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Development of nickel oxide electrode for application in dopamine detection

Miss Chanita Wattanasomboon



A Thesis Submitted in Partial Fulfillment of the Requirements
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Department of Chemical Engineering

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งานวิจัยนี้ศึกษาการสังเคราะห์นิกเกิลออกไซด์ สำหรับใช้เป็นตัวเร่งปฏิกิริยาในการตรวจวัดสารโดพามีนด้วยระบบไฟฟ้าเคมีด้วยวิธีไซคลิกโวลแทมเมตรี โดยการนำไปปรับปรุงขั้วไฟฟ้าทำงาน ซึ่งระบบการทดสอบใช้ขั้วไฟฟ้าเงิน/เงินคลอไรด์เป็นขั้วไฟฟ้าอ้างอิงและแพลททินัมเป็นขั้วไฟฟ้าสนับสนุน การสังเคราะห์นิกเกิลออกไซด์ด้วยวิธีการตกตะกอนนำมาเปรียบเทียบกับระหว่างการใช้โซเดียมไฮดรอกไซด์(NaOH) และ ยูเรีย($\text{CH}_4\text{N}_2\text{O}$) เป็นตัวที่ทำให้ตกตะกอน และนิกเกิลออกไซด์ที่เติมสารลดแรงตึงผิวเพื่อควบคุมรูปร่าง พบว่าทั้งสองวิธีสามารถปรับปรุงค่าการตอบสนองทางไฟฟ้าเคมีเมื่อเปรียบเทียบกับขั้วไฟฟ้านิกเกิลออกไซด์ที่ไม่ได้ถูกปรับปรุง การศึกษาปริมาณของนิกเกิลออกไซด์ที่นำมาปรับปรุงลงบนขั้วไฟฟ้าต่อค่าการสนองทางไฟฟ้าพบว่าปริมาณที่เหมาะสมคือ 0.078 มิลลิกรัม การปรับปรุงคุณสมบัติของนิกเกิลออกไซด์ด้วยการประยุกต์ใช้สารลดแรงตึงผิว และการทำไฮโดรเทอร์มอล ทรีตเมนต์ในการสังเคราะห์นิกเกิลออกไซด์เพื่อนำมาปรับปรุงขั้วไฟฟ้า พบว่าสภาวะที่ให้ค่ากระแสที่ดีที่สุดของการสังเคราะห์นิกเกิลออกไซด์ด้วยการใช้ยูเรียเป็นตัวตกตะกอนคือ การใช้สารลดแรงตึงผิวทั้งสองชนิดผสมกันมีค่าความเข้มข้นของโซเดียม โดเดซิล ซัลเฟต(SDS) และปิวตะนิล-1-4-บิฟไทมิลโดเดซิลแลมโมเนียม โบรไมด์($\text{C}_{12}\text{-C}_4\text{-C}_{12}, 2\text{Br}$)เท่ากับ 0.04 และ 8.2 มิลลิโมลาร์ ตามลำดับ โดยใช้อุณหภูมิในการทำไฮโดรเทอร์มอล ทรีตเมนต์ที่ 120 องศาเซลเซียส การตรวจวัดโดพามีนวัดได้จากอิเล็กตรอนที่เกิดจากการออกซิเดชันของโดพามีนที่ศักย์ไฟฟ้า 0.3 โวลต์ ซึ่งเกิดจากการเร่งปฏิกิริยาของนิกเกิลออกไซด์ ความเข้มข้นของโดพามีนเป็นสัดส่วนโดยตรงกับค่ากระแสที่วัดได้ในสภาวะ 10 มิลลิโมลาร์ของสารละลายฟอสเฟสบัฟเฟอร์ พีเอช 7.0 การปรับปรุงนิกเกิลออกไซด์ขั้วไฟฟ้ามีช่วงความเป็นเส้นตรงในการตรวจวัดโดพามีน 2 ช่วง คือ 3.125 – 100 และ 100 – 500 ไมโครโมลาร์ ซึ่งความไวต่อโดพามีนเท่ากับ 0.0498 และ 0.01 ไมโครแอมแปร์ต่อไมโครโมลาร์ ตามลำดับ และมีระดับการตรวจพบที่ต่ำที่สุดที่ความเข้มข้นของโดพามีนเท่ากับ 1.75 ไมโครโมลาร์

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CHANITA WATTANASOMBOON: Development of nickel oxide electrode for application in dopamine detection. ADVISOR: PROF. SUTTICHAH ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: SUWIMOL WONGSAKULPHASATCH, Ph.D., 81 pp.

This research studied the synthesis of nickel oxide as a catalyst for dopamine detection to modified working electrode by electrochemical with cyclic voltammetry. In the system, the potentiostat connect electrode with silver/silver chloride reference electrode and platinum counter electrode. In this study, the synthesis of nickel oxide by precipitation method was compared between using sodium hydroxide (NaOH) and urea ($\text{CH}_4\text{N}_2\text{O}$) as a precipitating agent and with/without surfactant adding. It was found that nickel oxide from both precipitating agents showed an improvement of the current response when compared with unmodified nickel oxide electrode. The study of nickel oxide loading on the electrode showed the highest current response at 0.078 mg of nickel oxide loading. The modification of nickel oxide by addition of surfactant and hydrothermal treatment that found the highest current response obtain from nickel oxide modified electrode that synthesized from precipitation with urea by addition of mixed surfactant of butanediyl-1, 4-bis(dimethyldodecylammonium bromide)(C12-C4-C12,2Br⁻) 0.04 mM and Sodium dodecyl sulphate(SDS) 8.2 mM and hydrothermal at 120 °C. Determination of dopamine by oxidation of dopamine was improved electrochemical response by nickel oxide modified electrode at 0.3 V of apply voltage. The detection of dopamine was operated in 10 mM phosphate buffer solution, pH 7.0 show two linear range that are 3.125 – 100 and 100 – 500 μM with sensitivity 0.0498 and 0.01 $\mu\text{A}/\mu\text{M}$, respectively. The limit of detection was 1.75 μM .

Department: Chemical Engineering Student's Signature

Field of Study: Chemical Engineering Advisor's Signature

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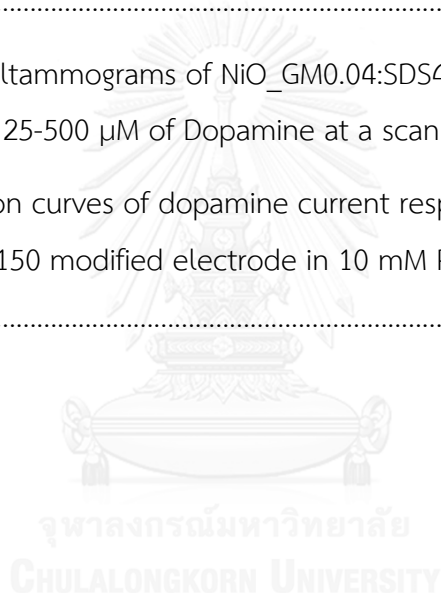
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CHAPTER I

INTRODUCTION

1.1 Rationale

Dopamine (3, 4-dihydroxyphenyl ethylamine) is one of the most important neurotransmitter that is produced in the adrenal glands and several areas of the brain. Low level of dopamine or abnormal of dopamine concentration could lead to many neurological diseases such as Parkinson's disease, attention deficit hyperactivity disorder (ADHD), restless legs syndrome (RLS) Schizophrenia [1]. As a consequence, detection of dopamine especially in micro molar level of concentration would be of importance for diagnosis or other applications related pharmaceutical or medicine. Dopamine can be detected by many analytical techniques such as chromatographic method, spectrophotometry, mass spectroscopy, etc. However, these methods have some disadvantages, including long analysis time, high cost and require a lot of sample[2]. Biosensor is another technique that has been drawn much attention in dopamine detection because when compare to conventional methods. The advantages of biosensor are that analyte can be directly detected without sample pretreatment, fast analysis and low cost.

Biosensor with electrochemical method is an interesting method used to detect dopamine as dopamine is strong electrochemical activity and in the incunabulum stage, enzyme based biosensor has been used for dopamine detection due to highly sensitive. However, disadvantages of this technique are low stability over long time operation and temperature [3]. Another problem of dopamine detection is an interference from ascorbic acid (AA) and uric acid (UA) due to close oxidation potential to dopamine in electrochemical method effect to overlapping of voltammetry response [4], which results in poor selectivity and sensitivity of dopamine detection. In the conventional electrochemical sensor method, direct determination of dopamine is rare and poor dopamine response. Thus, the chemical modification of electrode surfaces has been developed to enhance the sensitivity of sensors. In order to improve sensor's activity of dopamine detection, electrode can be improved by various

materials such as metal oxide nanoparticle, carbon based material, nanocomposite material, etc.

Among various materials, metal oxide is used as modifying agent because it possesses long term stability, high surface reaction activity[4]. Nickel oxide (NiO) is an attractive material due to its good electrocatalytic property in term of electron transfer between Ni^{2+} and Ni^{3+} , good oxygen ion conductivity, biocompatibility, nontoxic, high chemical stability, high surface area and high structure stability [5].

To improve sensitivity of biosensor, nickel oxide has been selected to use as electron transfer because nickel oxide was found high in absorption, electron transfer, isoelectric point, IEP 10.7 [6]. In addition, nickel redox show high catalytic activity toward the oxidation of some organic compounds with a lower cost when compared to others (especially, nobel metal) [7].

In this work, we aim to improve sensitivity of biosensor by investigating the effect of morphologies of nickel oxide on dopamine detection. Study the effect of nickel oxide loading on electrode. Synthesis method, the addition of surfactants, temperature, are subjects of investigation.

1.2 Objective

To develop nickel oxide modified electrode for dopamine detection.

1.3 Scope of work

Study the effect of precipitating agent in precipitation synthesis by using two precipitating agent: sodium hydroxide and urea

- Use different ratios between Gemini surfactant (butanediyl-1, 4-bis (dimethyldodecylammonium bromide), (C12-C4-C12,2Br)) and anionic surfactant (Sodium dodecyl sulphate, SDS)
- Use different hydrothermal temperatures

Study the performance of dopamine detection in electrochemical analysis

- Study the effect of nickel oxide loading on electrode
- Study the performance of nickel oxide as sensor in dopamine detection

CHAPTER II

THEORY

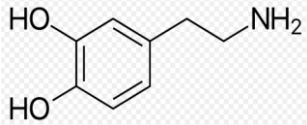
In this chapter information relating dopamine detection via electrochemical analysis, including dopamine, nickel oxide and dopamine o-quinone as well as analytical methods relating to this research (biosensor and electrochemical) are provided.

2.1 Properties of chemical compounds studied in this research

2.1.1 Dopamine

Dopamine or 3,4-dihydroxyphenethylamine is a neurotransmitter in the group of catecholamine that widely distributed in the central of neural system and used as chemical messenger. Dopamine is important to human and animal because it can affect the cardiovascular and renal system. Dopamine can be synthesized by changing organic group of L-DOPA (L-3,4-dihydroxyphenylalanine) to amino group in the brain and kidneys. Dopamine can also be synthesized in some plants and animals (<https://th.wikipedia.org>). Some properties of dopamine are summarized in Table 2.1.

Table 2.1: Structure and properties of dopamine

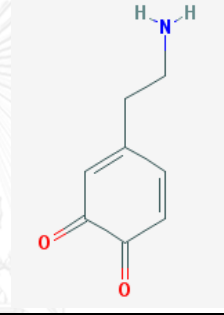
Molecular formula	$C_8H_{11}NO_2$
Structure	
Molecular weight	153.178 g/mol
Melting point	128 °C
Boiling point	227 °C at 23 mmHg.
Solubility in water	60.0 g / 100 ml water
Solubility	In water, methanol and hot ethanol

(<https://pubchem.ncbi.nlm.nih.gov>)

2.1.2 Dopamine o-quinone

Dopamine o-quinone (dopamine quinone) or 4-(2-aminoethyl) cyclohexa-3,5-diene-1,2-dione is produced by oxidation of dopamine. Dopamine o-quinone and free radicals that produced by autoxidation of dopamine can poison cells, this mechanism may lead to cell lose that occur in Parkinson's disease. (<https://en.wikipedia.org/wiki/>) Some properties of dopamine o-quinone are summarized in Table 2.2.

Table 2.2: Structure and properties of dopamine o-quinone

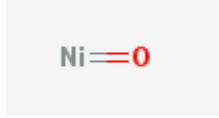
Molecular formula	$C_8H_9NO_2$
Structure	
Molecular weight	151.162 g/mol

(<https://pubchem.ncbi.nlm.nih.gov/>)

2.1.3 Nickel oxide

NiO is a chemical compound that in the mineral form is bunsenite. It is in the group of basic metal oxide. NiO can be prepared by several methods such as precipitation, sol-gel, hydrothermal etc., where nickel reacts with oxygen to produce nickel oxide. NiO is used in many applications such as production of alloys, catalyst, electrochemical material etc. (<https://en.wikipedia.org/wiki/>). Some properties of nickel oxide are summarized in Table 2.3.

Table 2.3: Structure and properties of NiO

Molecular formula	NiO
Structure	
Molecular weight	74.693 g/mol
Melting point	1,955 °C
Density	6.72 g/cm ³
Solubility in water	None
Solubility	Ammonium hydroxide , Potassium cyanine

(<https://pubchem.ncbi.nlm.nih.gov>)

2.2 Surfactant

Surfactants are organic compounds that are amphiphilic. They have hydrophobic groups (tail) and hydrophilic groups (head). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at the interface between liquid and liquid or at the interface between liquid and solid. For example, the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase. Surfactants are compounds that decrease the surface tension (or interfacial tension) between liquid and solid/gas/liquid interface. Surfactant will use in detergents, wetting agents, emulsifiers, foaming agents, and dispersants. (<https://en.wikipedia.org>)

2.2.1 Type of surfactant

Dependent on the nature of the hydrophilic group, surfactants are classified as anionic, nonionic, cationic or amphoteric.

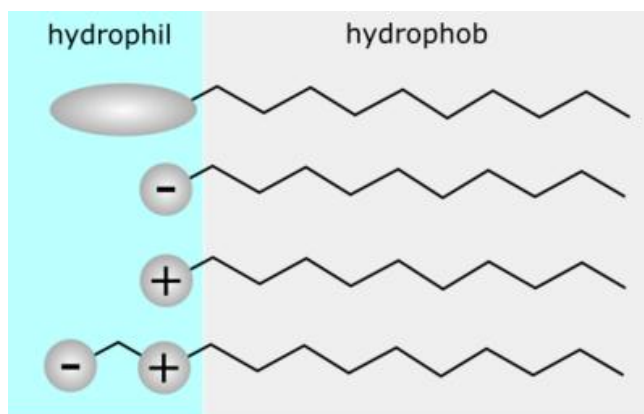


Figure 2. 1 Surfactant classification by comparison of head group: nonionic, anionic, cationic, amphoteric. (<https://en.wikipedia.org>)

- **Anionic surfactants**

Anionic surfactants are the hydrophilic group consists of a negatively charged group i.e. sulphonate, sulphate or carboxylate, etc. Basic soaps are anionic surfactants. Over the last 50 years many soaps have been replaced used surfactant such as alkyl sulphates, alkyl sulphonates and alkyl benzene sulphonates. Anionic surfactants are sensitive to water hardness.

- **Cationic surfactants**

Cationic surfactants are the hydrophilic group consists of a positively charged. The most typical applications are for softeners and antistatics. The cationic surfactants are used in proteins or synthetic polymers to provide desirable surface characteristics. Hair conditioners and fabric softeners use cationic surfactant

- **Nonionic surfactants**

Nonionic surfactants are a non-charged hydrophilic group. They are well suited for cleaning purposes and is not sensitive to water hardness. Nonionic surfactants have wide applications ranging from cleaning detergents.

- **Amphoteric surfactants**

Amphoteric surfactants are surfactant that the charge of the hydrophilic part is controlled by pH of the solution. This means that the amphoteric can act as anionic surfactant in an alkalic solution or as cationic surfactant in an acidic solution. Amphoteric surfactants are widely used in shampoos. (<http://www.eco-forum.dk/>)

2.2.2 Micellization

When surfactant concentration of a solution is high enough, it can be energetically more favorable for monomers to combine into a certain form. The minimum concentration at which micelle forms is called Critical Micelle Concentration (CMC). Different surfactants have different CMC values. The simplest micelles are spheres but as surfactant concentration increases the micelles grow and form rods. At high surfactant concentrations the rods form larger structures such as hexagonally packed rods and palisade arrangements. As these structures increase in size they take on a greater degree of order until, for the biggest structures, they occur as liquid crystals. In surfactant technology the micelle structure can be manipulated to give a product with the desired morphology. (<http://www.rsc.org/>)

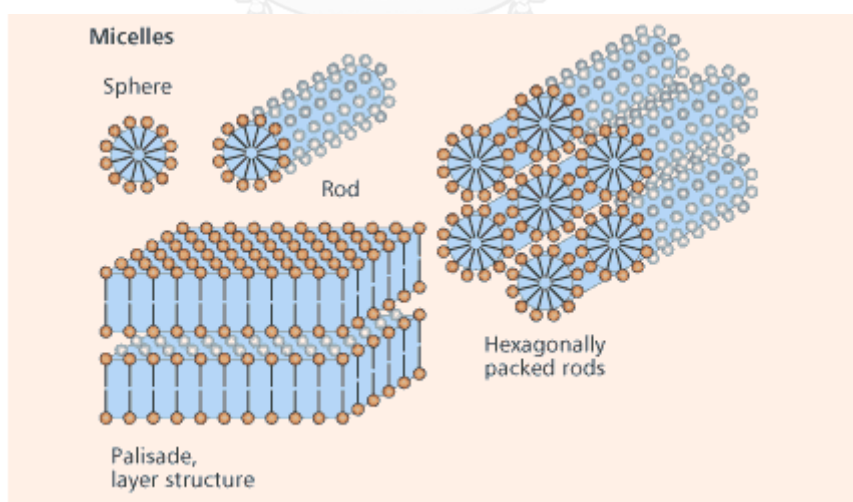


Figure 2. 2 micell structures of surfurfactant. (<http://www.rsc.org/>)

2.3 Gemini Surfactants

Gemini surfactants are made by two hydrophobic chains and two polar/ionic head groups covalently connected by a spacer group at the level of or in close vicinity to the head groups. Gemini surfactants have potential applications in detergents, cosmetics, the chemical industries, pharmaceutical and biological systems and material preparation etc [8].

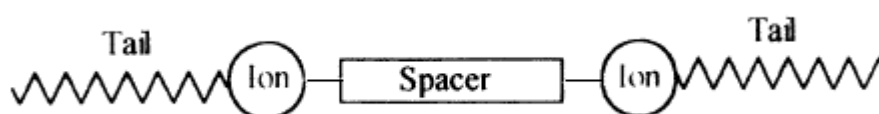


Figure 2. 3 Schematic representation of gemini surfactant [9]

Comparison between conventional and Gemini surfactants:

- Gemini surfactant have lower C_{20} values (a measure of their tendency to adsorb at an interface) than conventional surfactant.
- Gemini surfactants have lower critical micelle concentration (CMC) values (a measure of their tendency to form micelles) than conventional surfactants.
- Gemini surfactant are closer connecting head groups than conventional surfactants.
- Gemini surfactants have stronger interactions with oppositely charged surfactants at the aqueous solution/air interface. In addition, they are more soluble in water and some Gemini surfactants exhibit unique rheological properties [10].
- Micelle shape of gemini surfactant is dependence on surfactant structure, solution conditions such as concentration, temperature and ionic strength [9].

Gemini surfactants exhibit greater water solubility and higher surface activity when compared to conventional surfactants. This property makes them potential candidates for the use in new laundry washing machines, which limit the use of water. Their low CMC values promise greater efficiency in the solubilization of water-insoluble material, since solubilization occurs only above the CMC. The interfaces are closer packing of hydrophobic chains when compared to conventional surfactants that means a more laterally cohesive interfacial film which implying better foaming, dispersing, and emulsifying properties, whereas the 1:1 molar interaction of ionic geminis with oppositely charged surfactants makes them more compatible than comparable conventional surfactants [10].

