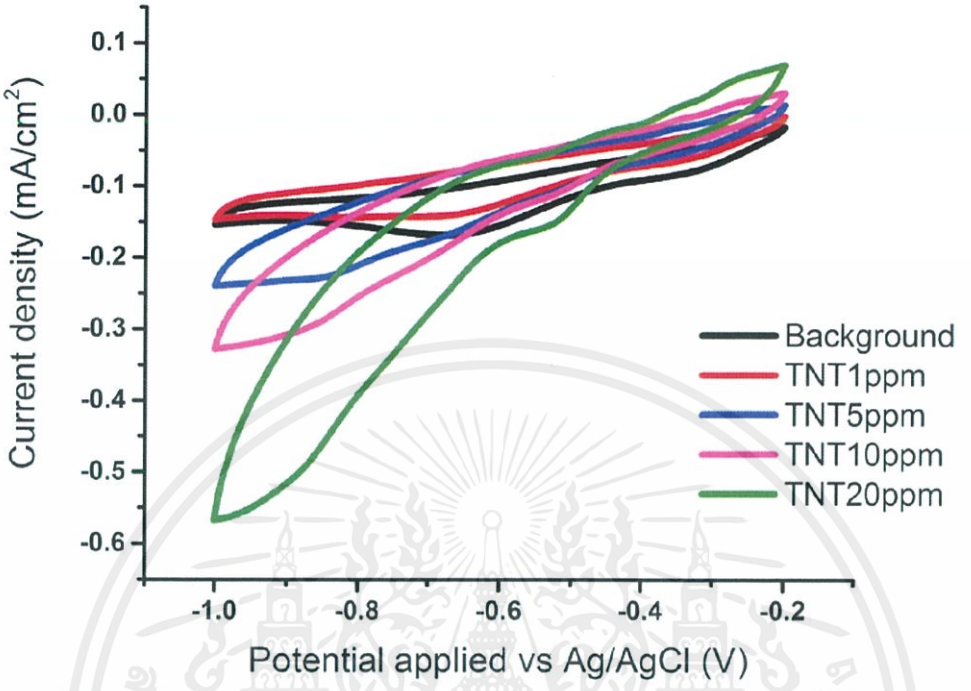


**Figure 4.6** Cyclic Voltammogram of gold electrode immersed in EtOH+EG(1:1) in 0.1 M KCl 30%water

## 4.2 The study of effect of printed circuit boards as electrode for nitroaromatic detection

Previous study presents the effect of electrolyte, the results shown the gold and GC electrode provided the best electrolyte for detecting TNT which was EtOH+EG(1:1) in 0.1 M KCl 30%water electrolyte. However, the drawback of gold and GC electrode is not suitable to modified because of an expensive cost. Therefore, the experiment examined the ability to detect explosive using unmodified gold and Carbon PCB which cheaper, easy to modified and portable. Figure 4.7 demonstrated the cyclic voltammogram of unmodified carbon-PCB in EtOH+EG(1:1) in 0.1M KCl 30%water electrolyte. The unmodified carbon-PCB exhibited the completely no reduction peak at all. This electrode was expected to have specific reduction peak after modification. Figure 4.8 represented the cyclic voltammogram of unmodified gold-PCB in EtOH+EG(1:1) in 0.1M KCl 30%water electrolyte. The unmodified gold PCB exhibit the reduction peak of nitro group in TNT at -0.5 to -0.55 V. All the TNT concentration are provided the similar signal with different

