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Polyaniline/Cellulose acetate composite and its ammonium ion sensing applications

A Thesis Presented

by

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to

The Graduate School

in Partial Fulfillment of the

Requirements

for the Degree of

Master of Science

in

Materials Science and Engineering

Stony Brook University

May 2014

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Abstract of the Thesis

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Conducting polymers have been investigated for years, since their discovery in 1977. Among them, polyaniline exhibits high electrical conductivity, leading to versatile applications, such as sensors, actuators, and catalysts.

In this thesis, emeraldine salt polyaniline (ES-PANI) and cellulose acetate (CA) have been employed to produce composite fiber and films by three different methods: electrospinning, drop coating, and spin coating.

The morphology and size of produced composites were studied by SEM. The results showed that the diameter of electrospun composite fiber decreases to nanosize, generating a nanofiber matrix that immobilize polyaniline particles.

Sensing experiments were carried out at room temperature. Three types of sensors, each made by a different method, were tested for their respective responses to ammonia hydroxide. Their sensitivity and stability in ammonium hydroxide environment has been assessed. Ammonia

hydroxide at different concentrations of 2.5 ppm, 10 ppm, 25 ppm and 50 ppm, were used as the analyte. As a result, the electrospun sensor exhibited far greater sensitivity and stability than the sensors made by drop coating and spin coating. With increasing concentration, the sensitivity rises, demonstrating this to be a good sensor in the application of ammonium ion detection.

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Acknowledgments

The work in this thesis would not be completed without the support of family, friends and co-workers.

First, I would like to extend my sincere gratitude to Professor Perena Gouma, my Master thesis' advisor, for providing me this great opportunity to study in the field of polyaniline sensing. Your profound knowledge, personal guidance and encouragement have been of an excellent basis for my Master's research.

I must also extend thanks to my other committee members, Milutin Stanaćević and Gary Halada. Thank you for your insightful suggestions and great supports, which providing great help of my project.

During this work, I have collaborated with many colleagues for whom I have great respected, and I wish to thank to all those who have helped me with my project. I am grateful to Shantanu Sood, Dr. Jusang Lee, Dr. Jim Quinn and Dr. Yutaka Nomura. Without your support, I would not have overcome so many barriers and finally complete my thesis.

Thanks to all the friends I met with. Your friendship was a nice addition to my graduate life.

Chapter 1

1. Introduction

1.1 Environmental and health impacts of ammonia

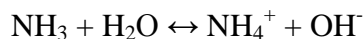
Ammonia, the product of natural nitrogen-containing compounds, can be employed in many areas. Since it provides a good source of plant nitrogen nutrition to terrestrial organisms, it is primarily applied in agriculture as fertilizer[1], to promote the growth of plants. In addition, its thermodynamic and vaporization properties make ammonia a natural refrigerant[2]. While Freon is the most common used refrigerant it suffers from disadvantages such as its toxicity and role in ozone depletion. Ammonia refrigerant not only keeps high heat transfer efficiency and gas to liquid transformation, but also is less toxic. Based on these merits, ammonia is used as one kind of natural refrigerant to replace Freon. Thirdly, ammonia solution can be used during fermentation to adjust pH and have influence on microorganism activities. In 1990, Sarkar[3] investigated ammonia effects on bacillus fermentation of soybeans, with increasing ammonia concentration, the pH during fermentation first decrease from 6.9 to 6.4, and then increase to 8.2 in 32h, controlling activity of bacillus. Besides the above mentioned applications, ammonia also can be used as antimicrobial agent[4], energy fuel[5], household cleaning products[6] and in other fields.

However, ammonia is still a toxic and hazardous compound with a pungent odor, causing health problems to human beings. For example, ammonia is considered to be responsible for a neuropsychiatric syndrome named hepatic encephalopathy[7].

Currently, there are many areas that are difficult to secure stable drinkable water due to water contamination. Among various pollution source, ammonia contamination has become one of most important threat to drinking water.

There are many sources that may contaminate drinking water, for instance, when ammonia is applied in agricultural fertilizer, ammonia can dissolve in surface water, also, organics that contain nitrogen are able to be reduced to ammonia and then absorbed by water. With the water penetrating underground, it brings negative influence on underground water, which is regarded as an indispensable source of drinking water[8]. In addition, water resource from industry offal, such as ammonia refrigerant, fertilizer factory, may be affected. Plenty of examples can be shown that how our drinking water resource are possibly contaminated. According to the report[1] from the Oregon Department of Human Services, the environmental limits for ammonia in water ranges from 0.25 to 32.5 mg/l (ppm). Hence, for drinking water safety concern, efficient evaluating techniques should be employed to check if the water meets the requirement of human drinking. Particularly, detecting the ammonia component in the water is very important[9].

When ammonia (NH₃) dissolves in water, it converts to ammonium ions (NH₄⁺), so there is a chemical equilibrium between ammonia and ammonium ion. The equilibrium is shown below.



Ammonium ion, however, can be determined by an ion sensor analytically[10, 11]. After ion detection, ammonia concentration can be deducted according to percent of conversion in specific environment. For example, in 1993, Spotte[9] presented a table containing the ratio ammonium

ion and ammonia with the consideration of pH, temperature and salinity. In this way, ammonia concentration in water can be indirectly derived.

1.2 Sensors

A sensor is a device which converts unreadable signals to other measurable signals, such as electrical: resistance, voltage, current or optical, which can be recognized by human beings. As

shown below, sensors are composed of three parts:

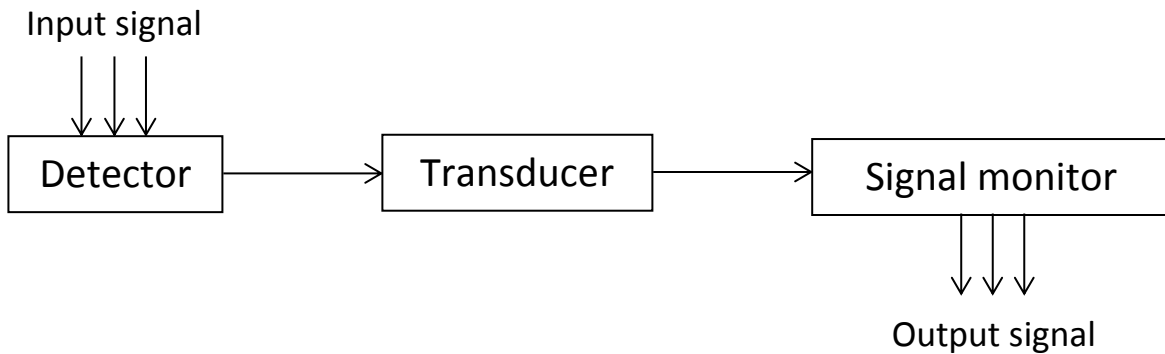


Figure 1 Sensor transduction process

The detector interacts with incoming stimulus, generating unreadable input signals, usually in chemical, physical or biological forms. Then transducer converts input signal to understandable and measurable output signals, including electrical, optical or mechanical forms. Finally, by monitoring readable output signal, human beings can detect the interaction between analytes and detector.

Sensor can be classified according to its output signal: resistive sensors, amperometric sensors, potentiometric sensors. Besides electronic output, optical and other physical signals also can be of use.

The idea of using a sensor to detect ammonia in water has been investigated for years, different materials, manufacturing approaches and testing methods have been adapted and received considerable momentum. Among these ammonia aqueous sensors, there are many advantages, such as high efficiency, fast response, environmental friendly. Among these materials that were used for ammonia sensor, polyaniline not only possess above positive point, but also exhibits thermal stability, cost effective, demonstrating to be ideal material for aqueous ammonia sensing.

The below table is ammonia aqueous sensor classification according to diverse output signals:

Sensor output	Material	Reference
Electronic		
Resistive	Polyaniline-(acrylonitrile-butadiene-styrene) composite film	[11]
Amperometric	Dodecylbenzene sulfonate (DBSA)-doped polyaniline nanoparticles, enzyme-gel(Urease, glutaminase and poly(carbamoylsulphonate) hydrogel) solution deposited on the surface of the PANI-modified electrode	[12, 13]
Potentiometric	Photocured poly(n-butyl acrylate) membrane with immobilised nonactin, SiO ₂ /ZrO ₂ /phosphate-NH ₄ ⁺ composite	[10, 14]
Optical	Immobilization of glutamate dehydrogenase and diaphorase in chitosan film and thiazolyl blue tetrazolium bromide as color indicator	[15]

Table 1 Ammonia aqueous sensor classification according to diverse output signals

1.3 Chemoresistive sensor

Chemoresistive sensor transforms the chemical reaction to electrical resistance change when exposed to a gaseous or liquid analyte. Here, the resistance change accounts for the charge carriers exchange between sensor and analyte during reaction.

There are five key parameters determine the effect and efficiency of a resistive sensor, they are sensitivity, selectivity, response time, recovery time and stability[16, 17].

Sensitivity: The sensitivity can be defined as electrical change when the sensors are exposed to the analyte. Certain input stimulation should create a detectable resistance change, therefore, output can be monitored. An equation can be used to represent the magnitude of resistance change, that is:

$$S = \frac{\Delta R}{R_0}$$

Here, $\Delta R = R_f - R_0$

R_f stands for final electrical resistance when sensors are exposed to specific gas or liquid, and R_0 is the resistance during the sensor exposure to the control. Therefore, ΔR is the resistance change when the sensor moving from the baseline condition to the analyte atmosphere. S represents resistance change proportion. The increasing difference between resistance values in the control and in analyte atmosphere, lead to greater magnitude of S , indicating the higher sensitivity of employed sensor.

Selectivity: in a normal condition, ideal sensing environment cannot be achieved, therefore, a good sensor must be sensitive to one certain analyte and avoid interference in testing environment. The selectivity indicates anti-interference ability while testing assigned analyte.

$$\text{Selectivity} = \frac{\text{Sensor sensitivity for interfering liquid}}{\text{Sensor sensitivity for analyzed liquid}}$$

Response time: when an analyte touches sensor, it takes time for the interaction, to quantify this parameter, the response time reflects the time that the sensor resistance changes from the start of baseline to 90% of final value when exposed to the analyte. A good sensor should have a short response time in the order of milliseconds-seconds.

Recovery time: when sensor returns to the control environment, it need time to return to previous resistance, to quantify this parameter, the recovery time is measured as the time that the sensor resistance changes return to 10% of its above mentioned response final value. Also, the short recovery time indicates the efficiency of applied sensor.

