NICKEL-GRAPHENE COMPOSITE AMPEROMETRIC SENSOR FOR THE DETECTION OF FORMALDEHYDE

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Thesis
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ABSTRACT

Formaldehyde is the most active aldehyde with disinfection ability, killing bacteria and stopping bacteria from growing, although it has been banned internationally from food and food-related products due to high toxicity that leads to dizziness, vomiting and, in extreme cases, death. In this work, the sensor was fabricated relying on catalytic activity of nickel nanoparticles immobilized on graphene support (Ni-graphene composite), and was operated in an amperometric mode of an electrochemistry work station. The factors affecting formaldehyde detection studied in this work include; Formaldehyde concentration, %Ni loading in composite material, pH value of background solution, and the presence of interfering substances. The best sensor showed good responses to 1-60 ppm of formaldehyde in pH 13 alkali solution with a sensitivity of ~0.09 ppm^{-1}, and the LOD of 3.05. No significant cross sensitivities were observed against 1,000 ppm benzoic acid (preservative), 1,000 ppm sodium hydrosulfite (bleach) and 250 ppm sodium tetra borate (food additive) at tested concentrations. This research suggested that the sensor can be used for formaldehyde detection in food and food-related products.

KEY WORDS: FORMALDEHYDE/ AMPEROMETRIC SENSOR/ GRAPHENE / NICKEL NANOPARTICLES/ COMPOSITE MATERIAL

58 pages

การตรวจวัดฟอร์มาลดีไฮด์ด้วยระบบเซนเซอร์โดยใช้วัสดุร่วมนิกเกิลบนแกรฟีนเป็นวัสดุตรวจวัด
A NICKEL-GRAPHENE COMPOSITE AMPEROMETRIC SENSOR FOR THE DETECTION OF FORMALDEHYDE

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บทคัดย่อ

ฟอร์มาลดีไฮด์เป็นสารในกลุ่มแอลดีไฮด์ที่มีความไวต่อการเกิดปฏิกิริยาได้ไวที่สุด มีคุณสมบัติในการฆ่าและยับยั้งการเจริญเติบโตของแบคทีเรีย โดยองค์กรนานาชาติได้จัดให้ฟอร์มาลดีไฮด์อยู่ในกลุ่มสารอันตรายและห้ามใช้ในอาหาร หรือผลิตภัณฑ์ที่เกี่ยวกับอาหาร เนื่องจากความเป็นพิษทำให้เกิดอาการปวดหัว อาเจียน และในกรณีร้ายแรงอาจทำให้ถึงแก่ความตาย โดยในงานวิจัยนี้อาศัยคุณสมบัติการเร่งปฏิกิริยาของอนุภาคนาโนของโลหะนิกเกิลที่ถูกตรึงอยู่บนแผ่นแกรฟีน (วัสดุร่วมนิกเกิล-แกรฟีน) มาประดิษฐ์เป็นอุปกรณ์เซนเซอร์ในระบบการตรวจวัดการเปลี่ยนแปลงของกระแสไฟฟ้า (Amperometric mode) โดยอาศัยหลักการไฟฟ้าเคมี โดยในงานวิจัยนี้ได้ศึกษาปัจจัยที่มีผลต่อการตรวจวัดฟอร์มาลดีไฮด์คือ ปริมาณความเข้มข้นของสารฟอร์มาลดีไฮด์ ปริมาณนิกเกิลในวัสดุตรวจวัด ค่าพีเอช และสารรบกวนในระบบ เซนเซอร์ที่ดีที่สุดในงานวิจัยนี้สามารถตอบสนองต่อฟอร์มาลดีไฮด์ในช่วงความเข้มข้น 1-60 มิลลิกรัมต่อลิตร (ppm) ในสารละลายมาตรฐานที่มีสภาวะเป็นเบส (พีเอชเท่ากับ 13) โดยมีค่าความไวที่ 0.09 ลิตรต่อมิลลิกรัม (ppm^{-1}) และค่าความเข้มข้นต่ำสุดที่สามารถตรวจวัดได้ (LOD) ที่ 3.05 ซึ่งเซนเซอร์ที่ผลิตได้มีความเสถียรต่อการตรวจวัด และไม่มีการตอบสนองต่อสารรบกวนอื่นได้แก่ กรดเบนโซอิก (สารกันบูด) โซเดียมไฮโดรซัลไฟต์ (สารฟอกขาว) และ โซเดียมเตรตะโบเรต (สารปรุงแต่งอาหาร) จากงานวิจัยเซนเซอร์จึงมีความเหมาสมในการตรวจวัดสารฟอร์มาลดีไฮด์ที่เจือปนในผลิตภัณฑ์อาหาร

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CHAPTER I
INTRODUCTION

The chapter I shows the introduction of research project, which is composed of Motivation, Objectives and Scopes of research as followed;

1.1 Motivation

Currently, meat and agricultural products, such as fresh vegetable, meat and seafood were found to be illegally contaminated with hazard chemicals in hope to prolong their shelf life and prevent them from being spoiled during transportation. List of hazardous chemicals, according to the Ministry of Public Health report [1], includes preservatives such as bleach (Sodium hydrosulfide) and formalin.

Formalin is an aqueous solution of formaldehyde (37-40%) with methanol (10-15%). On the other hand, formaldehyde is a colorless gas with strong odor that is used heavily as a main reactant for production of urea-formaldehyde, phenolic, melamine, pentaerythritol, and polyacetal resins [2]. It is normally presence in adhesive for wood, plastic board and furniture (Figure 1.1). Although formaldehyde can kill bacteria and keep raw food fresh during transportation, it is a suspected carcinogen and harmful to human, causing eye irritation, severe stomachache, dizziness, and even death. The US Environmental protection agency (EPA) has suggested formaldehyde concentration in drinking water to not exceed Longer-term Health Advisory-draft of 5 mg/L for a child and 20 mg/L for an adult [3]. Arts and his teams [4] studied relation between volume of formaldehyde and carcinogenic in body, and concluded that formaldehyde is carcinogenic.

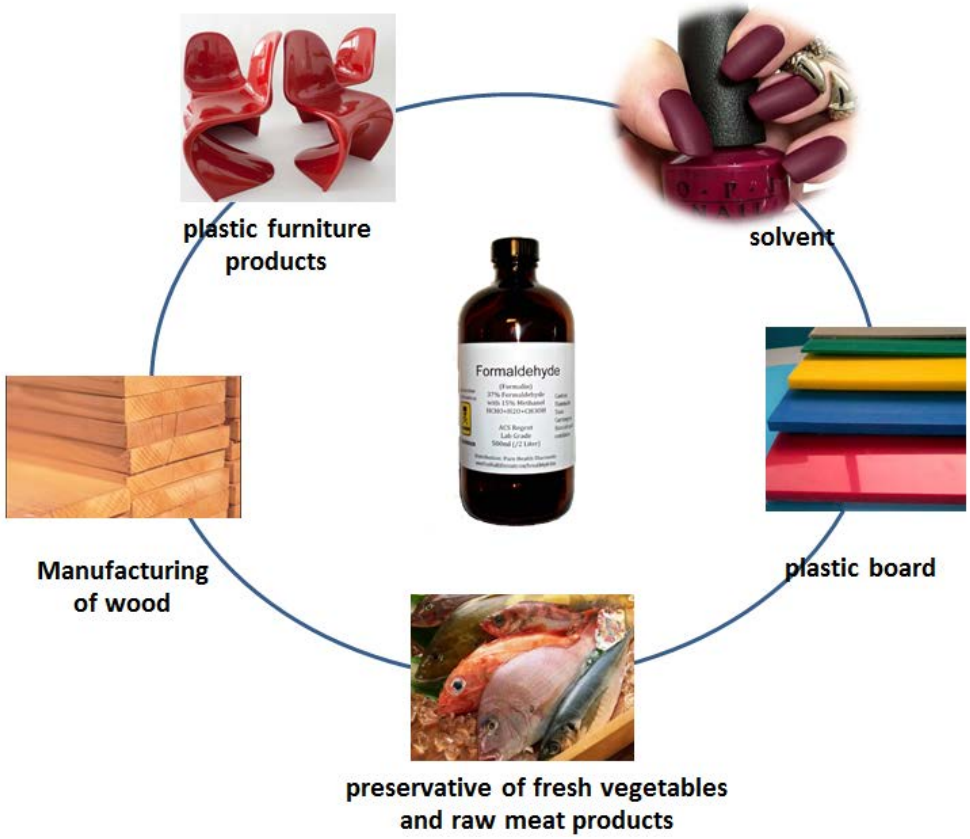

Figure 1.1 Uses of formaldehyde

Different methods, including colorimetry, spectroscopy and chromatography, have been demonstrated and employed for formaldehyde detection. For example, dye chemicals, such as 2,4-dinitrophenyl hydrazine, was coupled with formaldehyde [5] yielding color changes that could be monitored using spectroscopy (colorimetric approach [6]). However, the detection limit was poor and ppm level of formaldehyde detection cannot be achieved. Analytical instruments, HPLC [7], etc., have been used as a standard method in detecting down to few ppm level of formaldehyde. The main issue regarding analytical method test concerns cost and time in sample analysis and requirement on trained personnel.

Amperometric sensor is an electrochemical sensor (Figure 1.2) that relies on 3 electrodes cell which consist of working electrode (WE), reference electrode (RE), and counter electrode (CE). Chemical reactions and physical interactions that lead to charge donation and withdrawing from the WE would generate electrochemical current that would be monitored and recorded as sensor signals. Nickel nanoparticle is an amazing catalyst, showing strong catalytic activity toward formaldehyde [5]. However, an issue regarding nanoparticles is their surface electrostatic charges that attract nanoparticles to come close to one another and become agglomerated.

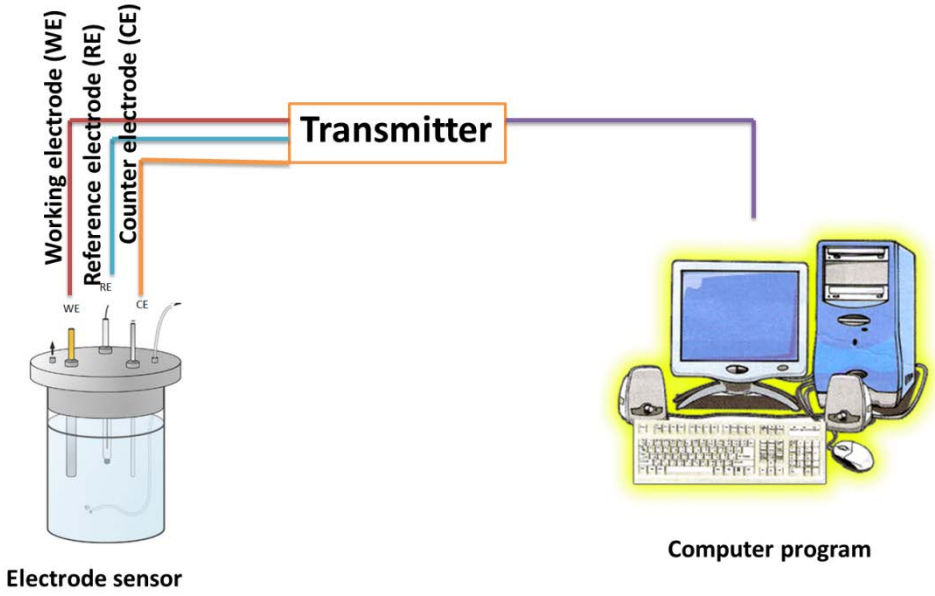

Figure 1.2 Electrochemical sensor systems

In this work, we enhanced the catalytic activity of Ni nanoparticles by compositing it with a charge-transfer promoting graphene support [6], maximizing active area of the Ni nanoparticles. The Ni-graphene composite was synthesized through chemical path whereby Ni nanoparticles were chemically deposited, and immobilized on graphene sheet. The composite was implemented to a WE, and was demonstrated as an amperometric formaldehyde sensor.

1.2 Objectives

Objectives of research include the synthesis of Ni-rGO composite material, the study and characterization of composite behaviors, and the determination of a suitable condition in developing formaldehyde amperometric sensor using Ni-rGO composite.

1.2.1 To synthesize Ni-rGO composite material.

1.2.2 To study sensing performances and mechanisms of Ni-rGO composite for formaldehyde sensing.

1.2.3 To develop a protocol for formaldehyde detection using the Ni-graphene sensor.

1.3 Scopes

Scopes of research consist of the synthesis of Ni-rGO composite via chemical reaction path, the utilization of Ni-rGO composite into WE as amperometric sensor in a 3-electrode system, and the effect of different variables on formaldehyde sensing.

1.3.1 Ni nanoparticles were synthesized and immobilized on graphene support, following chemical reaction approach.

1.3.2 The Ni-graphene composite was incorporated to working electrode of a 3-electrode electrochemical cell, and is operated in amperometric mode.

1.3.3 Variables of interest are %Ni loading (15-50%Ni loading), pH of solution (10-13), formaldehyde concentration (0.1- 60 ppm), chemical interferences (against benzoic acid, sodium hydrosulfite and borax), reproducibility and reusability of the sensor.

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Properties and detection of formaldehyde

2.1.1 Properties of Formaldehyde

Formaldehyde is the smallest and most active aldehyde (Figure 2.1) with colorless property and strong odor. It is a suspected carcinogen, causing eyes and respiratory irritation at low concentration and causing conscious lost and even death at high concentration. Formaldehyde is commonly used as adhesive resins in the manufacturing of wood and plastic furniture products [7], and as reactants and solvent in chemical industries [8]. It is also used as a precursor for the synthesis of Melamine formaldehyde, Urea formaldehyde, Phenol-formaldehyde, Polyacetal, and 1,4 Butanediol (Figure 2.2). Formaldehyde is also used as disinfectant, insecticide and illegally used as preservative in fresh vegetables and raw meat products [9]. World Health Organization (WHO) has reported limitation for formaldehyde concentration in various food and food related products, as shown in Table 2.1 and 2.2 [10].

