CHAPTER I

INTRODUCTION

1.1 Introduction

Ammonia is a compound with the formula NH_3. This gas is colorless with a characteristic pungent odor. Ammonia is an important industrial gas but it is high toxicity, even low concentration level (ppm). Examples of its use in industry are the production of nitric acid and ammonium salts, particularly the sulfate, nitrate, carbonate, and chloride, as well as the synthesis of hundreds of organic compounds including many drugs, plastics, and dyes. Its dilute aqueous solution finds use as a household cleansing agent. Anhydrous ammonia and ammonium salts are used as fertilizers, and anhydrous ammonia also serves as a refrigerant, because of its high heat of vaporization and relative ease of liquefaction. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Moreover, ammonia can occur in large quantities as a pollutant emission in the case of fertilizer production, livestock farming and slurry processing. Ammonia is also releasing from humans and animals from their urine. Although in wide use, ammonia is both caustic and hazardous. People are usually exposed to ammonia by breathing air that contains the gas and direct contact with the liquid. Larger amounts of ammonia can be detected near farms and industries. Farms have high levels of ammonia due to animal waste storage and the use of liquid ammonia as fertilizer. Industrial sites can release high levels in case of chemical leaks or spills and in sewage treatment plants. Transportation accidents may also release dangerously high amounts of ammonia. Lastly people who keep a lot of pets indoors and do not clean up the animal waste may also source of ammonia. Today, most of the ammonia in our atmosphere is emitted direct or indirect by human activity. The worldwide emission of ammonia per year was estimated in 1980 by the European community commission for environment and quality of life to be 20–30 tetragrams [1].

The maximum value allowed at the working place for 8 hours exposure is only 25 ppm (18 mg/m^3 of air) and the olfactory limit of detection of ammonia gas is 55 ppm [2]. Ammonia levels below 1 ppm are not expected to cause health problems. Exposure to more concentrated levels (above 25 ppm) for long term exposure (more than 8 hours) can cause headaches, nausea, and intense burning of eyes, nose, throat, and skin. At high concentration levels, ammonia gas can cause serious health damage, irritating and/or burning nasal passages and lungs. Individuals with asthma and emphysema may be particularly sensitive to ammonia. With the global population boom, more and more human lives are being endangered by the effects of ammonia gas exposure. Therefore, development and fabrication of systems for detecting ammonia gas at low level are of great contemporary interest. Choice of suitable sensing materials along with efficient microelectronics for the detection system is the key step in such efforts for ammonia.

1.2 Literature Review

Generally, detecting ammonia could be done in many ways. One of them is differentiating odor. If ammonia concentration is high, it was easy to detect because the gas had a very strong odor. In general, human nose is sensitive to strong odor. Thus, it is not surprising why human is sensitive to ammonia. However, human nose could not determine the concentrations of ammonia. Therefore, ammonia detectors are researched. Techniques that widely used were metal-oxide gas sensors, catalytic ammonia detectors, conducting polymer ammonia analyzers and optical ammonia detection. Presently, the developing of electrically conductive polymers for ammonia gas sensing applications was conducted. The primary goal of the development was to create a reliable, highly sensitive and selective to ammonia gas.

Researchers have studied conducting polymers and developed them as sensing materials in gas sensor applications. Many types of conducting polymers- polypyrrole (PPy), polyaniline (PANi), polythiophene (PTh) and their derivatives were used as the active layers of gas sensor and showed good improvement. Comparing with those of commercial sensors, the one made of conducting polymers had high sensitivities and

short response. In addition, conducting polymer was easy to synthesize through chemical or electrochemical processes and can be easily modified by copolymerization or structural derivations. Conducting polymers also produced proper mechanical properties that allow a facile fabrication of sensors [3]. For this reason, the conducting polymers sensors have been received much more attentions from many researchers and many related articles were published.