Stability: Operating stability is another key features, it is about whether the sensors can maintain the effectiveness and efficiency when exposed to analyte repeatedly and at different times. In the cases that analytes are kept interacting with sensors and cannot be removed, the baseline will not back to origin. Without ability to return to original baseline, sensors are announced to be contaminated and cannot be used. Moreover, further use of contaminated sensor will create more baseline deviation from the origin.

Since resistance is easy to be measured and analyzed, many researches have been investigated and applied in a wide range of aqueous sensing. One application that has received much attention is electronic tongue, which is to mimic tongues of human beings and used as discriminating

flavors of various liquids. Electronic tongue works as comprehensively analyzing a sample instead of acquiring certain information of individual specimen [18]. Sensor arrays from electronic tongue interacts with sample, then transducing to readable signal pattern, after statistical analyzing sensor data, a comprehensive conclusion about quality of sample can be drawn. Electronic tongue can be classified depending on output pattern signals, many of them are potentiometric, voltammetric and optical sensors[19].

Sensor output	Testing liquid	Major material	Reference
Electrical			
Potentiometric	Ammonium and alkaline ions (sodium, potassium)at different measuring sites in the states of Mexico and Hidalgo	Polyvinyl chloride, Ionophores nonactin, valinomycin, bis[(12-crown-4)methyl]-2-dodecyl-2-methylmalonate, tri-N-dodecylamine	[20]
Voltammetric	Ten teas and twelve detergents	Gold, iridium, platinum and rhodium	[21]
Impedentiometric	Fifty solution for 5 basic taste salty, sour,	Polyvinyl alcohol, polyallylamine, carbon nanotubes, Polylactic aci, poly(3,3-dipentoxy-2,2-bithiophene) and poly(3,3-	[22, 23]

	sweet, umami and bitter.	dipentoxy-2,2:5,2-terthiophene)	
Optical	Na ⁺ and K ⁺ ions in natural waters	polyvinyl chloride, crown ether-type ionophore	[24]

Table 2 Electronic tongue classification depending on output pattern signals

1.4 Polymer chemoresistive sensor

Conducting polymers, with its alternative single and double bonds, allow charge carrier to transfer in direction of the polymer backbone. Also, low cost becomes another advantage for considering conducting polymers as gaseous and liquid sensing elements[17]. When compared with metal oxide sensor, polymer exhibits some other advantages, such as great thermal stability, mechanical flexibility, wide range working temperature, easy processing and cost effective. Hence, conducting polymers that applied in sensor have been researched for years. In 2000, Heeger, MacDiarmid and H. Shirakawa received Nobel chemistry prize for discovery and development of conducting polymer. Currently, conducting polymers, like polypyrrole[25], polyaniline[26], poly(3,4-ethylenedioxythiophene)[27] and so on, were employed to resistive sensor. Besides materials options, various fabrication methods, including chemical polymerization[28], electrospinning[29], inkjet-printed[12], produce diverse structures, such as film[30], nanofiber[29], nanorods[27].

1.5 Polyaniline

Polyaniline is a type of conjugated polymers that has been recognized as gas and liquid sensor material because of its high conducting electricity and conductivity change with chemical reaction[26]. Other key features are thermal stability, low cost and ability to work under room temperature. The surface of polyaniline may interact with analyte, causing the structure change. Therefore, it may result in an increase or decrease in electrical resistance of the polymer. By monitoring resistance changes, interaction and concentration of analyte can be deduced.

However, polyaniline also has drawbacks, such as, infusibility and insolubility in most solvents, relatively low conductivity when compared with metals[31]. The first two disadvantages mentioned above lead to difficulties in fabrication and the last disadvantage renders to limited application. To figure out these problems, recently, many attempts have been made. One method to improve polyaniline processability is to use a suitable dopant. Some functional sulfonic acids, such as dodecylbenzene sulfonic and camphor sulfonic can be used as dopant, with introducing specific dopant, polyaniline proved to be dissolved in some solvents[32, 33], and hence become more easily processed. Another processing method uses commercial polymers as matrices in composites, so when polyaniline is mixed with other matrix polymers, polyaniline can be immobilized and its electronic properties remain intact. By introducing a matrix, the composite becomes easily processed with improved mechanical property. Saikia et al.[34]produced starch/polyaniline composites by using oxidative polymerization method. In this experiment, the author combined antioxidant property of pure polyaniline and biocompatibility of starch, starch component helped reduced the cytotoxicity of polyaniline, therefore, the antioxidant property of polyaniline can be applied in a bio-environment. Another example is cellulose acetate and polyaniline composite [35]. The durability and film-forming property of cellulose acetate makes

it an ideal matrix for the composite. Polyaniline exhibits stability in terms of its DC electrical conductivity.

The conductivity of polyaniline is lower than metal. To improve its conductivity, metal oxides are incorporated in it. Recently, many metal oxides have been used to form polyaniline composites, including tin dioxide(SnO_2)[36], indium oxide(In_2O_3)[36], Zinc oxide(ZnO)[37],titanium dioxide(TiO_2)[38]. In Wang's[38] experiment, titanium dioxide-polyaniline/polyamide 6 composite was fabricated to be tested in ammonia gas with concentration ranging from 50 to 250 ppm. Then, to demonstrate the increasing conductivity function of titanium dioxide, TiO_2 -PANI/PA6 and PANI/PA6 were compared for sensing; as a result, due to the formation of the P-N junction by p-type PANI and n-type TiO_2 , TiO_2 -PANI/PA6 composite exhibited greater response sensitivity and recovery. Furthermore, various gases, such as ammonia, methanol, ethanol and acetone, were used for selectivity tests, the results showing that TiO_2 -PANI/PA6 composite had magnificent selectivity for ammonia detection.

Although polyaniline itself has drawbacks, with recent research, these drawbacks can be overcome, leading to great future applications of polyaniline.

1.6 Measurement of electrical conductivity change

Conductivity alters when liquid analyte touches sensor. This is because when analyte touches sensor, there is chemical reaction between analyte and sensor, causing surface structure change of the sensor. With the change, sensor conductivity can be modified. Generally, there are two types of interaction between analyte and sensor that account for electrically conducting change:

one is a polymer redox reaction after treating oxidizing or reducing agents; the other one is a doping and dedoping process.

For polyaniline, there are three different states of polyaniline, leucoemeraldine, emeraldine, pernigraniline. All three of them can transfer through redox process. In addition, each state can be divided to base and salt type. Doping and dedoping are the methods that transfer between base and salt. The below is a figure that shows structure and transition of different polyanilines[39].

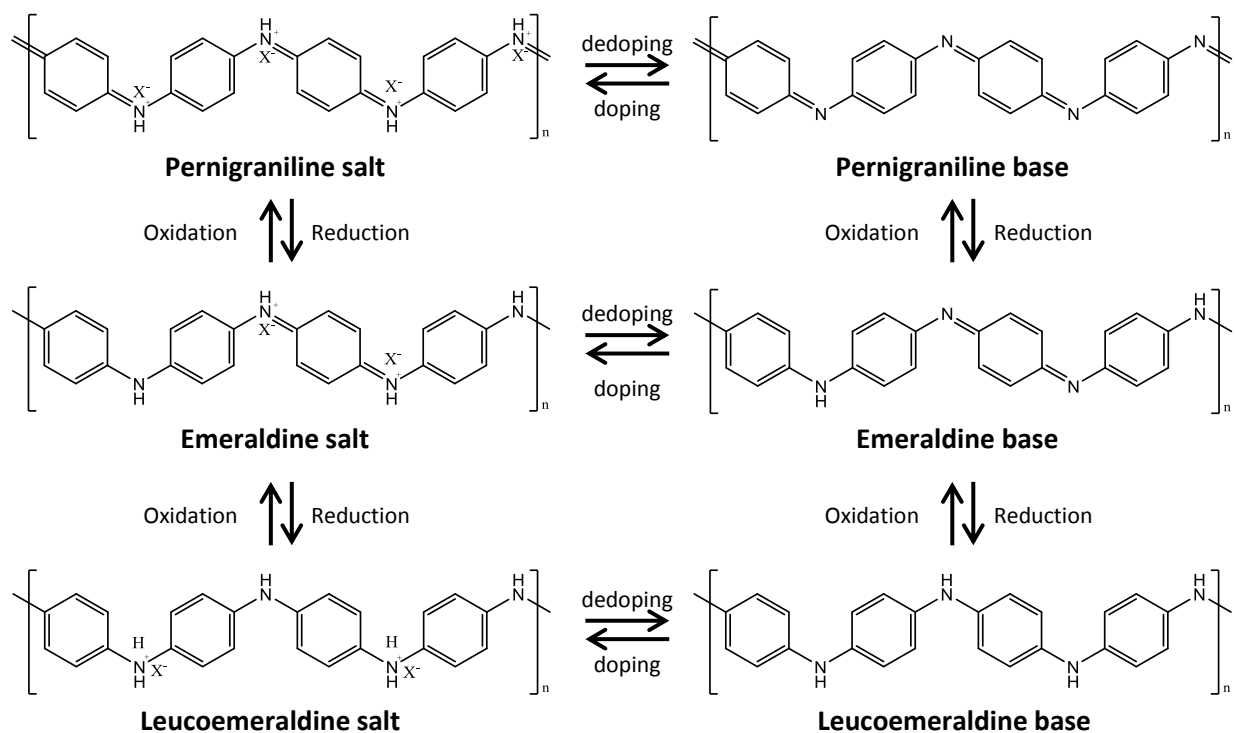


Figure 2 The reversible transformations of different polyaniline forms

By monitoring this electrical change, scientists can deduce the chemical reaction between analyte and sensor. As mentioned above, there are two ways of structure transformation, redox reaction and doping/dedoping process. For redox reaction, analyte should be able to oxidize or reduce

polyaniline structure to make its state change, resulting in conductivity altering. For doping and dedoping process, as the figure shown below[40], acid doping largely increase the conductivity of polyaniline, forming its salt state from base state. On the contrary, with the impact of base, salt state polyaniline can be led to base state with decreasing conductivity. Therefore, doping and dedoping process influence the conductivity.