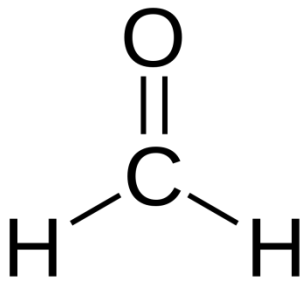

Figure 2.1 Molecular structure of formaldehyde [7]

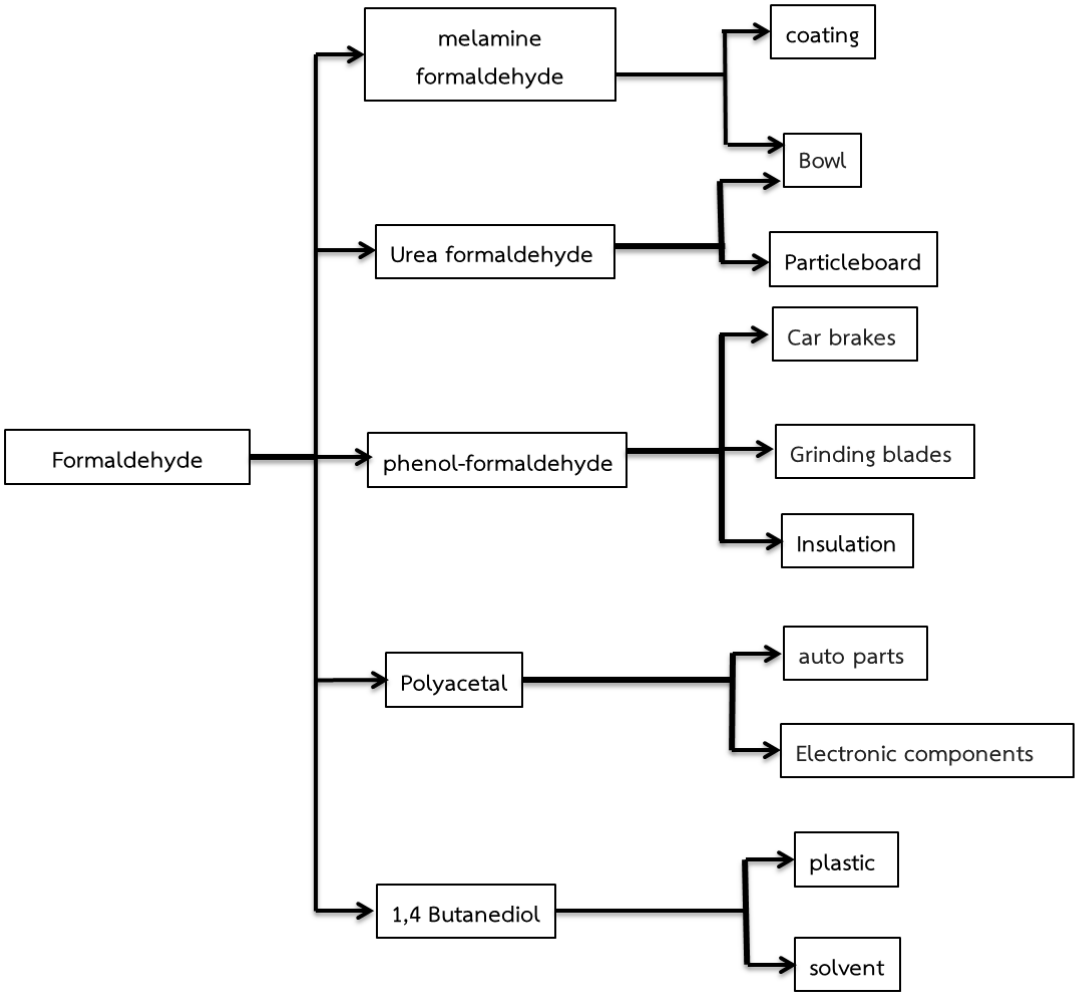

Figure 2.2 Applications of formaldehyde in chemical industries

Table 2.1 Formaldehyde concentration in meat, seafood, and dairy products [10]

Food and product type	Level (ppm)
Meat products	
Beef	4.6
Pig	5.8-20
Sheep	8
Poultry	2.5-5.7
Processed meat products (including ham and sausage)	<20.7
Liver paste	<11.9
Seafood	
Cod	4.6-34
Shrimp	1-1.4
Squid	1.8
Fish ball	6.8
Crustacean	98
Bombay-duck	<140
Dairy products	
Goat’s Milk	1
Cow’s Milk	<3.3
Cheese	<3.3

Table 2.2 Formaldehyde concentration in fruits, vegetables and others food type [10]

Food and product type	Level (ppm)
Fruits and Vegetables	
Apple	6.3-22.3
Apricot	9.5
Banana	16.3
Beetroot	35
Bulb vegetable	11
Cabbage	5.3
Carrot	6.7-10
Cauliflower	26.9
Cucumber	2.3-3.7
Grape	22.4
Green Onion	13.3-26.3
Kohlrabi	31
Pear	38.7-60
Spinach	3.3-7.3
Potato	19.5
Water melon	9.2
White radish	3.7-4.4
Shiitake mushroom (dried)	100
Shiitake mushroom (raw)	6-54.4
Others food type	
Alcoholic beverage	0.02-3.8
Soft drinks	8.7
Brewed coffee	3.4-4.5
Syrup	<1-15.4

2.1.2 Formaldehyde detection

Several methods were introduced for detection of formaldehyde, such as chemical method, colorimetric precipitation, high performance liquid chromatography, and spectrometry.

a. Chemical precipitation

Chemical precipitation is a method relying on reactions of adenosine (Figure 2.3) and formaldehyde producing insoluble precipitate [11]. Formaldehyde concentration can be determined by measuring the obtained precipitate. A detection limit, defined as formaldehyde concentration at which detection signal is 3 times higher than the signal to noise ratio, of 0.5 mg/kg can be achieved via this method.

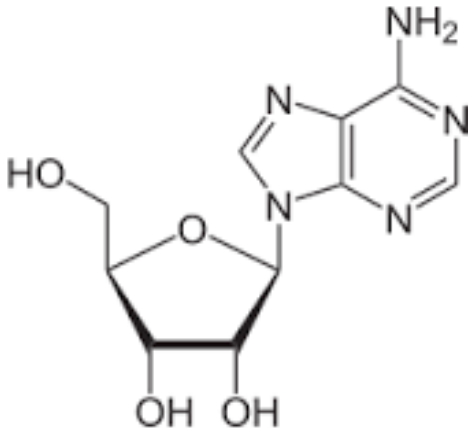

Figure 2.3 Molecular structure of adenosine [11]

b. Colorimetry method

Colorimetry formaldehyde detection utilizes reactions of dyes in concentrated sulfuric acid and formaldehyde solution at 100 ^{o}C to produce quinone, which is purple in color [12]. The color intensity of the solution is measured using UV-vis spectrophotometer (wavelength 578 nm), and calibrated for formaldehyde concentration. A reported detection limit of formaldehyde is 5- 20 µg/ml. An example of utilizing Colorimetry method in formaldehyde detection was demonstrated by Wang x. and et al. [13] Methyl Yellow was used for formaldehyde detection. From

equation 2.1, Methyl Yellow in sulfuric acid (hydroxylamine sulfate: $(NH_2OH)_2 \cdot H_2SO_4$) react with formaldehyde molecules, changing the color of Methyl Yellow from yellow to red. Formaldehyde concentration was determined from the solution's color intensity via UV-Vis spectrometry.

$$2HCHO + (NH_2OH)_2 \cdot H_2SO_4 \rightarrow 2H_2C{=}NOH + H_2SO_4 + 2H_2O \quad \text{(Equation 2.1)}$$

c. High performance liquid chromatography (HPLC)

High performance liquid chromatography (Figure 2.4) is an analytical technique, relying on separation capacity of HPLC column in separating and distinguishing liquid components [14]. HPLC separation potential depends strongly on interactions between stationary phase (coated material on column's surface) and the mobile phase (targeted analytes). The formaldehyde sample is diluted in the mobile phase, and fed through the column. Each chemicals in the solution is separated from one another due to the different interaction with the stationary and mobile phase, and is monitored by a detector. Correlation of detected exited components and time of exiting is plotted, creating chromatograms. One disadvantage regarding HPLC measurement concerns high instrumental cost and need of trained personnel. The limit of detection for formaldehyde is in part per million (ppm) scales.

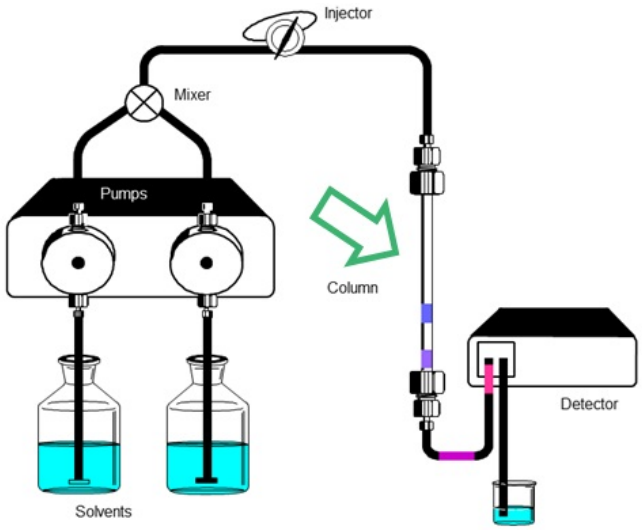

Figure 2.4 Diagram of High performance liquid chromatography [15]

From the research of P. wahed et.al. [16], formaldehyde concentration in fruits, vegetable, milk, fish etc. was determined with HPLC method. HPLC has limit of detection of 0.39, 0.32 and 1.75 mg/l for mango, milk, and fish respectively. The highest formaldehyde concentration was reported in kachki fish, rice, and cauliflower respectively (Figure 2.5).

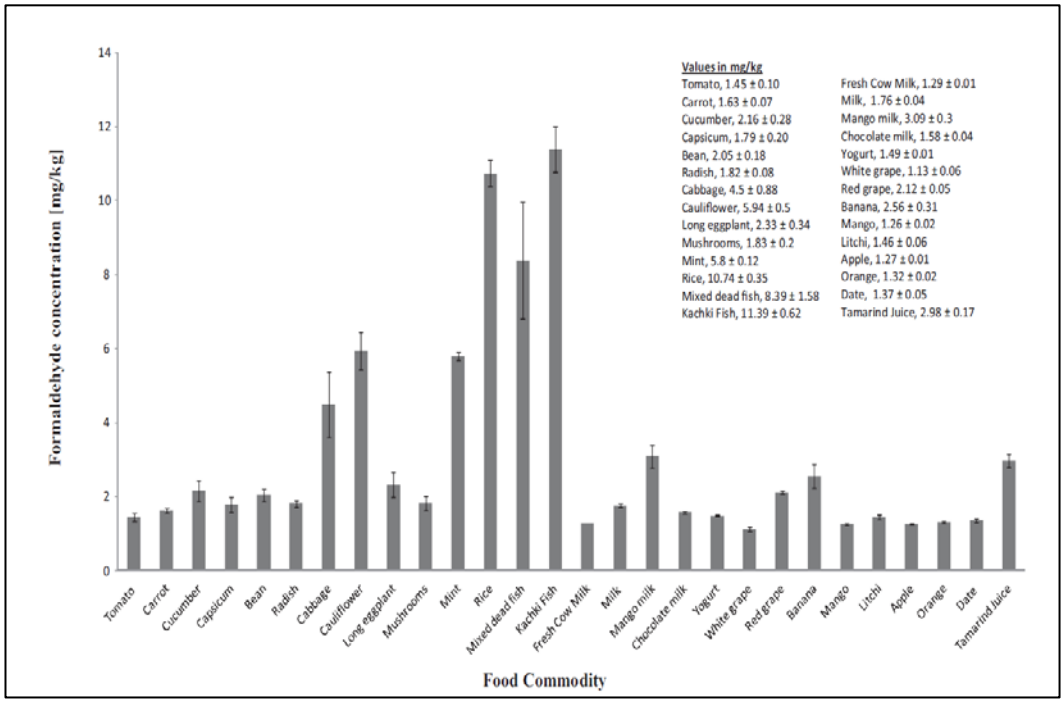

Figure 2.5 Formaldehyde content (expressed as mean ± std. dev) determined in different food products. [16]

d. Spectrometry

Spectrometry is a technique in analytical chemistry that utilizes optical properties of different compounds [17]. The concentration of formaldehyde can be interpreted from the scattering pattern of visible light after passing light through the sample solution while the light adsorption was determined. Major advantages of spectrometry method are good detection sensitivity, low cost measurement, and ease of processing with a detection limit of formaldehyde on the scale of part per million (ppm).

C. Xiaojun et.al [18] exercised spectrophotometric method in detecting formaldehyde by mixing Rhodamine (RhB) (25ml 9.19 x 10^5 mol/l), sulfuric acid (H_2SO_4) (1.5 ml 0.3 mol/l), and bromate solution ($KBrO_3$) with different concentration of formaldehyde. The solution was heated at 100 ^oC for 6 mins, and cooled in tap water for 3 mins. An aliquot was taken and filled in a quartz cell and analyzed with UV-vis (515 nm). The adsorption spectra can be interpreted that as formaldehyde concentration increase, the absorption spectra will decrease (Figure 2.6).

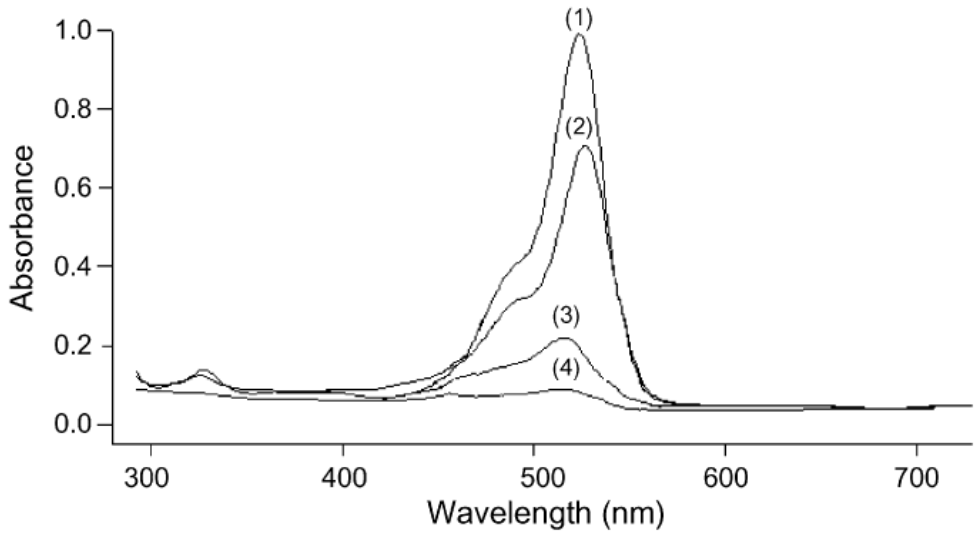

Figure 2.6 Absorption spectra of different systems: (1) RhB–H_2SO_4; (2)RhB–H_2SO_4–$KBrO_3$; (3) RhB–H_2SO_4–$KBrO_3$–HCHO (40µg/ml); (4) RhB–H_2SO_4–$KBrO_3$–HCHO (100µg/ml) [18]

2.2 Sensor detection and electrolytic cell

2.2.1 Electrolytic cell application in sensor

Electrolytic cell is an electrochemical system [19], used in quantitative analysis of chemical concentration, consisting of two reactions; oxidation and reduction. An example of electrolytic reaction is splitting water molecules using electricity, as shown in Equation 2.2 – 2.4.

Equation 2.2 shows the oxidation reaction at the anode, in which water molecule is splitted into electrons, protons, and oxygen gas. Equation 2.3 shows the reduction reaction at the cathode, in which protons combine with electrons, forming hydrogen gas. Equation 2.4 is the combination of Equation 2.2 and Equation 2.3, known as redox reaction, causing electrochemical current flow. Thus, the extent of the reaction can be determined quantitatively by measuring the electrical potential/current.

Anode reaction: $2H_2O \rightarrow 4H^+ + 2e^- + O_2$ (Equation 2.2)

Cathode reaction: $4H^+ + 4e^- \rightarrow 2H_2$ (Equation 2.3)

Redox reaction $2H_2O \rightarrow 2H_2 + O_2$ (Equation 2.4)

At present, the application of electrolytic cell as sensor includes the detection of various ions (Fe^{3+}, Cr^{3+}, Cr^{6+}, Cl^-), formaldehyde and monosaccharide. Responding electrical current is the results of oxidation and reduction reaction. An electrode sensor consists of 3 components; working electrode (WE), counter electrode (CE) and reference electrode (RE) (Figure 2.7).

a. Working electrode (WE)

Working electrode is the targeted electrode that electrochemical changes (potential, current, capacitive, etc.) can be monitored. It can be made out of platinum, gold, glassy carbon, or any metal/metal oxide/semiconductor. Chemical reactions and physical interactions that occur at the WE can be detected, and recorded as a sensor signal. The key to achieve an excellent sensing signal is to provide high surface area WE (good sensitivity), to select a proper material for WE (selective to a target analyte), and to promote a stable WE that is not corroded or deteriorated during operation.

b. Reference electrode (RE)

Reference electrode is a standard electrode, functioning as zero-setting electrode, whereas overpotential value of the electrolyte could be continually monitored and set as "zero". The applied potential provided at the WE would be monitored versus the RE. In other words, the role of RE is to minimize effects from nonspecific disturbances, such as temperature, electrolyte concentration, and medium vaporization, etc. RE is commonly made of silver wire, employed in a glass vessel along with potassium chloride (saturated with silver chloride) solution.

c. Counter electrode (CE)

Counter electrode is used to complete the other side of the redox reaction, as related to the WE. For example, if oxidation reaction occurs at WE, reduction reaction must take place at CE. It can be made out of platinum or graphite.