2.4 Biosensor

Biosensor is analytical device used to detect chemical compounds or analytes by combining a biological substance with a physicochemical detector or transducer. (<https://en.wikipedia.org/wiki/>)

Biosensor works by electrochemical analysis, called electrochemical biosensor, and it is used to analyze chemical or biological compounds such as cell, blood, urine, saliva, food samples and environmental samples. Target analytes can directly interact with specific biological substance or bioreceptor that coat on transducer element, leading to a produce of biochemical reaction. This results in the change in electron, visible, thermal properties of substances. Biosensor composes of five main parts:

Bioreceptor: a part that is used to specify biological component through interaction with analyte.

- Electrical interface: this is where active biological reaction is occurred.
- Transducer: element that converts specific biochemical reaction into an electrical signal.
- Signal processor: electronic signal that is used to convert chemical parameter to electrical parameter.
- Display: this part is used to show the results.

Components of biosensor is shown in Fig. 2.4

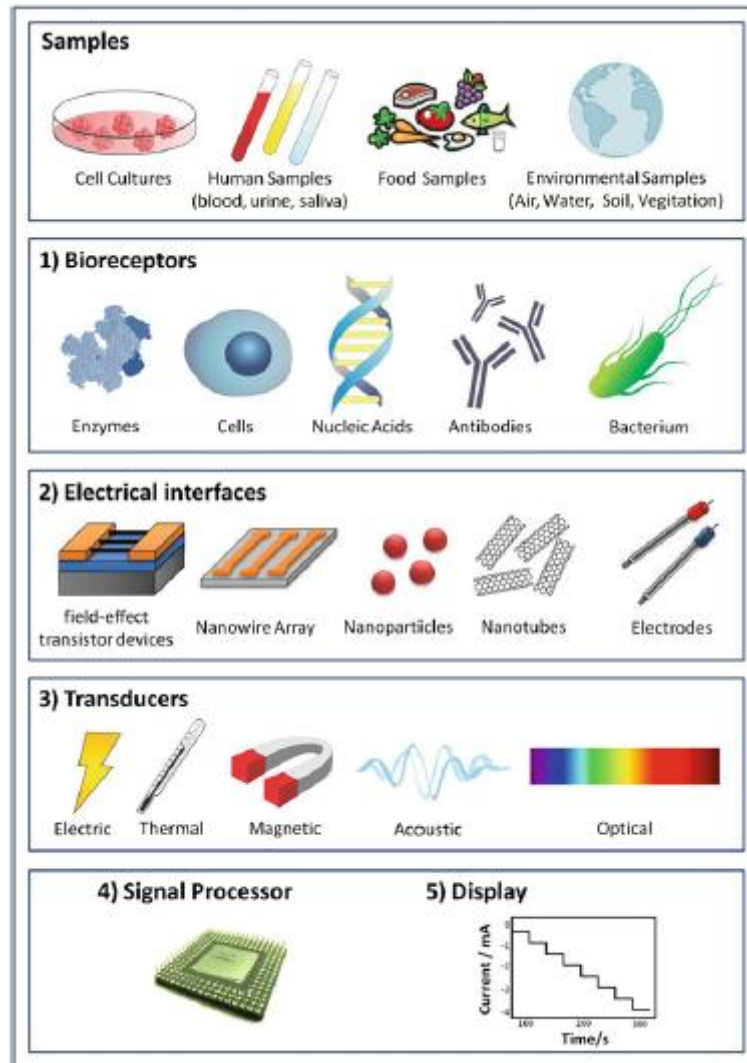


Figure 2. 4 Components of biosensor[11]

2.4.1 Type of biosensor

Type of biosensor can be classified as follows.

- **Resonant biosensor**

This type uses an acoustic wave transducer combine with bioreceptor. This sensor focuses on a change in the mass of bioreceptor that resulted from interaction between analytes and bioreceptor.

- **Optical detection biosensor**

It is use a silicon wafer that connect with protein molecule by covalent bond. The wafer is sensitive to UV light that affect to antibody. A signal is generated by the formation of diffusion grafting when put the wafer in the analytes.

- **Thermal detection biosensor**

Thermal detection biosensor is temperature detector connect with the immobilized enzyme. A concentration of analytes is measured by heat of reaction that produce from interaction between enzyme and analytes.

- **Ion sensitive biosensor**

This type of sensor works by interaction between ion and semiconductor. The result comes from the change of electric potential at semiconductor surface.

Electrochemical biosensor

For this type, analytes reacts with a biological component on the electrode surface. Electrical potential array shows the change in electrical current.

2.4.2 Advantages of biosensor

- Biosensor can detect nonpolar molecules that not response to other common devices
- Biosensor are specific to each analytes due to immobilization on them.
- Response time of detection is short.
- Detection is swift and continuous control.

2.4.3 Disadvantages of biosensor

- Biosensor cannot detect in heat sterilization condition because it affects to biological materials.
- Stability of biological material such as enzyme, cell, antibody, tissue, etc. depends on the natural property of each molecule that can deactivate under some conditions such as pH, temperature, or ion.
- The cell in biosensor can become intoxicated by some other molecules.

2.5 Electrochemical biosensor

Electrochemical biosensor is a new way to develop analysis of biomaterial with electrochemical. The advantages of this system are great specificity, sensitive, highly selective and lower cost when compared to other methods. Electrochemical biosensor can sense material without damaging the system. The use of electrochemical biosensor to apply in industrial and environment such as control of food manufacturing process, evaluation of food quality, detection of fermentation and monitoring of organic pollutants, etc.

Detection principle of electrochemical biosensor are different according to transducer type. Bioelectrochemical reaction will generate a measurable current, potential or charge accumulation, or conductivity. This method detects analyte related with the change of electrical signal and has an electrical signal as output data. For example, the intensity of the current, potential energy and electrical conductivity of the electrode change.

2.5.1 Electrochemical cell

In Electrochemical cell, electrode is an important part that affect performance of electrochemical biosensor as surface of electrode material effect detection ability.

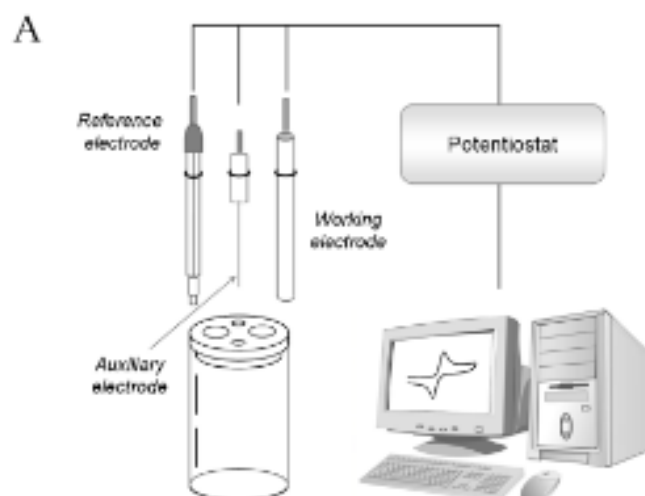


Figure 2. 5 Electrochemical cell with a three-electrode system [12]

Electrode can be classified as follows:

- **Reference electrode**

This electrode is usually produced from inert material. This electrode offers stable potential in electrochemical system. The most common reference electrodes are hydrogen electrode, Ag/AgCl electrode that is a Ag wire coat with AgCl, saturation-calomel or mercurous chloride(Hg_2Cl_2) electrode that consist of mercury, saturated potassium chloride solution and paste (mixture of mercury(I) chloride powder and potassium chloride) .

- **Counter electrode**

This electrode is a function as a cathode (working electrode as an anode). This electrode has a surface area higher than working electrode. The half reaction occurring at the counter electrode should occur fast enough not to limit the process at the working electrode. This electrode is often made from electrochemically inert materials such as gold, platinum or carbon.

- **Working electrode**

The reaction occurs on this electrode can be referred to as either cathodic or anodic, depend upon the reaction on this electrode: reduction or oxidation. The examples of working electrode are glassy carbon electrode, screen printed electrode, indium tin oxide coated glass electrode, carbon paste electrode etc.

2.5.2 Signal detection method

- **Amperometry**

It is operated at a given applied potential between the reference electrode and working electrode. It generates signal that is related to concentration of target analyte. The current signal is generated as a function of reduction or oxidation of product on the surface of working electrode. (http://www.sirebi.org/open/Intro_Biosensing)

- **Voltammetry**

It is the most useful technique in electrochemical analysis. Both the current and the potential are measured. The position of peak current is related to analyte and the peak current density is related to the concentration of analyte.

- **Cyclic Voltammetry (CV)**

Cyclic voltammetry that working electrode potential changes linearly with time. Cyclic voltammetry experiment end when it reaches a set potential value and inverse to the initial potential. The plot of the current at working electrode and the potential give cyclic voltammogram of reaction[13]. The potential was scanned to more positive values that show oxidation of analyte's reduced form (R) to analyte's oxidized form (O). The reverse directions scan to more negative potentials that show reduction of O to R. The overall reaction was shown in equation 2.1.



In Figure 2.6 show the relationship between added potential and time. The initial potential start to positive potential value and switch to negative potential value.

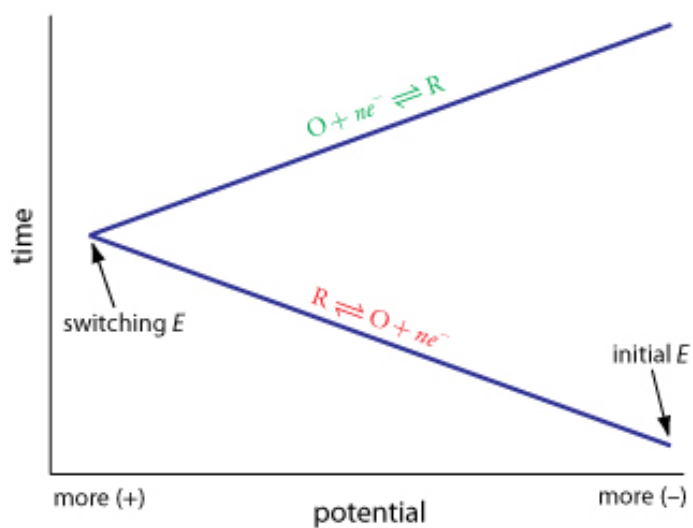


Figure 2. 6 The potential value in the present of time

The results of voltammogram was shown in Figure 2.7. The voltammogram was separated peak for the oxidation and the reduction reaction. Characterization of each peak by a peak of potential and peak of current.

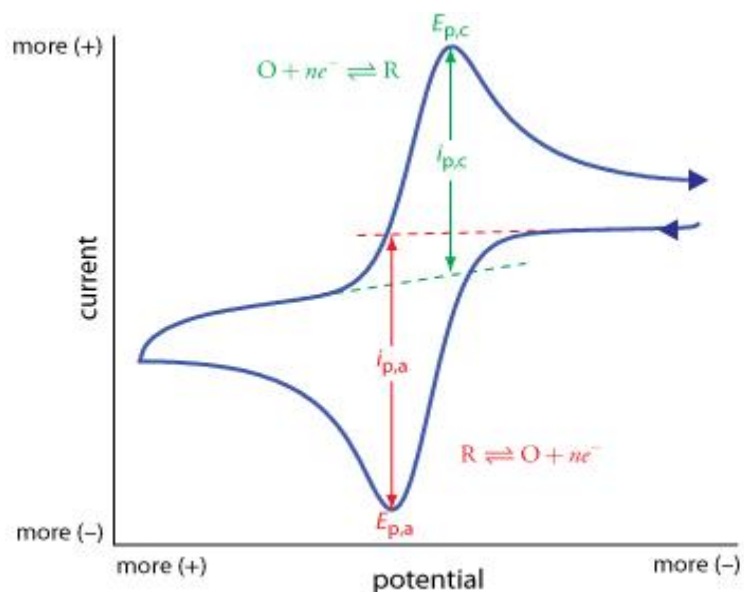


Figure 2. 7 The cyclic voltammogram present in the function of peak currents and peak potentials

The peak current in cyclic voltammetry is given by the Randles-Sevcik equation

$$i_p = \left(2.69 \times 10^5 n^{\frac{3}{2}}\right) A D^{\frac{1}{2}} \nu^{\frac{1}{2}} C = KC \quad (2.2)$$

where, n = the number of electrons in the redox reaction

A = the area of the working electrode

D = the diffusion coefficient for the electroactive species

ν = the scan rate

C = the concentration of the electroactive species at the electrode.

For a best system, the anodic and cathodic peak currents will equal, and the ratio $i_{p,a}/i_{p,c}$ is 1.00. The half-wave potential, $E_{1/2}$, is midway between the anodic and cathodic peak potentials.

$$E_{1/2} = \frac{E_{p,a} + E_{p,c}}{2} \quad (2.3)$$

2.5.3 Influence of Mass Transport on the Faradaic Current

Mass transport that affect the rate which reactants and products move at the electrode surface have three mode.

Diffusion occurs when the concentration of a molecule at the electrode surface is different from the bulk solution. For example, when apply a potential sufficient to completely reduce $\text{Fe}(\text{CN})_6^{3-}$ at the electrode surface, the result of a concentration gradient are show in Figure 2.8. Before apply the potential ($t = 0$) the concentration of $\text{Fe}(\text{CN})_6^{3-}$ is the same along the surface of electrode. After applying the potential, its concentration at surface of electrode decreases to zero and $\text{Fe}(\text{CN})_6^{3-}$ diffuses to the electrode from bulk solution. The longer time for apply the potential show the greater the distance over diffusion occurs. The dashed line shows the extent of the diffusion layer at time t_3 . These profiles assume that convection and migration do not significantly contribute to the mass transport of $\text{Fe}(\text{CN})_6^{3-}$.

The region of solution that diffusion occurs is the diffusion layer. In the absence of other modes of mass transport, the width of the diffusion layer, δ , increases with time as the $\text{Fe}(\text{CN})_6^{3-}$ must diffuse from increasingly greater distances.



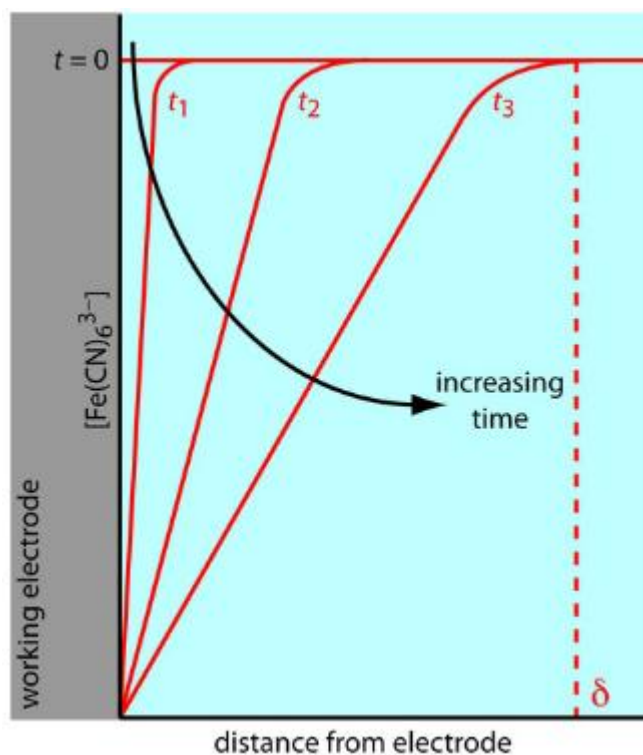


Figure 2. 8 The concentration gradients of $\text{Fe}(\text{CN})_6^{3-}$ complete reduces to $\text{Fe}(\text{CN})_6^{4-}$ when apply the potential

Convection occurs when the solution was mechanically mixed. The reactants go to the electrode and the products remove from the electrode. The most common form of convection is stirring the solution with a stir bar. Other methods that have been used include rotating the electrode and incorporating the electrode into a flow-cell.

Migration occurs when a charged particle in solution is attracted to an electrode that have a surface charge. If the electrode have a positive charge, an anion will move toward the electrode and a cation will move toward the bulk solution.

The movement of material to and from the electrode surface is a complex function of all three modes of mass transport. When the diffusion is the only significant form of mass transport, the current in a voltammetric cell is equal to

$$i = \frac{nFAD(C_{\text{bulk}} - C_{x=0})}{\delta} \quad (2.4)$$

where n = the number of electrons in the redox reaction,

F = Faraday's constant

A = the area of the electrode

D_i = the diffusion coefficient for the species reacting at the electrode

C_{bulk} and $C_{x=0}$ = the concentrations in bulk solution and at the electrode surface

δ = the thickness of the diffusion layer.

2.5.4 Shape of Voltammograms

The shape of a voltammogram is determined by several experimental factors. For the voltammogram in Figure 2.9a, the current increases from a base line current to a limiting current, i_l . Because the faradaic current is inversely proportional to δ (equation 2.4), a limiting current can only occur if the thickness of the diffusion layer remains constant because a stirring of the solution. When the absence of convection in the diffusion layer increases with time, the voltammogram has a peak current instead of a limiting current. As shown in Figure 2.9b

For the voltammograms in Figures 2.9a and 2.9b, the current as a function of the applied potential was measured. It can show the change in current, Δ , following a change in potential. The resulting voltammogram has a peak current. It is shown in Figure 2.9c.

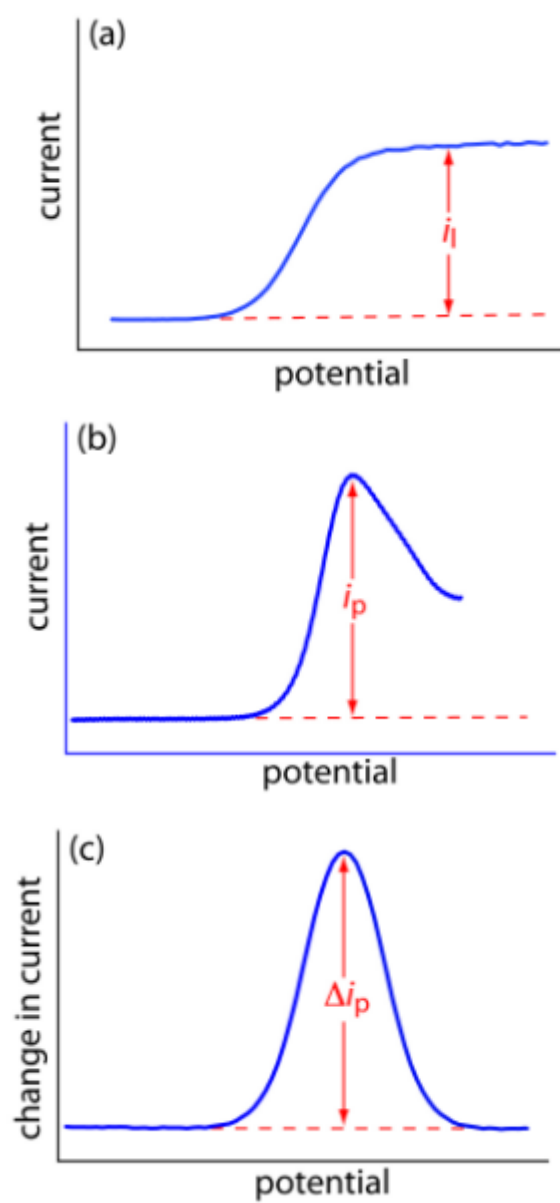


Figure 2. 9 The three common shapes for the voltammograms.

(<http://chem.libretexts.org/>)

CHAPTER III

LITERATURE REVIEWS

This chapter presents review of literatures concerning electrochemical biosensor for dopamine detection and the development of nickel oxide used in electrochemical biosensor.