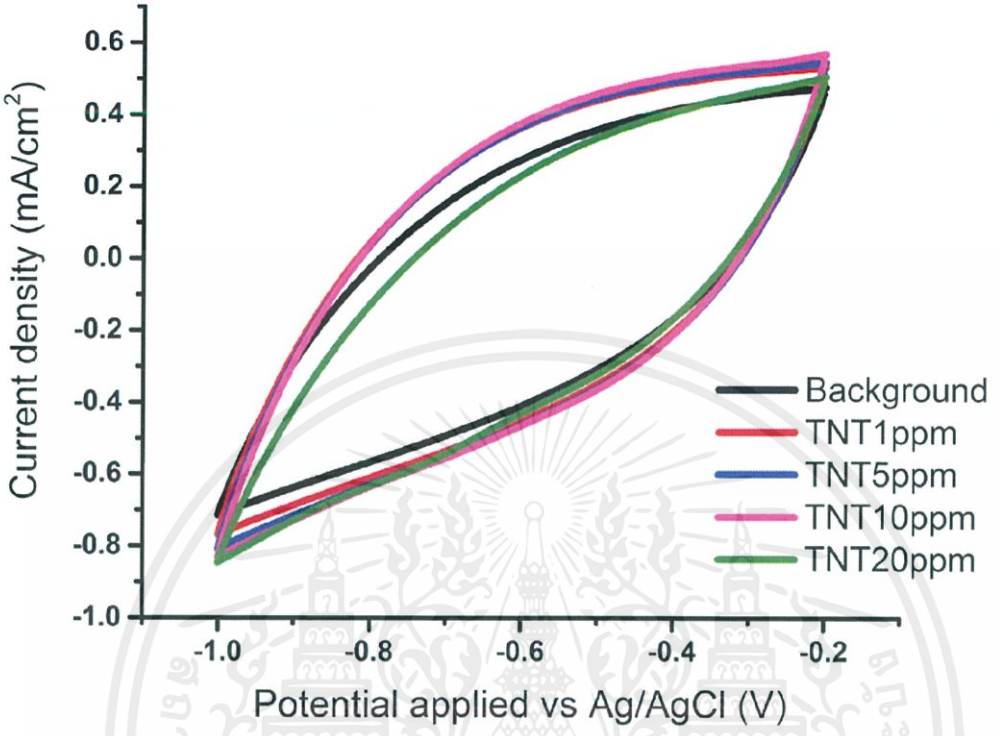


Figure 4.7 Cyclic voltammogram of carbon PCB immersed in EtOH+EG(1:1) in 0.1M KCl 30%water

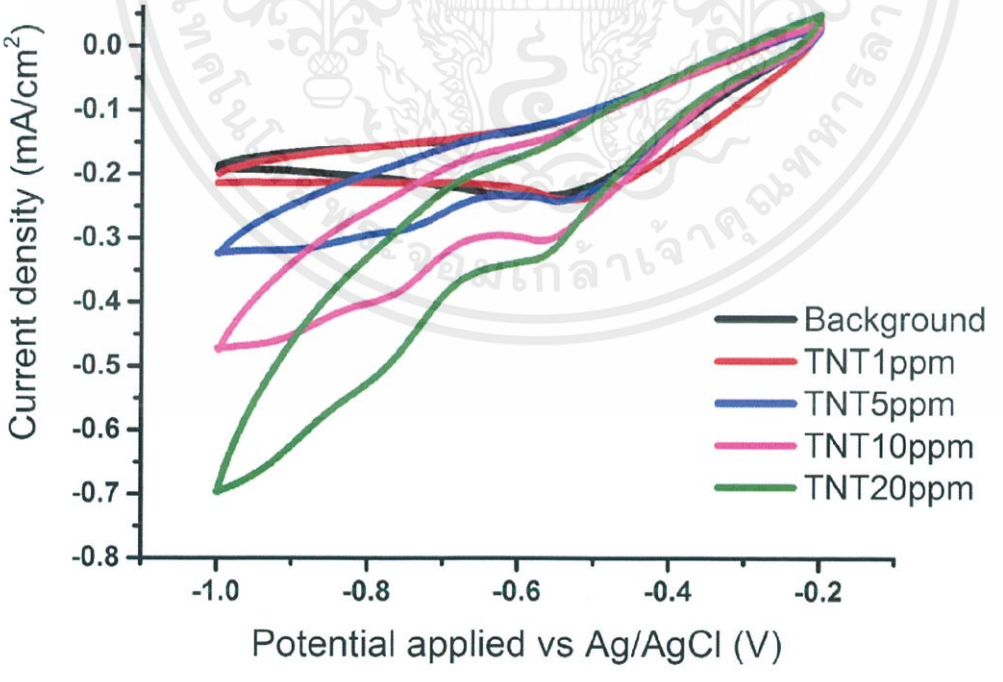


Figure 4.8 Cyclic voltammogram of gold PCB in EtOH+EG(1:1) in 0.1M KCl 30%water

intensity which significantly increased. These two PCB electrodes were expected to provide increased reduction current of nitro group in TNT when modified.