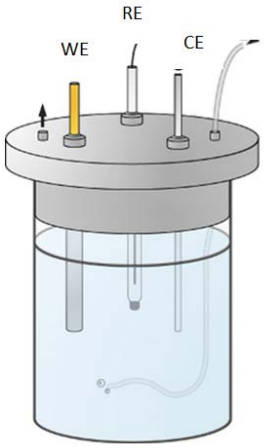

Fig 2.7 Diagram of a 3-Electrode electrochemical cell [20]

2.2.2 Electro analytical methods

Electrolytic cell is used in quantitative chemical analysis. Most commonly used electro analytical methods are cyclic voltammetry and amperometric techniques.

a. Cyclic voltammetry technique

Cyclic voltammetry technique (CV) is an electrochemical analysis method, where the applied potentials (at WE) are scanned forward from one value a to b(Figure 2.8), and scanned backward from t_0 to t_2. The graph obtained from CV analysis is called cyclic voltammogram (Figure 2.9), showing the relation between electrochemical current and voltage change in the electrochemical system.

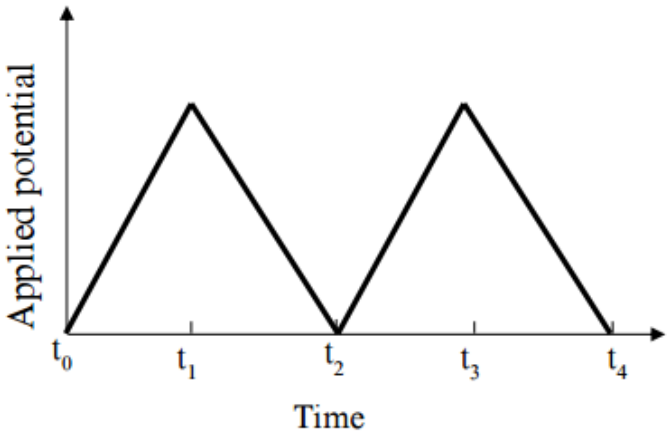

Figure 2.8 Potential waveform of cyclic voltammetry [21]

Cyclic voltammetry has two periodic scans, forward and reverse. In the forward scan, the potential applied to the working electrode increases, leading to an oxidation reaction, while, in reverse scan, the applied potential decreases, leading to a reduction reaction. When one scan is completed, the graph then formed a loop (Figure 2.9), in which x-axis is the potential scan and y- axis is the responding electrochemical current measured on the working electrode. The height of two peaks measured during forward and backward scan corresponds to anodic peak current (Ipa) and cathodic peak current (Ipc), respectively, while the position of two peaks correspond to anodic peak potential (Epa) and cathodic peak potential (Epc), respectively. The values of Epa, Epc, Ipa, Ipc will change depending on the chemical types and concentration.

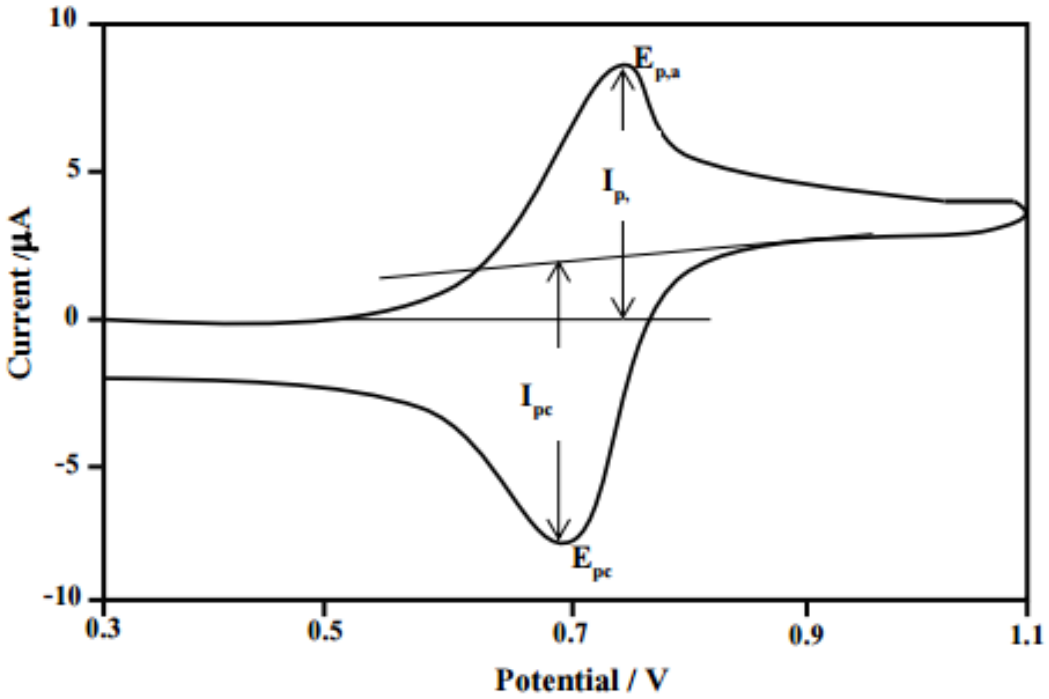

Figure 2.9 Cyclic voltammogram [22]

C. Zhao and his team [5] used nickel electrode to detect formaldehyde in Staircase Voltammetry mode (Figure 2.10). Cyclic voltammogram was obtained by scanning applied potentials from 0 to 0.65 V. in background solution of sodium hydroxide (0.1M). Significant changes in oxidative/reductive peaks were observed in presence and absence of formaldehyde. Anodic and cathodic peak potential of the background solution was observed at 519 mV and 448 mV, respectively (curve 1). When adding 3.90×10^{-6} M formaldehyde, anodic and cathodic peak potential was observed at 480 mV and 418 mV, respectively (curve 2).

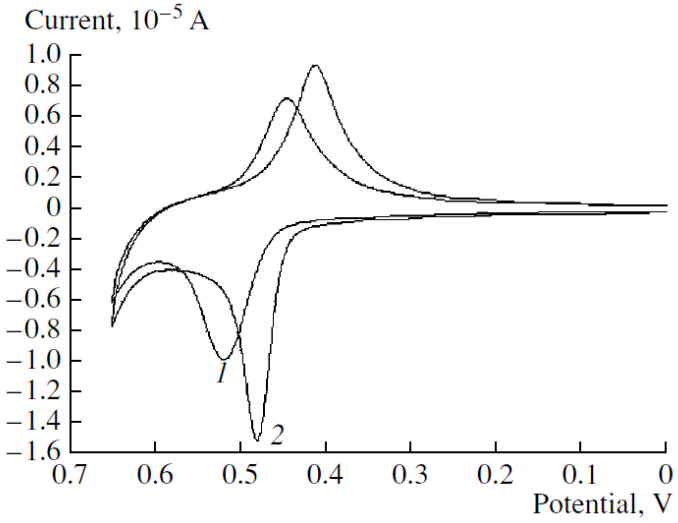

Figure 2.10 Cyclic voltammograms showing electroactivity of the nickel electrode in the absence (1) and presence (2) of 3.90×10^{-6} M HCHO in 0.1 M NaOH. (Scan rate; 100 mV/s). [5]

Catalytic performance of Ni and Ni-graphene composite were demonstrated in various research works. Reduction of formaldehyde, under Ni catalyzed reactions, is shown in equation 2.5 and 2.6 [5]. The reaction started by having the Ni(II) components oxidized, releasing an electron and becoming Ni(III) (Equation 2.5). Then, formaldehyde (HCHO) reacts with OH^- from NaOH in presence of Ni(III), resulting in charge transfer between Ni (III) and formaldehyde, reducing Ni(III) to Ni(II) (Equation 2.6). The charge transfer give rise to electrical signals as corresponded to formaldehyde concentration.

$$Ni(II) \rightarrow Ni(III) + e^- \quad \text{(Equation 2.5)}$$

$$Ni(III) + HCHO + 2OH^- \rightarrow Ni(II) + CH_2(O)O^- + H_2O \quad \text{(Equation 2.6)}$$

b. Amperometric technique

Amperometric technique is an electrochemical analysis method, which measure the electrochemical current from redox reaction. The reactions cause electrons to be transferred from working to counter electrode. Research example includes Isoprenaline detection on glassy carbon electrode modified by iridium oxide nanoparticles [23]. Graph obtained from the analysis, is a relation between current (y-axis) and time (x-axis). From Figure 2.11, current increase when concentration of isoprenaline increase periodically.

At present, amperometric technique is a popular quantitative analysis of chemical concentration. Applications include the detection of formaldehyde in drinking water, monosaccharide level in blood, and heavy metal in wastewater.

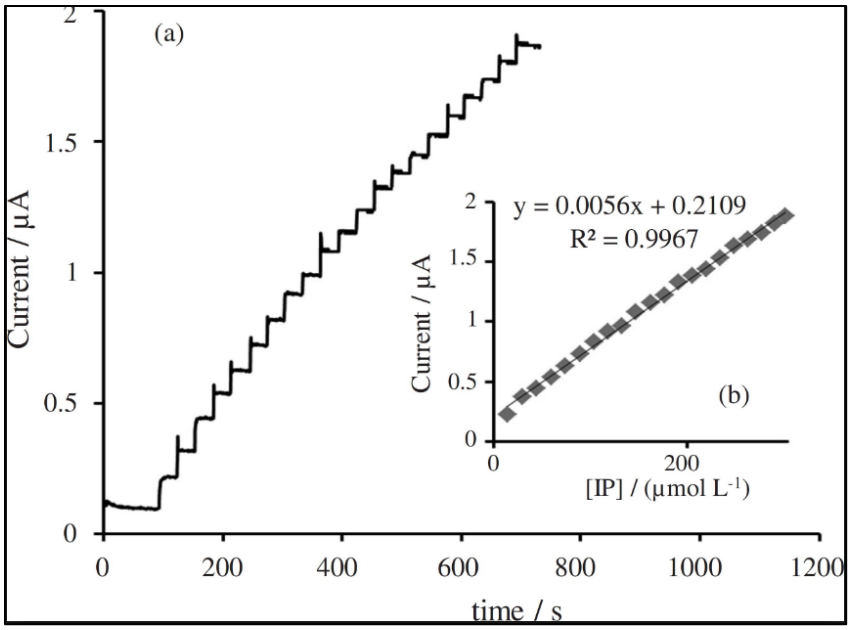

Figure 2.11 Amperometric curve [23]

N.A. Seyed and his teams [24] reported an amperometric detection of formaldehyde using Nickel/ P anozeolite modified electrode. A fixed potential of 0.58 V was applied to the electrode while formaldehyde concentration was increased periodically from 0.02 to 11.5 mM. The sensitivity of detection is 43.07 μA/mM^{-1}, and the detection limit is 5.8 mM (Figure 2.12).

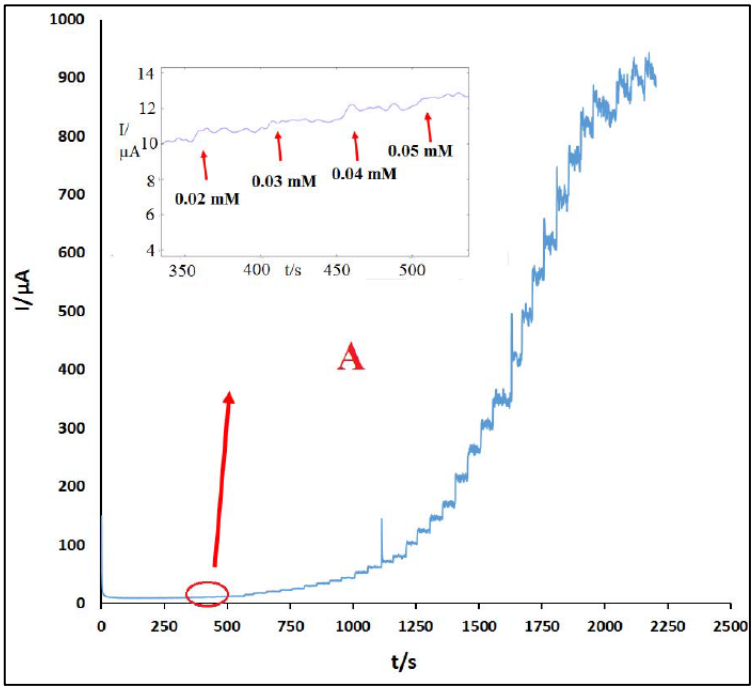

Figure 2.12 Amperometric curve of Nickel/ P nanozeolite modified electrode given a fixed potential of 0.58 V, as formaldehyde concentration increased periodically from 0.02 to 11.5 mM [24]

2.3 Graphene and composite material

2.3.1 Properties of graphene

Graphene is one layered graphite, an allotrope of carbon, consisting of carbon atoms covalently bond to one another via sp^2 hybridization. Graphene is the thinness material ever discovered with thickness of an atom, providing two-dimensional structure (2D) (Figure 2.13) with high chemical stability, outstanding electrical properties and remarkable mechanical properties [25]. Different graphene applications have been proposed and demonstrated, mainly focusing on fabrication of electronic devices such as hard disk, electrodes, and sensors.

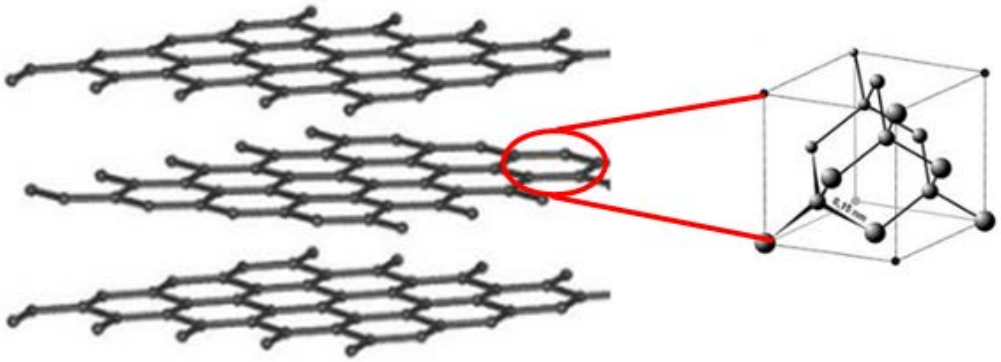

Figure 2.13 Graphene structure [26]

2.3.2 Industrial application of graphene composite material

a. Electronic industry

Various electronic components such as n-type and p-type transistor can make use of graphene as an advanced material. One example is FFT transistor (Figure 2.14 a) that utilizes superconductive property of graphene. Graphene is 4 times more conductive than copper and displays remarkable electron mobility at room temperature (~15000 $cm^2v^{-1}s^{-1}$) [27]. This makes graphene suitable for the application in hard disk. Graphene helps enhance the conductivity between magnetic electrodes in hard disk. (Figure 2.14 b shows the schematic of graphene based hard disk)

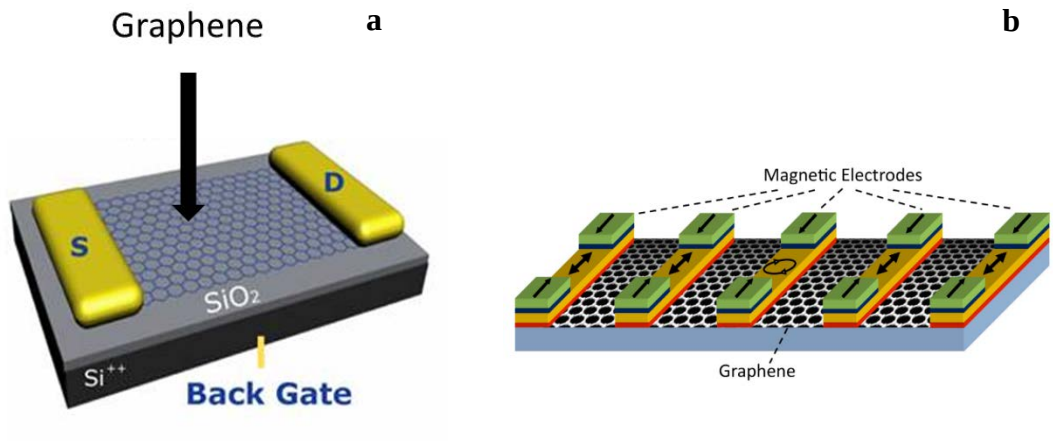

Figure 2.14 a) Graphene in FFT transistor b) the schematic of graphene based hard disk [27]

b. Catalyst application of graphene

Graphene can also be used as supporting material for catalysts in composite, utilizing random defects on graphene structure that create electron nodes for metal deposition. The metal/metal oxide composited with graphene can be used as catalyst in waste treatment, chemical synthesis and sensor technology. For example, Nickel-graphene composite was used for sulfur dioxide (SO_2) removal, whereas SO_2 reacts with reducing agent with an assistant of nickel catalyst to form Ni_2S [28]. Titanium dioxide (TiO_2)-graphene composite was known for its photocatalytic activity toward Hexavalent Chromium (Cr (VI)). Cr(VI) can be converted to Cr (III) (Figure 2.15) [29]. The role of the graphene here was not only to support catalyst nanoparticles, but also to help reduce the effect of catalyst deterioration during SO_2 treatment.