Dopamine is consider neurotransmitter. Detection of dopamine at high or low levels is important because abnormal level leads to negative effect in human body. Methods to detect dopamine are, for example, fluorometry, gas chromatography(GC), electrochemiluminescence, calorimetric, high performance liquid chromatography(HPLC), or electrochemical, etc. [14]. However, some methods have own intrinsic limitations such as GC and HPLC are uncomfortable for appliing in a portable detection due to large-scale and expensive instrument [15]. Electrochemical sensor detection, a main technique used to detect dopamine, offers high sensitivity, simplicity, portability (20), good controllability, rapid response and real-time detection. Dopamine can detect conveniently because of its electroactive property [16]. Electrochemical sensor can be divided into two parts: biosensor and chemical sensor. Biosensor is a device that uses biological recognition element, which directly contact with electrochemical transduction element, whereas chemical sensor contains non-biological active element [17]. Development of electrochemical biosensor for the detection of dopamine has been focused on the improvement of sensitivity, selectivity, stability and bio-compatibility by modified electrode. Unmodified conventional electrodes are not appropriate for dopamine detection due to the interference electrochemical signal, high oxidation potential and low selectivity [18]. Interference in real sample include ascorbic acid (AA) and uric acid (UA) showed poor selectivity and sensitivity in dopamine detection because oxidation of AA and UA is closed to the same potential, resulting in the overlap of voltammetric response for oxidation in real sample. Nurzulaikha et al. [19] reported that this problem could be solved by improving the electrocatalytic performance on electrode surface to separate their oxidation potential and selective interaction with dopamine on the electrode

surface. Electrode surface was modified by various compounds such as polymer [20-26], metal oxide [27-31], nanoparticle [1, 32-35], carbon based material [36, 37] and nanocomposite [38, 39].

Extensive studies have been focused on operating condition and modified electrode because it is found to be an important part that can affect performance on dopamine detection. In the modification of surface electrode, metal oxide becomes important material that can provide an effective surface to enhance sensing characteristics. Metal oxide has shown physical and electrical properties that can affect sensing of biomolecules. The immobilization of bio-receptor on metal oxide nanoparticle is also affect biosensor performance. The formation and property of nanobiointerface depend on nature of metal oxide such as effective surface area, surface charge, energy, roughness and porosity, valence and conduction state, functional group and physical state etc. The rate of electron transfer depend on the characteristic of the immobilized biomolecule and metal oxide interaction. It is considered to improve sensitivity, detection limit, shelf life and lower cost for biosensor. Various metal oxides used in biosensing applications are, for example, tungsten trioxide [14], zinc oxide [29], tin dioxide [31], copper oxide [40], cobalt oxide [41], iron oxide [42], etc. Among these, nickel oxide has been of interest to use as dopamine sensor due to its high electrocatalytic property, oxygen ion conductivity, biocompatibility, nontoxicity, high chemical stability, and high electron transfer. The high of isoelectric point (IE = 10.7) of nickel oxide is also advantageous in binding biomolecules that have a low IEP via strong electrostatic interaction [43].

Liu et al. [27] modified electrode by using nickel and copper oxide combined with graphene composite. The morphology of synthesized material was found to be flake-like and crimple shape. The modified electrode was obtained by electropolymerization method. The study of electrochemical operation in 0.1 M PBS from pH 2.0 to 11.0. It showed the oxidation peak currents increased with the increasing of pH and the highest peak current was found at pH 8. The relationship between the oxidation currents of analytes and metal oxides for a particular Ni-Cu oxide composition on the surface of electrode was investigated for different compositions,

varied from 1:1 to 3:3. The results showed that the composition of 3:1 was an optimal electro-deposition parameter due to the highest current peak was observed. Volumetric response of dopamine showed 0.5 -20 μM in linear detection range (LDR) and 0.167 μM in the detection limit and 9.406 in the sensitivity. Liu et al.[44] modified electrode by using copper-nickel hydroxide composite combined with nitrogen doped graphene and coating with nafion. Electrochemical parameter was studied, supporting electrolytes are PBS, Britton-Robinson, HCl, HAc, NaAc-HAc, KCl with different pH values ranging between 6 and 8.5. It was found that dopamine showed favorable redox property on PBS electrolyte (0.1mol/L) and peak current was largest at pH 6.5. The response of dopamine showed 1×10^{-4} to 4.6×10^{-2} μM in linear detection range (LDR) and 3.3×10^{-5} μM . The stability of electrode was investigated for 1 week and the results showed that electrochemical response was unchanged and decreased for 5.6% in one month. Jahani and Beitollahi modified electrode by using nickel oxide nanoparticle decorated on graphene nanosheets. The modified electrode was prepared by graphene/screen-printed electrode (GR/SPE) was soaked in nickel nitrate solution at a potentiostatic potential of -1.1V for 7 s. The characterization of modified electrode by scanning electron microscopy (SEM) show bumpy with some granules morphology. The electrochemical analysis was studied by cyclic voltammetry (CV) in 0.1 M PBS and pH 7 because electrocatalytic oxidation of dopamine at the surface of modified electrode was more favored in under natural condition. The result from CV responded of 75.0 μM dopamine concentration show modified electrode have higher anodic peak current for dopamine oxidation than unmodified electrode. They study effect of scan rate on electrocatalytic oxidation of dopamine show the oxidation peak potential shift to positive potential when increase scan rate. Performance of modified electrode in the presence of dopamine concentration at pH 7.0 and scan rate 50 mV/s. The results showed 1×10^{-3} to 5.0×10^{-1} μM in linear detection range (LDR) and 3.14×10^{-4} μM . The percent recovery of modified electrode in the presence of interference show 98% dopamine recovery. Reddy et al.[45] modified electrode by synthesis of NiO-ZnO hybride nanoparticle via a micro-emulsion method with the use of sodium dodecyl sulfate surfactant (SDS) surfactant and co-surfactant hexanol as a template. The characterization of hybrid material showed only NiO and ZnO compositions in the

hybrid material and 28 nm of average particle size was obtained. The SEM result showed flaked shaped structure with thickness around 40 -50 nm and long around 500 nm with some irregular shaped particle show less than around 40 nm. The results showed ΔE_p was 0.061 V. However, a well-defined redox wave of dopamine was observed at the MCPE and the peak currents increased with the anodic peak potential shifting to 0.146 V and the corresponding cathodic peak potential is 0.097 V. The result of ΔE_p is 0.049 V. due to the modified electrode showed fast electron transfer process. In addition, the effect of concentration of dopamine by differential pulse voltammetric technique for the analysis of dopamine was also investigated in this work. Dopamine concentration was varied from 1 μM to 600 μM and the results for the modified carbon paste electrode prepared with NiO/ZnO hybrid nanoparticles showed that increasing the concentration of DA from 1 μM to 600 μM resulted in an increase in anodic peak current with three linear ranges (1 μM to 6 μM , 6 μM to 100 μM and 100 μM to 600 μM). Roychoudhury et al.[46] modified electrode for dopamine sensor by using nickel oxide nanoparticle and tyrosinase enzyme conjugate on ITO electrode (Tyrosinase/NiO/ITO). Nickel oxide was prepared by precipitation method using sodium dodecyl sulphate (SDS) anionic surfactant as a template to control size of synthesized nickel oxide nanoparticles. The surface morphology of modified NiO/ITO and Tyrosinase/NiO/ITO were studied by atomic force microscopy (AFM). The AFM micrograph of NiO/ITO electrode showed rough surface with uniformly nanoporous granular morphology. After immobilization of tyrosinase enzyme molecules, the nanoporous granular morphology of NiO/ITO surface converted into regular smooth globular morphology. The Nickel oxide nanoparticle film provided nanoporous surface lead to an enhancement of enzyme loading on NiO/ITO electrode and the immobilization of enzymes occurred may be due to electrostatic interaction between positively charged Ni^{2+} ions on the NiO/ITO surface and negatively charged carboxyl group (COO^-) of tyrosinase enzyme molecules. The modified electrode was analyzed by cyclic voltammetry (CV) method. The studies of bare ITO, NiO/ITO and Tyrosinase/NiO/ITO electrodes were conducted in PBS (50 mM, pH 6.5, 0.9% NaCl) at 100 mV/s of scan rate in the potential range of -1.0 V to +1.5 V. The presence of

tyrosinase as a biocatalyst in the redox reaction enhanced the kinetics of reaction and hence leads to higher sensitivity of detection. The study with ITO and NiO/ITO electrodes redox peaks in the presence of dopamine appeared as expected, due to catalytic activity of metal oxide with respect to phenolic group. However, the outcome of CV studies in the presence of dopamine indicated that the large of peak current during reduction of o-dopaquinone (I_{pc} , 10.27 mA) of Tyrosinase/NiO/ITO electrode is 38% higher than the peak current (I_{pc} , 7.46 mA) of NiO/ITO electrode. This is due to availability of active binding sites in enzyme and enhanced electron transfer between active sites of the enzyme and electrode. The Volumetric response of dopamine showed 1.04 μM of the detection limit, 0.06 $\mu\text{A}/\mu\text{M}$ of the sensitivity and 2-100 μM of the linear detection range (LDR). The sensor response time of Tyrosinase/NiO/ITO electrode with dopamine concentration of 500 μM in PBS (50 mM, pH 6.5, 0.9% NaCl) showed 90% of biosensor response obtained within 45 s. The reusability of modified electrode for 100 μM dopamine solution after 100 cycles showed 85% of response compared with original response. The shelf-life and storage stability of modified electrode by measuring amperometric current response for o-dopaquinone at keep of 1 day up to 10 days and then after a gap of 5 days. It has been found that the modified electrode retained response by up to 91% after 5 days, 84% after 10 days, 80% after 30 days and decrease to 77% after 45 days when stored under refrigerated condition (4 °C).

Table3. 1 Summary of condition modified electrode for dopamine detection.

Electrode			Method	Condition		Ref.
Working	Reference	Counter		pH	solution	
NiO/GR/SPE	Ag/AgCl	graphite	CV	7.0	0.1M PBS	[7]
NiO-CuO/GR/GCE	Saturated calomel	Pt	CV	8.0	0.1M PBS	[27]
Nafion/Cu-Ni(OH) ₂ /N-GR/CGE	Ag/AgCl	Pt	CV	6.5	0.1M PBS	[44]
NiO/ZnO/graphite	Saturated calomel	Pt	CV	7.4	0.2M PBS	[45]
Tyrosinase/NiO/ITO	Ag/AgCl	Pt	CV	6.5	0.5mM PBS	[46]
Nafion/Ni(OH) ₂ /MWCNT/GCE	Ag/AgCl	Pt	DPV CA	7.0	0.1M PBS	[47]

Table3. 2 Summary of performance of modified electrode for dopamine detection.

Modified electrode	Linear range (μM)	Sensitivity	Limit of detection (μM)	Ref.
NiO/GR/SPE	1–10 10–500	0.040 ($\mu\text{A}/\mu\text{A}$) 0.005 ($\mu\text{A}/\mu\text{A}$)	0.314	[7]
NiO-CuO/GR/GCE	0.5–20	9.406 ($\mu\text{A}/\mu\text{A}\cdot\text{cm}^2$)	0.167	[27]
Nafion/Cu-Ni(OH) ₂ /N-GR/CGE	0.1–46	-	0.033	[44]
NiO/ZnO/graphite	1–6 6–100 100–600	-	0.062	[45]
Tyrosinase/NiO/ITO	2–100	0.060 ($\mu\text{A}/\mu\text{A}$)	1.0	[46]
Nafion/Ni(OH) ₂ /MWCNT/GCE	(DPV) 0.05–2.5 (CA) 0.25–23	-	0.015 0.110	[47]

CHAPTER IV

EXPERIMENTAL

The investigation in this work is focused on the synthesis of nickel oxide to use as coating material on working electrode. In this chapter, the details of nickel oxide preparation, techniques of material characterization, including XRD, SEM and TGA, and experimental details of electrochemical biosensor analysis are presented.

4.1 Chemicals

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as precursor for nickel oxide (NiO). Sodium hydroxide (NaOH) was used to control pH of solution and accelerate precipitation. Urea ($\text{CH}_4\text{N}_2\text{O}$) was used to accelerate precipitation. Sodium dodecyl sulphate, SDS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) and butanediyl-1, 4-bis(dimethyldodecylammonium bromide), (C12-C4-C12,2Br) were used to control structure of NiO. Ethanol ($\text{C}_2\text{H}_6\text{O}$) and de-ionized water were used to wash the precipitated solids. Sodium phosphate, Monobasic (NaH_2PO_4), sodium phosphate, Dibasic (Na_2HPO_4) and sodium chloride (NaCl) were used to prepare phosphate buffer saline (PBS). Dopamine hydrochloride ($(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{NH}_2 \cdot \text{HCl}$) was used to prepare dopamine solution at various concentrations.

4.2 Material preparation

4.2.1 Synthesis of NiO by precipitation method

A 200-ml of 20 mM nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was mixed with 40 mM sodium hydroxide (NaOH) solution until pH to 11.5-12 and continuously stirred for 2 hrs at room temperature. The green precipitates solids were obtained in the solution. The precipitate was separated by filtration and washed with 50 ml of de-ionized water three times and 50 ml of ethanol three times. The product was dried in an oven at 70 °C for 24 hrs. The green powder was calcined at 800 °C for 1.5 hrs and NiO was obtained. For NiO synthesis with the addition of surfactant into the system, sodium dodecyl sulphate, SDS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) and butanediyl-1, 4-

bis(dimethyldodecylammonium bromide), (C12-C4-C12,2Br) were dissolved in 200-mL DI water. The surfactant solution was mixed together before mixing with nickel nitrate hexahydrate. The ratio between (C12-C4-C12,2Br) and SDS concentration are 0.0 : 8.2, 0.04 : 4, 0.04 : 8.2, 0.04 : 12, 0.04 : 0.00 in mM. For the method with hydrothermal treatment, the solution was transferred to a Teflon bottle and placed in carbolite in various hydrothermal temperature (100, 120, 150 °C).

4.2.2 Synthesis of NiO by precipitation with urea hydrolysis with hydrothermal treatment

A 40 mmol of urea ($\text{CH}_4\text{N}_2\text{O}$) was dissolved in 200 ml of de-ionized water. A 20 mmol of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was slowly added to the solution of urea. The solution was continuously stirred for 2 hrs at room temperature. The green solution was obtained. The solution was transferred to a Teflon bottle and placed in the oven at various hydrothermal temperatures (100, 120, 150 °C). Precipitated solids were obtained after hydrothermal treatment. The solids were separated by filtration and washed with 50 ml of de-ionized water followed by 50 ml of ethanol. Then, the product was dried in an oven at 70 °C for 24 hrs. The green powder was calcined at 800 °C for 1.5 hrs and NiO was obtained. For the addition of surfactant, A surfactant was dissolved in de-ionized before adding urea. The ratios between (C12-C4-C12,2Br) and SDS concentration are varied the same as conducted in section 4.1.1.

4.3 Characterization of nickel oxide

The characterization of modified nickel oxide was examined by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Thermal gravimetric analyzer (TGA). X-ray Diffraction is used to determine the crystalline phase and purity of modified NiO. S-3400N HITACHI Scanning electron microscope (SEM) is used to determine the structural morphology of modified NiO. Thermal gravimetric analysis, SDT Q600 TA instrument is used to analyze the decomposition of precipitate in this study.

4.4 Electrochemical biosensor analysis

4.4.1 Preparation of modified working screen printed electrode

The modified electrode was prepared by mixing of 31 mg of nickel oxide and 1 ml of de-ionized water with sonication for 5 minute. The concentration of suspension was obtained at 31 mg/ml. The suspension was varied as 15.5, 7.75, 3.87, 1.94, 0.97 mg/ml. A 5 μ l of NiO/H₂O suspension in various concentrations was dropped on graphite working electrode. The modified working electrode was dried in desiccator for 1 hr and ready for electrochemical analysis. Figure 4.5 show the screen printed electrode that used for this study. The area of working electrode is 7.065 mm².

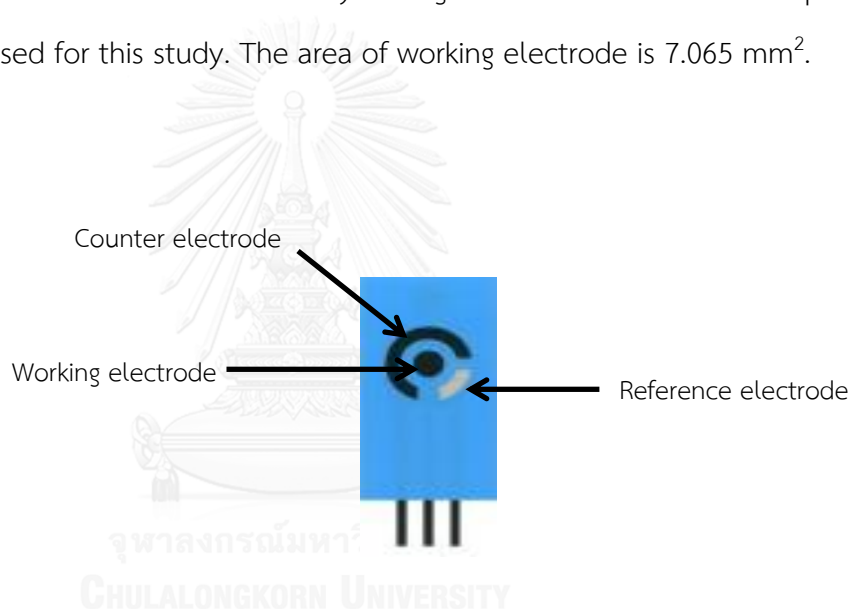


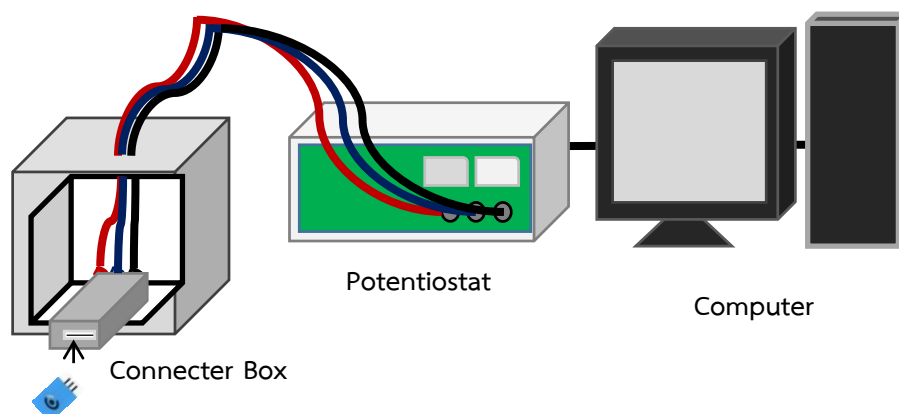
Figure 4. 1 Screen printed electrode for electrochemical study.

4.4.2 Preparation of Dopamine stock solution

A 0.948 g of dopamine hydrochloride was mixed with 100 ml of de-ionized water to obtain 50 mM of dopamine concentration. The solution was diluted to 500, 400, 300, 200, 100, 50, 25, 12.5, 6.25, 3.12 μM . with 10 mM phosphate buffer saline, PBS (pH 7). The preparation of 10 mM PBS of pH 7 was prepared using sodium phosphate monobasic, sodium phosphate dibasic and sodium chloride were used to prepare phosphate buffer saline (PBS). The pH was adjusted with hydrochloric acid or sodium hydroxide solution.

4.4.3 Electrochemical biosensor for dopamine detection analysis

The measurements were conducted on electrochemical analyzer using three electrode system with modified screen printed electrode (SPE). The electrochemical measurements of the modified electrodes were performed by Autolab potentiostat (PGSTAT302N) using NOVA1.11 software. The screenprinted electrode (Quasense, Thailand) 12.5mm \times 30mm (width \times length) consists of three main parts, which are a graphite counter electrode, a silver/silver chloride reference electrode (Ag/AgCl) and a graphite working electrode with 3 mm of working electrode diameter. The 100 μl of 1 – 400 μM dopamine solution was added to screen printed electrode before electrochemical analysis. The cyclic voltammetry (CV) was used to detect dopamine concentration at 50 mV/s of scan rate in the potential range -0.5 to 0.5. The square wave voltammetry was tested in the frequency at 25 Hz. and potential range 0 to 0.6. Figure 4.5 show experimental equipment for electrochemical biosensor study.



Screen printed
electrode

Figure 4. 2 Experimental equipment for electrochemical biosensor study



CHAPTER V

RESULTS AND DISCUSSION

This chapter presents the investigation on the effects of synthesis methods, surfactant, and temperature of hydrothermal treatment for synthesis of nickel oxide on electrochemical performance of dopamine detection by electrochemical sensor.