## 4.3 Modified the electrode and studied the effect

According to the effect of electrode toward TNT detection described earlier, the gold-PCB was promoted as good candidate for electrode modification. The gold-PCB were modified by PAA, CNT and nano$TiO_2$ particles. Carbon-PCBs were modified by nano$TiO_2$ particles. Figure 4.9 demonstrated the cyclic voltammogram of PAA modified gold-PCB that provided a very good electrochemical signal. It was clearly distinguishing the environment containing TNT from the environment with no TNT contained, because the $COOH^-$ in PAA can interacts through hydrogen bonding with $NO_2$ group in nitroaromatic. These hydrogen bonding expected to absorbed more TNT molecule toward working

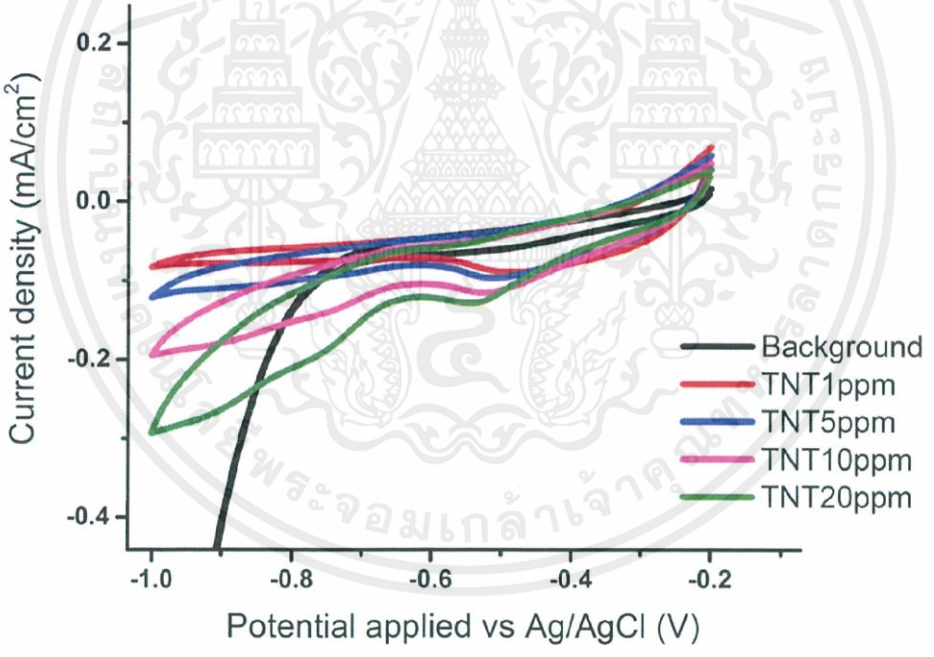


**Figure 4.9** Cyclic voltammogram represented current response of PAA modified gold-PCB electrode

electrode. Nano$TiO_2$ particles modified on carbon-PCB capable of distinguishing the different of the environment with and without TNT molecule as shown in figure 4.10 which the signal exhibited the reduction peak at -0.58 V in the solution containing TNT molecule. Nano$TiO_2$ particles predicted to increase the surface area of the active area of working electrode. Besides $TiO_2$ nanoparticles trend to absorb TNT molecule after negative

polarized $TiO_2$ nanoparticles with large band gap Fermi level increased resulting in increased electron concentration. High electron concentration attracted TNT molecule move toward working electrode. Figure 4.11 shown the CV graph of CNT modified gold-