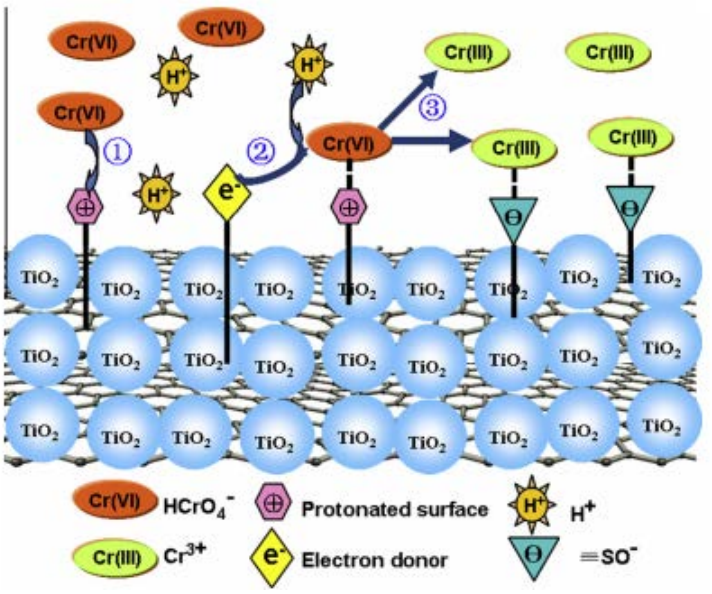

Figure 2.15 Proposed mechanism of Cr (VI) reduction and removal by TiO_2-Graphene composite. [28]

Nickel-graphene composite material was used to detect the presence and concentration of formaldehyde in solution. This is due to the specific reactivity of nickel to formaldehyde molecule. From the research of C. Zhao et al [5], nickel working electrode was used in formaldehyde detection by staircase voltammetry. From the work of N.A. Seyed et al. [24], a new sensor for the detection of formaldehyde based on Nickel/ P nanozeolite modified electrode was fabricated. This sensor relies on the specific reactivity to formaldehyde of nickel and the high specific surface area of graphene to help increase catalytic activity.

c. Sensor technology application of graphene

Graphene has been demonstrated as sensitive material for sensor device due to its high charge transfer ability and thermal stability. It also possess an advantage over other sensitive material in containing random defects on its structure that become active node for a formation of metal nanoparticles. For example, TiO_2-graphene composite was used for Cr (VI) detection in water [28]. Platinum (Pt)–graphene composite was used for hydrogen gas detection in vapor phase [29]. Copper sulfide-graphene composite was used for peroxide (H_2O_2) [31] detection, and nickel-

graphene composite was used for formaldehyde detection in water. Different methods have been used for the synthesis of nickel/nickel oxide-graphene composite material. These include physical method (Hydrothermal), electrochemical deposition, and chemical method (Sol-gel).

From the research of M. Tao et al. [32], nickel-graphene composite was used in the decomposition of ammonia into hydrogen. Nickel-graphene composite was synthesized at high temperature by hydrothermal method. Graphene oxide, synthesized by modified hummer method, was mixed with nickel nitrate solution then calcined at 450 ºC (Figure 2.16).

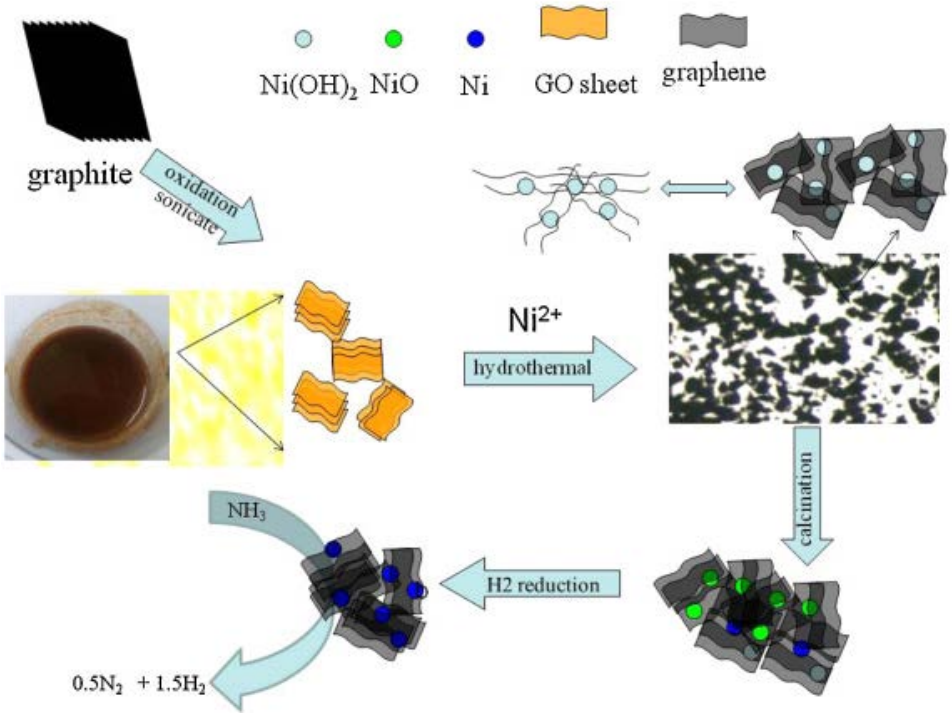

Figure 2.16 Schematic of nickel-graphene composite synthesis at high temperature [32]

From the work of X. Zhonghua et al. [33], electrochemical process was utilized in the synthesis of nickel-graphene composite (Figure 2.17). Nickel nitrate was mixed with graphene oxide, then a bare glassy carbon electrode (GCE) was immersed in the solution. An electrical potential of 0.6 to 1.4 V was applied to the GCE, forming nickel graphene composite at the surface of GCE.

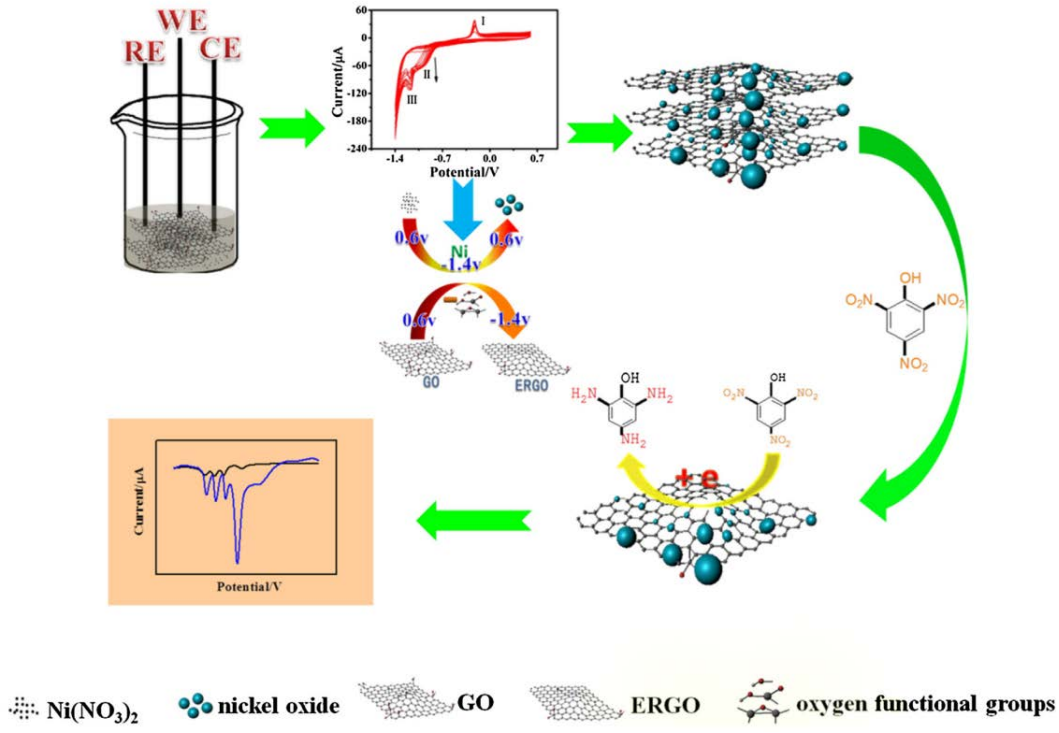

Figure 2.17 Schematic of nickel-graphene composite synthesis utilizing electrochemical process [33]

From the research of W. Zhaigng et al [6], Ni-Nanospheres/reduced graphene oxide (Ni-rGO) was synthesized with microwave-assist sol-gel method. $Ni(NO_3)_2$ $6H_2O$ was mixed with graphene and ethylene glycol, then hydrazine monohydrate was added. The mixture was placed in a microwave reflux at 300 W for 20 min. Afterward, the mixture was filtered and dried at 60 ^oC for 12 h. Figure 2.18 shows the SEM and TEM images of Ni- rGO. The composite was analyzed with FT-IR. From the FT-IR spectra (Figure 2.19), C=O vibration band (1723 cm^{-1}) had disappeared from the Ni-rGO curve. This is due to the successful reduction of GO to rGO when using hydrazine as a reducing agent.

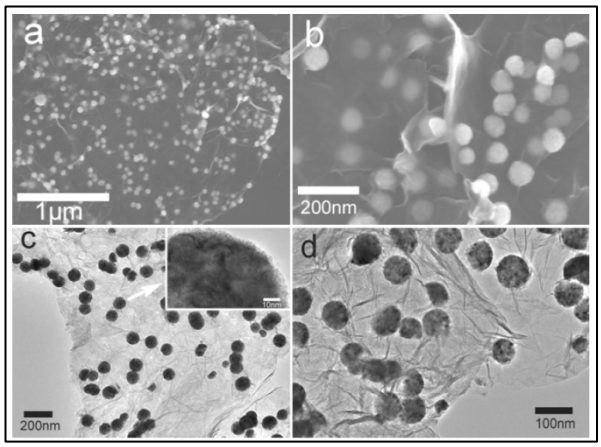

Figure 2.18 (a) Low-magnification and (b) high-magnification SEM image of the as-prepared Ni-rGO, (c) Low-magnification and (d) high-magnification TEM image of the as-prepared Ni-rGO. [6]

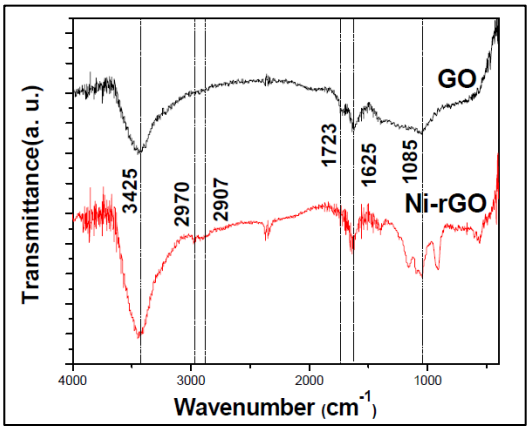

Figure 2.19 FT-IR spectra of the as-prepared GO and Ni-rGO [6]

CHAPTER III
MATERIALS AND METHODS

Chapter III discusses material and methods and research methodology, composing of Catalyst preparation, Synthesis of GO, Synthesis of Ni-rGO composite, formaldehyde detection, and application. Overall research methodology is concluded in figure 3.1.

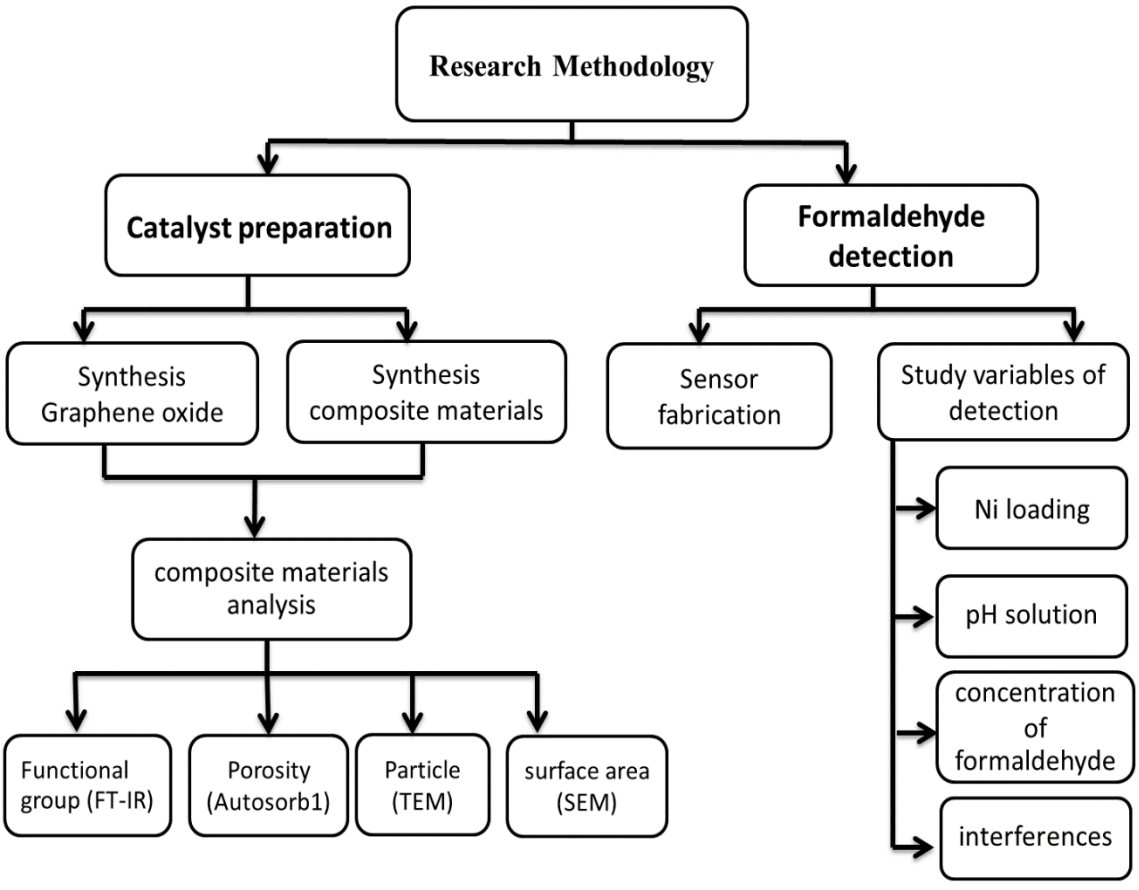

Figure 3.1 overall research plans

3.1 Materials and methods

All solutions were prepared using reagent grade chemicals and deionized water. Graphene oxide (GO) was synthesized from natural graphite flakes (-10 mesh Reagent grade, 99.9% A Johnson Matthey Company) via a modified Hummer's method. All chemicals/reagents, including sodium nitrate ($NaNO_3$: reagent grade, 99.0%), potassium permanganate ($KMnO_4$: reagent grade Ajax Finechem pty Ltd), hydrogen peroxide (H_2O_2: analytical grade, 30% Emd millipore corporation), hydrochloric acid (HCl: analytical grade, 37%V.S.Chem house), sulfuric acid (H_2SO_4: analytical grade, 98%, V.S.Chem house), nickel(II)nitrate hexahydrate ($Ni(NO_3)_26H_2O$: Analytical grade 99.9%, BDH Laboratory Supplies), ethylene glycol (EG: analytical grade,98% , Fluka Chemika), formaldehyde solution (HCHO: analytical grade, 40% , BDH Laboratory Supplies), and sodium hydroxide (NaOH: analytical grade, 97% Ajax Finechem pty), were used with no further treatment.