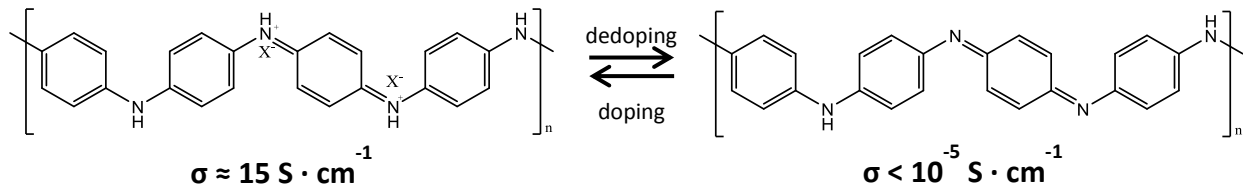


Figure 3 Polyaniline emeraldine base/salt transformation

1.7 Doping mechanism

For the purpose of increasing conductivity, certain impurities are introduced to pure materials, hence, the above process is called doping. In the case of polyaniline, emeraldine salt polyaniline (ES-PANI) performs the best conductivity, which is 15 S/cm, however, other forms of polyaniline only reach 10^{-5} S/cm[41]. To employ the best conductivity, all three base states should convert to emeraldine salt. Therefore, two most applicable ways of producing emeraldine salt polyaniline.

The first is oxidative doping from leucoemeraldine base polyaniline (LEB-PANI). Leucoemeraldine is totally reduced form of polyaniline. To achieve ES-PANI with higher conductivity, full reduction state should first be oxidized, then doped with strong acids. During the oxidation, part of electrons will be removed from the backbone chain and forming imine group, then, acids connect to the chain on the same site, increasing the conductivity. Usually the

oxidation doping takes two chemicals, oxidant and strong acid to fulfill the process, however, chlorine can be both oxidant and acid dopant, therefore, it takes only one step to fabricate.

Another doping method is acid doping, strong acid was used for its protons incorporating on the imine sites. First, electron transferred to the proton that binds to imine. Then, charge resonance results in electron delocalize, forming polaronic structure as emeraldine salt, increasing the conductivity. The difference between two doping processes is that acid doping does not change oxidation state and lose of electrons. Right now, acid doping is the most common method to be applied in doping mechanism.

1.8 Methods of fabricating polyaniline

There are many techniques of synthesizing polyaniline.

The most classical way of fabricating polyaniline is chemical synthesis, the basic materials for chemical synthesis are aniline, an oxidant and strong mineral acid. The most commonly used oxidant, ammonium persulfate, is added to aniline and acid, such as hydrochloric acid and sulfuric acid for fabrication.

During the processing, proton gaining from acid incorporates in aniline monomer, then with oxidant addition, radical cation is formed, according to resonance theory, electron transfers to para-position of benzene ring due to inductive effect and absent steric hindrance[41]. After electron transferring, two resonance forms can connect head to tail, becoming dimers. Then, dimers start to head-to-tail link, deriving long chain polyaniline.

The figure shown below is transformation steps.

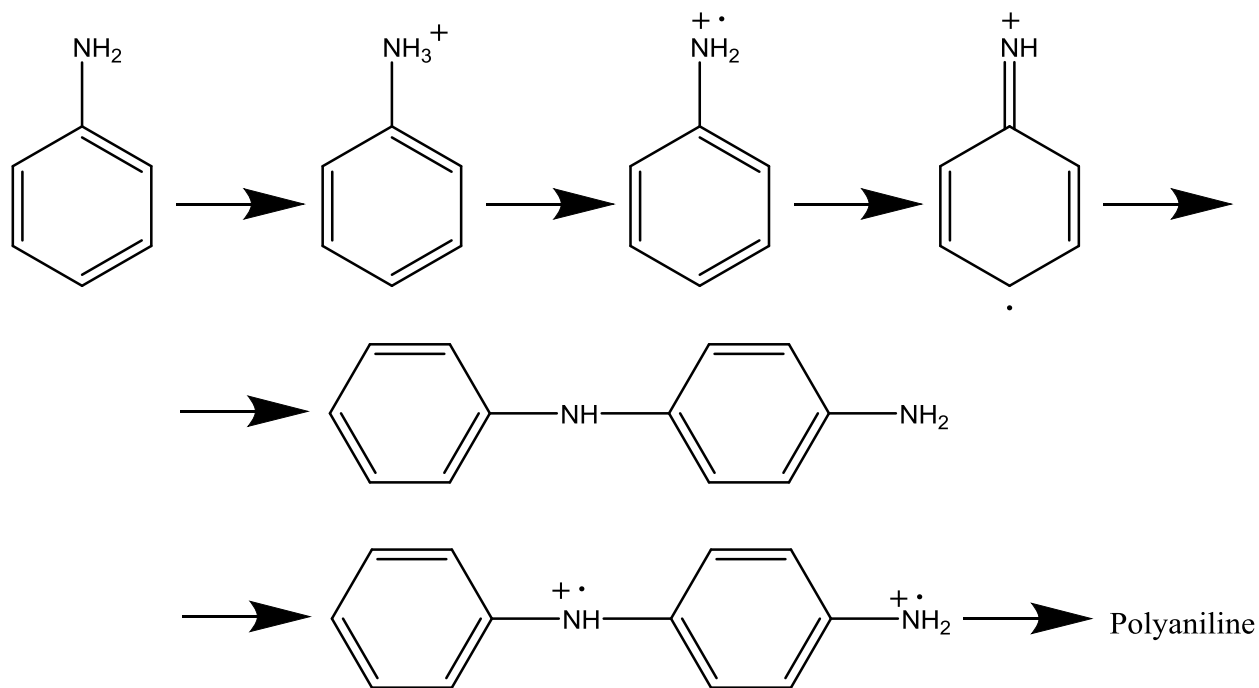


Figure 4 Polyaniline polymerization mechanism

Furthermore, with the advance of process, templates, such as nanoporous membranes[42], surfactant[43], were used for directing structure. Recently, Jiaying Huang found that with the use of immiscible organic/aqueous biphasic system, the nanosized polyaniline can be produced in large quantities[44].

Another method is electrochemical polymerization, when potential was applied in solution by electrical device, the conducting polyaniline can be deposited on the electrodes of electrochemical setup. The electrochemical process can be regarded as two steps. The first step is formation from aniline to polyaniline and deposit on the surface of electrode. After the first layer of polyaniline covering the electrode, subsequently, more polyaniline formed and deposited on the surface of previous polyaniline layers[45]. The most advantage of electrochemical polymerization is operated in a relatively clean environment, without additional chemicals

polluting synthesis, as a result, obtaining pure material. Langer[46, 47] fabricated PANI with both micro and nano structure . H.X. He [48]combined mechanical break junction method with electrochemical polymerization, stretching 200 nm long nanowires, reducing its diameter from 20 nm to 6 nm.

The third method is called enzyme assisted growth, which is stable, environmental compatible and without bi-product generation. Besides, enzyme method is able to improve mechanical integrity of composite. Wang[49] prove all above advantages by using horseradish peroxidase(HRP) catalyze PANI/ sulfonated polystyrene (SPS) complex, and then dry-spinning. Also, Nabid [50] successfully synthesize core-shell structure PANI/TiO₂ composite with horseradish peroxidase(HRP) as catalyst, H₂O₂ as oxidation agent and sulfonated polystyrene (SPS) as matrix. However, the complexity of enzyme synthesis renders it limited application.

In addition, template synthesis of polyaniline is widely used due to its highly effectiveness and relatively simple structure. Because the polyaniline shape depends on template, therefore, template is designed according to the desired polyaniline shape. The polyaniline formed on the surface of template, then template dissolved or incinerated, deriving a material with desired structure. However, with such intriguing features, template synthesis also has some disadvantages: the first is during the template removing process, the solvent that dissolve template or high temperature incineration may also have influence on polyaniline itself, the solvent or high temperature are possible to change polyaniline structure, or even worse, completely destroy polyaniline. The second is after template remove, polyaniline with desired shape may be destroyed or aggregated without the support of template.

Mechanical stretching is a method that elongate material under certain load and environment, in the process, aligned nanomaterial can be derived. H.X. He[48] stretched polyaniline, reduced its diameter, improved its alignment, and correspondingly, increased conductivity of polyaniline. Also they found that, over-stretched will induce abrupt transitions between stable polymer chain configuration, causing the decrease in conductivity.

1.9 Electrospinning

Among those techniques, electrospinning, has been recognized as another novel method of fabricating nano-sized materials. It applies high voltage on the polymer to alter surface tension to form nano-structures. Various polymer solutions, such as polyacrylonitrile[51], polyvinyl alcohol[52], polyaniline[53], polyvinylchloride[54], cellulose acetate[55], have been successfully electrospun into nano-sized fibers.

The high voltage cause droplet electrical charging, inducing electrostatic repulsion, to a certain extent, the liquid erupts, forming jets. During the electrospinning process from ejecting to reaching collector, the solution jet evaporates or solidifies, and forming interconnected mats at the collector[56].

The complete electrospinning setup contains a DC high voltage power supply, syringe, programmable syringe pump, needle with different gauge size, collector. Moreover, the whole electrospinning setup should be applied under fume hood in case that volatile solution evaporates in the air.

The process of applying electrospinning should be in the following sequence: Firstly, solution is introduced into syringe with proper chosen gauge size of needle. Then, syringe is installed and fixed on the syringe pump, also, high voltage supplier are connected with needle and aluminum

substrate. With the force from syringe pump, solution can be ejected from needle, at the same time, the applied high voltage operated from needle to collector form jets and finally, the interjected fiber reach the collector[16, 57].