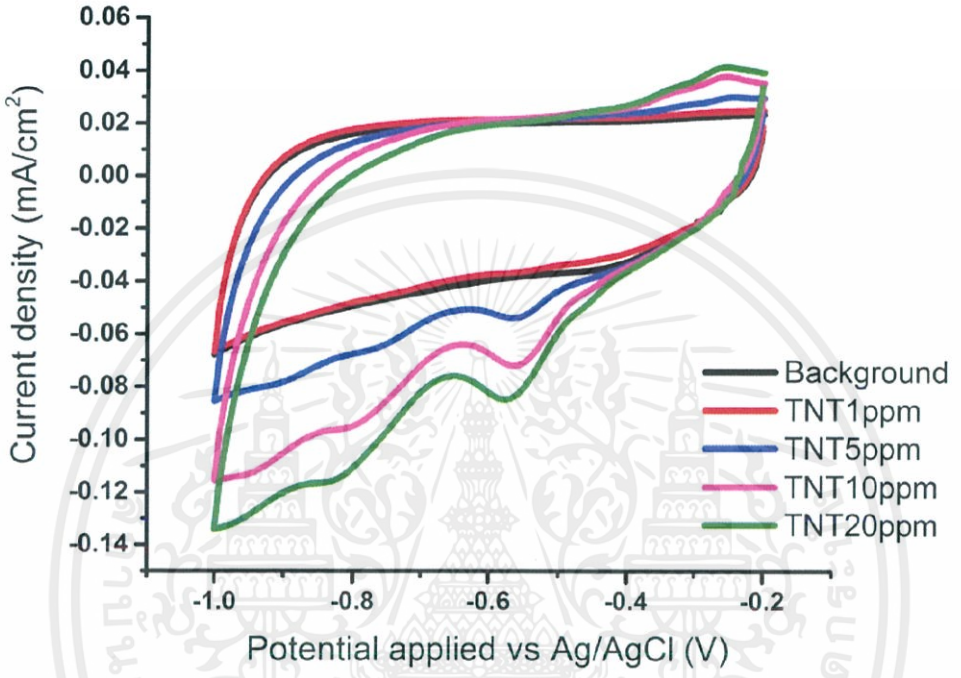


**Figure 4.10** Cyclic voltammogram represented current response of $TiO_2$ modified C-PCB electrode

PCB electrode which represented the reduction peak of nitro group in TNT molecule. CNT is known as good electrical conductivity and especially CNT provided the redox active sites which mean it can absorb more TNT molecule compare to other materials and gave high current reduction peak of nitro group. Figure 4.12 $TiO_2$ modified gold-PCB electrode represented the reduction peak at -0.58 V which is the reduction potential of nitro group in TNT. There is another reduction peak at -0.43 V which predicted as intermediate compound, which are 2-A-4,6-DNT, 4-4-A-2,6-DNT, 2,6-DA-4-NT and 2,4-DA-6-NT, occurred when TNT reacted with electrolyte. The intermediate compounds are also form the reactant which is the nitroaromatic thus intermediated compounds were not classified as interfering substances.

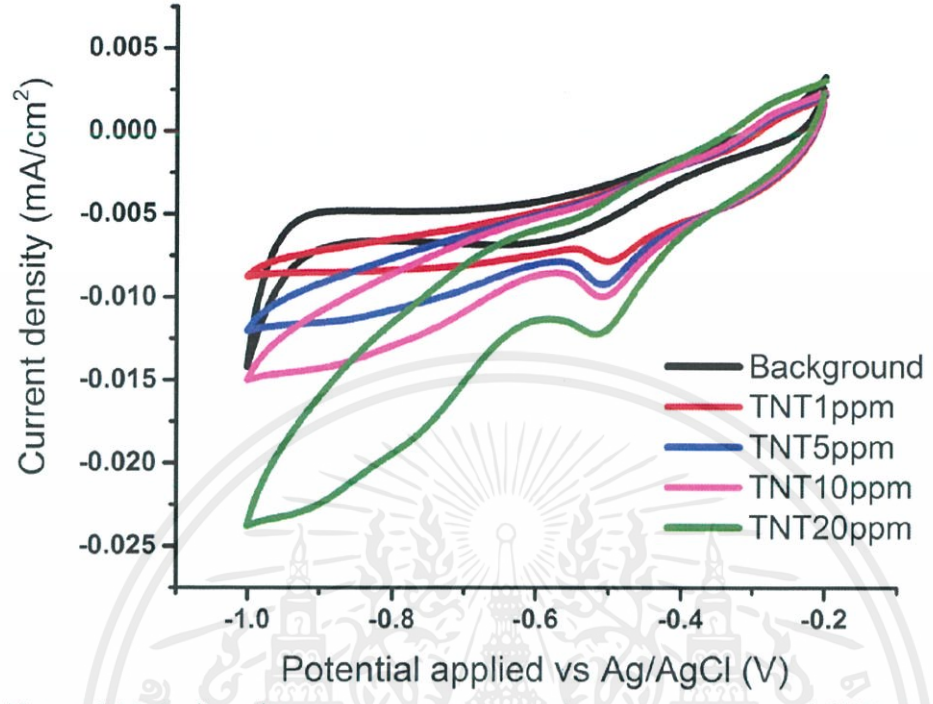


Figure 4.12 Cyclic voltammogram represented current response of CNT modified gold-PCB electrode