3.2 GO preparation

Graphene oxide (GO) was prepared following a modified chemical exfoliation method (Figure 3.2), proposed by Zhang and his team [34]. The process started by mixing 2 g. of natural graphite flakes, 1 g. of $NaNO_3$ and 50 ml of concentrated sulfuric acid in a 250 ml flask. The mixture was continuously stirred, and kept below 4°C in an ice-bath cooled system while 7.3 g. of $KMnO_4$ was slowly added in during a period of 2 hrs. Next, the mixture was removed from the ice bath, and warmed up to 35^{o}C for another 2 hrs, allowing oxidation reaction between graphite and $KMnO_4$ to occur. Next, DI water (90 ml) was poured in, decreasing mixture viscosity prior to an addition of H_2O_2 solution (7 ml H_2O_2+55 ml DI water). The GO power appeared in brownish color, and can be filtered from the mixture using vacuum filtration apparatus and glass microfiber filter paper (Glass Microfiber Filters. GE Healthcare Life Sciences). The GO powder was further rinsed several times using a solution of 3% (v/v) HCl followed by DI water, and was dried at 90 ^{o}C for at least 12 hrs. The obtained GO powder was kept inside a desiccant for future uses.

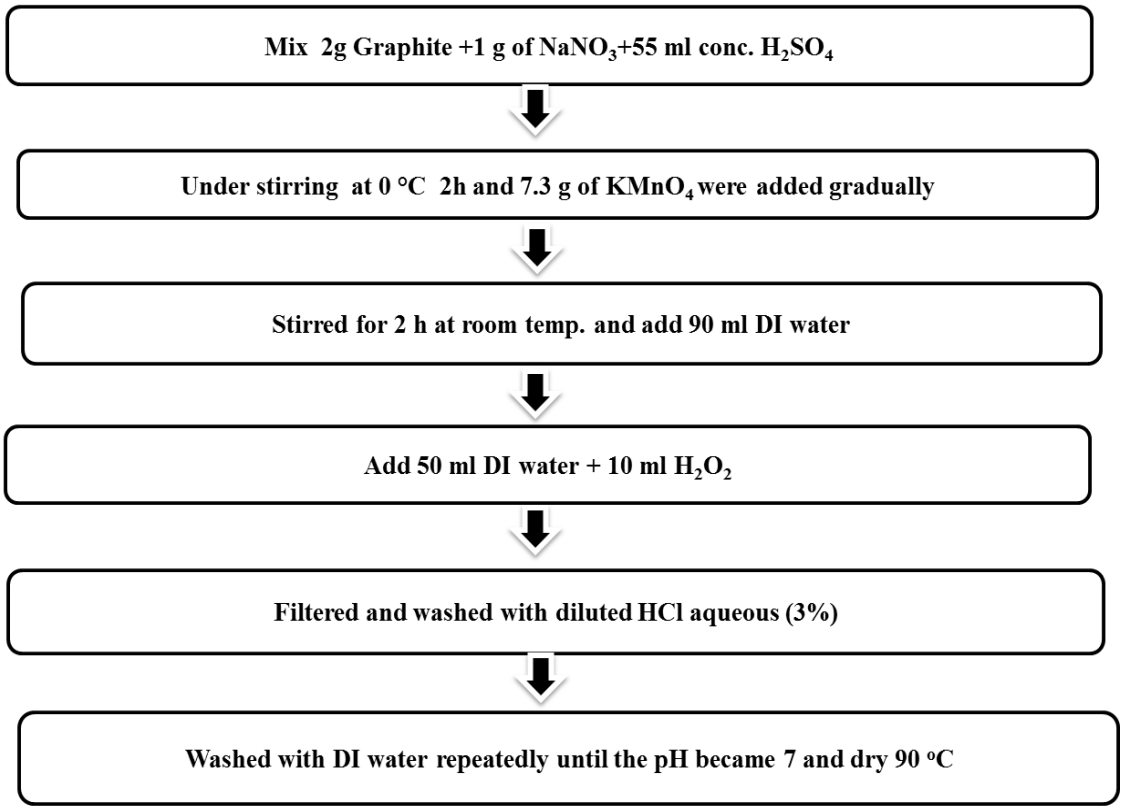

Figure 3.2 Modified chemical exfoliation method

3.3 Synthesis of Ni-rGO composite

To synthesize a Ni-graphene composite (Figure 3.3), 10 mg. GO and 58 mg. $Ni(NO_3)_26H_2O$ were dissolved in ethylene glycol and sonicated for 2 hrs. The mixture was immediately submerged to a 125 °C temperature controlled oil bath and stirred for 2 hrs. Next, 5 ml of hydrazine-monohydrate was added to the mixture. The Ni-rGO composite was obtained from the mixture using vacuum filtration apparatus and glass microfiber filter paper. The composite powder was calcined at 600 ^oC for 12 hrs. It's worth noting that the GO was partially reduced here as side effects from reducing environment during the synthesizing process, and was converted to reduced graphene oxide (rGO).

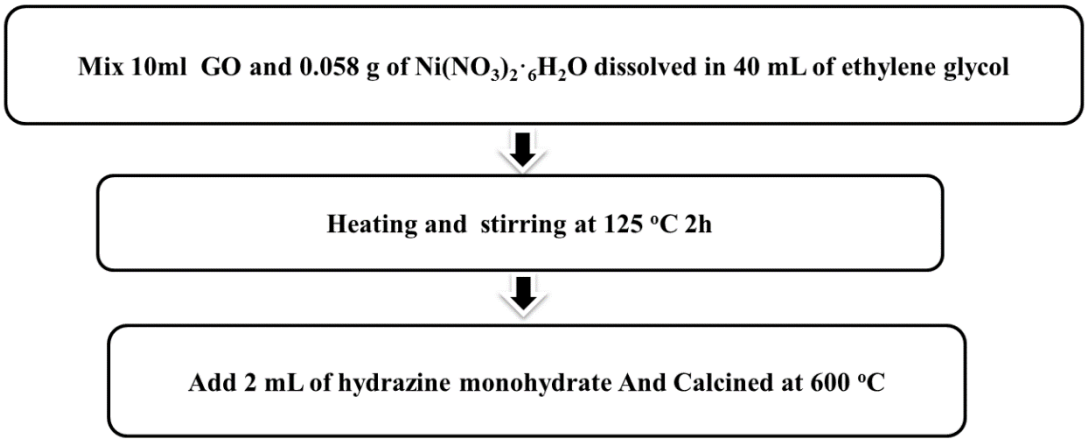

Figure 3.3 Synthesis of Ni-rGO composite method

3.4 Sensor fabrication

The Ni-rGO composite was re-suspended in DI water at a concentration of 2 mg/ml and sonicated for 1 hr to disintegrate the composite powder. The composite suspension was carefully casted on a glassy carbon electrode (GCE), and dried in an oven at 50 °C to form composite film layer. After several coatings, uniform layer of composite film was observed under the optical microscope. Then, the Ni-rGO composite coated GCE was employed as a working electrode (WE) in a 3-electrode electrochemical cell along with reference electrode (Ag/AgCl: CHI instruments), and platinum wire electrode (Pt wire: CHI instruments). The system was operated in an amperometric mode with a voltammetric bias of 0.6 volts in a solution of 0.1 NaOH (pH13). All electrochemistry experiments were performed using the electrochemical work station (CHI1206) (Figure 3.4). A desired concentration of formaldehyde, ranged from 0.1-60 ppm, was generated by adding formaldehyde solution to the 0.1 NaOH background solution.

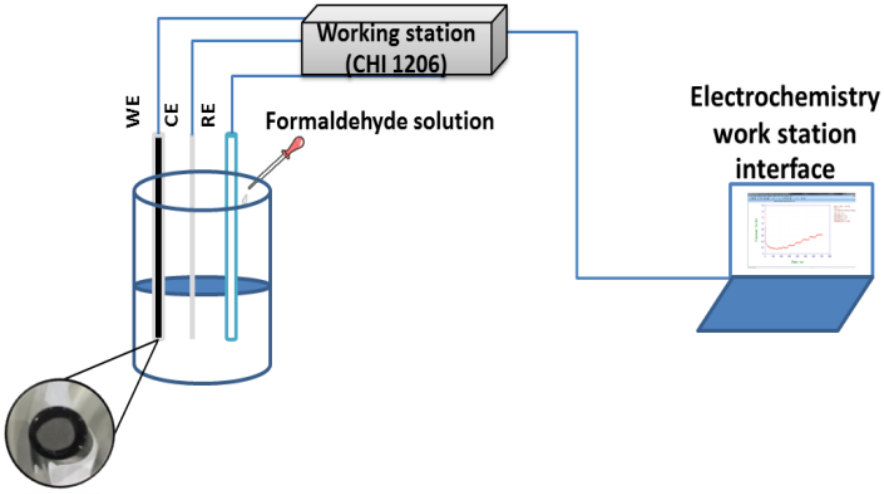

Figure 3.4 Schematic diagram of formaldheyde detection apparatus

3.5 Effect of formaldehyde detection

3.5.1 Effect of %Ni loading

In this work, %Ni loading of Ni-rGO composite was varied at 15%, 20%, and 50% on the working electrode. The sensor was operated in amperometric mode in alkali background solution with pH 13. A constant potential of 0.6 V was applied to the working electrode, while formaldehyde concentration in the background solution (1.0 M NaOH) was increased stepwise from 0.1 to 60 ppm. The performance of the sensor was determined using 4 parameters which include sensitivity, limit of detection, repeatability, and the number of damaged electrode.

3.5.2 Effect of solution pH

In this part, the pH value of the background solution was varied at 10, 12 and 13. The sensor was operated in amperometric mode using Ni-rGO with the optimal %Ni loading from the previous experiment as the working electrode. A constant potential of 0.6 V was applied to the working electrode, while formaldehyde concentration in the background solution (1.0 M NaOH) was increased stepwise from 0.1 to 60 ppm. The sensitivity of the sensor at each pH value was then determined.

3.5.3 Effect of interfering substances

In this part, the sensor was tested against solution containing formaldehyde and various interfering substances, commonly found in food products, including benzoic acid (preservative, 1000 ppm), sodium hydrosulfite (bleach, 1000 ppm), and sodium tetra borate (food additive, 250 ppm). The sensor was operated in amperometric mode using Ni-rGO with the optimal %Ni loading and pH value of background solution obtained from previous experiments. A constant potential of 0.6 V was applied to the working electrode, while formaldehyde concentration was fixed at 60 ppm.

3.6 Application of formaldehyde detection in food product

In this experiment, sensing performance of the sensor for the detection of formaldehyde in food product was demonstrated using raw squid. First, raw squid was cut into small pieces, immerse in 100 mL solution containing 8,000 ppm of formaldehyde concentration for 12 hours (1.0 µL of 8,000 ppm formaldehyde solution dispersed in 8.0 mL of background solution will yield a formaldehyde concentration of 10 ppm). Then 1.0 gram of raw squid soaked with formaldehyde was immerse in 1.0 mL of DI water or 1.0 mL of 1.0 M NaOH solution for 15 minutes to study the effect of solvent type in extracting formaldehyde. The obtained solutions were tested against sensor operated in amperometric mode using Ni-rGO with the optimal %Ni loading and pH value of background solution obtained from previous experiments. A constant potential of 0.6 V was applied to the working electrode. Finally, the sensing performance was determined.

CHAPTER IV
RESULTS AND DISCUSSION

Chapter IV involves characterizations of Ni-rGO composite, formaldehyde detection and sensing mechanisms, effect of %Ni loading on Ni-rGO composite, effect of pH solution for formaldehyde detection, and finally Effect of interferences for Formaldehyde detection.

4.1 Characterizations of Ni-rGO composite

4.1.1 FT-IR spectra

Chemical properties of GO and Ni-rGO samples were observed using FTIR (Figure 4.1). The transmittance at wave numbers of 3382, 1399 and 1626 cm^{-1} are assigned to hydroxyl groups (O-H: H bonded) [6]. Presence of hydroxyl groups could be attributed to moisture (H_2O molecules) and ethylene glycolwhile the peaks at 2350 cm^{-1} can be assigned to C≡N. It was observed that the C=O vibration (1723 cm^{-1}) and stretching vibration of C-O (1218 cm^{-1}) partially disappeared after GO was converted to Ni-rGO composite. This could be resulted from reducing environment during hydrazine addition and thermal reduction.

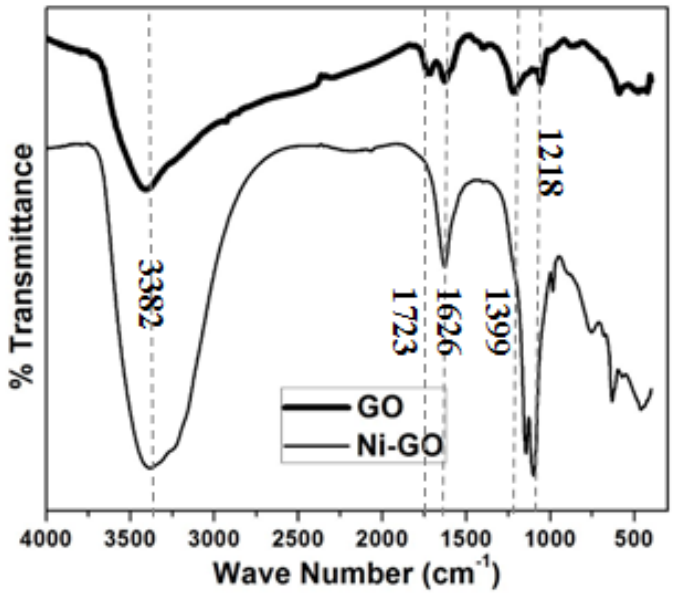

Figure 4.1 FT-IR spectra of the GO and Ni-rGO

4.1.2 TEM and EDS Analysis

The GO sheet was observed as thin sheets with 1x1 μm^2 in size under the transmission electron microscope (TEM) (Figure 4.2). The TEM image of the Ni-rGO composite reveals a well dispersed spherical Ni nanoparticles with diameter of ~20 nm, decorated on the rGO supports. Elemental analysis using energy dispersive x-ray spectrometer (EDS) (Figure 4.3) indicates presence of Ni from Ni nanoparticles, C and O from graphene and Cu from the TEM copper grid. Small size and well distribution of Ni nanoparticles were attributed to surface tension reduction characteristic of the Ethylene glycol (EG) [6], allowing Ni^{2+} adsorption on rGO sheets.