The electrospinning setup is shown below

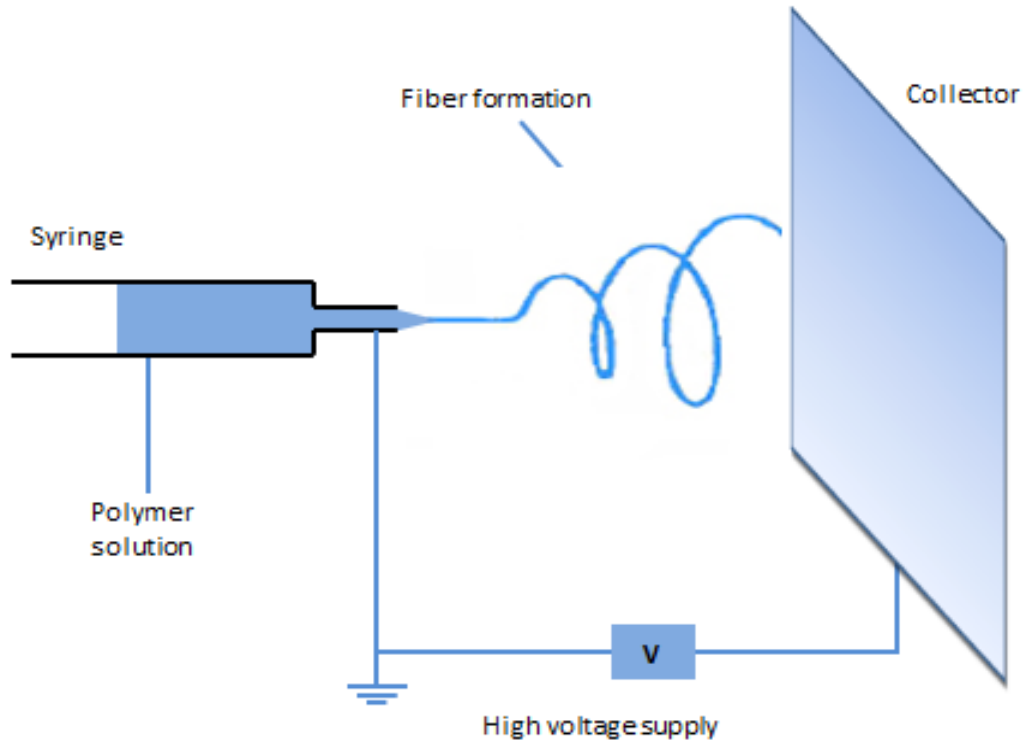


Figure 5 Electrospinning setup

Both vertical and horizontal electrospinning setup can be used. Each of them has its own advantages, the gravity in vertical setup induce solution down to the collector. On the other hand, the tilting angel of syringe will modify nano-fibers.

There are three key parameters that electrospinning setup influence the diameter of fibers, they are voltage, flow rate and distance between needle and collector.

Voltage[58]: with the increase of voltage, however, the fiber diameter enhancing the electrostatic repulsion, leading to stronger surface break, therefore, the fiber diameter decrease. Moreover, increasing voltage results in uniformity of fiber mat. On the contrary, reducing voltage will increase fiber diameter and reduce uniformity.

Flow rate[59]: high flow rate provide large amount solution ejecting from the needle, however, excess amount of solution cause the solution lacking of stretching strength and sufficient time for evaporation, leading to increase of fiber diameter. In the opposite, lower flow rate generate enough stretching strength and evaporation time, reducing fiber diameter.

Distance between needle and collector[57]: the longer distance results in smaller fiber diameter. Inversely, shorter distance gives rise to larger diameter size.

Besides above three parameters, there are some other parameters, such as viscosity, surface tension and solution temperature. Solution viscosity depends on the nature of solution and concentration of solution. Higher concentration increases viscosity, therefore, resulting in large electrospun fiber diameter.

By employing electrospinning technique, micro or nano-sized material or composite with high surface to volume ratio and porosity can be produced. Besides changing surface to volume ratio, electrospinning increases flexibility in surface functionalities and mechanical property. Also, the electrospinning method is easy to control and cost effective.

However, with above advantages of electrospinning, it has some drawbacks [56]. First is about uniformity, the setup cannot control the fiber diameter consistently, usually, the setup only can determine a certain range of diameter. Although some researches have been done saying that electrospinning operating on high temperature lead to more uniformity than in the room

temperature, this theory has not been generally proved[56]. Another problem is about forming of beads, higher concentration renders to form beads. These beads decrease the uniformity, and hence influencing the conductivity.

For instance, Liu[55] succeed electrospun cellulose acetate with three different solvents, acetone, acetic acid and dimethylacetamide (DMAc) and studied the impacts of solution properties and substrate materials on electrospinning and derived morphology of cellulose acetate. In the study of solvents, above three solvents were selected due to their different values among viscosity, boiling temperature and solubility, which were considered to be key parameter to decide electrospun material. The result showed that cellulose acetate in acetone : DMAc at ratios 2 : 1 predicted continuous and stable electrospinning process , also the fiber size was able to be diminished to 100 nm. In the study of collector materials, aluminum foil tended to form more tight structure, less porous and thicker than paper.

1.10 Drop coating

Drop coating is one material producing method that employs continuous solution drop depositing on substrate. After dropping process, the solvent evaporate, forming thin film. The material itself and solvent are two major influences on thin film formation. Moreover, during the drop coating process, the deposition speed of droplet and drying time also have impact on forming thin film. Slower dropping and drying rate predict better uniformity and reduce thickness. Even though drop coating is easy to operate, there is a disadvantage that film uniformity is poor.

Watanabe[60] utilize alternate drop coating to derive dual biointerfaces with polyelectrolyte multilayers. Then, multilayers were capable of adsorbing model protein called serum albumin and using as protein reservoir, demonstrating drop coating process is a novel fabrication method.

1.11 Spin coating

Spin coating is a method to producing uniform thin film on a plain substrate. Its principle is by using high speed rotation, generating centrifugal force to make material spreading on the substrate. There are several procedures when employing spin coating. First, specified materials, usually composites, were deposited on the center of substrate. Then, the rotation started to accelerate, with the increase of angular speed, deposited materials were spread from the center to the edge of substrate. Finally, with drying process, solution came out of the composite, leaving the drying composites solidify, after that, thin films were derived[61].

Thickness and uniformity are the two major factors that describe the quality of thin film. As an advanced film formation process, there are two aspects to determine the thickness and uniformity of derived products. One aspect is about nature of raw material, such as viscosity, composite ratio, surface tension. For instance, if the viscosity of composite is high, indicating that the composite is hard to spread through the surface of substrate, therefore, greater centrifugal force and rotation time should be increased for composite spreading.

The other aspect is spin coater parameter: spin speed and spin time:

Spin speed: according to centrifugal force equation shown below:

$$F = mrw^2 = \frac{mv^2}{r}$$

Here, F, w and v represent centrifugal force, angular speed and linear speed, respectively. As shown, centrifugal force is proportional to the square of speed, indicating that higher speed results in greater force for composite solution spreading. Typically, rotation speed ranges from

1500 rpm to 6000 rpm, to ensure enough force for extension and control uniformity and thickness. Increasing spin speed renders to thinner film and greater uniformity.

Spin time: time is another important parameter in spin coating, enough spin time ensures material can spread through the whole substrate uniformly and film can be reduced to certain thickness.

With both speed and time increasing, thinner film can be achieved. However, when both speed and time increase to critical point, thickness reaches to minimum.

Besides spin speed and spin time, drying rate also influence film thickness and uniformity. The cause can be divided into two parts, one is internal cause, the material itself property plays major impact on drying rate. The other is external cause, such as temperature and humidity. With the slow drying rate, film thickness decrease and uniformity increase.

1.12 Polyaniline based sensors for aqueous ammonia sensing

Some works have been done for polyaniline in the use of aqueous ammonia sensing. Different composites materials, fabrication methods and sensing tests lead to different results. Some of them showed great effective and efficient sensing, demonstrating polyaniline to be excellent sensor for ammonia liquid.

For example, Koul [11] fabricated polyaniline/acrylonitrile-butadiene-styrene (PANI-ABS) composite film through chemical oxidative polymerization and studied its aqueous ammonia sensing response. Hydrochloric acid and ammonium persulphate were used as dopant and oxidant. Then, aqueous ammonia test was carried, it showed that the baseline ranged from 300 to 1.302 k Ω and increased to maximum 10^{11} Ω when exposed to different concentrations of aqueous ammonia ranging from 1N to 10^{-5} N.

Another sensor example is doped polyaniline produced by inkjet-printed as the deposition technique[12]. Then sensor experiment were carried out for testing aqueous ammonia, the results showed that the detection limit of ammonia was at least 2×10^{-5} M. With the increase of concentration, the sensor exhibited higher sensitivity. Also, sensor was tested in the period of 15 days with injection of 18 ppm ammonium, demonstrating its good daily stability. In the last, sensor with a bunch of interferences from refrigerant was measured for selectivity, however, high concentration of sodium chloride proved to have negative influence on the sensor.

Even though current work of polyaniline in the use of aqueous ammonia sensing show good response when the sensors are applied in the environment of ammonia, sensitivity, selectivity and stability have been demonstrated to be applicable in ammonia sensing, however, no sensors can be described as an ideal one, there exists some disadvantages, such as unstable baseline and relatively complicated processing method.

The present paper discusses the response behavior of electrospun polyaniline/cellulose acetate (PANI-CA) composites fibers to aqueous ammonia at different concentrations. Also, a comparative study of PANI-CA film produced by drop coating and spin coating has been carried out.

Chapter 2

2. Material synthesis and characterization

2.2 Materials and equipment

In order to produce ES-PANI/CA composite for the sensor, emeraldine salt polyaniline (Fluka-Selectophore), cellulose acetate (Sigma-Aldrich) and acetone (Pharmco-aaper) were used in this fabrication process. For the sensing test, deionized water (Pharmco-aaper 0.22 micron filtered) and ammonium hydroxide (J.T.Baker) were used.

For fabrication, electrospinning setup contained syringe pump (kd Scientific), syringe, 20 gauge needle, high voltage supplier (Gamma high voltage), and collector. Spin coating used spin coater (Chemat technology kW-4A). For sensing test, resistance measurement instrument (Agilent 34401A digit multimeter) was used.

2.2 Material synthesis

ES-PANI/CA Hybrids

Emeraldine Salt Polyaniline and Cellulose Acetate were mixed together in acetone solution. Samples of polyanilic and cellulose acetate, in the ratio of 1:4, were deposited onto alumina substrates with interdigitated electrodes, as shown below. Three different methods, electrospinning, drop coating and spin coating were used for deposition by using the same 1:4 ratio. For electrospinning, 20 gauge needle, 22 kV voltage, flow rate of 0.2 ml/min and 80mm distance between needle and collector were applied; For drop coating, sample solution consecutively dropped on the substrate until cover the whole surface of interdigitated electrodes,

then kept at room temperature overnight for drying process; For spin coating, 3500 rpm was applied for 40s, then kept at room temperature overnight for drying process.