5.1 The effect of precipitating agent in synthesis nickel oxide by precipitation method

The synthesis of nickel oxide by precipitation method with different precipitating agents is provided below as well as the properties of the synthesized nickel oxide.

5.1.1 The physical properties of nickel oxide

In this study, sodium hydroxide and urea were used as precipitating agents. Nickel oxide synthesized from precipitation with sodium hydroxide as a precipitating agent is denoted as NiO_SH and nickel oxide synthesized from precipitation with urea as precipitating agent is denoted as NiO_UH. Figure 5.1 shows XRD patterns of the synthesized NiO from the two precipitating agents. The results show that both synthetic nickel oxides show patterns corresponding to NiO. The main diffraction peaks of the synthetic nickel oxides were observed at $2\theta = 37.29, 43.40, 62.95, 75.42$ and 79.43 . This finding confirms that the precipitate was completely decomposed to NiO. No impurity peak was observed in the XRD patterns.

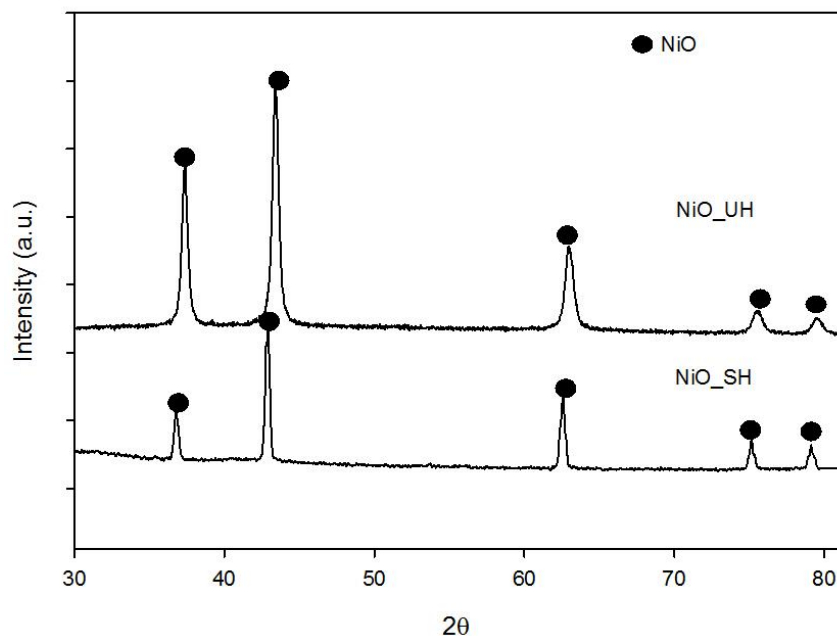


Figure 5. 1 XRD patterns of NiO from different precipitating agents

The thermal gravimetric analysis of nickel hydroxide was studied to find the calcination temperature of nickel hydroxide to obtain synthetic nickel oxide as shown in Figure 5.2. The weight loss starting from room temperature to 1000 °C was detected. The first weight loss between 100 - 200 °C is due to the loss of molecule associated with nickel hydroxide. The weight loss between 200 - 400 °C is due to the decomposition of nickel hydroxide to nickel oxide. The weight loss around 700 °C is due to the loss of intercalated anion such as CO_3^- , HCO_3^- or NO_3^- [48]. The results show complete decomposition of nickel hydroxide at 800 °C. So, this temperature was chosen as the calcination temperature of nickel hydroxide to nickel oxide.

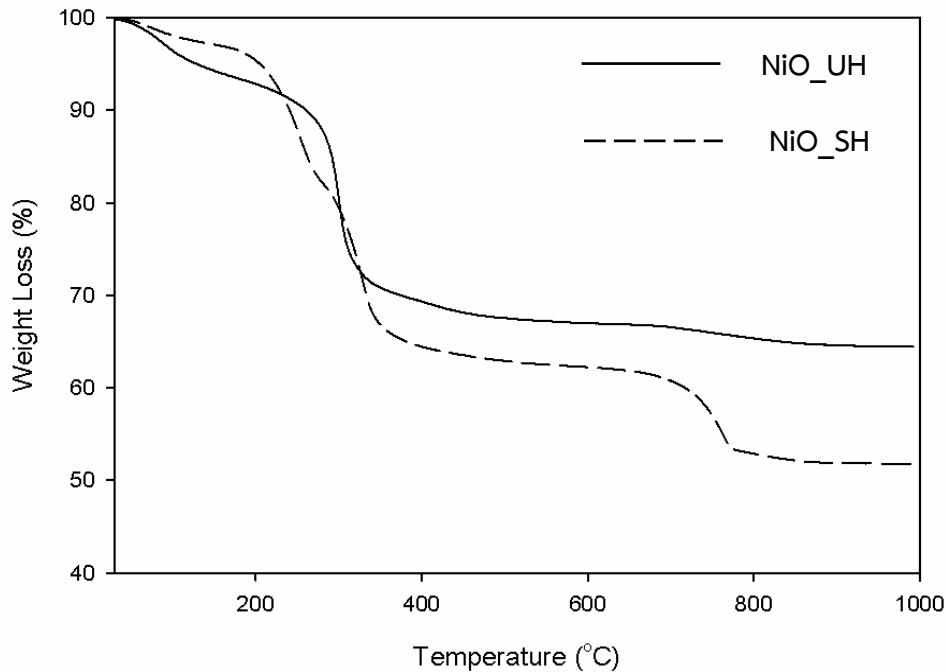
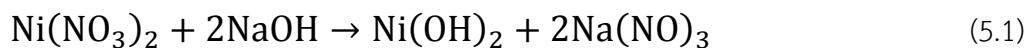
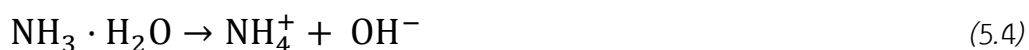
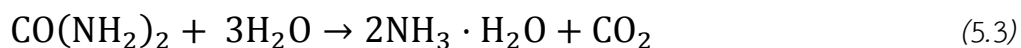


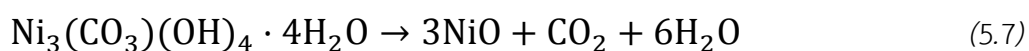
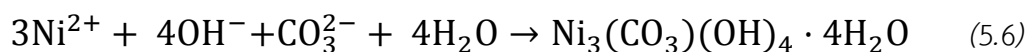
Figure 5. 2 TGA of nickel oxide from different precipitating agents

Morphology of synthetic nickel oxide is shown in Figure 5.3, the synthetic nickel oxide from the precipitation method using urea as a precipitating agent (NiO_UH) shows the fuzz morphology with more porosity than the one synthesized from sodium hydroxide (NiO_SH), which shows denser packing particles. This is because of the effect of the intercalated ion in the nickel hydroxide layer before the calcination step. The synthesis reaction mechanisms of nickel oxide by precipitation method using sodium hydroxide as a precipitating agent are shown by Roychoudhury et al. 2015[46].



The synthesis reaction mechanisms from urea as a precipitant are shown by Miao et al. year (49)





From the above equations, it can be seen that precipitation by sodium hydroxide shows the nitrate ion in the nickel hydroxide layer but the precipitation by urea shows nitrate ion and carbonate ion. So, the calcination of nickel hydroxide that have more intercalated ion would provide more porous nickel hydroxide.

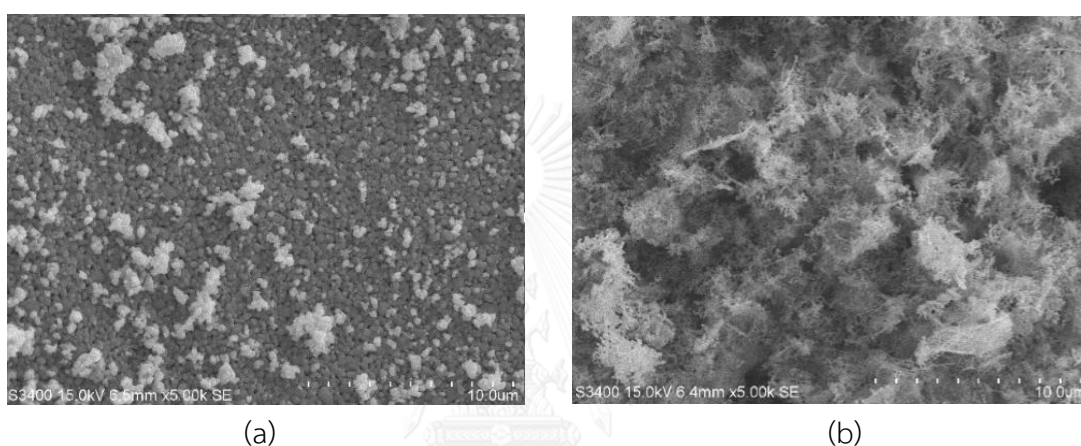


Figure 5. 3 Morphology of synthetic nickel oxide from different precipitating agents a) NiO_SH and b) NiO_UH

5.1.2 Dopamine detection by electrochemical sensor of synthetic nickel oxide

Electrochemical analysis of dopamine detection was used to study the effect of precipitating agent in the precipitation synthesis. Cyclic voltammetry (CV) is the method used to examine performance of all of the electrodes. The reaction mechanism of electrochemical dopamine detection is shown in Figure 5.4.

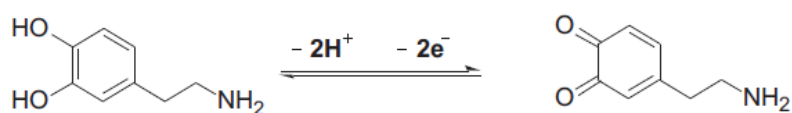


Figure 5. 4 Reaction mechanism for electrochemical dopamine detection[27]

In electrochemical detection, dopamine is oxidized to dopamine-o-quinone when potential is scanned to more positive value, obtaining anodic peak current, I_{pa} . When the potential is reverse scanned to more negative potential, dopamine-o-quinone is reduced to dopamine, obtaining cathodic peak current, I_{pc} . The detection was catalyzed by the Ni(III)/(II) redox couple reaction at the surface of electrode. The reaction was shown in Equation 5.8 [49].



The electrochemical activity of bare electrode and synthetic nickel oxide electrode was examined by cyclic voltammetry in a 50 μM Dopamine in PBS 10 mM, pH 7.0 at a scan rate of 50 mV/s shown in Figure 5.5. The anodic peak potential for dopamine oxidation of bare electrode is around 0.37 V. When compared to the nickel oxide modified electrode, the anodic peak potential is observed at 0.3 V, which shifts to negative value around 0.07 V. The anodic peak current response of bare electrode and nickel oxide modified electrode is shown in Figure 5.6. The results show that the nickel oxide modified electrode obtained higher anodic peak current than the bare electrode. The NiO_UH shows the highest anodic peak current at 2.18 μA whereas the NiO_SH shows anodic peak current at 1.83 μA , which is higher than that of the bare electrode that shows anodic peak current at 1.01 μA . This could be because NiO_UH has higher surface area for electron transfer than NiO_SH as shown by SEM images depicted in Figure 5.3.

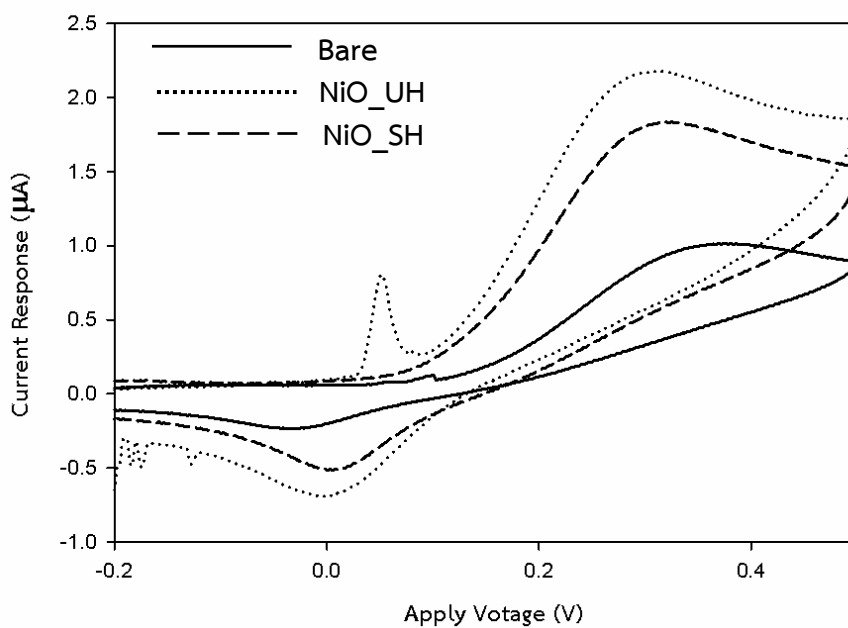


Figure 5. 5 Cyclic Voltammograms of the bare electrode and synthetic nickel oxide modified electrode from different precipitating agents in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S

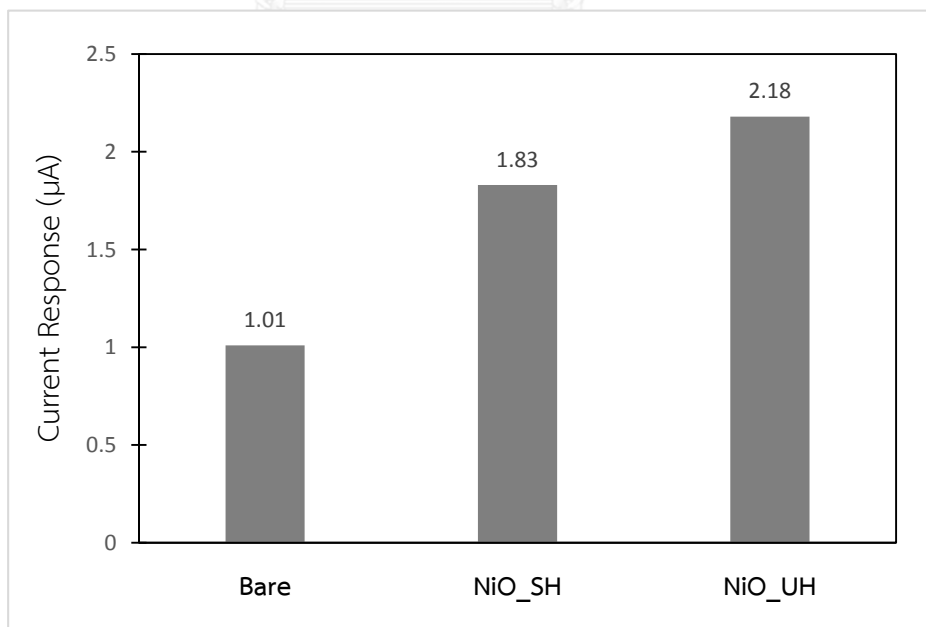


Figure 5. 6 Current response of bare electrode and synthetic nickel oxide modified electrode from different precipitating agents

5.2 The effect of nickel oxide loading on dopamine detection

The amount of nickel oxide loading on electrode was studied by using the nickel oxide synthesized by urea as a precipitating agent with adding gemini surfactant 0.04 mM, denoted as NiO_GM0.04:SDS0_UH. The cyclic voltammograms of NiO_GM0.04:SDS0_UH modified electrode was shown in Figure 5.7.

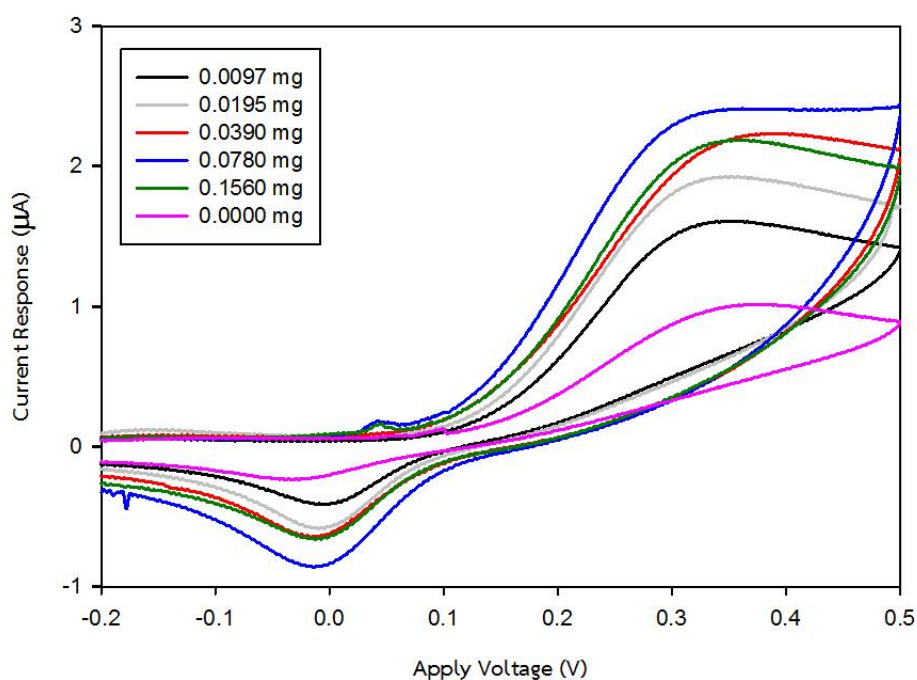


Figure 5. 7 Cyclic voltammograms of NiO_GM0.04:SDS0_UH modified electrode in 10 mM PBS (pH 7.0) containing 50 μ M of Dopamine at a scan rate of 50 mV/S with different nickel oxide loading

The anodic peak potential of NiO_GM0.04:SDS0_UH modified electrode corresponding to the oxidation peak potential of dopamine is observed at 0.35 V. The anodic current response of NiO_GM0.04:SDS0_UH with different amounts of nickel oxide loading was shown in Figure 5.8, the anodic peak current was continuously increased with increasing of nickel oxide from 0.0 to 0.0780 mg. For more than 0.0078 mg, anodic current response decreases. This result could be attributed to the coverage of nickel oxide on electrode. The loading of nickel oxide more than 0.078 mg results

in too thick layer of nickel oxide on electrode, unfavorable for electron transfer and diffusion of dopamine to the nickel oxide modified electrode, and leading to lower anodic current response [50]. So, the 0.078 mg of loading of nickel oxide was used in this study for further study.

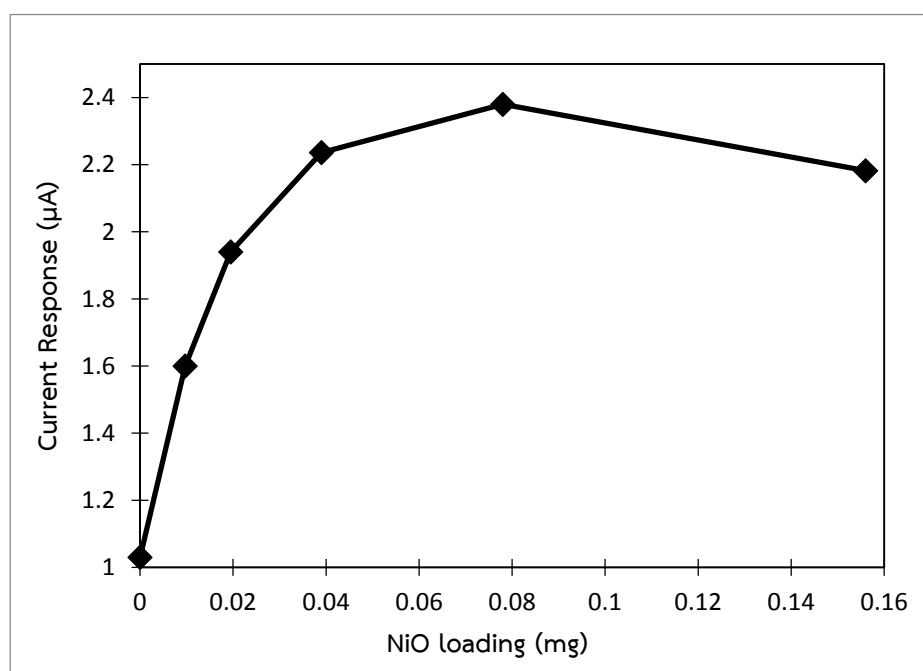


Figure 5. 8 Anodic peak current response of NiO_GM0.04:SDSO_UH modified electrode with different nickel oxide loading

5.3 The effect of surfactant on synthesis of nickel oxide by urea as a precipitant

Surfactant was added in the synthesis to act as a template that provides porous nickel oxide after calcination of precipitate. The use of different types and concentrations of surfactant could alter morphology and size of nickel oxide [51]. The surfactant was added during the synthesis of nickel oxide by urea as a precipitating agent with hydrothermal treatment at 150 °C.