Due to high sensitivity, reversible response, shorter response time, ease of synthesis and stability under ambient conditions, PANi was an appropriate option for gas sensing [4]. PANi can be synthesized by both chemical and electrochemical oxidative polymerizations of aniline in aqueous acid media by variety of oxidizing agents (Figure 1.1). It has a general structure in polyemeraldine base (PANi-EB), which consists of alternating reduced and oxidized repeating unit [5].
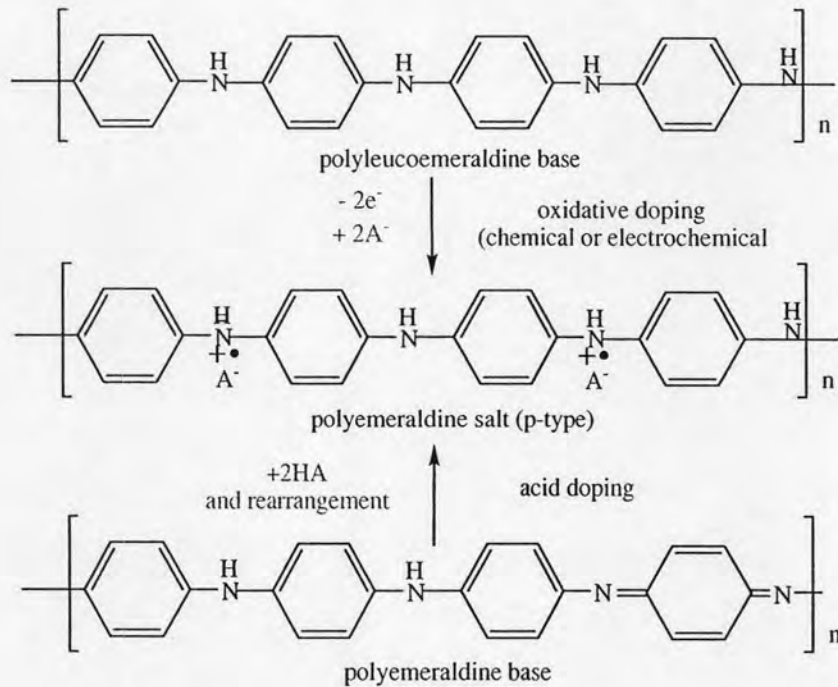
Figure 1.1 Acid doping and oxidative doping of PANi.

In the case of ammonia sensors, the principle of operation is based on a change in some property of PANi such as resistance of the material when interact with

a gas/odor. A lot of studies are dealing with the improvement of sensitivity and selectivity of PANi layer. The development was aimed on the nature of dopant, the presence and the nature of substituants of PANi on aniline ring, the deposition method of sensitive layer, the PANi post-treatment by an organic vapor, the use of threads woven into a fabric mesh as substrate and the use of a composite sensitive film with PANi. Other parameters like electrode geometry [9] and temperature [10] were studied, particularly the response of gas-sensitive chemo-resistors.

According to Jiakun et al. [6], a high sensitivity of PANi to ammonia gas at room temperature was reported with low resistivity, good selectivity, and reliability.Ammonia molecules represented as donors after being adsorbed and formed an electric barrier near the surface of the PANi. As a result, the resistance of PANi increased. Dhawan et al [7] also observed the changed of the resistance of PANi film when exposing to aqueous ammonia. PANi was synthesized by electrochemical polymerization and doped with 5-sulphonic acid and p-toluene. The surface resistance of the doped PANi changed from 10^2 to 10^{10} ohms. Piletsky et al. [8] reported the use of PANi as the sensitive element for ammonia microsensor. A multi-purposed silicon chip with a system of heaters and thermometers were used to construct a microsensor. Likewise, to study the sensor characteristic of PANi, the sensitivity of polymer film with a wide range of ammonia gas concentration in the range of 1 – 2000 ppm was monitored. A physicochemical model detailed the change in the conductivity of PANi with the absorbed ammonia molecules. The model shown that the change in conductivity occurred due to the reversible protonation of PANi molecule in ammonia removal. Moreover, the use of PANi for ammonia sensors was satisfied because of it high chemical stability in oxidizing ambient.

Many compounds were study as PANi dopant. The mineral acid HA (A = Cl$^-$, HSO$_4^-$, ClO$_4^-$) are most frequently used. The layer resistance increases, when the sensor is kept in an ammonia atmosphere [8, 11, 12]. Note that ammonia is the gas generally detected by PANi layers because of the similar role played by nitrogen atoms of both compounds in the establishment of the coordination bonding with protons [8, 12].