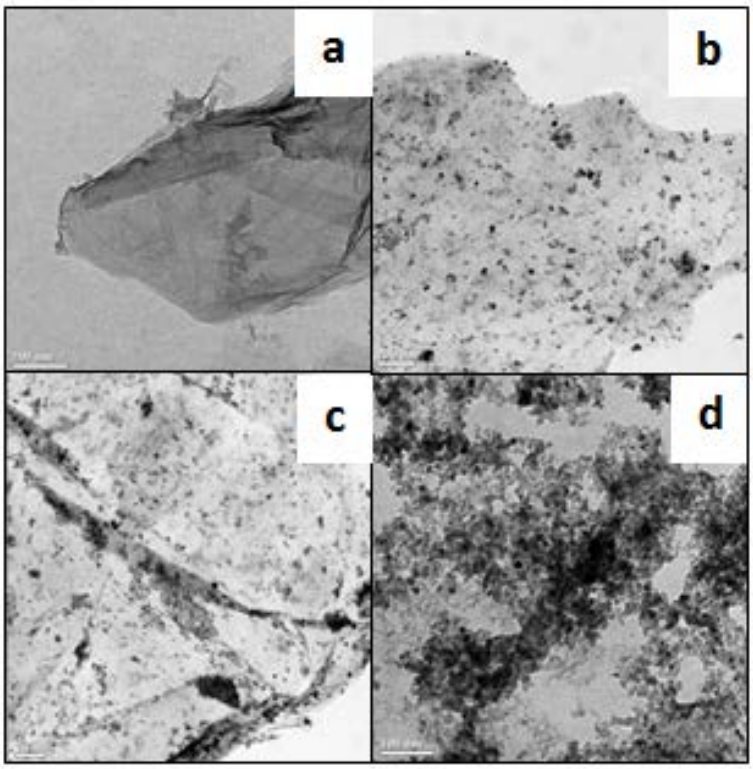

Figure 4.2 TEM images of a) GO sheet, b) 15%Ni- rGO, c) 20%Ni- rGO, and d) 50% Ni- rGO

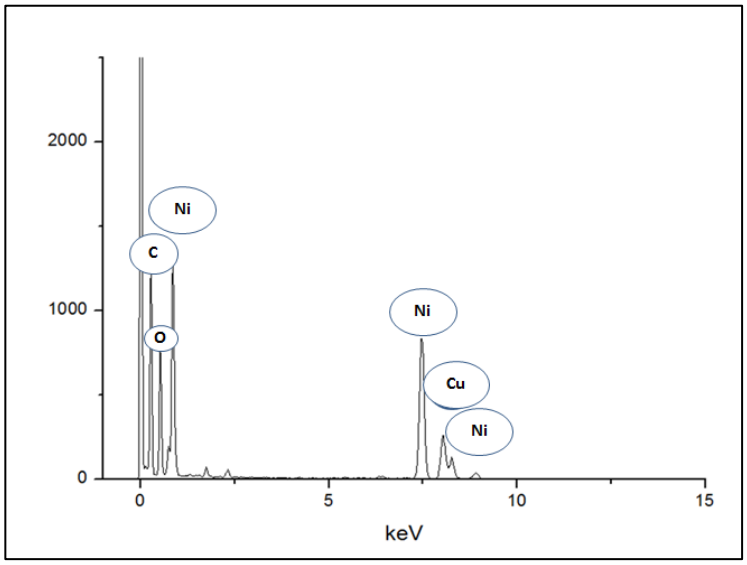

Figure 4.3 Energy dispersive x-ray spectrometer (EDS) of Ni-rGO

4.1.3 Bet surface area Analysis

It was determined from the BET analysis (Autosorb) that the Ni-rGO with 50%Ni loading provides the highest surface area and pore size. This can be attributed to the right portion of Ni and GO supports, doping a good amount of Ni nanoparticles while maintaining the highest surface area.

Table 4.1 Ni-rGO Composite Bet Analysis

	SURFACE AREA(m^2/g)	PORE VOLUME (ml/g)	PORE SIZE (Å)
NiO	2.151	$7.643x10^{-4}$	113.80
GO	6.289	$2.235x10^{-3}$	143.70
Ni(15%)-rGO	56.910	$2.023x10^{-2}$	93.41
Ni(50%)-rGO	75.980	$2.7x10^{-2}$	90.74

4.2 Formaldehyde detection and sensing mechanisms

4.2.1 Cyclic voltamogram analysis

Composite-coated GCE was employed as WE in an electrochemical cell along with RE and CE while the potential was scanned in CV mode (0.2-0.8 V, 100 mV/s scan rate) in 1.0 M NaOH background solution. Electroactivity of Ni-rGO on WE was observed against formaldehyde solution (1-46 ppm) as 2 distinct peaks, observed at 0.50 and 0.60 V, correspond to the cathodic peak potential (Epc) from the reduction reaction [22] and anodic peak potential (Epa) from the oxidation reaction [22], respectively (Figure 4.4). The peaks represent catalytic activity of Ni-rGO to formaldehyde and poise a suitable bias potential for amperometric operation to be 0.6 V.

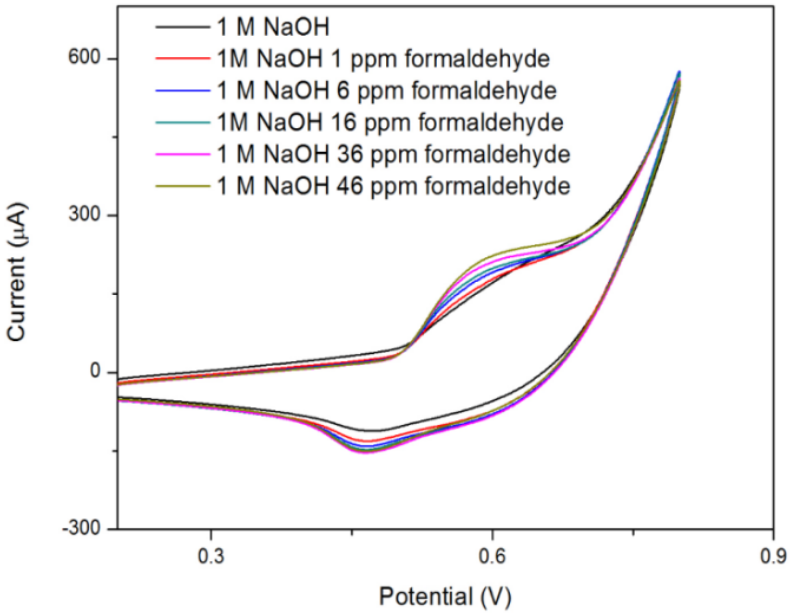

Figure 4.4 Cyclic voltamograms (0.2-0.8 V, 100 mV/s scan rate, pH 13 solution)

4.2.2 Formaldehyde detection

The composite was drop-casted on the GCE electrode and employed as working electrode (WE) in an electrochemical cell along with reference (RE) and counter (CE) electrodes. Constant potential of 0.6 V was applied to the WE (vs. Ag/AgCl reference) while the electrochemical currents were monitored and recorded as function of time (Figure 4.5, amperometric mode). When sensor baseline was reached, formaldehyde solution was added cumulatively in the medium, generating formaldehyde concentrations of 1 to 60 ppm. It was observed from Figure 4.5 that electrochemical current increased as formaldehyde concentration increased.

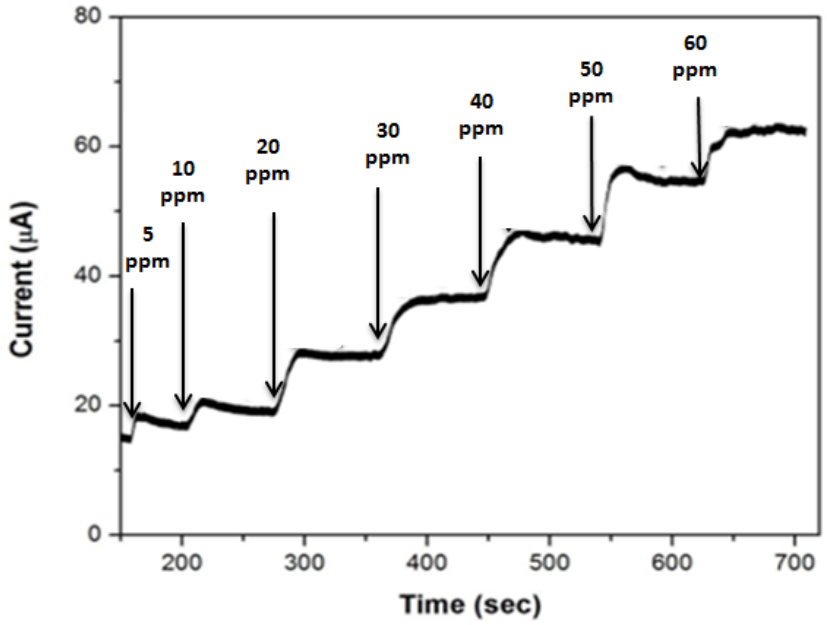

Figure 4.5 Sensing curve (Electrochemical current vs. time) 15% Ni-rGO pH 13

Prospected mechanisms for formaldehyde oxidation in alkali solution are shown in Equation 2.4 and Equation 2.5 (Figure 4.6), involving oxidation reaction of formaldehyde on nickel surface. In an aqueous solution, formaldehyde is hydrated, forming water-formaldehyde complexes- methylene glycol (CH_2 $(OH)_2$) that stays in deprotonated form ($CH_2(OH)O^-$) in an alkali solution [24]. The methylene glycol can be oxidized with an assistant of Ni(III) catalyst, and can be converted to $CH_2(O)O^-$ (Equation 2.4). Ni(II) is reversibly oxidized to Ni(III) (Equation 2.5) providing 1 electron to the electrode for electrochemical current, creating sensing signal.

$$Ni(II) \rightarrow Ni(III) + e^- \quad \text{(Equation 2.4)}$$

$$Ni(III) + HCHO + 2OH^- \rightarrow Ni(II) + CH_2(O)O^- + H_2O \quad \text{(Equation 2.5)}$$

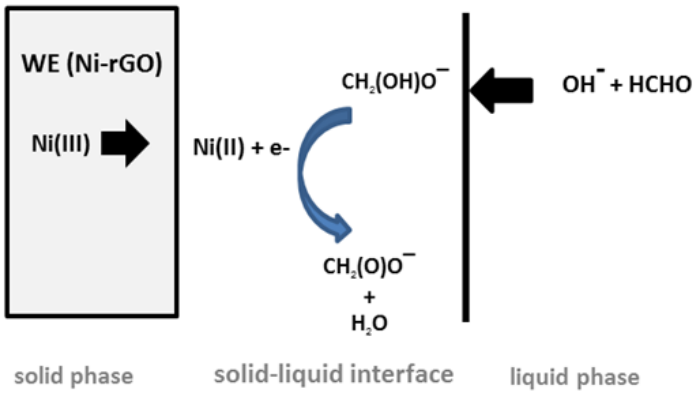

Figure 4.6 The electrocatalytic oxidation mechanism of formaldehyde (HCHO) on nickel electrode.

4.3 Effect of %Ni loading on Ni-rGO composite

Amount and size of Ni nanoparticles can significantly affect quality of the sensor. Sensing performance of the Ni-rGO composite with 15, 20, and 50 %Ni loading were determined using 4 parameters including sensitivity, limit of detection (LOD), repeatability, and reproducibility. Firstly, sensors with different Ni loading yielded sensitivity (slope of calibration curves, Figure 4.7) of 0.13, 0.06, and 0.09 ppm^{-1}, respectively. Sensitivity of sensor depends on reaction of WE (Equation 2.4 and 2.5). 15% Ni nanoparticles are more disperse than 50% Ni nanoparticles on graphene sheets (Figure 3), resulting in 15% Ni loading has the highest sensor sensitivity.

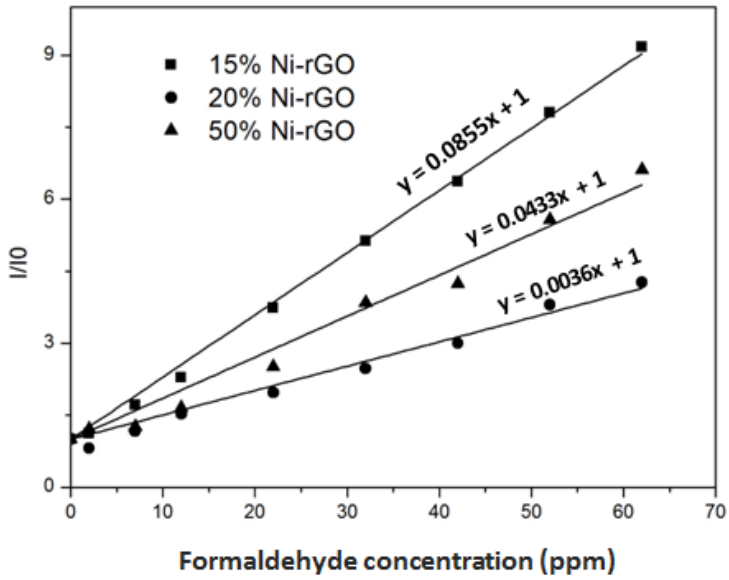

Figure 4.7 Calibration curves of normalized current (I/I_0) versus formaldehyde concentrations, obtained from Ni-rGO composite (15, 20 and 50% Ni loading (pH 13))

Secondly, the LOD values were determined from 3 times of signal noise divided by the sensitivity (Calculation of LOD is shown in appendix A), giving LOD values of 2.04, 3.13, and 3.05 ppm for 15, 20, and 50 %Ni on Ni-rGO, respectively. The comparison of various formaldehyde detection methods is shown in table 4.2. Conventional methods for formaldehyde detection include chemical precipitation, and colorimetric method that are not very specific and provide low sensitivity. Analytical instruments such as Spectroscopy and HPLC can sense formaldehyde at very low concentration, but are costly and require high expertise to operate. In this work, we proposed a new method for formaldehyde detection, relying on electrochemical sensor. Great advantages of the sensor are its portability, high sensitivity and real-time analysis. Material preparation and synthesis is simple, and has low cost.

Table 4.2 LOD valve Conventional methods and **Sensor detection**

Method	Materials for detection	LOD valve
Conventional methods		
Chemical precipitation [11]	2,4-dinitrophenyl hydrazine	~5ppm
Spectrometry [17-34]	2-amino-6-(piperazin-1-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NPz)	5-20 ppm
High performance liquid chromatography (HPLC) [15]	-	0.04 ppm
Sensor detection		
Staircase Voltammetry [6]	Nickel Electrode	0.5-1 ppm
Amperometric sensor	Nickel/ P nanozeolite modified electrode [23]	0.2 ppm
	NiO-rGOcomposite	0.3 ppm

Thirdly, based on sensitivity and LOD values, the sensors with 15 and 50 %Ni loading were qualified for the next performance test on repeatability, in which the sensors were exposed to 2nd and 3rd round of formaldehyde additions (Figure 4.8 and 4.9). An ideal sensor should be able to recreate the same responses, same value of sensitivity and LOD. However, it was observed that the Ni-rGO composite sensors at both 15 and 50 %Ni loading showed significant deterioration in responses when the sensors were re-used against formaldehyde for 2nd and 3rd round. This could be a drawback from the sensing mechanisms of Ni nanoparticles and formaldehyde that involved composite corrosion. Then, it was realized that the Ni-rGO composite was not reusable, but could be applied as a disposable formaldehyde sensor.