5.3.1 The physical property of nickel oxide

Physical property of nickel oxide could affect sensitivity of surface electrode for electrochemical dopamine detection. The synthesis of nickel oxide was carried out using urea as a precipitating agent with hydrothermal treatment at 150 °C. Figure 5.9 shows the XRD patterns of the synthesized nickel oxide, showing only peaks of nickel oxide. There are no diffraction peaks from other impurities observed in this XRD patterns. The diffraction peaks in this XRD pattern are narrow and sharp, indicating the good crystallinity of synthesized nickel oxide.

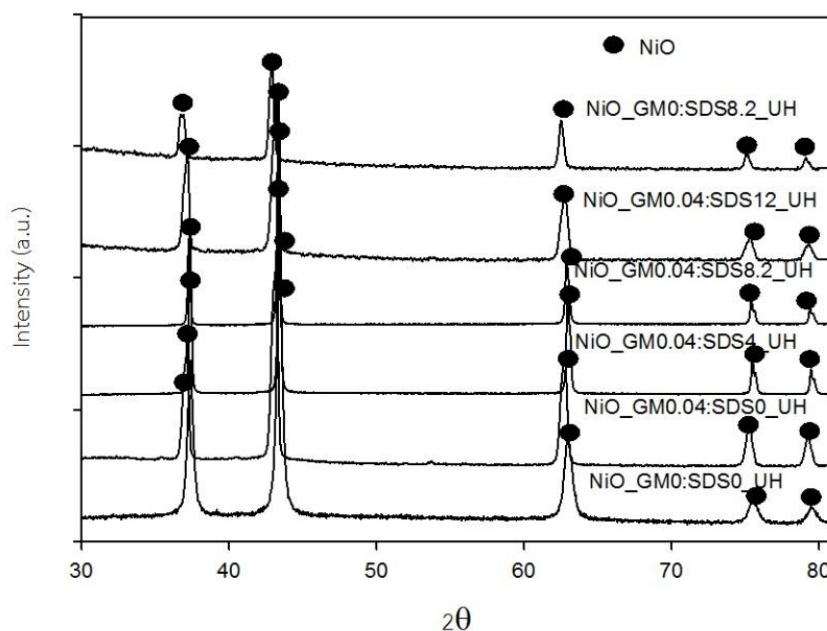
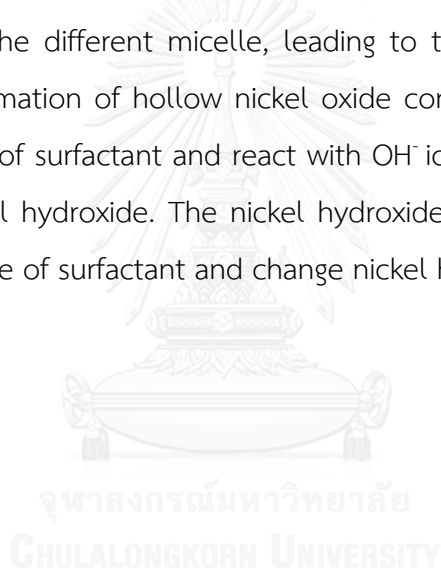


Figure 5. 9 XRD patterns of the synthesized nickel oxide by urea as a precipitating agent with different surfactant concentrations

Morphology of nickel oxide modified with different concentrations of surfactant is shown in Figure 5.10. Unmodified nickel oxide shows fluffy morphology (Figure 5.10 (a)). The addition of surfactant provides spherical particle of nickel oxide, Figures 5.10 (b), 5.10(c), 5.10(d), 5.10(f) but nickel oxide in Figure 5.10(e) shows thin layer morphology different from the others. The results show the adding of surfactant can change the morphology of the synthesized nickel oxide. The adding of only one surfactant shows the spherical particle, addition of gemini surfactant shows smaller particle of nickel oxide than the addition of only SDS probably due to the smaller of micelle of gemini surfactant. The addition of different concentrations of two surfactants during the synthesis affects the monomer of SDS and gemini surfactant which are connected to form the different micelle, leading to the different morphologies of nickel oxide. The formation of hollow nickel oxide comes the connection between Ni^{2+} ion with micelle of surfactant and react with OH^- ions from hydrolysis of urea at 150 °C to form nickel hydroxide. The nickel hydroxide was calcined in combustion process to decompose of surfactant and change nickel hydroxide to nickel oxide[52].



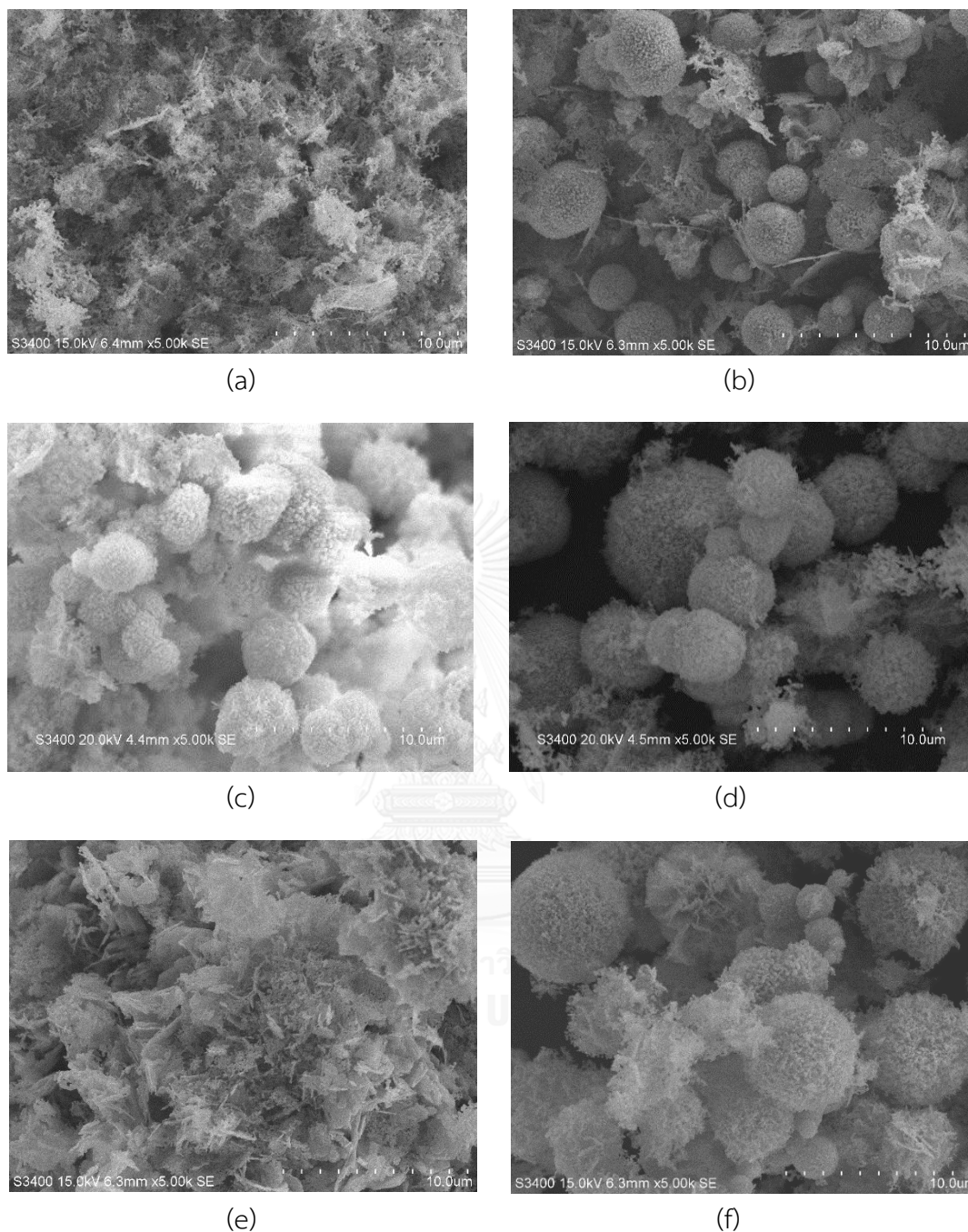


Figure 5. 10 Morphology of synthesized nickel oxide by using urea as a precipitating agent with different of concentration of surfactant (a) NiO_GM0:SDS0_UH, (b) NiO_GM0.4:SDS0_UH, (c) NiO_GM0.04:SDS4_UH, (d) NiO_GM0.4:SDS8.2_UH, (e) NiO_GM0.4:SDS12_UH, (f) NiO_GM0:SDS8.2_UH.

5.3.2 Dopamine detection by electrochemical sensor of synthesized nickel oxide

The effect of surfactant on nickel oxide modified electrode for detection of dopamine was shown by cyclic voltammograms in Figure 5.11. The results show that all modified electrodes have an anodic potential at 0.3 V, which is a negative shift from 0.37 of anodic potential of the bare electrode. The current response was increased for both of the anodic and cathodic currents. The anodic current response of nickel oxide modified electrode was shown in Figure 5.12. All of the nickel oxide modified electrode except NiO_GM0.4:SDS12_UH can improve the current response when compared with nickel oxide (no addition of surfactant) modified electrode. This result shows more efficient electron transfer of nickel oxide modified electrode. The spherical shape of nickel oxide modified electrode shows higher anodic current response than others. A NiO_GM0.4:SDS8.2_UH shows the highest anodic peak current response. These results were evidenced by SEM images of NiO_GM0.4:SDS8.2_UH.

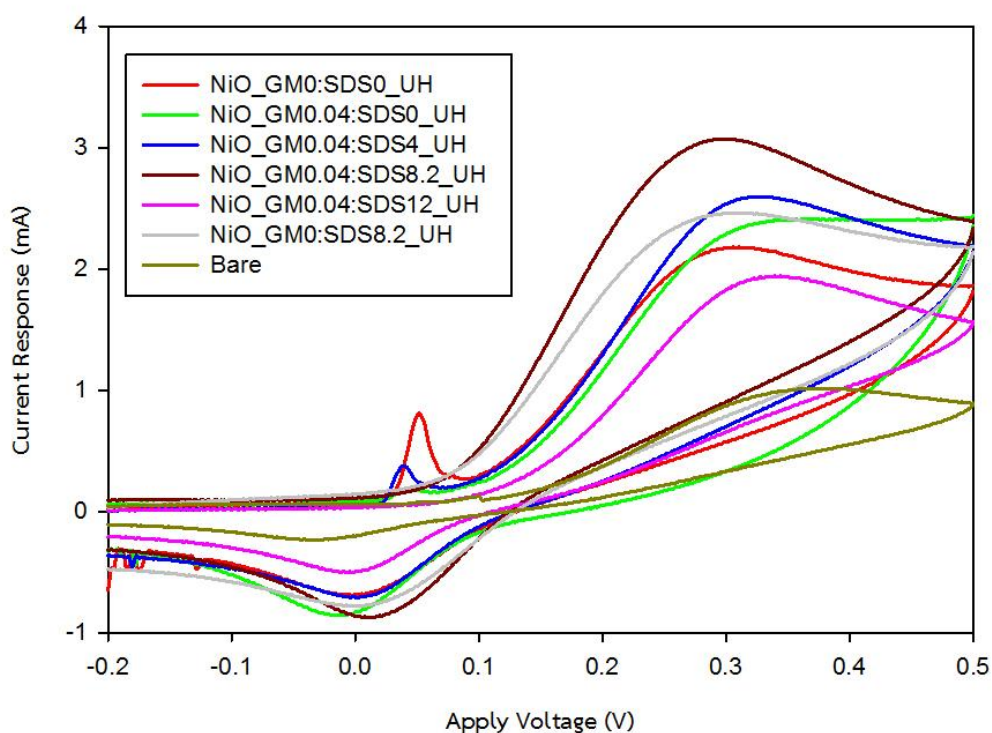


Figure 5. 11 Cyclic voltammograms of NiO synthesis by urea as precipitating agent with different surfactant concentrations in 10 mM PBS (pH 7.0) containing 50 μ M of Dopamine at a scan rate of 50 mV/S.

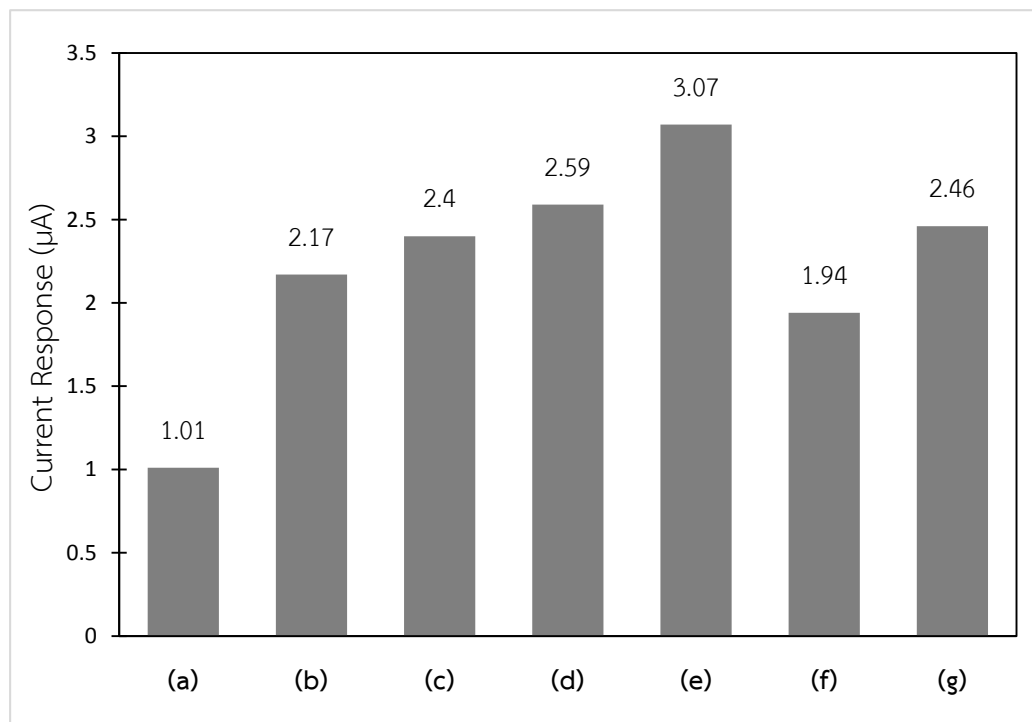


Figure 5. 12 Current response of NiO synthesis by urea as precipitating agent with different surfactant concentrations in 10 mM PBS (pH 7.0) contained 50 µM of Dopamine at a scan rate of 50 mV/S. (a) Bare electrode (b) NiO_GM0:SDS0_UH, (c) NiO_GM0.4:SDS0_UH, (d) NiO_GM0.04:SDS4_UH, (e) NiO_GM0.4:SDS8.2_UH, (f) NiO_GM0.4:SDS12_UH, (g) NiO_GM0:SDS8.2_UH

5.4 The effect of surfactant on synthesis nickel oxide by sodium hydroxide as a precipitating agent

This section reports the effect of surfactant addition during synthesis of nickel oxide by sodium hydroxide as a precipitating agent with hydrothermal treatment at 150 °C, the same condition as the synthesis using urea as the precipitating agent.

5.4.1 The physical property of nickel oxide

The XRD patterns of modified nickel oxide are shown in Figure 5.13. The results show only peaks of nickel oxide and the addition of surfactant does not affect phase of nickel oxide. The diffraction peaks of XRD pattern are also narrow and sharp, which indicates good crystallinity, similar to the modified nickel oxide by urea.

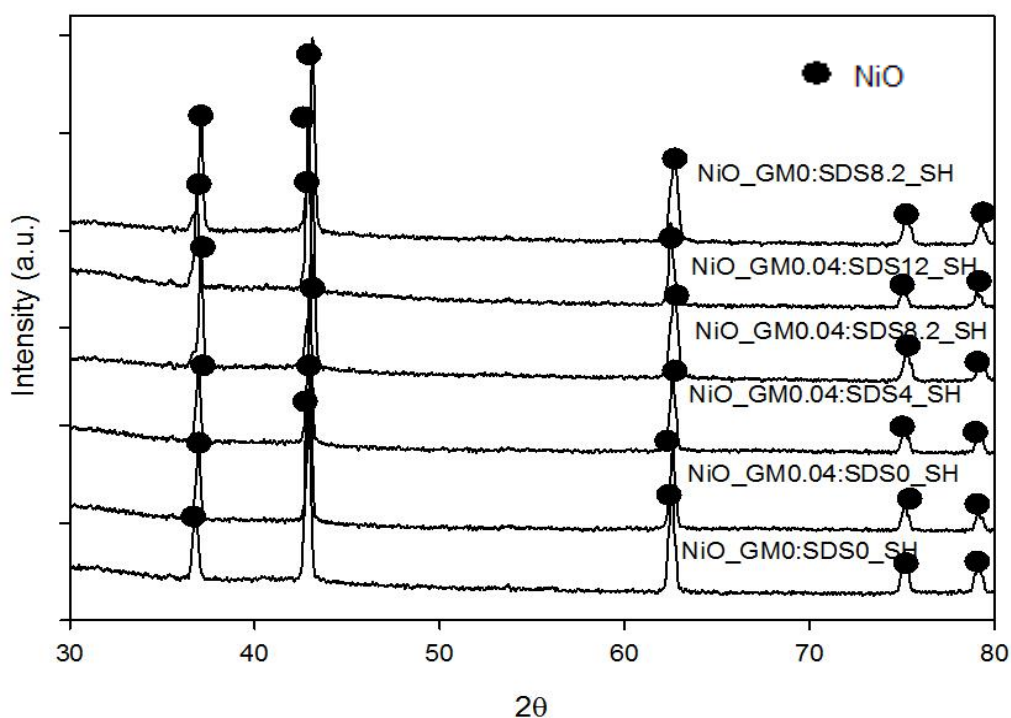


Figure 5. 13 XRD patterns of the synthesized nickel oxide by sodium hydroxide as a precipitating agent with different surfactant concentrations

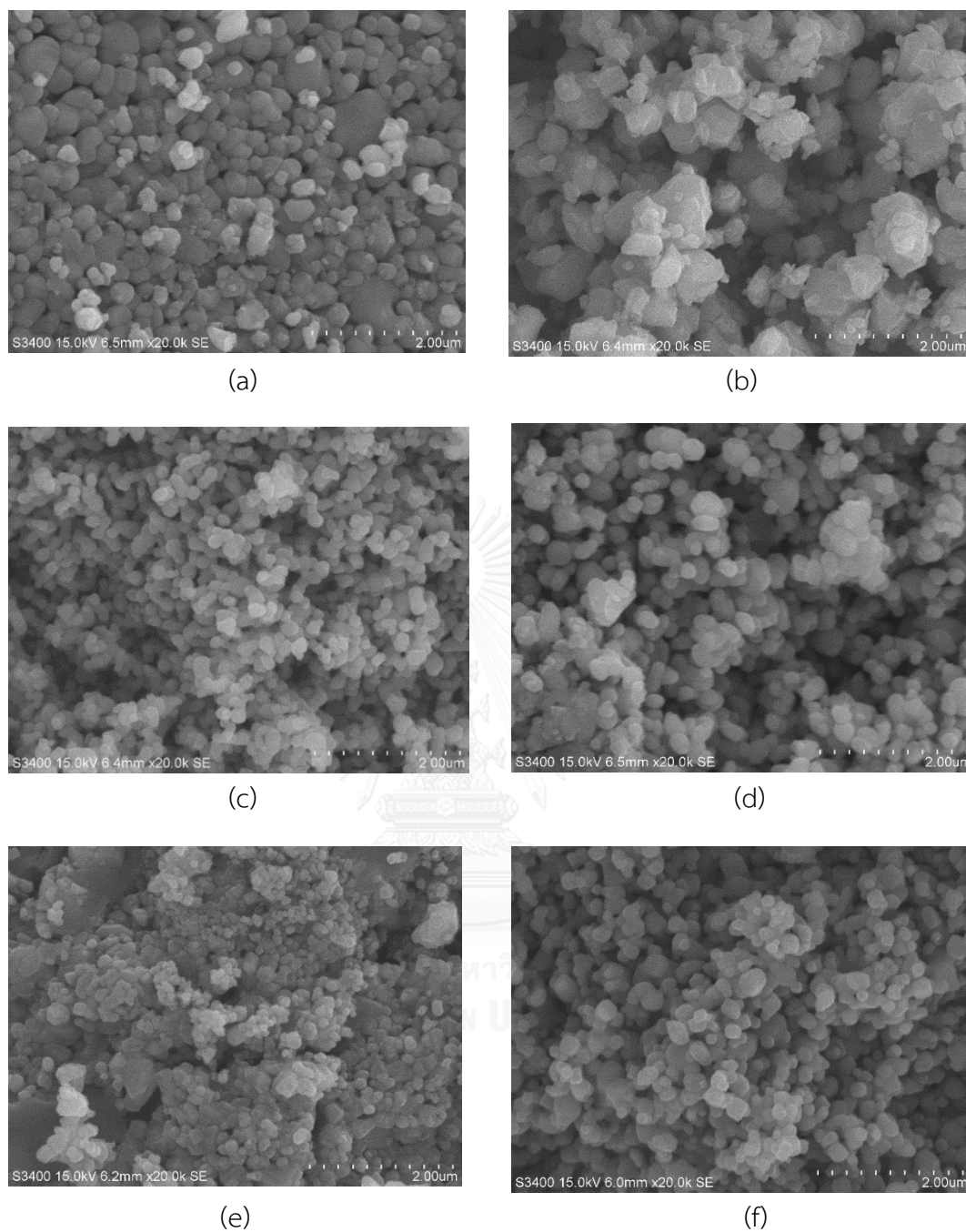


Figure 5. 14 Morphology of the synthesized nickel oxide by using sodium hydroxide as precipitating agent with different concentrations of surfactant (a) NiO_GM0:SDS0_SH, (b) NiO_GM0.4:SDS0_SH, (c) NiO_GM0.04:SDS4_SH, (d) NiO_GM0.4:SDS8.2_SH, (e) NiO_GM0.4:SDS12_SH, (f) NiO_GM0:SDS8.2_SH

Morphology of modified nickel oxide is shown in Figure 5.14. The unmodified nickel oxide shows dense packing of nickel oxide. The addition of only gemini surfactant or SDS during the synthesis show more porosity when compared with the unmodified nickel oxide. The addition of mixed surfactant shows greater porous nickel oxide, the increase of SDS concentration from 4 to 8.2 mM with a fixed gemini surfactant concentration at 0.04 mM shows the larger particle of nickel oxide.