Recently, many researches are being conducted about the use of a composite film with PANi as sensitive layer. Ogura et al. [13] have used a composite film of PANi-EB and polyvinyl alcohol to detect CO_2. The CO_2 adsorption leads to an increase of the film conductivity assigned to the transformation of PANi-EB in polyemeraldine salt by the incorporation of carbonate ions formed from CO_2 hydrolysis in the PANi-EB film. Chatuporn et al. [14] have studied the response under ammonia gas of layers made from citric acid doped PANi blends with polyvinyl alcohol. The conductance of PANi-PVA blended film increased when it exposed to ammonia gas. Moreover, amount of citric acid as the dopant, thickness of layer as well as operating temperature and humidity were discussed. Matsuguchi et al. [15] have succeeded ammonia sensors based on polyaniline/polystyrene and polyaniline/polymethylmethacrylate (PMMA) blends. Dopant nature (HCl on bis (2-ethylhexyl) hydrogen phosphate), proportion of each polymer solution, solvent natures are studied. The polyaniline–poly (methyl methacrylate) blend film prepared with toluene as the solvent showed the fastest response and good reversibility, because the porous film was obtained only by this combination.

According to these authors, this kind of polymer blends improved the solubility of conducting polymers and their processability. The sensors from these conducting polymeric composites and blends can make in different ways [15, 16, 17]. It has been found that these films are subjected to electron-donating gases such as ammonia.

Polymeric nanofibers have recently received much attention for gas sensor. Polymeric nanofibers can be processed by a number of techniques such as drawing [18], template synthesis [19], phase separation, and self-assembly [20]. These chemical methods of making polymeric nanofibers usually require specific structure-directing materials added to the polymerization bath like templates (polymerizing the monomer with the aid of either a "hard" or a "soft" template [20]) or the self-assembly of functional molecule. Moreover, the removal of such templates was required and produced lower yields with less reproducibility. Physical methods like electrospinning have been used to make nanofibers without using a template in

nanofiber production. Electrospinning or electrostatic spinning is an interesting technique that employs electrostatic forces to produce polymer fibers, ranging in diameter from sub-micrometers down to nanometers. Due to the high surface area to volume ratio, high porosity, very small size, and light weight of the electrospun fibrous, they have a variety of applications such as tissue scaffolding, highly efficient filtration membranes, nanowires, nanocomposites and electrical and optical materials [21,22]. The electrospinning process is the use of electrostatic force as the main driving force for fiber formation. In the process, a high voltage power supply is used to charge a polymer solution or melt through a metal contact, e.g. normally a needle, across a metal collection screen. The applied potential is in the range of 5 to 30 kV, depending on the collection distance. Electrospinning process provides a potential way to fabricate infinite continuous nanofibers.

Reneker and Chun et al [23] have reported that polyaniline fibers can be successfully formed into a sulfuric acid coagulation bath. The nanofibers contact the liquid on their passage towards a submerged ground plate. A liquid collector device might be used when electrospinning from solvents that are not readily volatile; in place of solvent evaporation the fiber is generated by precipitation in solution. Moreover, more than 20 polymers, including polyethylene oxide, nylon, polyimide, DNA and polyaramide have been electrospun using this system. In addition, Yu et al [24] have prepared nanofibers of HCl- or H_2SO_4-doped PANi by adopting dilute sulfuric acid bath as collector, using hot sulfuric acid as solvent. The conductivity of resulting homogeneous PANi sub-micron fibers were 52.9 S/cm, which prepared via optimizing electrospinning parameters. The effect of H_2SO_4 concentration in coagulation bath, HCl- or H_2SO_4-doped PANi concentration in hot H_2SO_4 solution, the doping acid type and the voltage applied to the electrospinning solution were discussed. Cardinas et al. [25] have also reported the formation of pure PANi fibers by the electrospinning process. The fiber diameters were ranging from hundreds of nanometers to a few micrometers and fiber lengths were of hundreds of micrometers. The fibers were collected on SiO_2/Si and Si wafer pieces in the form of isolated fibers. Moreover, they have been found that the implementation of the acetone bath was of key importance for the formation of fibers. The current–voltage characteristics are