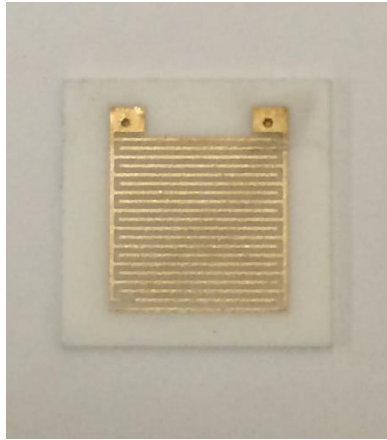


Figure 6 Al_2O_3 with Au electrodes transducer



Figure 7 Produced Sensor (From left to right: electrospun, drop coated, spin coated)

2.3 Material characterization

2.3.1 Scanning Electron Microscopy (SEM) analysis

SEM characterization for electrospun, drop coated and spin coated samples were conducted by using JEOL 7600F SEM for electrospun and drop coated samples and LEO 1550 for spin coated sample. Before SEM characterization, gold sputtering process was carried on the surface of samples in the environment of argon plasma. 20 kV was applied with the back scattering detector and the working distance is between 7mm and 8mm.

2.3.2 Sensing analysis

Sensing tests were carried out for derived ES-PANI/CA composite under ammonium hydroxide environment at room temperature. Electrodes transducer connects multimeter measurement instrument through gold wire for resistance monitoring. Different concentrations of ammonium hydroxide, 2.5 ppm, 10 ppm, 25 ppm and 50 ppm were used to test electrospun sensor to investigate the concentration influence of sensor and calculate sensitivity values. Then drop coating and spin coating fabricated sensors were test under 25 ppm ammonium hydroxide environments for comparing electrospun sensor efficiency.

Chapter 3

3. Results and discussion

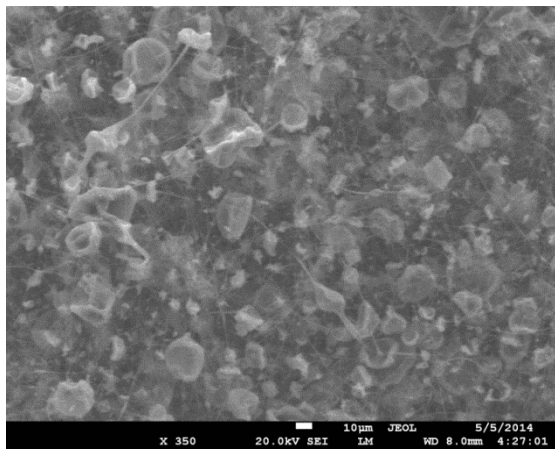
Cellulose acetate, as one of most important esters of cellulose, has been researched and widely used for a long time. There are several advantages for employing cellulose acetate, first is its ideal immobilizing property and solubility in many solvents, therefore, cellulose acetate has been applied as matrix to immobilize other polymers or metal oxides, forming composites to extend the application of immobilized material. In addition, cellulose acetate is easy to be shaped and inexpensive. Different forms, film, membrane and fiber, can be made depending on applications. Last but not the least, cellulose acetate is structural stable and hydrophobic. Being insoluble in water makes it perfect material that can be used in the aqueous environment.

With these advantages, cellulose acetate was employed to incorporate emeraldine salt polyaniline for ammonium hydroxide sensing. And acetone, which can dissolve cellulose acetate, was chosen to be the solvent.

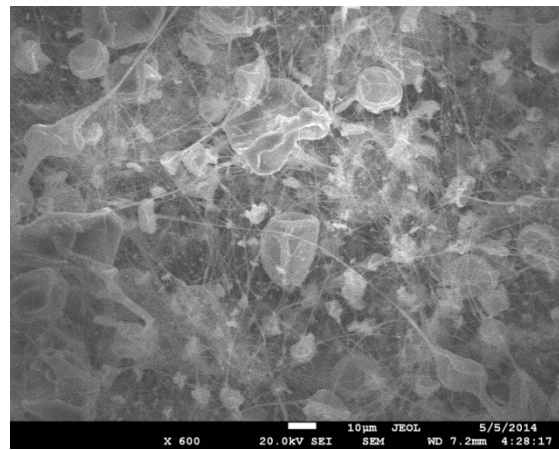
Electrospinning, drop coating and spin coating were successfully employed to produce PANI/CA composite in the ratio of 1:4. Electrospinning produced composite fiber, however, both drop coating and spin coating formed composite films. Because spin coating fabricate film by rotation, it led to better uniformity, nevertheless, drop coated film is formed by continuous dropping process, cannot promise the uniformity.

3.1 Structural characterization - SEM

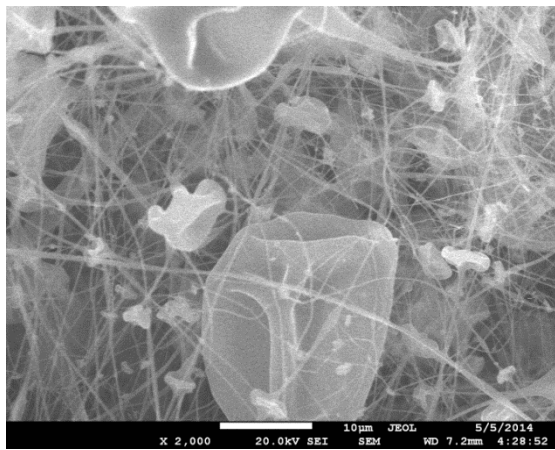
The below figures show ES-PANI/CA composite produced by electrospinning.



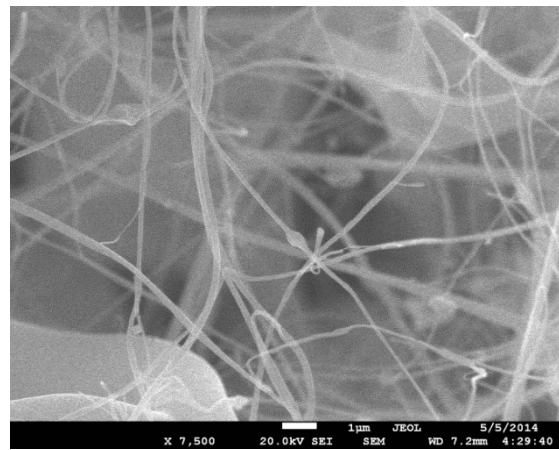
(a)



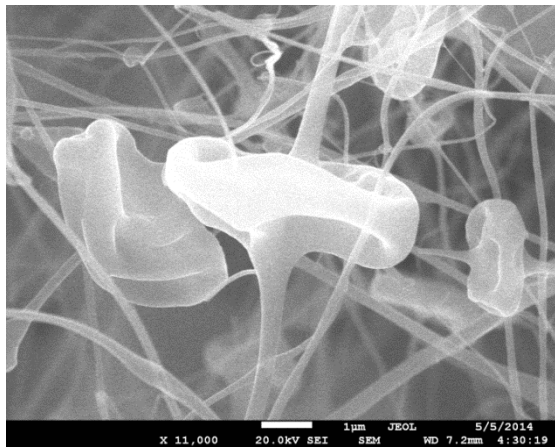
(b)



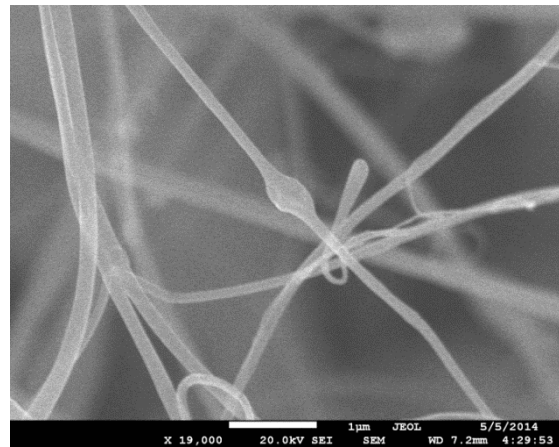
(c)



(d)



(e)



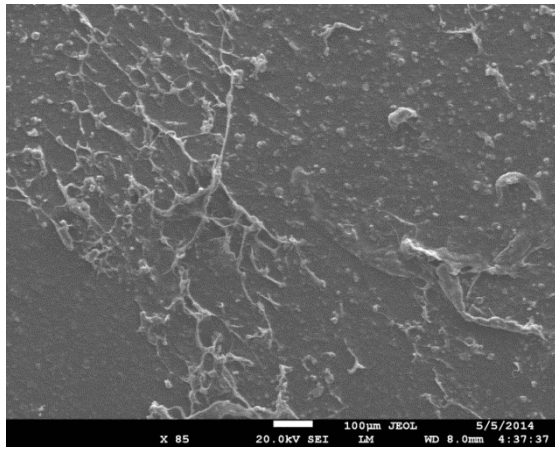
(f)

Figure 8 SEM image of electrospun ES-PANI/CA at (a) 350X, (b) 600X, (c) 2KX, (d) 7.5KX, (e) 11KX, (f) 19KX

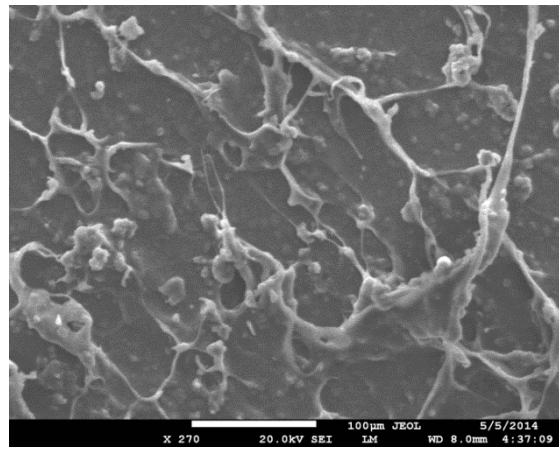
Based on above SEM figure, clearly, PANI particles were dispersed in the matrix fiber instead of being dissolved. The reason is that emeraldine salt polyaniline is not soluble in most solvent, the most common solvents that applied in polyaniline dissolution are N-methyl-2-pyrrolidone (NMP), toluene and trichloromethane. However, the solvent that used in this experiment, acetone, cannot dissolve polyaniline, but to dissolve cellulose acetate, therefore, polyaniline particles were only dispersed in the cellulose acetate/acetone solution after sonication. Then, with employing electrospinning, cellulose acetate was electrospun on the substrate forming fiber matrix and polyaniline particles were dispersed in the matrix of cellulose acetate. Therefore, from above low magnification figures (a), (b), (c), the particles were easy to be recognized between the fibers.