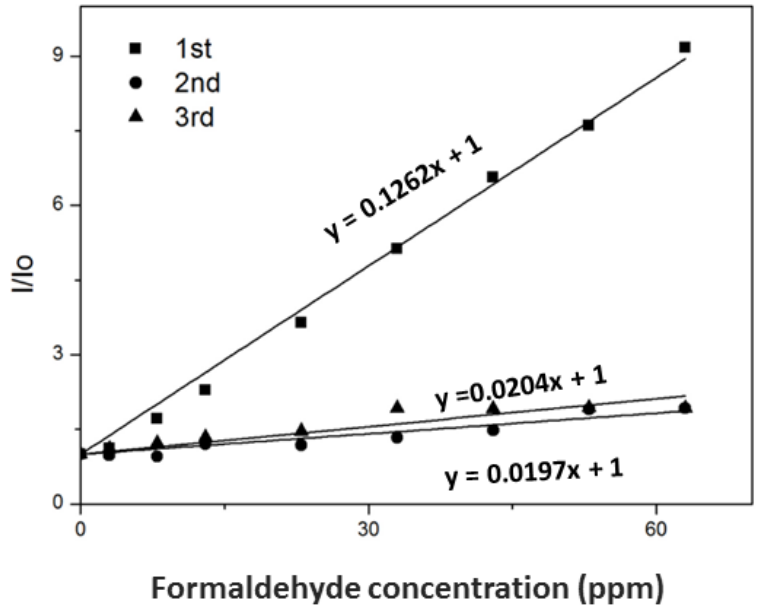

Figure 4.8 Repeatability of sensor 15%Ni loading at voltage 0.6 V at solution pH of 13

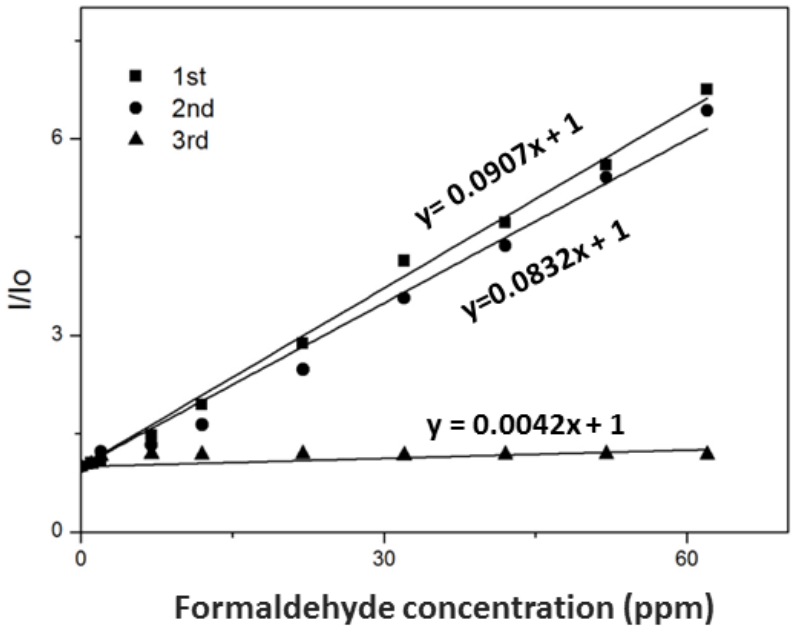

Figure 4.9 Repeatability of sensor 15%Ni loading at voltage 0.6 V at solution pH of 13

Fourthly, sensor reproducibility was determined by observing surviving rate of the synthesized electrode after it was employed in the electrochemical cell. We produced 15 electrodes for each 15 and 50 %Ni composite sensors and tested the electrodes for formaldehyde sensing. Sensors that provided good sensing though the whole formaldehyde range were considered "good" while sensors that failed during the test were labeled "damaged" (Table 4.3). It was found that only ~50% of the 15 %Ni loading sensor survived the test while over 80% of the 50 %Ni loading sensor remain active the whole test. This could be explained since redox reaction of formaldehyde over Ni catalyst can lead to catalyst corrosion. The sensor with lower percent of Ni loading (15 %) could be less durable than the sensor with higher percent of Ni loading (50 %).

It's worth mentioning that higher percent Ni loading, 60 and 100 %Ni, were also synthesized, but were proved to provide poor adhesion to the electrode. The composite film fell off the electrode prior to the sensing operation. Then, it was concluded that the Ni-rGO sensor with 50 %Ni loading was most suitable for further studies.

Table 4.3 Numbers of damaged electrode at 15% and 50% Ni loading

	Numbers of electrode (n)	Numbers of damaged electrode	Percent damaged (%)	variability
15% Ni loading	15	8	53.33	0.25
50% Ni loading	15	2	13.33	0.11

4.4 Effect of pH solution for Formaldehyde detection

The fact that formaldehyde needs to couple with OH^- prior to electro catalytic oxidation led us to study effect of solution pH to the sensor response. Values of solution pH were varied at 13, 12 and 10 (Figure 4.10), revealing significant reliance of Ni-rGO sensor on solution alkalinity [5, 22]. Sensor sensitivities against formaldehyde decreased from 0.086 to 0.043 and 0.004 ppm^{-1} as the solution pH decreased from 13 to 12 and 10, respectively. Results of cyclic voltammetry analysis at solution pH of 10, 12 and 13 are shown in figure 4.11 anodic peak current (Ipa) of oxidation reaction (0.6V) decreased from 3.41, 61.21 and 191.60 µA respectively. At pH 13, the sensor exhibited the highest response to formaldehyde solution. From the Equation 2.5, the amounts of OH^- from NaOH affect the reactions particularly in electron donating-receiving process. Then, it was important for Ni-rGO sensor to be operated at high pH to obtain the best sensing result.

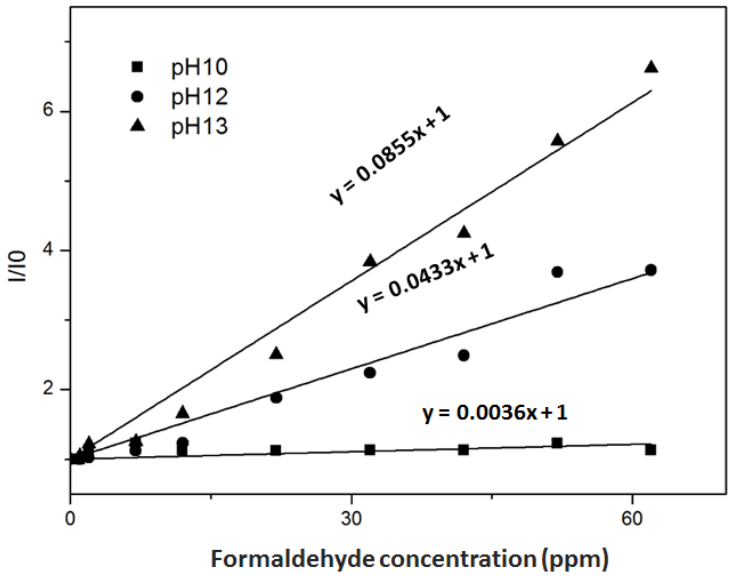

Figure 4.10 Effect of pH (10-13) solution for Formaldehyde detection at 50%Ni loading voltage 0.6

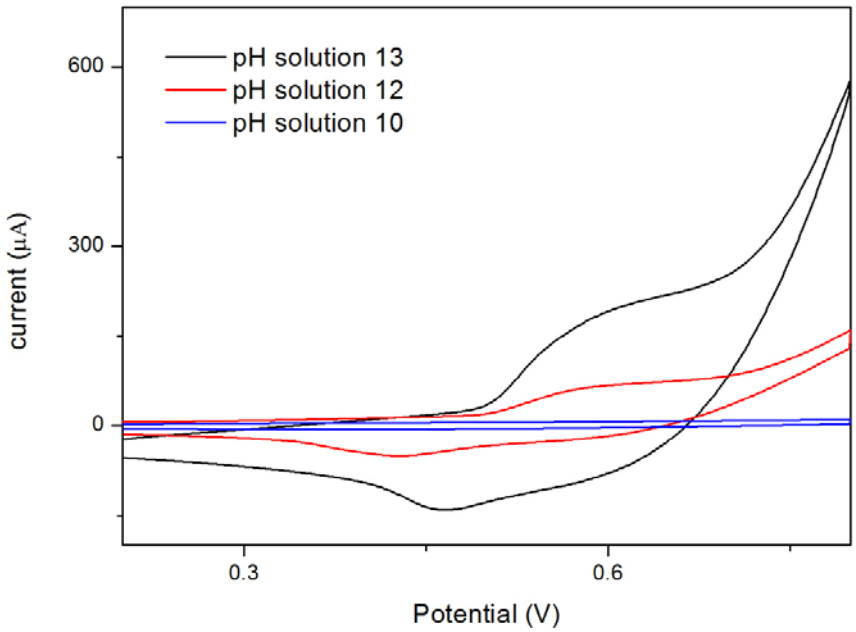

Figure 4.11 Cyclic voltamograms (0.2-0.8 V, 100 mV/s scan rate, pH solution 10-13)

4.5 Effect of interferences for Formaldehyde detection

Other substances found in fresh vegetables and raw meat products includes preservative (benzoic acid), decolorizer (Sodium hydrosulfite) and borax (sodium tetra borate). These are combined with formaldehyde in fresh vegetables and raw meat products. The research has also studied the effect of interferences for Formaldehyde detection. From experimental results, Ni-rGO composite has specific reactivity with formaldehyde. Figure 4.12 shows the sensor percentage of responses. The sensor has a very low responses with interferences, because Ni metal has specific reactivity with formaldehyde [6]. pH value also affected formaldehyde detection. Benzoic acid can be detected very well in acidic condition at solution pH of 4-5. [36] Sodium hydrosulfite and sodium tetra borate can be detected very well in neutral condition at solution pH of 7 [37]. While formaldehyde react well with Ni in basic condition at solution pH of 12-13 [5, 22]. In this work, we can conclude that the Ni-rGO composite on WE sensor has specific reactivity with formaldehyde.

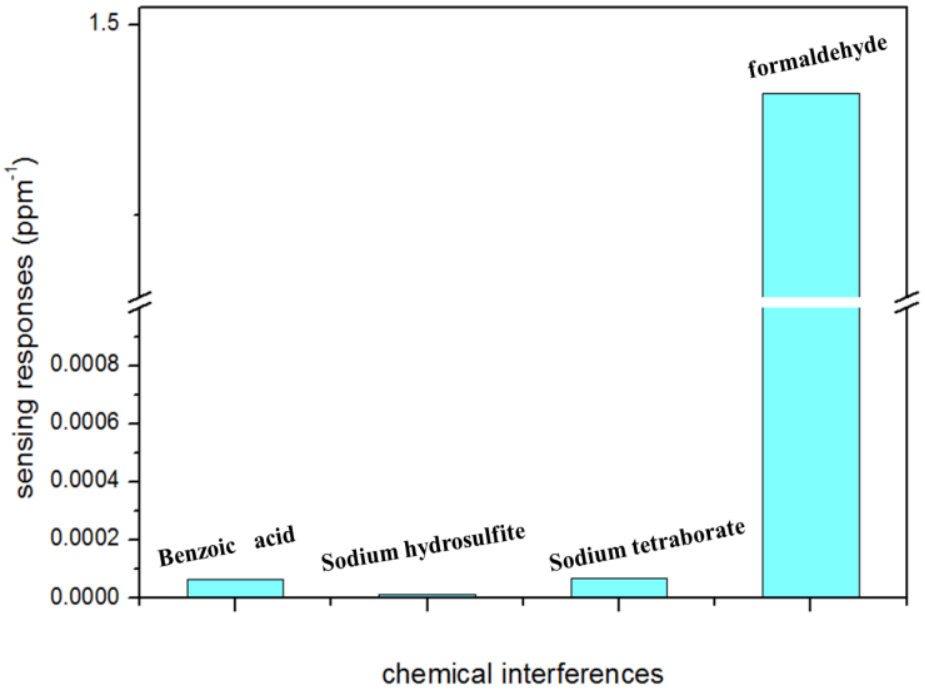

Figure 4.12 Effect of interferences for Formaldehyde detection at solution pH of 13 50%Ni loading voltage 0.6 V

4.6 Application in formaldehyde detection

According to the World Health Organization (WHO) reports, formaldehyde-contaminated food products include raw meat, vegetable, and seafood. We used squid as a model for an establishment of formaldehyde detection method.

In this work, we demonstrated the use of amperometric sensor for the detection of formaldehyde contaminant in squid. First, raw squid was cut into small pieces, and immersed in formaldehyde solution with formaldehyde concentration of 8,000 ppm (Figure 4.13) A 1.0 µL of 8,000 ppm formaldehyde solution was diluted in 8.0 mL of background solution, yielding formaldehyde concentration of 10 ppm. Then, 1.0 gram of raw squid soaked with formaldehyde was immersed in either 1.0 mL water, or 1.0 mL of 1.0 M NaOH solution to compare the effect of different solvent in extracting formaldehyde. The experimental results revealed that 1.0 M NaOH solution provide superior performance in extracting formaldehyde, as compared

to water (Table 3). This was attributed to the reaction between formaldehyde molecule (HCHO) and NaOH that converted formaldehyde into $CH_2(OH)O^-$ [24], with better dissolution ability as compared to formaldehyde. From this work, we can conclude that NaOH is the most suitable solution for the extraction of formaldehyde from food product.

Figure 4.13 detection of formaldehyde contaminant in squid

Table 4.4 Absorbed and Diffused formaldehyde in squid

Solvent type	Concentration of formaldehyde in extracted solvent (ppm)	Absorbed formaldehyde in Squid (%)	Diffused formaldehyde in Squid (%)
Water	8.20	18.0	82.0
1 M NaOH	9.42	5.8	94.2

CHAPTER V
CONCLUSION

In Chapter VI, conclusions of the research project were summarized. Suggestions from the experiments were also discussed for future work.

The Ni-rGO composite was synthesized and demonstrated for a fabrication of formaldehyde amperometric sensor. The best results was obtained from 50 %Ni loading which showed a sensitivity of 0.09 ppm^{-1} and limit of detection of 3.01 ppm for formaldehyde with good rate of reproducibility. The pH of solution most suitable for the detection of formaldehyde was observed at pH value of 13.

Sensing mechanisms depended on formaldehyde oxidation with an assistant of Ni nanoparticle catalyst. The Ni-rGO sensor showed excellent sensing performance in sensing formaldehyde with no significant responses against benzoic acid, sodium hydrosulfite and borax at tested conditions. The sensor was also tested against extracted formaldehyde solution from raw squid using different type of solvent. NaOH was determined to be the best solvent for the extraction of formaldehyde from food product.

Suggestion

1. The calcination of Ni-rGO composite at 600 ºC should be done in step-wise approach to ensure good settling of Ni nanoparticles on graphene sheet.

2. In the cyclic voltammetry and amperometric analysis, the stirring rate of the background solution should be kept constant to minimize the noise signal.

REFERENCES

1 World Health Organization. (1998). Environmental Health Criteria for Formaldehyde. World, Health Organization.

2 Chia, S., Ong, C., Foo, S. & Lee H. (1992). Medical students exposure to formaldehyde in a gross anatomy dissection laboratory. J Am Coll Health., 41(3),115-9.

3 World Health Organization. (2005). Formaldehyde in Drinking-water. World Health Organization.

4 Agency for Toxic Substances & Disease Registry. Formaldehyde. [serial online]. Available from: https://www.atsdr.cdc.gov/toxprofiles/tp111-c7.pdf. Accessed April 7, 2016.

5 Zhao, C., Li, M., Jiao, K. (2006). Determination of formaldehyde by staircase voltammetry based on its electrocatalytic oxidation at a nickel electrode, Journal of Analytical Chemistry, 61(12), 1204-1208.

6 Wang, Z., Hu, Y., Yang, W., Zhou, M., Hu, X. (2012). Facile One-Step Microwave-Assisted Route towards Ni Nanospheres/Reduced Graphene Oxide Hybrids for Non-Enzymatic Glucose Sensing Sensors, 12(4), 4860.

7 Science Lab. Material Safety Data Sheet Formaldehyde solution MSDS. [serial online].Available from: http://zabam.tau.ac.il/.upload/MSDS/Formaldehyde.pdf. Accessed April 8, 2016.

8 IARC Working Groups. Formaldehyde. [serial online]. Available from: http://monographs.iarc.fr/ENG/Monographs/vol100F/mono100F-29.pdf. Accessed June 8, 2016.