5.4.2 Dopamine detection by electrochemical sensor of synthesized nickel oxide

The study of the effect of surfactant on nickel oxide modified electrode for detection of dopamine are shown by cyclic voltammograms in Figure 5.15. The results show all of the modified electrodes have a negative shift of anodic potential from the bare electrode at an anodic potential of 0.37. The current response also increases for both anodic and cathodic currents similar to the nickel oxide modified electrode by urea with surfactant. The anodic current response of nickel oxide modified electrode are shown in Figure 5.16. Nickel oxide modified electrode can improve the current response when compared with the nickel oxide (no addition of surfactant) modified electrode. The porous surface of nickel oxide modified electrode (NiO_GM0.4:SDS4_SH) shows the highest anodic peak current response. This result is consistent with the SEM image of NiO_GM0.4:SDS4_SH, which shows small particle size with porous surface that leads to higher sensitive area for detection. So, NiO_GM0.4:SDS4_SH was chosen to study the effect of hydrothermal temperature.

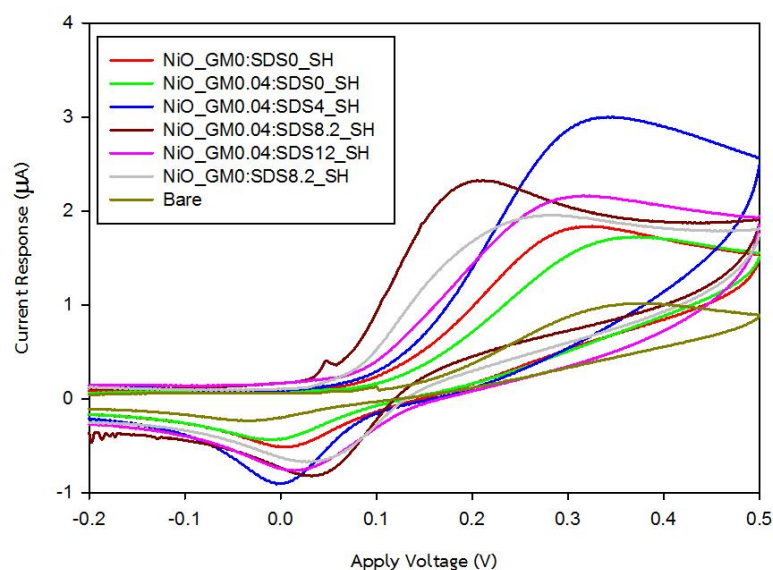


Figure 5. 15 Cyclic voltammograms of NiO synthesis by sodium hydroxide as a precipitating agent with different surfactant concentrations in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S.

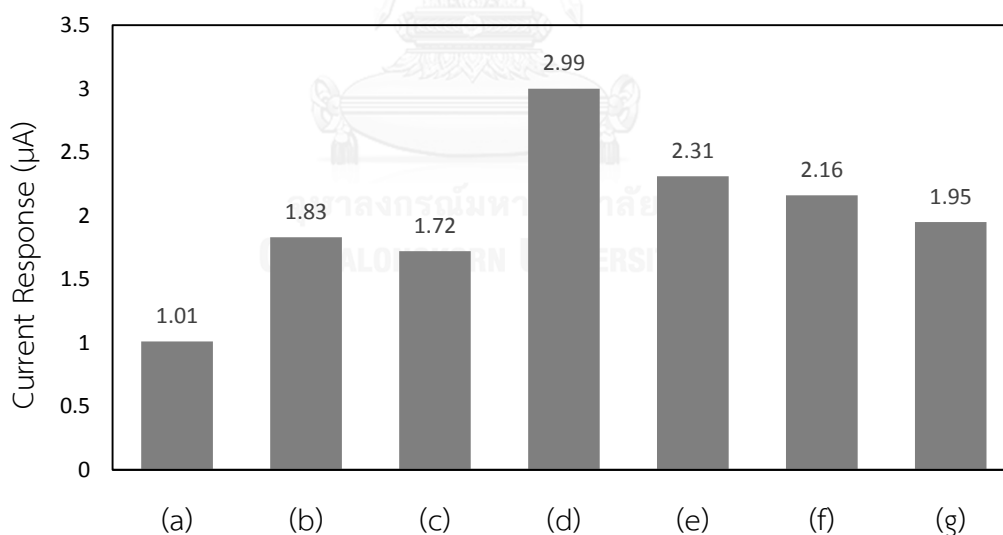


Figure 5. 16 Current response of NiO synthesis by sodium hydroxide as a precipitating agent with different surfactant concentrations in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S. (a) Bare electrode (b) NiO_GM0:SDS0_SH, (c) NiO_GM0.04:SDS0_SH, (d) NiO_GM0.04:SDS4_SH, (e) NiO_GM0.04:SDS8.2_SH, (f) NiO_GM0.04:SDS12_SH, (g) NiO_GM0:SDS8.2_SH

5.5 The effect of hydrothermal temperature in synthesis nickel oxide by precipitation method

The effect of temperature of hydrothermal treatment during synthesis on size, morphology and structural of nickel oxide was studied. The different temperature should lead to different detection sensitivities of nickel oxide modified electrode. In this study, the temperature of hydrothermal treatment was varied 100 °C, 120 °C, 150 °C.

5.5.1 The effect of hydrothermal temperature during synthesis by use urea as a precipitating agent

5.5.1.1 The physical property of nickel oxide

Physical property of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures is shown in Figure 5.17. The results show only peaks of nickel oxide. The different hydrothermal temperature does not affect to phase of nickel oxide. The diffraction intensity of modified nickel oxide is stronger and narrow with increasing hydrothermal temperature, which means higher crystallinity of synthesized nickel oxide. Morphology of nickel oxide with different hydrothermal treatments are shown in Figure 5.18. The results show hydrothermal temperature at 100 °C obtained irregular shaped with nanoplate of nickel oxide. When hydrothermal temperature was increased to 120 °C and 150 °C, the flower-like shape (connected nanoplate) and the hollow spherical shape of nickel oxide were observed, respectively. The different shapes of nickel oxide for different hydrothermal temperatures is because during the synthesis, at lower temperature of 100°C, nickel hydroxide are easily formed to nanoplate because of their intrinsic lamellar structure. When hydrothermal temperature was increased, the hydrolysis of urea provided more OH⁻ ions so that Ni²⁺ reacted with more OH⁻ ions to form the nickel hydroxide flower-like shaped and hollow spherical shaped respectively[52].

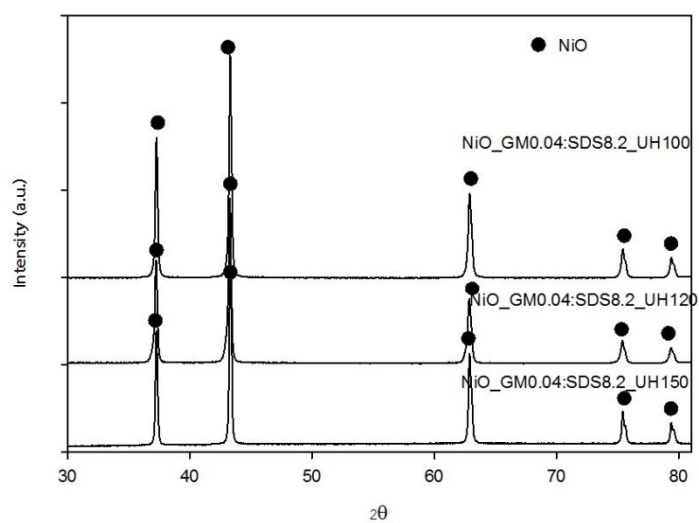


Figure 5. 17 XRD patterns of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures (100 °C, 120 °C, 150 °C)

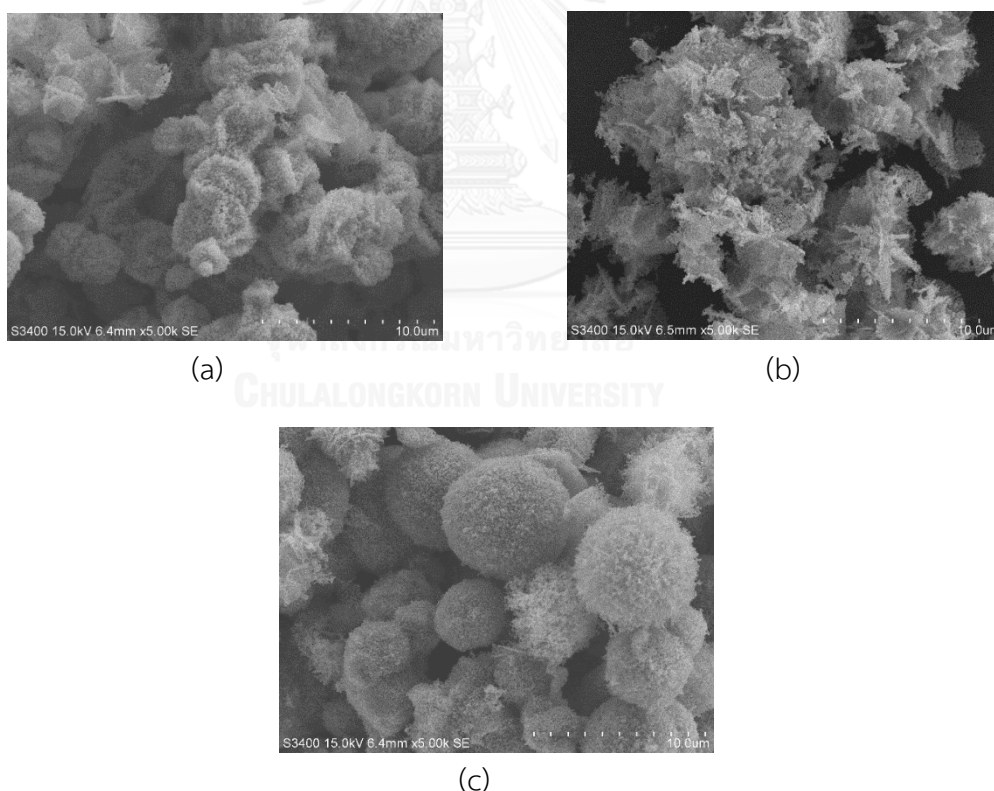


Figure 5. 18 Morphology of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures (a) NiO_GM0.04:SDS8.2_UH100, (b) NiO_GM0.04:SDS8.2_UH120 and (c) NiO_GM0.04:SDS8.2_UH150

5.5.1.2 Dopamine detection by electrochemical sensor of synthesized nickel oxide

The study of the effect of hydrothermal temperature on nickel oxide modified electrode for detection of dopamine is shown by cyclic voltammograms in Figure 5.19. NiO_GM0.04:SDS8.2_UH120 shows the highest anodic current response (in Figure 5.20) for dopamine detection at an anodic potential of 0.3 V. The result could be due to the star shape of NiO_GM0.04:SDS8.2_UH120 offering larger electron transfer area than the other nickel oxide modified electrodes.

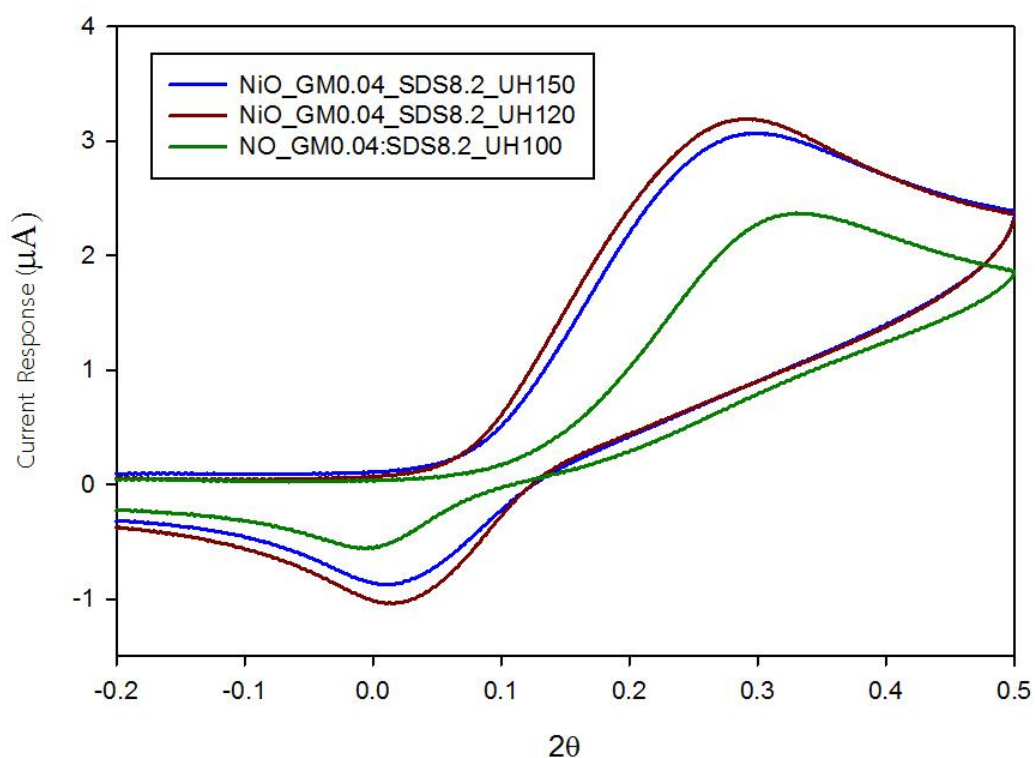


Figure 5. 19 Cyclic voltammograms of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S.

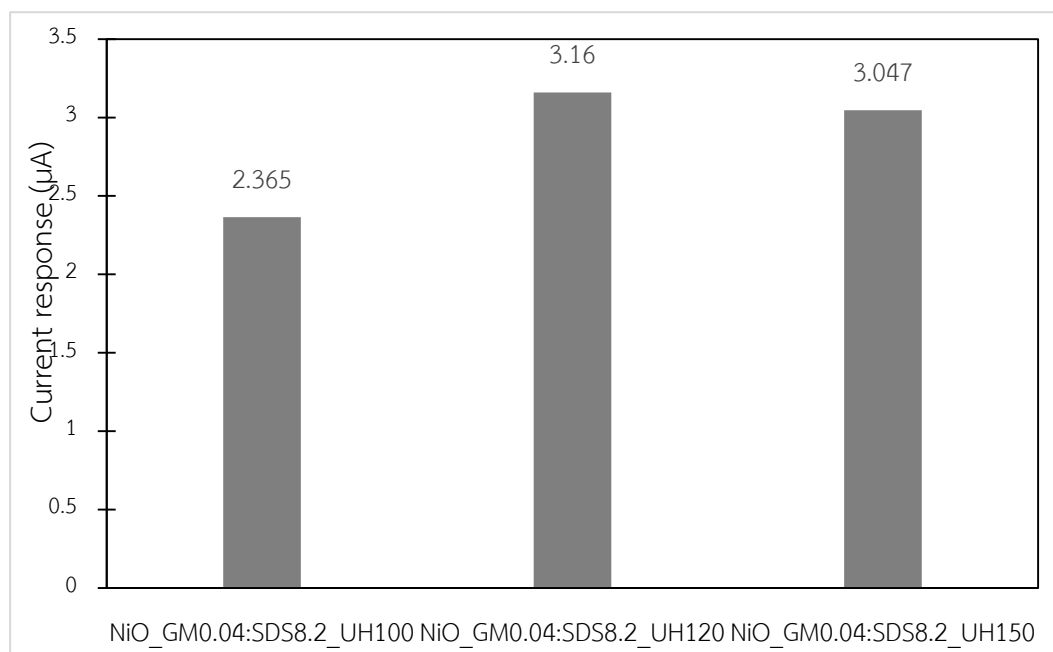
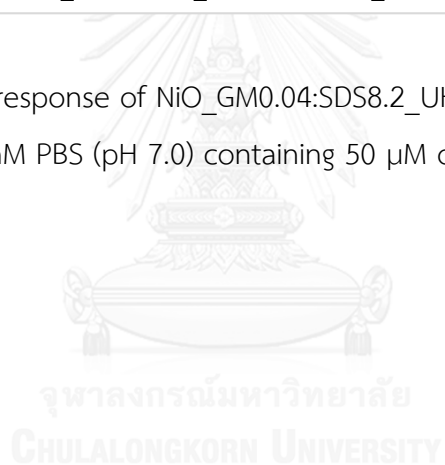


Figure 5. 20 Current response of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures in 10 mM PBS (pH 7.0) containing 50 µM of Dopamine at a scan rate of 50 mV/S.



5.5.2 The effect of hydrothermal temperature during synthesis by use sodium hydroxide as a precipitating agent

5.5.2.1 The physical property of nickel oxide

The physical property of NiO_GM0.04:SDS4_SH with different hydrothermal temperatures are shown in Figure 5.21. The result shows only peaks of nickel oxide, indicating that the different hydrothermal temperature does not affect phase of nickel oxide. The diffraction peaks in this XRD pattern are also narrow and sharp that show the good crystallinity of synthesized nickel oxide. Morphology of nickel oxide with different hydrothermal treatment is shown in Figure 5.22. The results show NiO_GM0.04:SDS4_SH150 has the smaller particle than others.