And figure 8 (f) clearly shows the diameter of matrix fiber, according to the scale, one can conclude is that nanosized diameters of cellulose acetate matrix fibers were derived through electrospinning method, providing high surface to volume ratio. Electrospinning has known to be an efficient method fabricating polymer nanofibers. Polymer solutions become to be charged by high voltage suppliers, generating electrostatic force. At the top of needle, when electrostatic force overcomes surface tension, solutions eject out and undergo elongation to make fiber thin and long, then the solutions evaporate and deposit on the surface of substrate, forming microsized or nanosized fibers.

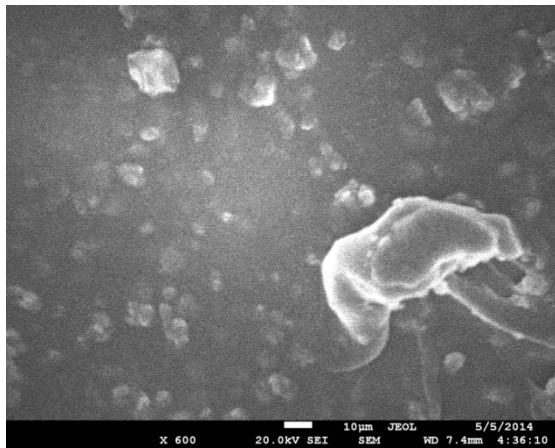
However, according to figure 8 (e), there are beads formed along the matrix fiber, influencing the continuity of fibers. In the study of electrospinning, beads formation is common and attributed to the viscosity of polymer solutions. Usually, higher concentration increase the viscosity, hence, with high viscosity, beads tend to be easily appeared.



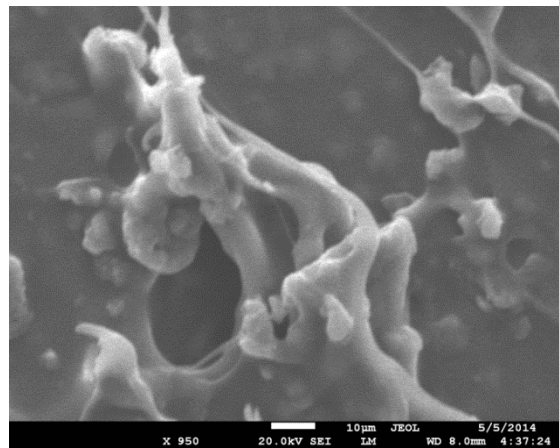
(a)



(b)



(c)



(d)

Figure 9 SEM image of drop coated ES-PANI/CA at (a) 85X, (b) 270X, (c) 600X, (d) 950X

The above figures display sample made by drop coating. The figures show non-uniformity surface with larger size compared with electrospun sample images. Furthermore, since it is film, it cannot show fibers across the images, giving us limit insight into its structure. Consecutive solution dropping can predict uniformity of polymer. Therefore, figures (a) and (b) display that polyaniline cannot be well dispersed. Plus, as figures (c) and (d) showed, the polyaniline exist in composite as a form of particle, so the surface of the drop coating made sample is not smooth.

Lastly, unlike electrospinning, drop coating is not a method to produce micro- or nano-composite, it is just the way of depositing film without changing its material structure or size, hence, the film size is not able to be diminished.

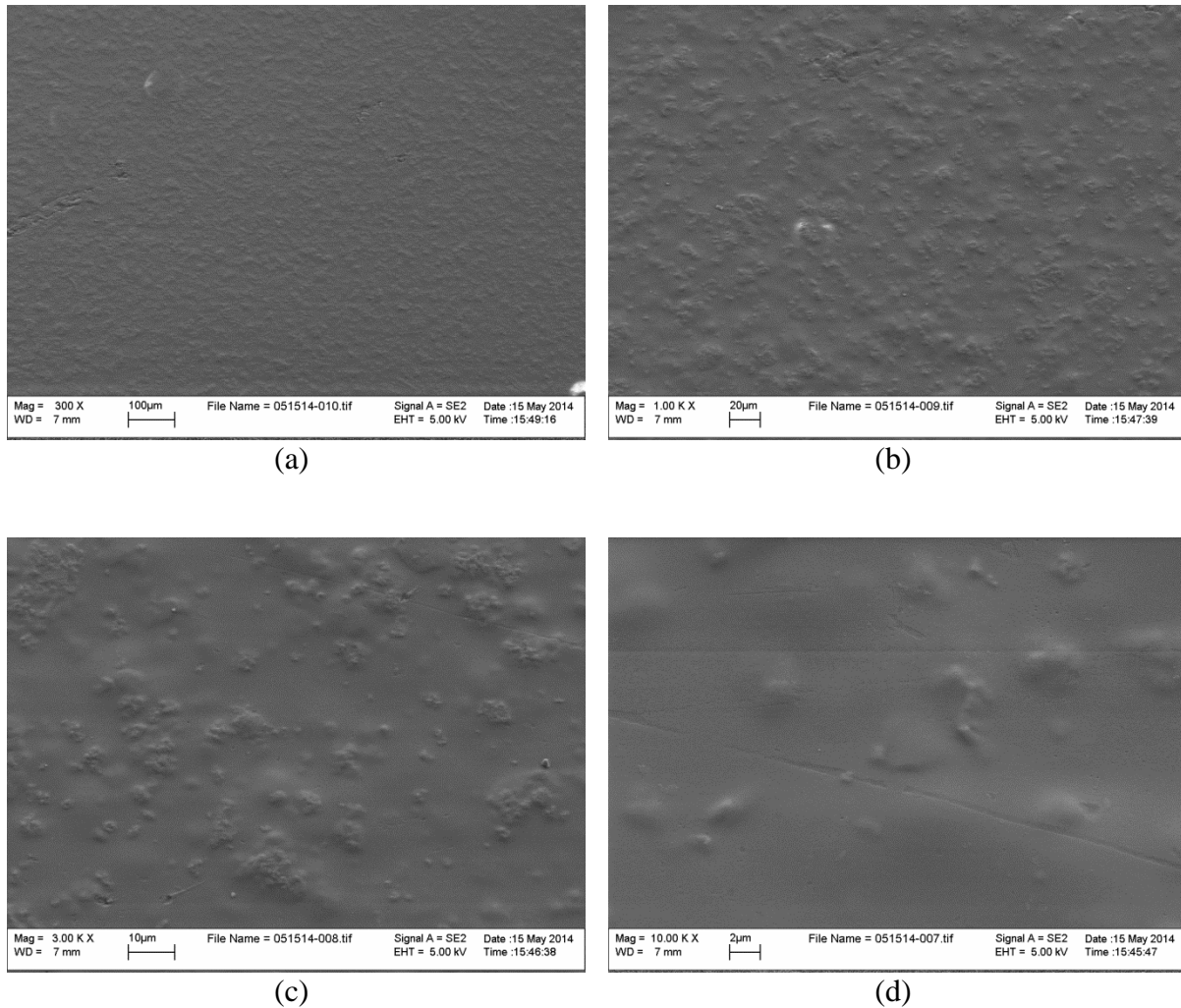


Figure 10 SEM image of spin coated ES-PANI/CA at (a) 300X, (b) 1KX, (c) 3KX, (d) 10KX

SEM sample image produced by spin coating also showed large size film, but when compared with drop coating sample, the advantage of spin coating high speed rotation, generating centrifugal force, make the film spread through the surface relatively uniform than drop coated

sample, as shown in figure 10 (a). Also, in figures 10 (b), (c), (d), there exist protuberances on the surface, and it is believe to be undissolved polyaniline.