9 World Health Organization. Formaldehyde in Food. [serial online]. Available from: http://www.cfs.gov.hk/english/programme/programme_rafs/programme_rafs_fa_02_09.html. Accessed June 8, 2016.

10 World Health Organization. (2003). Formaldehyde. [serial online]. Available from: http://whqlibdoc.who.int/hp/2002/a7769.pdf. Accessed June 8, 2016.

11 Maya, L., Angelina, K., Assya, K., Mariana, T., Maria, D. (2012). Allergic contact dermatitis from formaldehyde exposure. Journal of IMAB - Annual Proceeding (Scientific Papers). 18, 255-260.

12 Luks**,** E. (1992). Determination of formaldehyde using the colorimetric method with acetylacetone. I. Determination of formaldehyde in selected cosmetic products, 43(3-4), 289-93.

13. Wang, X., Si, Y., Wang, J., Ding, B., Yub, J. (2012). A facile and highly sensitive colorimetric sensor for the detection of formaldehyde based on electro-spinning/netting nano-fiber/nets, Sensors and Actuators B, 163, 186–193.

14 Giovann, B., Roberto, C. (2004). Determination of formaldehyde in spirits by high-performance liquid chromatography with diode-array detection after derivatization. Analytica Chimica Acta, 551,155–158.

15 Scientific Equipment center Prince of Songkla university. Formaldehyde. [serial online]**.** Available from: http://www.sec.psu.ac.th/webboard/?pid=view_replies&thread_id=212&forum_id=7. Accessed June 2, 2016

16 Wahed, P., Razzaq , A., Dharmapuri , S., Corrales, M. (2016). Determination of formaldehyde in food and feed by an in-house validated HPLC method. Food Chemistry, 202, 476–483.

17 Chemical Instrumentation Facility. Mass Spectrometry Tutorial. [serial online]**.** Available from: http://www.cif.iastate.edu/mass-spec/ms-tutorial. Accessed June 20, 2016.

18 Xiaojun, C., Guozhen, F., Liqin, J., Shuo, W. (2007). Kinetic spectrophotometric method for rapid determination of trace formaldehyde in foods. Analytica Chimica Acta, 590, 253–259.

19 Bodner research web. Electrolytic Cells. [serial online]. Available from: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/faraday.php . Accessed April 21, 2016.

20 Chemwiki. Typical electrochemical cell for voltammetry. [serial online]**.** Available from:http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Analytical_Chemistry_2.0/11_Electrochemical_Methods/11.4%3A_Voltammetric_Methods. Accessed June 20, 2016.

21 Shawn, G. (2012). Voltammetric Characterization Methods for the PEM Evaluation of Catalysts. Nelson Mandela Metropolitan University.

22 The Principles.Department of Chemical Engineering and Biotechnology. Linear Sweep and Cyclic Voltametry. [serial online]**.** Available from: http://www.ceb.cam.ac.uk/research/groups/rg-eme/teaching-notes/linear-sweep-and-cyclic-voltametry-the-principles. Accessed June 22, 2016.

23 Mahmoud, R.,Somayeh, F. (2015) Amperometric Detection of Isoprenaline Based on Glassy Carbon Electrode Modified by Iridium Oxide Nanoparticles. J. Braz. Chem. Soc, 26(5), 1034-1042.

24 Seyed, N., Shahram , G., Fatemeh, A. (2015). Nickel/ P nanozeolite modified electrode: A new sensor for the detection of formaldehyde, Sensors and Actuators15, 1-17.

25 Wikipedia. Graphene. [serial online]**.** Available from: https://en.wikipedia.org/wiki/Graphene. Accessed June 22, 2016.

26 Kuldeep, S., Anil, O., Dhawan, S. (2012).Polymer-Graphene Nanocomposites: Preparation, Characterization, Properties, and Applications. Nanotechnology and Nanomaterials, 38-40.

27 Jian, R. (2010), Controllable N-Doping in Graphene.Nano Lett, 10, 4975–4980.

28 Chun, C., Ching, W., Hung, W. (2004). Supported transition-metal oxide catalysts for reductionof sulfur dioxide with hydrogen to elemental sulfur .Chemosphere, 56, 425–431.

29 Zhao, Y., Zhao, D., Chen , C., Wang, X. (2013). Enhanced photo-reduction and removal of Cr(VI) on reduced graphene oxide decorated with TiO2 nanoparticles. Journal of Colloid and Interface Science, 405, 211–217.

30 Xiao, L.,Wen, F.,Hai , C.,Hao , Z., Jin , C.,Gui, Z., et al. (2012). Hydrogen evolution from water using semiconductor nanoparticle/graphenecomposite photocatalysts without noble metals. J. Mater. Chem., 22, 1539-1546.

31 Jing, B., Xiue, J., (2013) A Facile One-Pot Synthesis of Copper Sulfide-Decorated Reduced Graphene Oxide Composites for Enhanced Detecting of H_2O_2 in Biological Environments. Anal. Chem., 85(17), 8095–8101.

32 Tao, M., Qiana, X., Yin, L., Jian, C., Tie, R., Zhong Y. (2015). Nickle nanoparticles highly dispersed on reduced graphene oxide for ammonia decomposition to hydrogen. Journal of Industrial and Engineering Chemistry, 32, 373–379.

33 Zhonghua, X., Bo Y., Mengqian L., Honghong, R., Hui, W., Xiuhui, L. (2016). Direct electrodeposition of well dispersed electrochemical reduction graphene oxide assembled with nickel oxide nanocomposite and its improved electrocatalytic activity toward 2,4,6-Trinitrophenol. Electrochimica Acta, 192, 512–520.

34. Hummers, W.S., Offeman, R.E. (1958). Preparation of Graphitic Oxide. J. Am. Chem. Soc., 80(6), 1339–1341.

35 Dong, B., Song, X., Tang , Y., Lin, W. (2016). A rapid and facile fluorimetric method for detecting formaldehyde, Sensors and Actuators, B 222, 325–330.

36 Sciencelab, Benzoic acid- Material Safety Data Sheet (2013). p. 1-5.

37 Yu, D., Yong, D., Dong, S. (2013). A rapid and facile fluorimetric method for detecting formaldehyde, Journal of Environmental Sciences, 25,785–790.

APPENDICES

APPENDIX A

Calculation of Limit of detection

In an amperometric measurement of formaldehyde, the Ni-rGO sensor (15% No loading) was employed in an electrochemical cell that contained alkali solution as a background medium. Figure A.1 shows a response curve that was obtained from additions of formaldehyde solution (Arrows) to the medium. Electrochemical current increased as a result of formaldehyde addition.

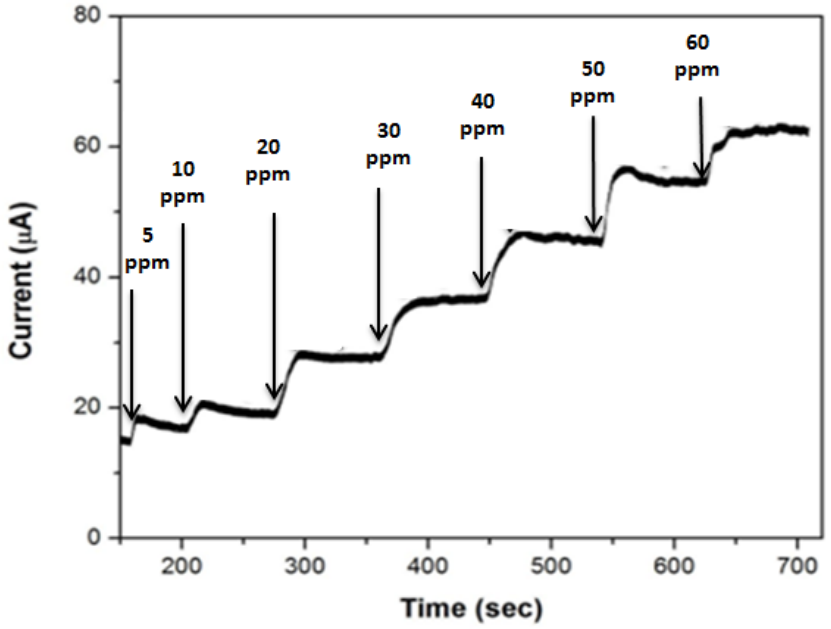

Figure A.1 Amperometric curve (Electrochemical current vs. time) obtained from additions of formaldehyde solution toNi –rGO (15% Ni loading)at applied potential of 0.6 V with pH 13 medium background

Heights of the electrochemical currents were plotted against formaldehyde concentrations, in which linear correlations were observed (Figure A.2). Slopes of each lines (Normalized current (I/Io) and Formaldehyde concentration) were determined as sensor sensitivity. Limit of detection was then calculated from equation A.1,

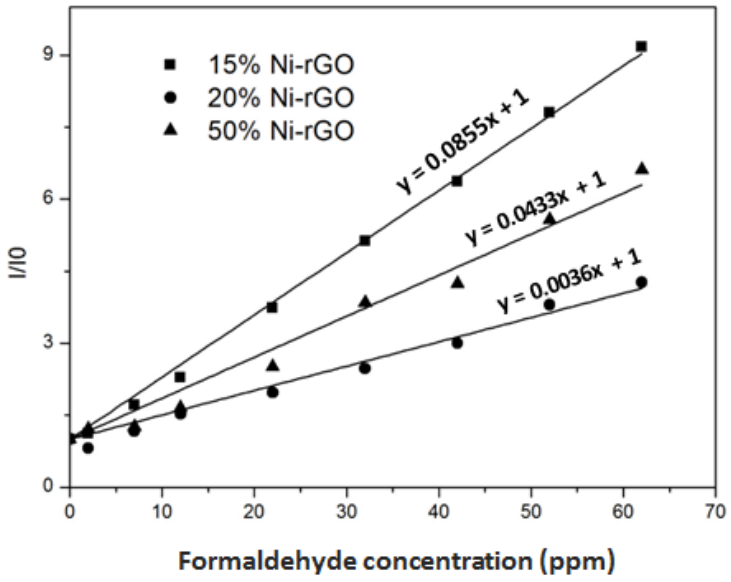

Figure A.2 Plots of normalized currents (I/I_0) and formaldehyde concentrations, obtained from Ni-rGO composite with 15, 20 and 50% Ni loading (pH 13 medium background)

$$\text{Limit of detection} = \frac{3 \times \text{std.}}{I_0 \times \text{sensitivity}} \qquad \text{equation A.1}$$

Std. is standard deviation

I_0 is the electrochemical current at baseline (NaOH 0.1 M)

Sensitivity is the slope of the curve of I/I_0 and formaldehyde concentration (Figure A.2)

APPENDIX B

Suggested protocol: Determination of formaldehyde in squid

1. Raw squid was cut into a small piece (1x1m^2), immersed in 100 mL solution containing 8,000 ppm formaldehyde for 12 hours.
2. The formaldehyde-soaked squid was immersed in 1.0 mL DI water or 1.0 mL 1.0 M NaOH solution for 15 minutes for formaldehyde extraction.
3. A 1.0 µL drop of extracted solutions were dispersed in 8.0 mL electrochemical cell (0.1 M NaOH background solution) while the Ni-rGO sensor was operated. The normalized current (I/I_0) was monitored as functions of operating time(Figure B.1) (Extract solvent: water).

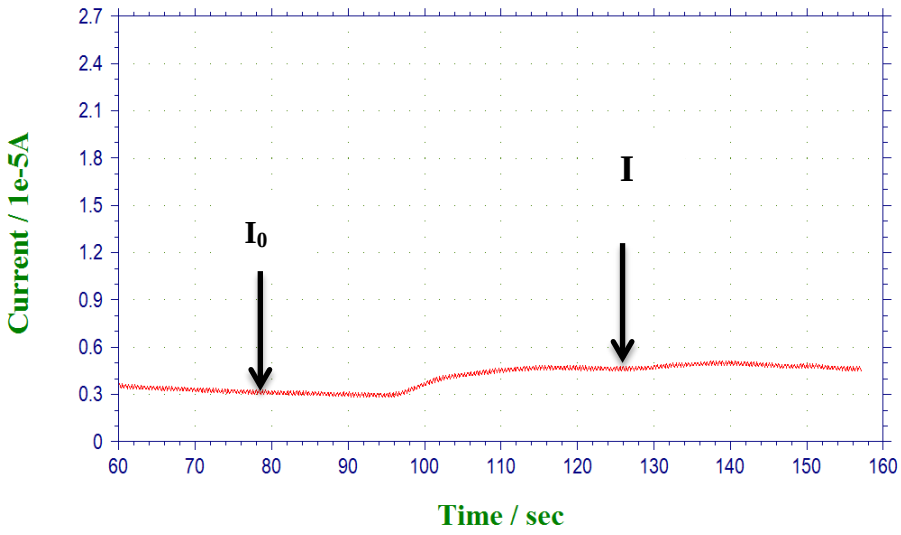

Figure B.1 Amperometric curve (Electrochemical current vs. time) of Ni –rGO sensor (50% Ni loading), introduced to squid extracted with water as the extract solvent.

4. The obtained value of I/I_0 was compared to the calibration curve (y axis). The formaldehyde concentrations in the squid extractswere determined (x axis).

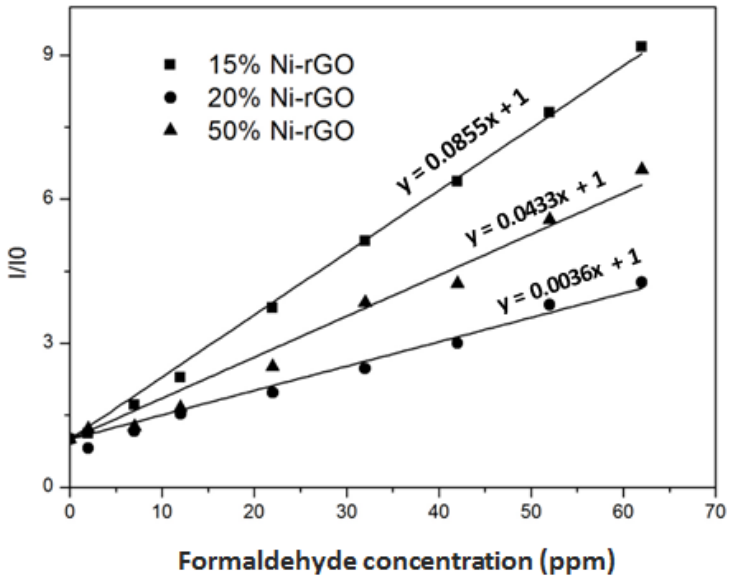

Figure B.2 Plots of normalized current (I/I_0) vs. formaldehyde concentrations, obtained from Ni-rGO composite with 15, 20 and 50% Ni loading (pH 13)

5. The concentration of formaldehyde in raw squid can be interpolated from the following equation;

$$C_1V_1 = C_2V_2$$

$$C_1\ (0.01) = 8.2(8)$$

$$C_1 = 6{,}560 \text{ ppm}$$

C_1 = Concentration of formaldehyde in raw squid (ppm)

C_2 = Concentration of formaldehyde in extracted solvent (ppm)

V_1= Volume of extracted solvent (mL)

V_2 = Volume of background solution (mL)

6. Absorbed formaldehyde percentage in raw squid can be calculated from;

$$\left(\frac{C_{in}- C_{out}}{C_{in}}\right) x\ 100 = \left(\frac{8{,}000-6560}{8{,}000}\right) x\ 100 = 18\%$$

Diffused formaldehyde percentage from raw squid into extracted solution (water) can be calculated from;

$$\left(\frac{C_{out}}{C_{in}}\right) x\ 100 = \left(\frac{6560}{8{,}000}\right) x\ 100 = 82\%$$

C_{in} is initial formaldehyde concentration (8,000 ppm)

C_{out} is finial formaldehyde concentration in solution (ppm)

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