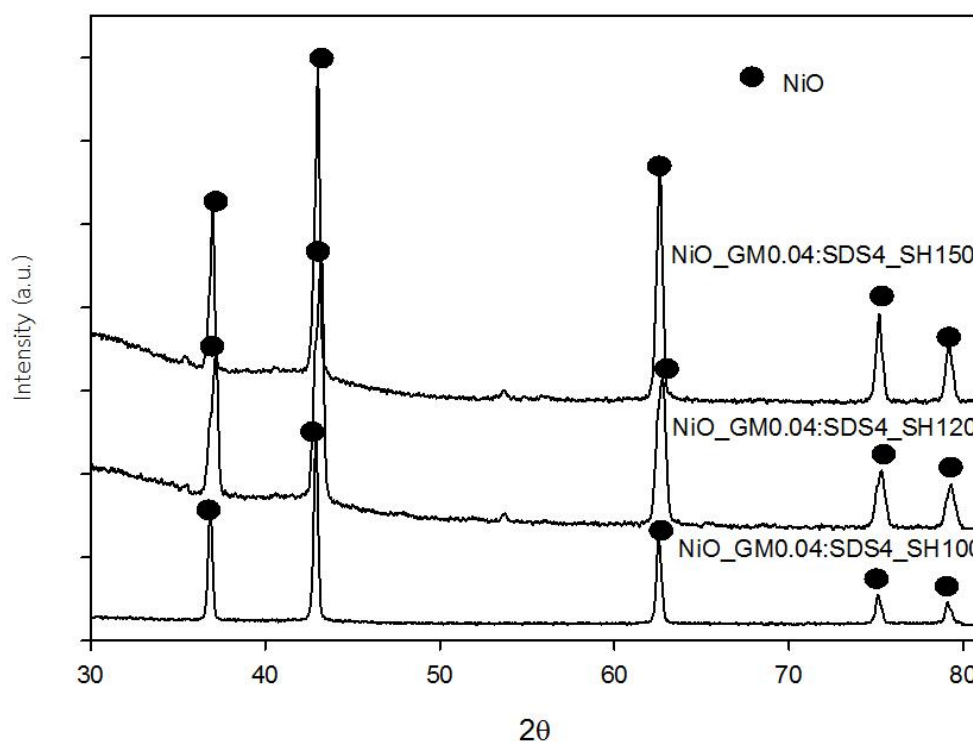


Figure 5. 21 XRD patterns of NiO_GM0.04:SDS4_SH with different hydrothermal temperatures (100 °C, 120 °C, 150 °C)

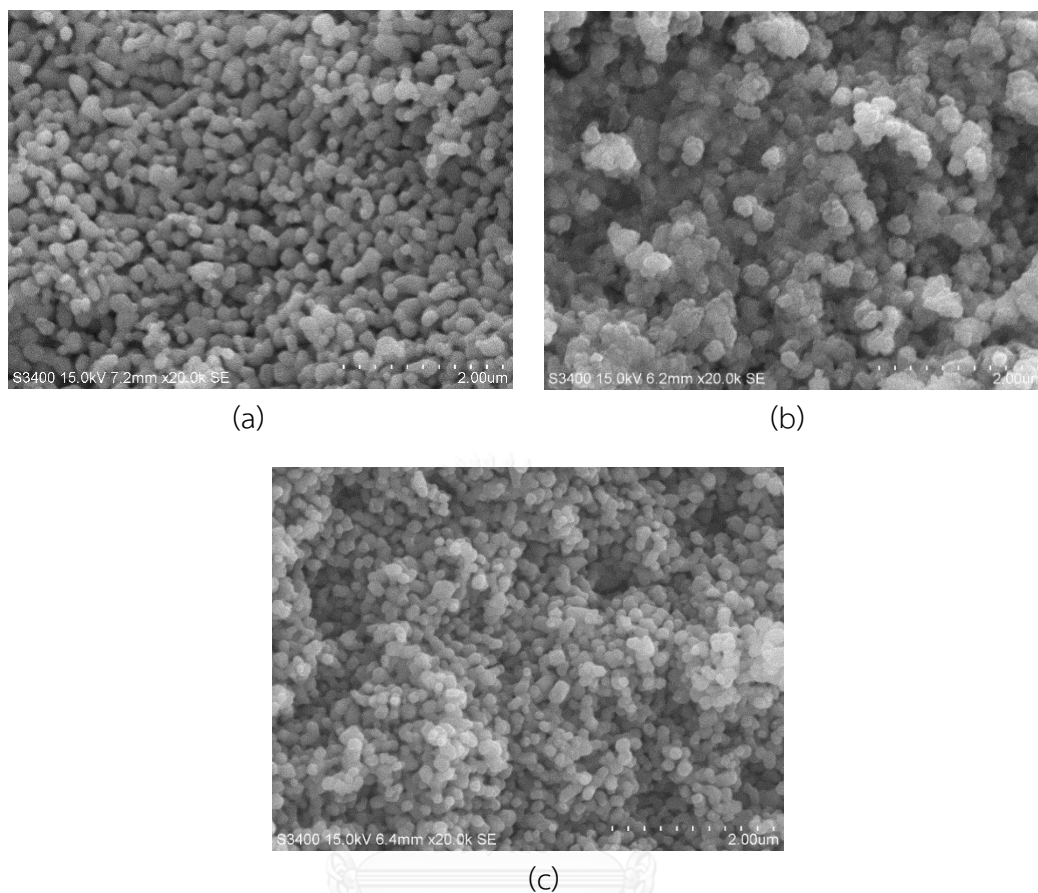


Figure 5. 22 Morphology of NiO_GM0.04:SDS8.2_UH with different hydrothermal temperatures (a) NiO_GM0.04:SDS4_SH100, (b) NiO_GM0.04:SDS4_SH120 and (c) NiO_GM0.04:SDS4_SH150

5.5.2.2 Performance of nickel oxide modified electrode for dopamine detection

The study of the effect of hydrothermal temperature on nickel oxide modified electrode for detection of dopamine is shown by cyclic voltammograms in Figure 5.23. NiO_GM0.04:SDS4_SH150 shows the same anodic potential at 0.3 V. and shows the highest anodic current response for dopamine detection (see Figure 5.24). The result is confirmed with SEM of NiO_GM0.04:SDS4_SH150, the smaller particle of nickel oxide shows larger electron transfer area than other nickel oxide modified electrodes.

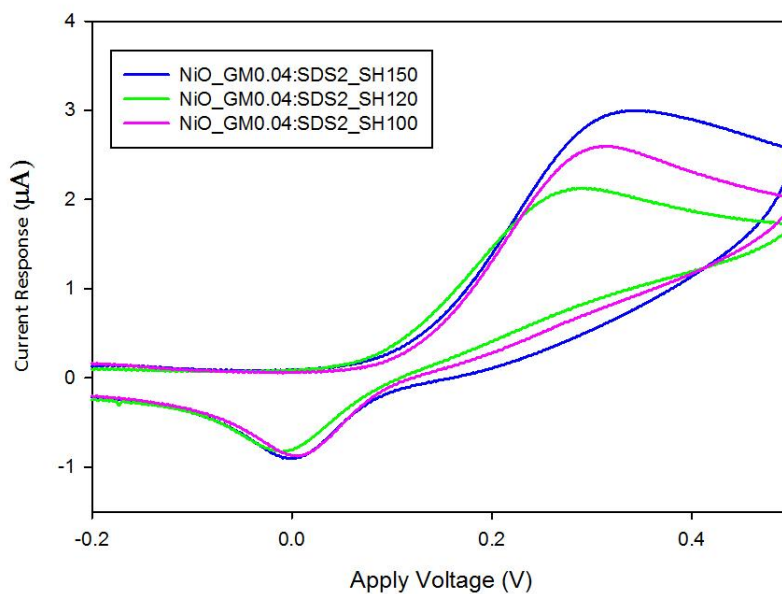


Figure 5. 23 Cyclic voltammograms of NiO_GM0.04:SDS4_SH with different hydrothermal temperatures in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S.

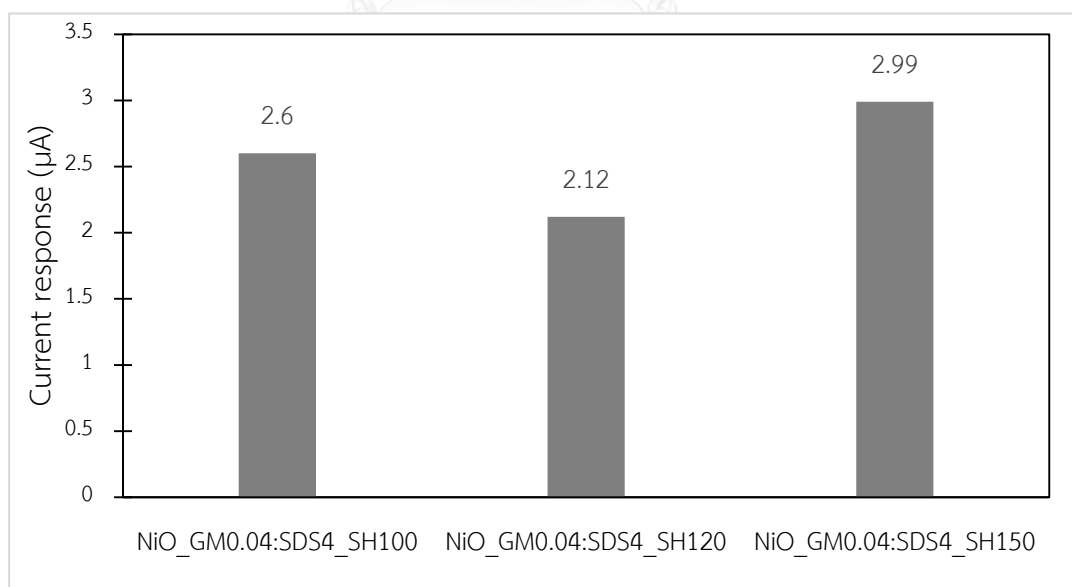


Figure 5. 24 Current response of NiO_GM0.04:SDS4_SH with different hydrothermal temperatures in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 50 mV/S.

5.6 Performance factor of nickel oxide modified electrode for dopamine detection

The performance factor of nickel oxide modified electrode was investigated by cyclic voltammetry. This section is to find the characteristics of nickel oxide modified electrode and the performance factors, which include linear range, limit of detection, sensitivity and reusability of nickel oxide modified electrode for dopamine detection.

5.6.1 Kinetic reaction behavior of nickel oxide modified electrode

The effect of scan rate on the response of nickel oxide modified electrode was investigated to study the kinetics of electrode reaction. Figures 5.25 and 5.27 show the cyclic voltammogram responses of NiO_GM0.04:SDS8.2_UH120 and NiO_GM0.04:SDS4_SH150 modified electrode in the range of scan rate from 25 – 300 mV/s. The results show that the anodic and cathodic peak currents increase linearly with increasing square root of scan rate as shown in Figure 5.26 and Figure 5.28. The linear regression equation of NiO_GM0.04:SDS8.2_UH120 modified electrode are calculated as:

$$I_{pa} = 0.3189\mathbf{V}+0.3218 \text{ (}\mu\text{A, mV/s, } R^2 = 0.999) \quad (5.9)$$

$$I_{pc} = -0.2409\mathbf{V}+0.8179 \text{ (}\mu\text{A, mV/s, } R^2 = 0.9996) \quad (5.10)$$

for NiO_GM0.04:SDS4_SH150 electrode are

$$I_{pa} = 0.4359\mathbf{V}+0.1007 \text{ (}\mu\text{A, mV/s, } R = 0.9998) \quad (5.11)$$

$$I_{pc} = -0.2817\mathbf{V}+1.0148 \text{ (}\mu\text{A, mV/s, } R = 0.9955) \quad (5.12)$$

The results indicates that the electrochemical reaction of dopamine at NiO_GM0.04:SDS8.2_UH120 electrode and NiO_GM0.04:SDS4_SH150 electrode was a diffusion-controlled electrochemical behavior.

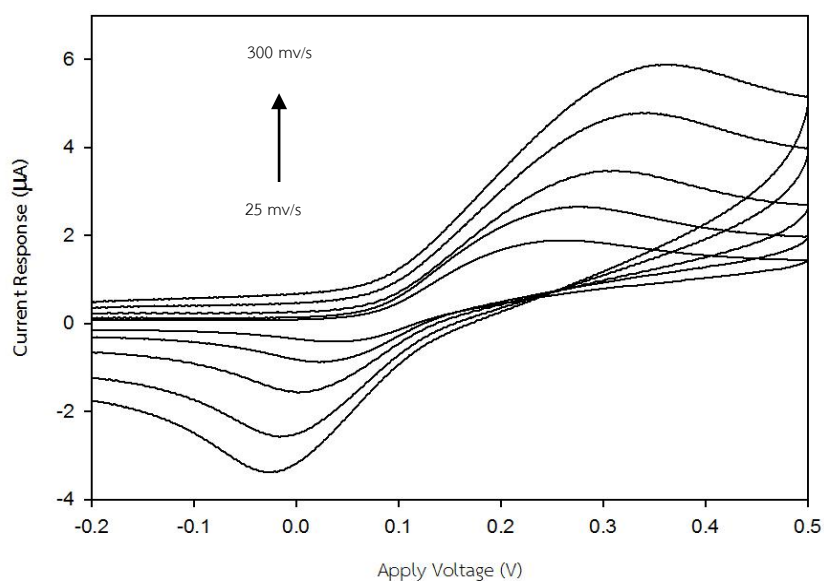


Figure 5. 25 Cyclic voltammograms of NiO_GM0.04:SDS8.2_UH120 in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine at a scan rate of 25-300 mV/s.

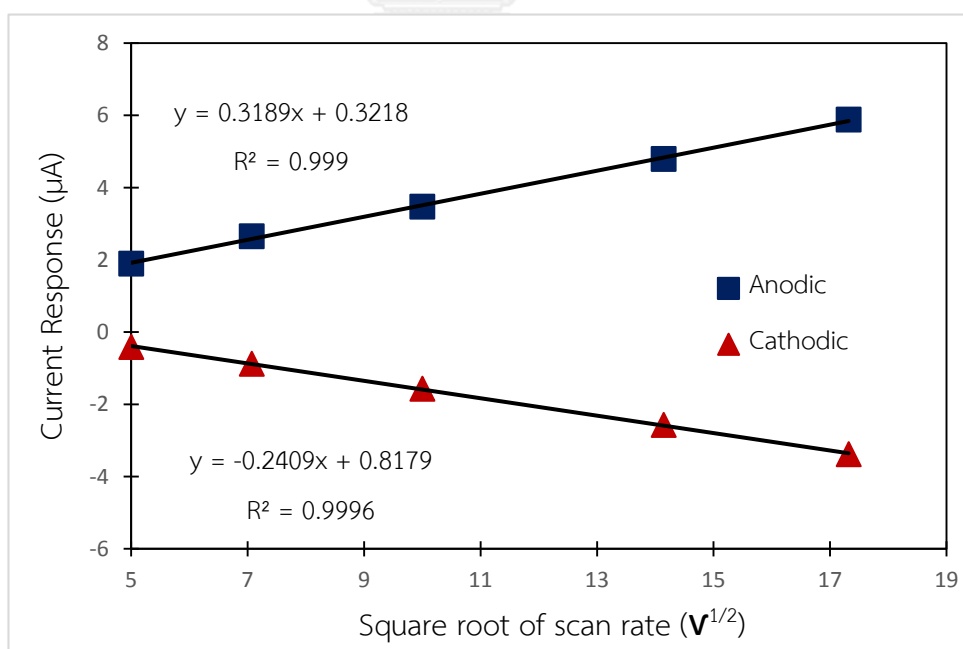


Figure 5. 26 Relationship between current response and square root of scan rate of NiO_GM0.04:SDS8.2_UH120 in 10 mM PBS (pH 7.0) containing 50 μM of Dopamine

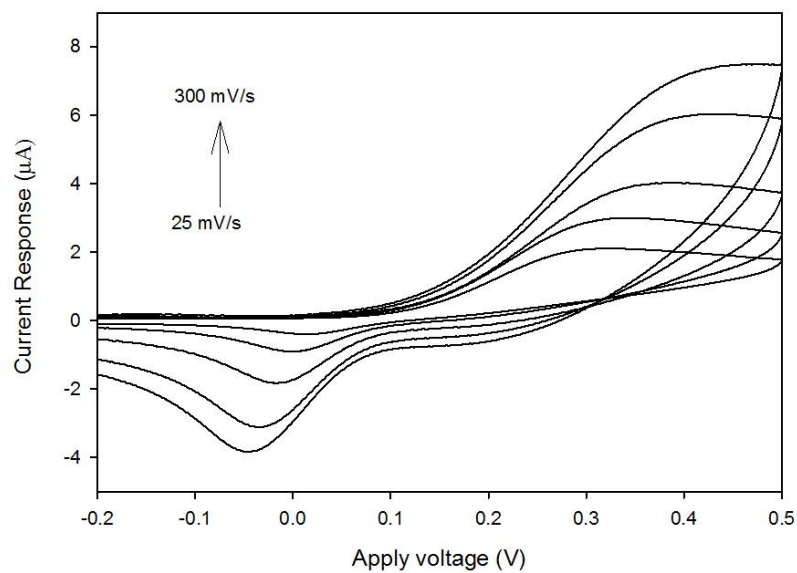


Figure 5. 27 Cyclic voltammograms of NiO_GM0.04:SDS4_SH150 in 10 mM PBS (pH 7.0) containing 50 µM of Dopamine at a scan rate of 25-300 mV/s.

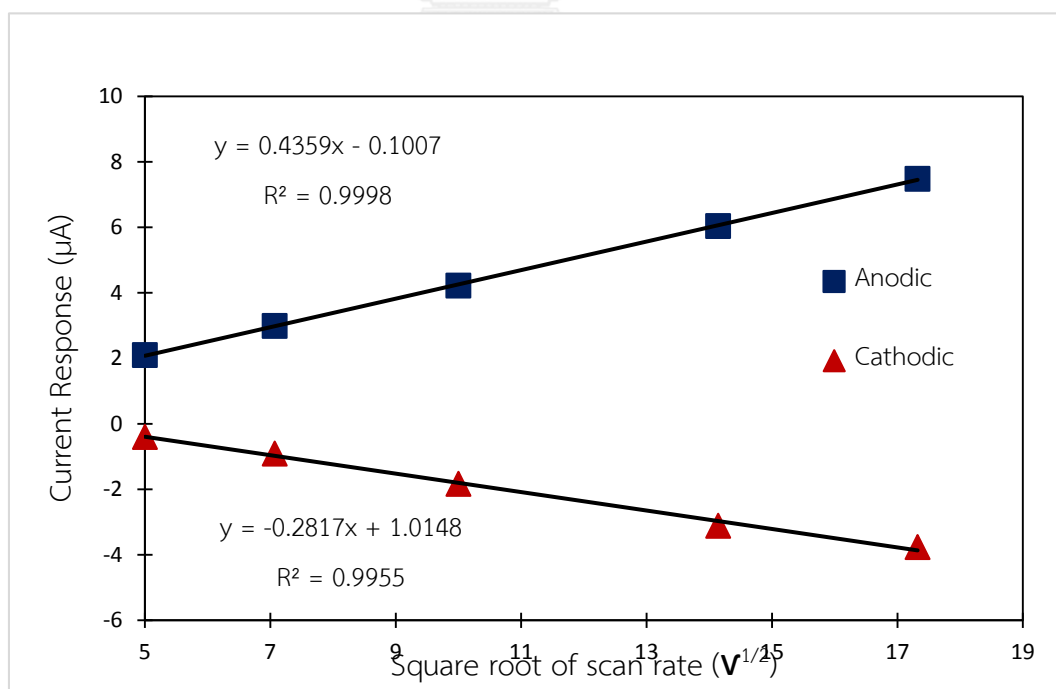


Figure 5. 28 Relationship between current response and square root of scan rate of NiO_GM0.04:SDS4_SH150 in 10 mM PBS (pH 7.0) containing 50 µM of Dopamine

5.6.2 Limit of detection

Limit of detection and sensitivity of nickel oxide modified electrode were determined for different dopamine concentrations as shown in Figures 5.29-5.32, respectively. The sensitivity of modified electrode was calculated from the ratio of current change to the concentration of dopamine change, which is a slope of calibration curve. The limit of detection was calculated from the following equation:

$$\text{Limit of detection} = 3S_d/m \quad (5.13)$$

where S_d is the standard deviation of the current response at the lowest detected concentration ($n = 3$)

m is the slope of anodic linear equation of dopamine detection at low concentration

The summary of the performance factor of nickel oxide modified electrode for dopamine detection is shown in Table 5.1. The cyclic voltammogram as a function of dopamine of NiO_GM0.04:SDS8.2_UH120 and NiO_GM0.04:SDS4_SH150 modified electrode are shown two linear ranges of for the range of concentration studied in this work. The first linear was found at 3.125 μ M – 100 μ M and the second linear range was found at 100 μ M – 500 μ M. Low linear concentration of both of nickel oxide modified electrode show higher sensitivity for dopamine response than high linear concentration. Limit of detection shows that NiO_GM0.04:SDS8.2_UH120 modified electrode can detect lower concentration of dopamine than NiO_GM0.04:SDS4_SH150.