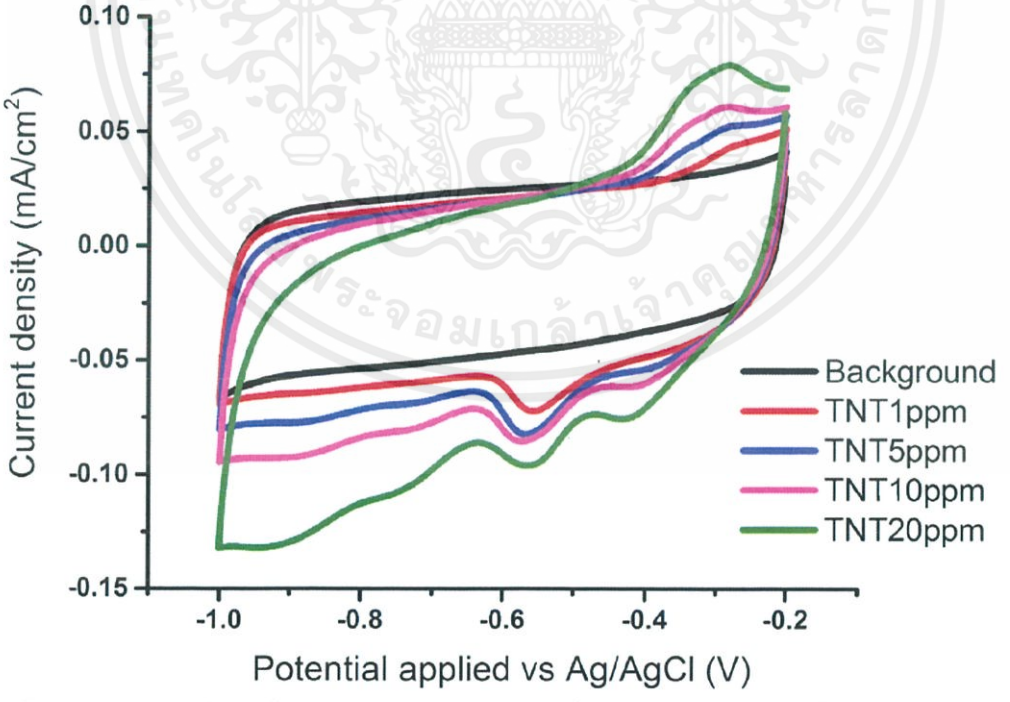


Figure 4.11 Cyclic voltammogram represented current response of $TiO_2$ modified gold-PCB electrode

# CHAPTER 5

# CONCLUSIONS

In this research, a mechanism of nitroaromatic detection via electrochemistry measurement was studied. The electrochemical technique was a good candidate for TNT detection due to the three nitro groups that attached to toluene were reduced when applied potential at -0.45 to -0.55 V by using three electrodes, Ag/AgCl as reference electrode, Pt as Counter electrode and modified working electrode. Gold and GC was used as working electrode to studied the effect of selective material in both of electrode commercial and printed circuit boards electrode. The modified membranes on working electrode was then studied to improve the detection ability. Each experiment will be summarized below:

- The effect of electrolyte toward the TNT detection of glassy carbon electrode was investigated. The EtOH+EG (1:1) in 0.1M KCl 30% water electrolyte exhibited the best electrochemical signal for GC electrode. Reduction activity of nitro group in 20 ppm TNT of can be detected at potential -0.5 V.
- The EtOH+EG(1:1) in 0.1M KCl 30% water was used in electrode material tested. Gold and GC electrode tips can present the reduction peak of TNT at 20 ppm. While gold and carbon printed screen board can be exhibited reduction peak in lower concentration. This experiment confirmed the ability to distinguish TNT in solution. Thus, gold and carbon printed screen board was more suitable to modified.
- Gold and carbon PCB was modified by PAA and nano$TiO_2$ particles. PAA on gold PCB provided the cyclic voltammogram with much more obvious reduction peak at -0.5 V. Carboxylic or carboxylate moiety ($COO^-$) of PAA can bound a hydrogen bonding with $-NO_2$ moiety in nitroaromatic compound, thus TNT molecule can move toward electrode and generated $NO_2$ reduction which increased reduction current in electrochemical detection. Nano$TiO_2$ particles on Carbon-PCB represented much better the cyclic voltammetric graph compare to the unmodified one at potential of -0.6 V.

Therefore, these modified working electrodes on gold or Carbon-PCBs can be applied to use as portable electrochemical detection because PCBs were smaller and cheaper.

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