linear and the conductivity in the range usually observed for partially doped polyaniline. However, it is difficult and complicated to electrospinning PANi by itself as limited by its molecular weight and solubility [21]. To overcome this problem, most of the researchers were blending PANi with other spinnable polymer. Macdiarmid et al. [26,27] reported the conductivity of 0.2 S/cm when electrospun 50 wt% PANi doped with *d,l* camphorsulfonic acid blended with polyethylene oxide (PEO) in chloroform. Nicholas et al (2008)were fabricated electrospun isolated camphor sulfonic acid-doped PANi nanofiber sensors and tested in the presence of various aliphatic alcohol vapors comparing to the response obtained from a cast nanofiber mat (prepared via chemical synthesis). PEO was added to assist in fiber formation by acting as a plasticizer. Sensors made from individual fibers exhibited larger responses, especially for bigger alcohol molecules, and also showed a true saturation upon exposure and removal of the alcohol vapor. Interestingly, the response of sensors made from electrospun nanofibers to small alcohol molecules was opposite to that observed for cast nanofiber mats and could be related to the doping process used in the preparation of the polymer in either case. A faster response and the ability to selectively deposit isolated nanofibers by electrospinning made this technique attractive in the fabrication of rapid response sensors. Bishop and Gouma (2007) have prepared electrospun of leucoemeraldine-based polyaniline (LEB-PANi)/ Polyvinyl Pyrrolidone (PVP) composites for NO_2 detection. Electrospinning LEB-PANi with PVP enhanced the dispersion of the LEB-PANi particles; PVP alone enhanced the overall reaction and the adsorption kinetics of NO_2 on the fibrous mat. Pure PVP is inherently insulating and has a high affinity to water, thus it can also be employed to amplify the sensitivity of polyaniline to humidity. At high humidity exposures, PVP transforms into a rubbery polymer, resulting in a change of the electrospun matrix morphology and overall chemical character of the fibrous mat. It has been observed that humidity levels above 40%RH was resulting in breakdown of mat structure. Therefore, this room temperature and 40% RH were suitable for measurement of NO_2 of electrospun PVP-PANi composite. Aussawasathien et al. [28] have prepared $LiClO_4$ doped polyethylene oxide (PEO) electrospun nanofibers for humidity sensing and camphosulfonic acid (HSCA) doped PANi/polystylene (PS) electrospun nanofibers for sensing H_2O_2 and glucose. The diameters of prepared polymeric

nanofibers are in the range of 400-1000 nm and achieved significant enhancing of sensitivity for the nanofiber sensor. According to Norris et al. [21], ultrafine fibers of PANi doped with camphorsulfonic acid blended with PEO with diameters less than 2 μm were prepared by electrospinning. By controlling the ratio of PANi to PEO in the blend polymer, fibers having a desired conductivity (comparable to that of PANi.HCSA/PEO cast films) were produced. The importance of the high surface to volume ratio provided by the electrospun fibers was evident at least one order of magnitude increase in the rate of the vapor phase de-doping and at least two orders of magnitude in the rate of spontaneous re-doping, compared to the cast film. Liu et al. [29] have successfully achieved nanofibers by scanning-tip electrospinning of droplet of the blend solution of the PANi doped with 10-camphosulfonic acid (CSA). The resulting nanowire detector of protonated PANi nanofibers react with NH_3, changing its electrical resistance and display threshold detection of 0.5 ppm of NH_3.

1.3 The purpose of the study

Using PANi as ammonia sensing was well-known and can be enhanced by blending with other polymer. Polymeric nanofibers can be beneficial the fabrication of sensor. Therefore, this research is interesting to study the fabrication of electrospun mats of citric acid-doped PANi blending with polyvinyl alcohol as an ammonia gas sensing. The effect of the eletrospinning processing variables on morphology and diameter of citric acid doped PANi-PVA fibers were investigated. The sensing performance of the electrospun mats to ammonia gas was examined. The effect of percent dopant, percent PANi and influence of solvent to produce electrospun mats were also studied. Finally, the sensing performance of electrospun mats to ammonia gas in real sample was employed.