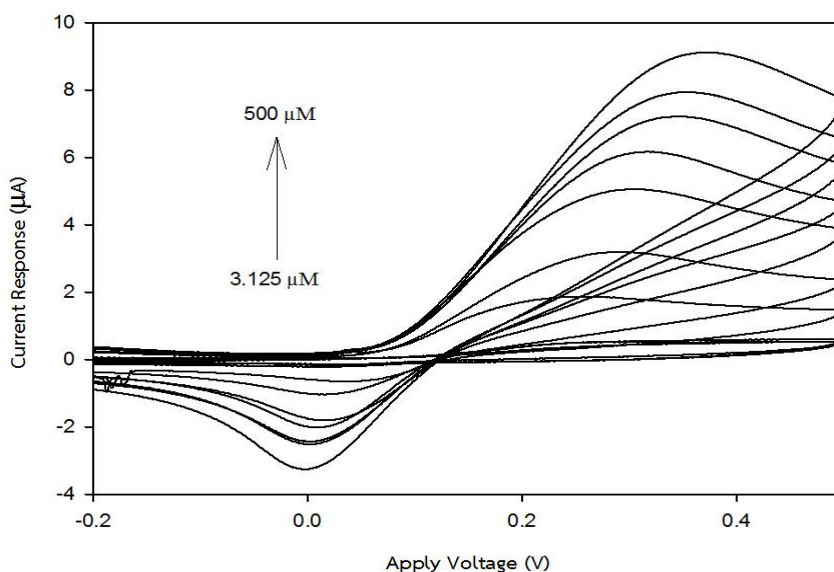


Figure 5. 29 Cyclic voltammograms of NiO_GM0.04:SDS8.2_UH120 in 10 mM PBS (pH 7.0) containing 3.125-500 μM of Dopamine at a scan rate of 50 mV/s.

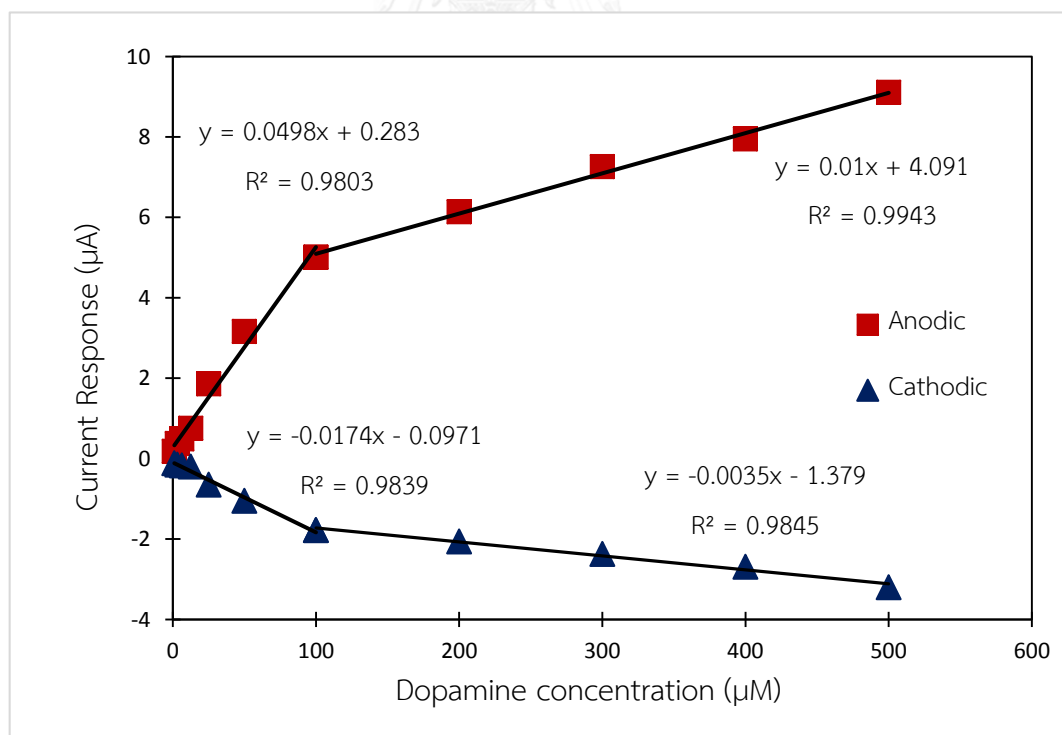


Figure 5. 30 Calibration curves of dopamine current response of NiO_GM0.04:SDS8.2_UH120 modified electrode in 10 mM PBS (pH 7.0) at a scan rate of 50 mV/s.

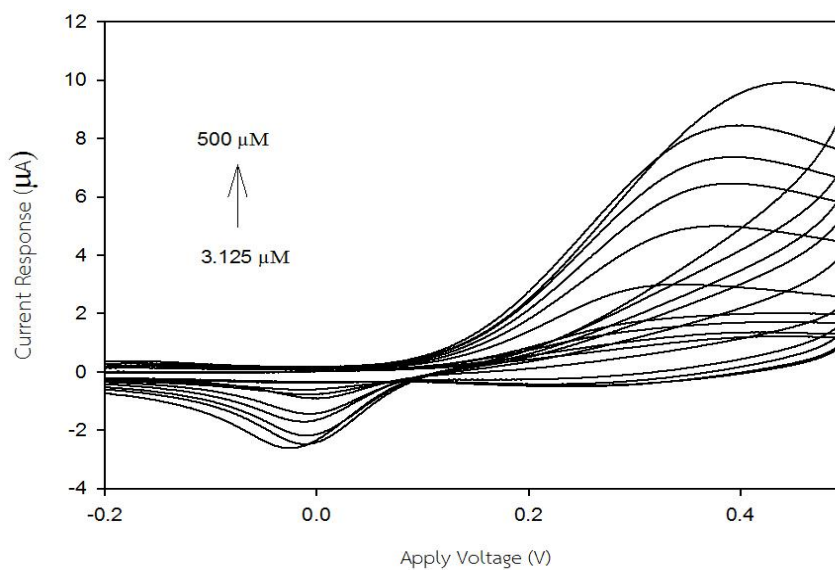


Figure 5. 31 Cyclic voltammograms of NiO_GM0.04:SDS4_SH150 in 10 mM PBS (pH 7.0) contained 3.125-500 μM of Dopamine at a scan rate of 50 mV/s.

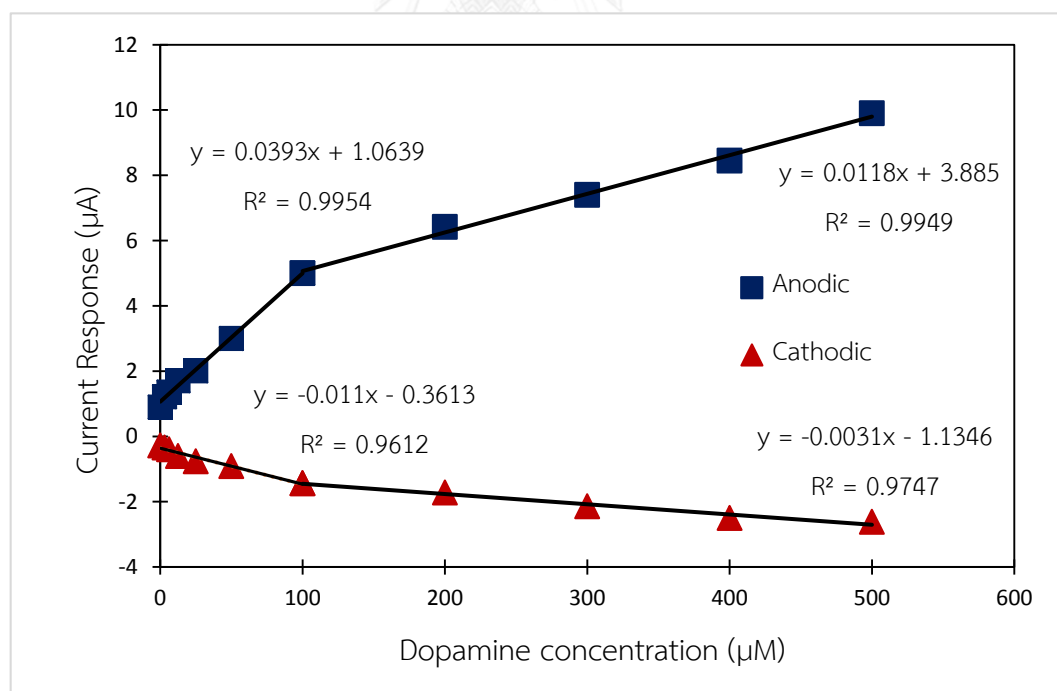


Figure 5. 32 Calibration curves of dopamine current response of NiO_GM0.04:SDS4_SH150 modified electrode in 10 mM PBS (pH 7.0) at a scan rate of 50 mV/s.

Table 5. 1 The performance factor of nickel oxide modified electrode for dopamine detection

Electrode	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Limit of detection (μM)
NiO_GM0.04:SDS8.2_UH120	3.125 - 100	0.0498	1.75
	100 - 500	0.01	
NiO_GM0.04:SDS4_SH150	3.125 - 100	0.0393	2.75
	100 - 500	0.0118	



5.6.3 Comparison of performance factors to other researches

The electrochemical parameters for dopamine detection were compared with other research and the results were listed in Table 5.2. It can be seen that the nickel oxide modified electrode for dopamine detection show high sensitivity and wide linear range.

Table 5. 2 Comparison of the performance factor for dopamine detection with other researches

Electrode	Morphology of NiO	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Limit of detection (μM)	Ref.
NiO/Graphene	granule	1 -10 10 -500	0.0399 0.0048	0.31	[7]
Enzyme/NiO	Semi-spherical	2-100	0.0600	1.04	[46]
NiO_GM0.04:SDS8.2_UH120	Star shaped	3.125-100 100-500	0.0498 0.0100	1.75	This work
NiO_GM0.04:SDS4_SH150	Spherical	3.125-100 100-500	0.0393 0.0118	2.75	

CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

This study investigated the use of modified nickel oxide as the catalyst for dopamine detection. The results showed that dopamine can be determined by cyclic voltammetry as electrons generated from dopamine under the potential at 0.3 V. The concentration of dopamine was directly proportional to the measured current.

The optimum condition and ability of nickel oxide modified electrode for dopamine detection are summarized as follows:

6.1.1 Precipitating agent affects morphology of nickel oxide. Nickel oxide using urea as a precipitating agent offered fuzzi morphology whereas nickel oxide using sodium hydroxide showed denser packing particle.

6.1.2 The increase of SDS concentration in mixed surfactants of SDS and C12-C₁₂Br provided larger size of NiO particle for both of nickel oxide synthesis by using sodium hydroxide and urea as a precipitant.

6.1.3 Hydrothermal temperature affects the morphology of the synthetic nickel oxide. For NiO_GM0.04:SDS8.2_UH with hydrothermal temperature at 120 °C and NiO_GM0.04:SDS4_SH with hydrothermal temperature at 150 °C gave higher sensitive area that show better dopamine response when compared to NiO modified at other temperatures.

6.1.4 Nickel oxide loading on the electrode of 0.078 mg or 0.011 mg/mm² provided the highest dopamine response.

6.1.5 NiO_GM0.04:SDS8.2_UH120 shows the best performance factor that have two detection ranges. The low concentration show detection at 3.125 to 100 µM and sensitivity of 0.0498 µA/µM. The high concentration show detection at 100 to 500 µM and sensitivity of 0.01 µA/µM. The limit of detection is 1.75 µM

6.2 Recommendation

6.2.1 The coating method and solvent for preparation of modified electrode are interesting for the future study in order to improve the dispersion of nickel oxide on electrode and time for preparation of modified electrode.

6.2.2 The study of interferences such as uric acid and ascorbic acid should be studied due to close oxidation potential of real samples.



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APPENDIX



APPENDIX

Raw Data

A lot of data obtain from cyclic voltammetry for one graph. So, this data were not shown. The tables show the response current that from cyclic voltammetry method.

Table A. 1 Peak response of cyclic voltammetry of bare electrode and nickel oxide modified electrode (potential -0.5 to 0.5 V, scan rate at 50 mV/s)

Electrode	Potential (V)		Current Response (μA)	
	E_{pa}	E_{pc}	I_{pa}	I_{pc}
Bare	0.37	-0.031	1.01	-0.234
NiO_UH	0.30	-0.007	2.18	-0.688
NiO_SH	0.31	-0.005	1.83	-0.516

Table A. 2 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO_GM0.04:SDS0_UH) (potential -0.5 to 0.5 V, scan rate at 50 mV/s)

NiO loading (mg)	Current Response (μA)	
	I_{pa}	I_{pc}
0.0000	1.01	-0.234
0.0097	1.60	-0.414
0.0195	1.94	-0.587
0.0390	2.24	-0.645
0.0780	2.38	-0.858
0.1560	2.18	-0.660

Table A. 3 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO synthesis by precipitation method with urea as a precipitating agent, hydrothermal at 150 °C and different concentration of surfactant) at potential -0.5 to 0.5 V, scan rate at 50 mV/s.

Electrode	Surfactant (mM)		Current Response(μ A)	
	C12-C4- C12,2Br	SDS	I_{pa}	I_{pc}
NiO_GM0:SDS0_UH	0.00	0.00	2.17	-0.691
NiO_GM0.04:SDS0_UH	0.04	0.00	2.40	-0.858
NiO_GM0.04:SDS4_UH	0.04	4.00	2.59	-0.699
NiO_GM0.04:SDS8.2_UH	0.04	8.20	2.68	-0.795
NiO_GM0.04:SDS12_UH	0.04	12.00	1.94	-0.504
NiO_GM0:SDS8.2_UH	0.00	8.20	2.46	-0.781

Table A. 4 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO synthesis by precipitation method with sodium hydroxide as a precipitating agent, hydrothermal at 150 °C and different concentration of surfactant) at potential -0.5 to 0.5 V, scan rate at 50 mV/s.

Electrode	Surfactant (mM)		Current Response(μ A)	
	C12-C4- C12,2Br	SDS	I_{pa}	I_{pc}
NiO_GM0:SDS0_SH	0.00	0.00	1.83	-0.516
NiO_GM0.04:SDS0_SH	0.04	0.00	1.72	-0.439
NiO_GM0.04:SDS4_SH	0.04	4.00	3.00	-0.849
NiO_GM0.04:SDS8.2_SH	0.04	8.20	2.31	-0.822
NiO_GM0.04:SDS12_SH	0.04	12.00	2.16	-0.765
NiO_GM0:SDS8.2_SH	0.00	8.20	1.95	-0.673

Table A. 5 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO_GM0.04:SDS8.2_UH) synthesis by precipitation method with urea as a precipitating agent, hydrothermal at 100, 120, 150 °C) at potential -0.5 to 0.5 V, scan rate at 50 mV/s.

Electrode	Hydrothermal Temperature (°C)	Current Response (μA)	
		I_{pa}	I_{pc}
NiO_GM0.04:SDS8.2_UH150	150	3.05	-0.875
NiO_GM0.04:SDS8.2_UH120	120	3.16	-1.037
NiO_GM0.04:SDS8.2_UH100	100	2.36	-0.557

Table A. 6 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO_GM0.04:SDS4_SH) synthesis by precipitation method with urea as a precipitating agent, hydrothermal at 100, 120 and 150 °C at potential -0.5 to 0.5 V, scan rate at 50 mV/s.

Electrode	Hydrothermal Temperature (°C)	Current Response (μA)	
		I_{pa}	I_{pc}
NiO_GM0.04:SDS4_SH150	150	2.99	-0.907
NiO_GM0.04:SDS4_SH120	120	2.12	-0.825
NiO_GM0.04:SDS4_SH100	100	2.60	-0.875

Table A. 7 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO_GM0.04:SDS8.2_UH120) synthesis by precipitation method with urea as a precipitating agent, hydrothermal at 120 °C at potential -0.5 to 0.5 V, scan rate at 25-300 mV/s.

Scan rate (mV/s)	Potential (V)		Current Response (μA)	
	E_{pa}	E_{pc}	I_{pa}	I_{pc}
25	0.26	0.037	1.89	-0.412
50	0.27	0.022	2.65	-0.877
100	0.31	0.003	3.47	-1.570
200	0.33	-0.017	4.79	-2.570
300	0.36	-0.024	5.88	-3.380

Table A. 8 Peak response of cyclic voltammetry of nickel oxide modified electrode (NiO_GM0.04:SDS4_SH150) synthesis by precipitation method with sodium hydroxide as a precipitating agent, hydrothermal at 150 °C at potential -0.5 to 0.5 V, scan rate at 25-300 mV/s.

Scan rate (mV/s)	Potential (V)		Current Response (μA)	
	E_{pa}	E_{pc}	I_{pa}	I_{pc}
25	0.32	0.012	2.10	-0.399
50	0.34	-0.004	2.99	-0.907
100	0.39	-0.017	4.22	-1.830
200	0.43	-0.036	6.04	-3.110
300	0.47	-0.043	7.48	-3.760

Table A. 9 Peak response of cyclic voltammetry of dopamine calibration curve of nickel oxide modified electrode (NiO_GM0.04:SDS8.2_UH120) synthesis by precipitation method with urea as a precipitating agent, hydrothermal at 120 °C at potential -0.5 to 0.5 V in 10 mM PBS, scan rate at 50 mV/s.

Dopamine concentration (μM)	Current Response (μA)						SD	RSD (%)
	$I_{pa(1)}$	I_{pc}	$I_{pa(2)}$	$I_{pa(3)}$	$I_{pa(4)}$	$I_{pa(avg)}$		
0	0.179	-0.115						
3.125	0.374	-0.152	0.377	0.394	0.337	0.369	0.029	
6.25	0.490	-0.172	0.500	0.447	0.577	0.533	0.054	12.98
12.5	0.754	-0.200						
25.0	1.860	-0.650						
50.0	3.160	-1.050	3.010	2.660	2.990	2.955	0.196	6.65
100.0	5.010	-1.780						
200.0	6.140	-2.060						
300.0	7.260	-2.370	7.040	7.210	7.710	7.305	0.286	3.91
400.0	7.950	-2.690						
500.0	9.110	-3.200						

Table A. 10 Peak response of cyclic voltammetry of dopamine calibration curve of nickel oxide modified electrode (NiO_GM0.04:SDS4_SH150) synthesis by precipitation method with sodium hydroxide as a precipitating agent, hydrothermal at 150 °C at potential -0.5 to 0.5 V in 10 mM PBS, scan rate at 50 mV/s.

Dopamine concentration (μM)	Current Response (μA)						SD	RSD (%)
	$I_{pa(1)}$	I_{pc}	$I_{pa(2)}$	$I_{pa(3)}$	$I_{pa(4)}$	$I_{pa(avg)}$		
0	0.900	-0.276						
3.125	1.217	-0.340	1.200	1.250	1.270	1.222	0.036	
6.25	1.358	-0.390	1.540	1.360	1.450	1.427	0.090	6.30
12.5	1.708	-0.600						
25.0	2.010	-0.760						
50.0	3.000	-0.907	3.150	3.200	3.290	3.160	0.071	2.45
100.0	5.000	-1.430						
200.0	6.420	-1.716						
300.0	7.400	-2.139	7.320	7.560	7.200	7.370	0.183	2.49
400.0	8.450	-2.496						
500.0	9.900	-2.614						

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