3.2 Sensing analyze

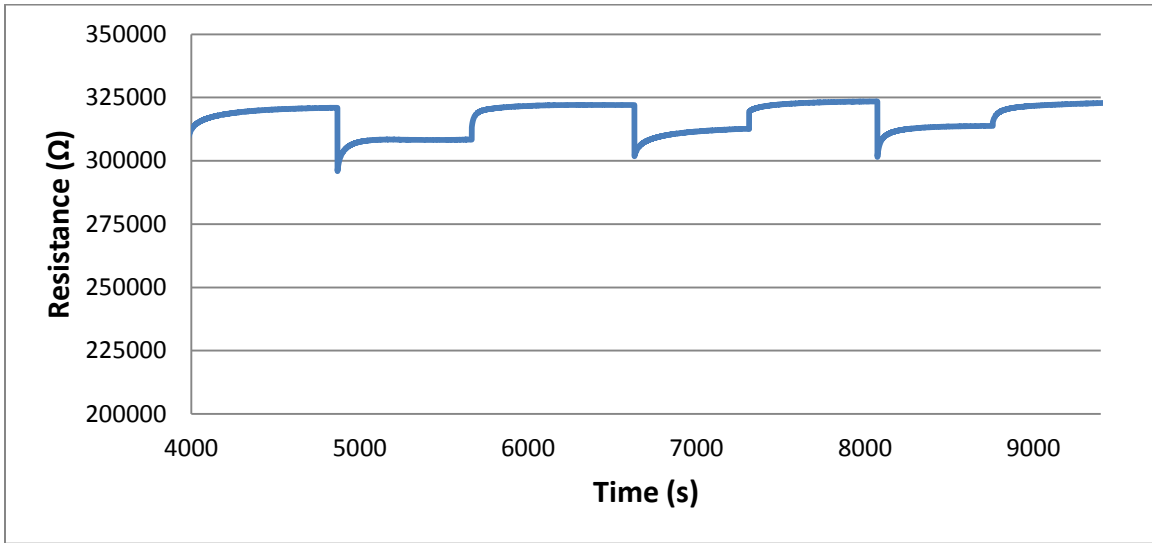


Figure 11 Graph of electrospun ES-PANI/CA response to 2.5 ppm ammonium hydroxide

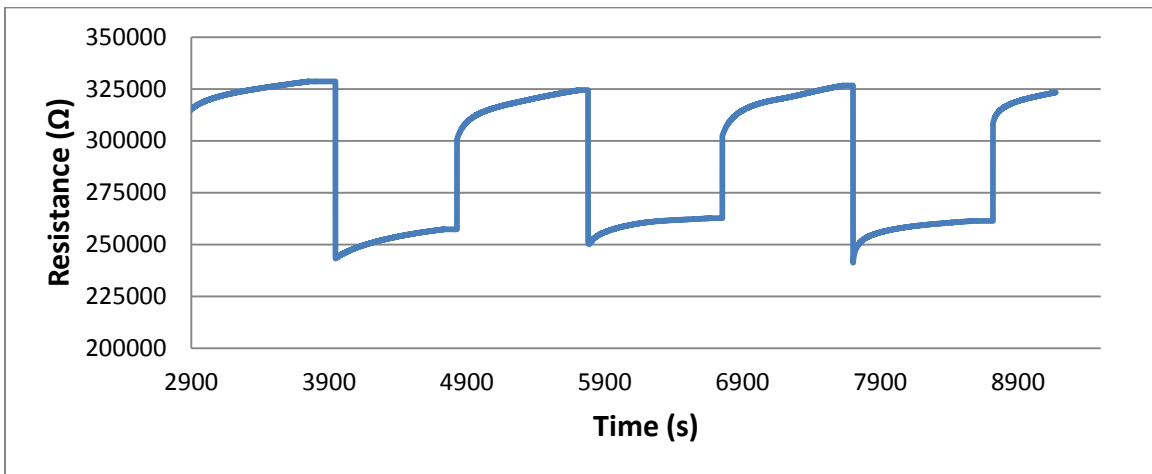


Figure 12 Graph of electrospun ES-PANI/CA response to 10 ppm ammonium hydroxide

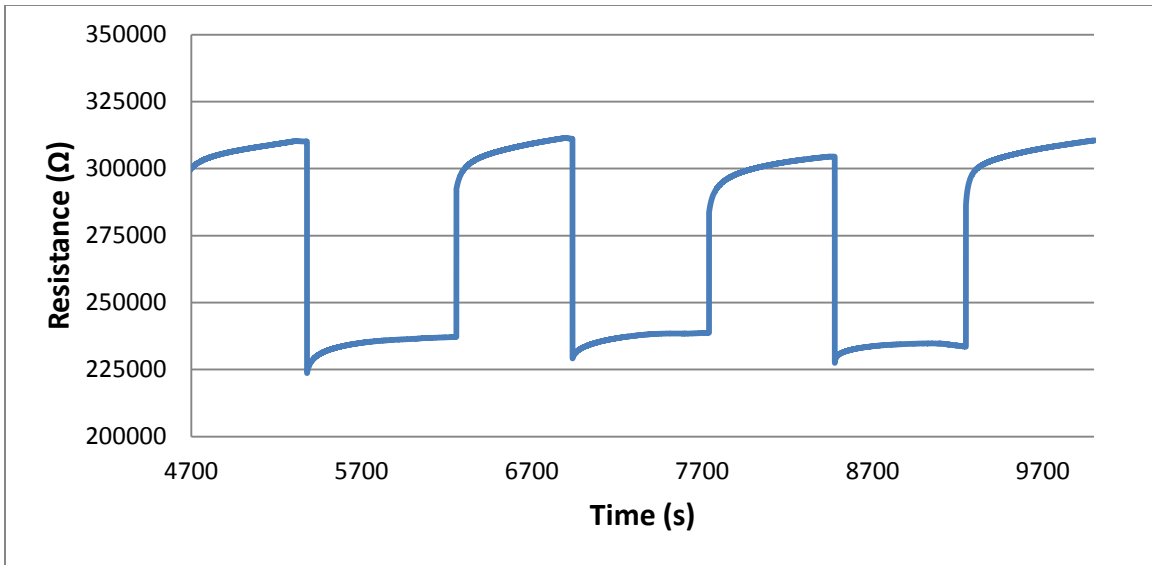


Figure 13 Graph of electrospun ES-PANI/CA response to 25 ppm ammonium hydroxide

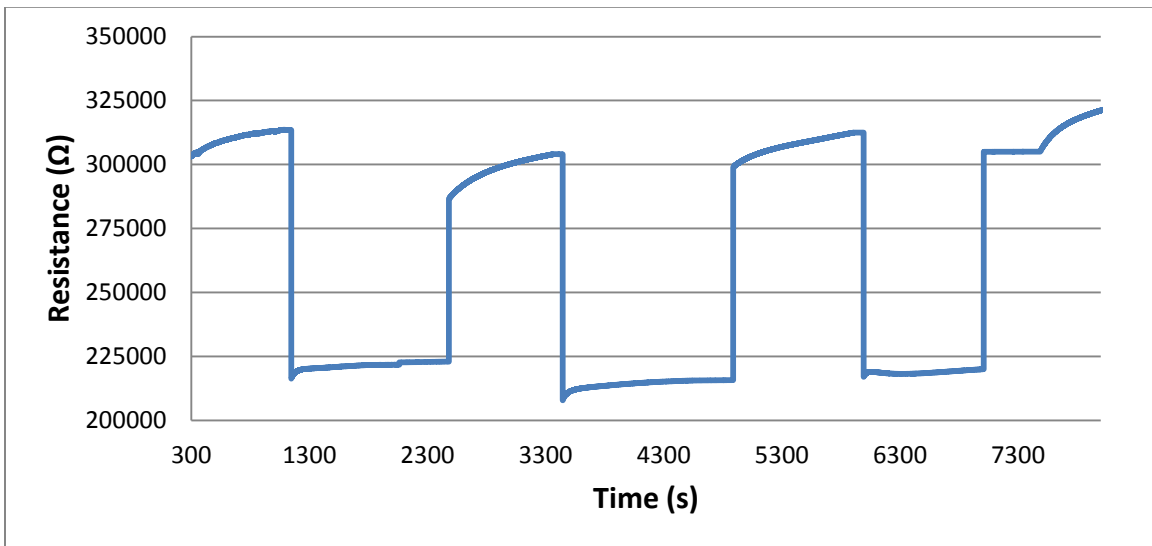


Figure 14 Graph of electrospun ES-PANI/CA response to 50 ppm ammonium hydroxide

Above figures reveal the sensor, made by electrospinning, response to ammonium hydroxide under different concentrations. To analyze sensing behavior, firstly, sensor was put into the deionized water for deriving stable baseline, generally, the resistance of ES-PANI/CA electrospun sensor remains 310-320 kΩ when immersed in deionized water. Then the sensor was

put into different concentrations of ammonium hydroxide. When immersed in the environment of ammonium hydroxide, the resistance drastically decreased from 320 k Ω , indicating the reaction between emeraldine salt polyaniline and ammonium hydroxide lead to the resistance change.

In this experiment, electrospun sensor under different concentrations had been tested. 2.5 ppm, 10 ppm, 25 ppm and 50 ppm of ammonium hydroxide had been employed, and then, the resistance decrease to 300, 260, 240, 215 k Ω , respectively. Thereby, one conclusion can be made that the concentration of ammonium hydroxide has direct influence on the resistance of electrospun composite sensor. With increasing concentrations, the resistances decrease further.

In addition, each sensing process under different concentrations repeated three times to demonstrate its stability. On the basis of above figures, in a sequence of experiment, both baseline and resistance in ammonium hydroxide remained in a certain range, proving good stability and reusability.

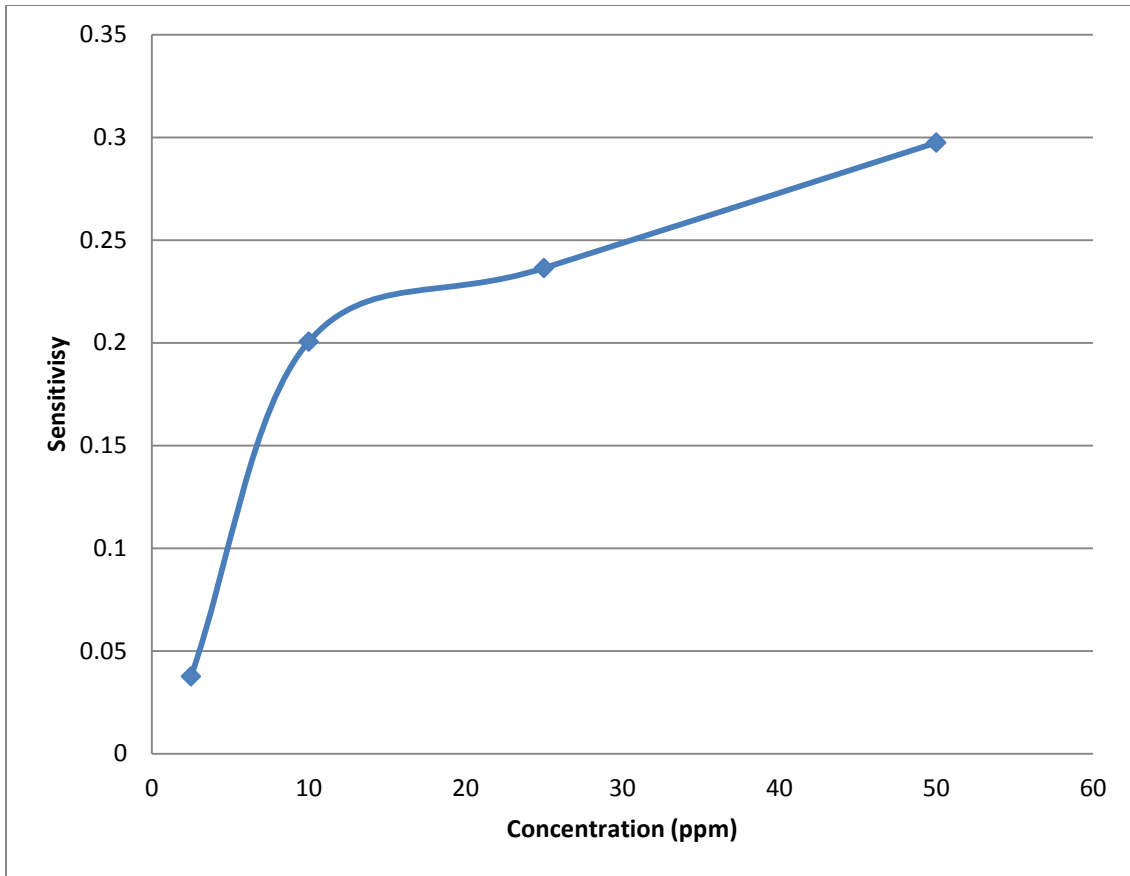


Figure 15 Graph pf electrospun ES-PANI/CA sensitivity to ammonium hydroxide

According to the sensing equation $S = \Delta R/R_0$, the resistance change can be translated to sensitivity, shown as above figure. When the concentration is 2.5 ppm, the sensitivity is relatively low ($S=0.038$). However, with the raising concentration of ammonium hydroxide, sensitivity increases. Sensitivity reaches 0.3 at 50 ppm concentration. For further deduction, sensitivity will keep increasing according to the figure trend.

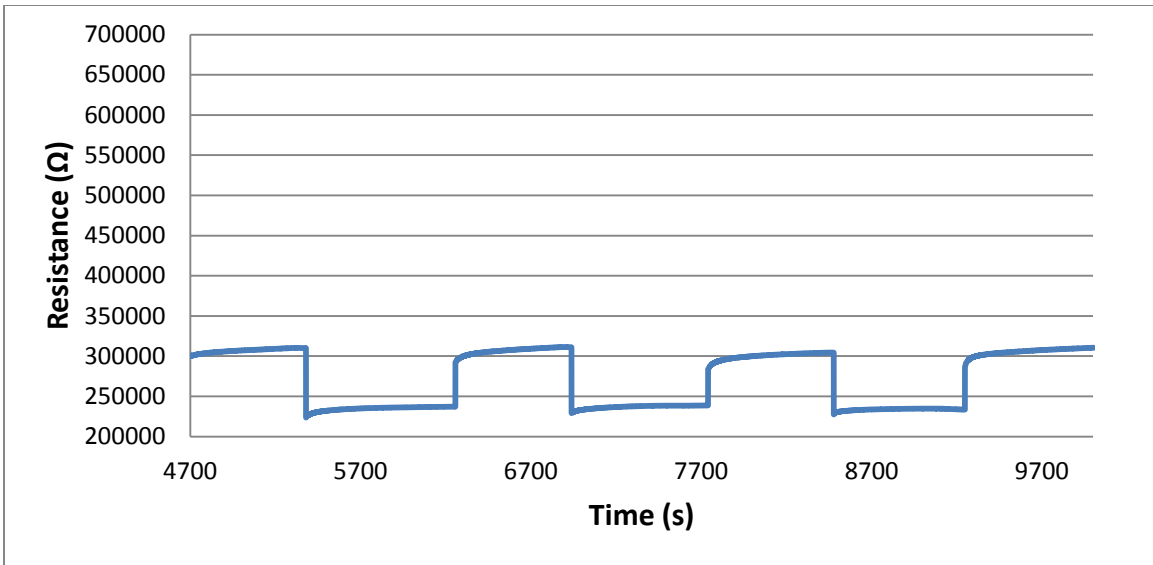


Figure 16 Graph of electrospun ES-PANI/CA response to 25 ppm ammonium hydroxide

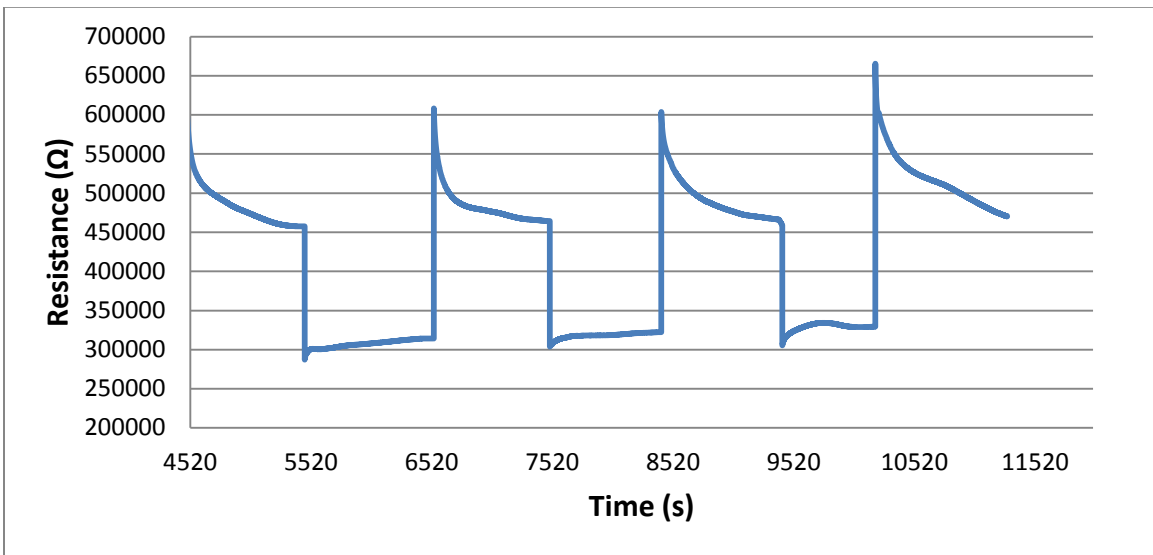


Figure 17 Graph of drop coated ES-PANI/CA response to 25 ppm ammonium hydroxide

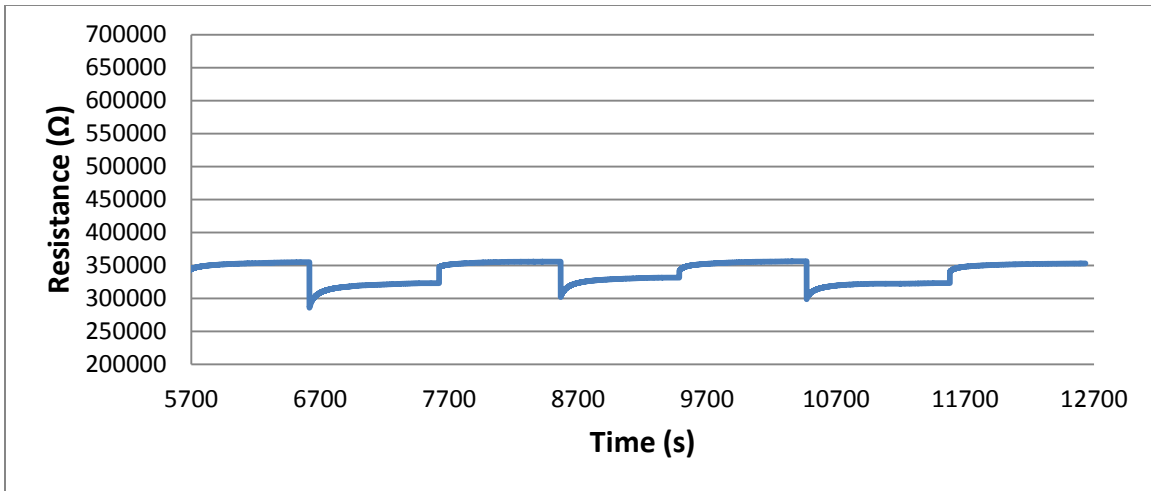


Figure 18 Graph of spin coated ES-PANI/CA response to 25 ppm ammonium hydroxide

Drop coated film and spin coated film were also applied in the test of 25 ppm ammonium hydroxide. The above figures display the resistance change comparison of three different methods made sensors in 25 ppm ammonium hydroxide. For the drop coated sensor, the resistance changed from 460 to 320 kΩ. When compared with electrospun sample, even though the resistance change is larger, the resistance is not stable. Therefore, without good stability, using resistance change to describe chemical reaction is not accurate. For spin coated sensor, the resistance decreased from 350 kΩ to 330 kΩ during the time that the sensor was moved from deionized water to ammonium hydroxide. Compared with electrospun sample, the resistance change is small, so that discriminate different concentration should be a problem.

A good sensor should have good sensitivity to detect certain analyte without interference. Tested solution concentration is decided by sensitivity, which is calculated by equation: $S=(R_f-R_0)/R_0$. When sensor is introduced to different concentrations, the sensitivities are supposed to be largely different for easy recognition, therefore, by analyzing sensitivities, accurate concentrations can be derived. If not, the sensitivities under different concentrations are close to certain value, it

becomes hard to discriminate the concentrations. Also, a sensor should be stable. If the sensor displays various values in the repeat times of use, it is hard to determine which time is valid and accurate sensing response behavior. After comparing three samples made by different methods, both drop coating and spin coating have disadvantages in sensing analyze. For drop coating, the sensor is not stable. For spin coating, the sensitivity of sensor is small. However, electrospun ES-PANI/CA composite sensor proved to be the ideal sensor for detecting ammonium hydroxide. It is believed that nanosized matrix fiber has positive influence on sensing behavior. High surface to volume ratio and nanosized fiber of cellulose acetate are attributed to electrospinning, since polyaniline is embedded in cellulose acetate, this property allows polyaniline more exposed to the analyte, increasing the possibility that polyaniline interacts with analyte. In addition, the cellulose acetate provides stable and firm matrix to immobilize polyaniline, leading to stability of the sensor.

Chapter 4

4. Conclusion

Polyaniline has been studied for sensing application for years. In this thesis, emeraldine salt polyaniline and cellulose acetate composites have been successfully fabricated by three different methods, electrospinning, drop coating and spin coating. Then SEM and sensing of ammonium hydroxide test have been employed to analyze samples made by different methods. For SEM tests, electrospun fiber diminished to nanosize, providing small diameter matrix to immobilize polyaniline. For sensing tests, all three samples resistances decrease when sensors in the environment of 25 ppm ammonium hydroxide. To compare three of them, the sensor made by electrospinning maintained superior sensitivity and stability than drop coating and spin coating. Then, electrospun sensor was tested in different concentration, 2.5 ppm, 10 ppm and 50 ppm. It clearly showed that higher concentration resulted in increasing sensitivity. These results indicate that electrospun ES-PANI/CA composite sensor is preferable in the application of detecting ammonium hydroxide.

Chapter 5

5. Future work

- ES-PANI/CA composite fabricated by electrospinning also produce beads along the matrix fiber. These beads have negative impact on continuity and uniformity of fibers, thereby affect conductivity of composite. The major reason that cause beads formation is high polymer solution viscosity. However, solution concentration direct influence viscosity. To eliminate beads along the fiber, concentration of polymer solution should be adjusted and electrospinning process parameter should be optimized.
- During the electrospinning process, dark green precipitate was observed growing on the top of needle. Based on color analysis, dark green material should be majorly emeraldine salt polyaniline. The existence of this phenomenon causes the loss of polyaniline and decrease the amount in ES-PANI/CA composite. The reason of compositional separation should be investigated and methods should be adopted to eliminate the polyaniline deposition.



Figure 19 Dark green deposition by electrospinning

- Ammonia presents in aqueous state in both ammonia and ammonium ions. There are several values, pH value, temperature and salinity that influence ammonia and ammonium ion transition. When moving sensor to real application, for example, test in saline water, these factors should be considered. Hence, the connection between three factors and ammonia and ammonium transition should be investigated for studying sensor response behavior.

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