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Preparation, Characterization and NH_3-sensing Test of HCl-doped Polyaniline Thin Films

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Abstract

This study is aimed to monitor the effects of varying the polymerization time of aniline on the morphology, electrical conductance, oxidation states, optical properties, and ammonia gas sensitivity of hydrochloric acid (HCl)-doped polyaniline (PAni) as the synthesized thin film. In this work, chemical oxidative polymerization of aniline was carried out using the rapid mixed method with ammonium peroxydisulfate, $(NH_4)_2S_2O_8$ as the oxidant and 0.4 M HCl as dopant. Temperature changes were also monitored from the start of the chemical reaction to describe the different phases of the chemical oxidative polymerization of aniline. The PAni thin films were deposited by taking the substrates from the reaction mixture after 2 minutes and 8 minutes polymerization time. FTIR spectroscopy, UV-vis spectroscopy and scanning electron microscopy (SEM) were used to conduct spectroscopic and morphological characterizations of the produced PAni, respectively. The two-probe method was used for electrical characterization of the samples. The FTIR spectrum of the 2-min deposited film with oxidation state of 43% revealed a band at 1309 cm^{-1} assigned to π-electron delocalization indicating that doping started at the onset of polymerization of aniline. With the 8-min deposited film, the $C\text{-}N^{+\cdot}$ stretching vibration in the polaron structure confirmed the formation of emeraldine-salt oxidation state of PAni . Along with this, energy band gap values of about 3.65 and 3.72 eV were obtained from UV-vis analyses. The degree of oxidation, conductance and ammonia sensing responses of the two film samples increased with polymerization time. The degree of doping, however, has no significant relationship with increasing time of polymerization. SEM micrographs of the samples showed porous nanostructures with interconnected networks of globular formations. The film produced within 8-min polymerization period has better sensitivity than the one produced within 2 minutes.

***Keywords**:* polyaniline, rapid mixed polymerization, FTIR, UV-vis

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1. Introduction

Polyaniline (*PAni*) has been proven to be a more conducting material compared with other polymers (Timmer *et al.,* 2005), making it of considerable interest in many theoretical and experimental studies involving chemical sensor materials in the family of conducting polymers. Its easy synthesis, which comes to completion within ten minutes (Stejskal and Sapurina, 2005) makes it a good choice for fabricating light-emitting diodes, electrode material, electromagnetic shield, and as a sensitive layer of chemical vapor sensors (Li *et al.,* 2009). Among the family of conjugated polymers, *PAni* is one of the most useful since it is air-and moisture-stable in both its conducting form and insulating form (Virji *et al.*, 2008). Thus, *PAni* film as a chemical vapor sensor has high environmental stability, stable electrical conduction and room temperature operation compared to metal oxide based gas sensors (Bavane *et al.*, 2010). In some studies involving the detection of aromatic organic compounds, however, humidity overrides the signal from a target analyte, resulting in an increase in resistance that may be due to polar water vapor causing a swell in the polymer networks. The hopping distance for the charge carriers may increase causing a decrease in conductivity and sensitivity. This phenomenon may be eliminated by flowing dry air into the test chamber before introducing the analyte (Li *et al.*, 2009).

It was considered that *PAni* gas sensors with excellent properties may be formed before the polymerization process terminates, a possibility which has not been attempted so far. In a study conducted by Stejskal *et al.,* (2008), polymerization of aniline was monitored and some samples were isolated after 4 min of reaction time but the product was not tested for NH_3 sensing. The focus was on the mechanism of oxidation, depending on the initial and the final acidity of the reaction mixture.

In this present work the samples were isolated after 2 minutes and 8 minutes of the reaction time and the focus was on monitoring the effects of varying the polymerization time of *PAni* thin films on its morphologies, electrical conductance, oxidation states, optical properties, and ammonia sensing characteristics. Thus, this study attempts to develop protonated emeraldine salt form of *PAni* that can be used to detect basic vapors, such as ammonia or organic amines. These gases can deprotonate the polymer and decrease its conductivity. Redox active chemicals such as Cl_2, F_2, Br_2, I_2, N_2H_4, NO_x, and SO_x can also be used as analyte since they can change the inherent oxidation state of *PAni*, which can also result in large changes in conductivity (Li *et* *al.*, 2008). The Polyaniline gas sensor can be used in environmental gas analysis, air quality control in the passenger compartment of automobiles, alarm systems in chemical industries and fertilizer factories where almost pure ammonia is used, and possibly in ammonia breath analyzers for the diagnosis of certain diseases.

2. Methodology

2.1 Sample Preparation

Polyaniline films were synthesized at room temperature by rapid mixed method using chemical oxidative polymerization of aniline. Ammonium peroxydisulfate, $(NH_4)_2S_2O_8$ / (APS) was used as the oxidizing agent and hydrochloric acid (HCl) as dopant. Hydrochloric acid has been used more frequently as dopant in producing protonated *PAni* film because unlike many other strong acids it is volatile, thereby preventing the presence of excess dopants in the *PAni* structure (Detsri and Dubas, 2009). This leads to the production of *PAni* conducting polymer (Stejskal, Sapurina, and Trchova, 2010) which can be used as an efficient NH_3 gas sensor.

The prepared APS solution was quickly poured into the aniline solution to ensure sufficient mixing before the polymerization begins. The first glass slide (borosilicate glass) was taken from the reaction mixture after 2 minutes of the reaction period and the second sample was taken after 8 minutes of the polymerization process. This polymerization time interval corresponds to the deposition time of *PAni* onto the glass substrates. After taking out each synthesized *PAni* film from the mixture, it was immediately washed with 0.2 M HCl and then similarly with ethanol. The *PAni* films were then dried out for characterization.

2.2 Thin Film Characterization

2.2.1 Conductance/Resistance and Ammonia Sensitivity Measurements of Samples

The ammonia gas sensor was fabricated (Figure 1) by applying a mesh of silver (Ag) paste on the film’s conductive part. Copper electrodes were attached to the Ag paste to establish contacts for resistance measurement

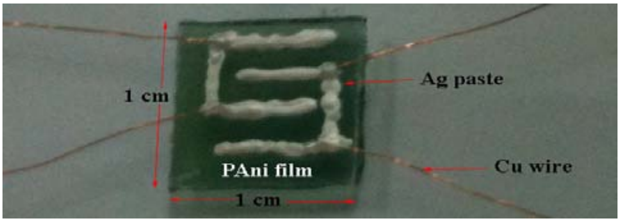


Figure 1. Silver-pasted PAni sample with attached Cu wires used for resistance measurement

using the two probe method. Two spare electrodes in the films served as reserved contacts in case of damage. Figure 2 shows the schematic diagram of the two-probe set-up. The current was supplied to the sample by the low current source and the corresponding voltage was determined from the voltmeter reading before exposing the *PAni* films in the ammonia environment.

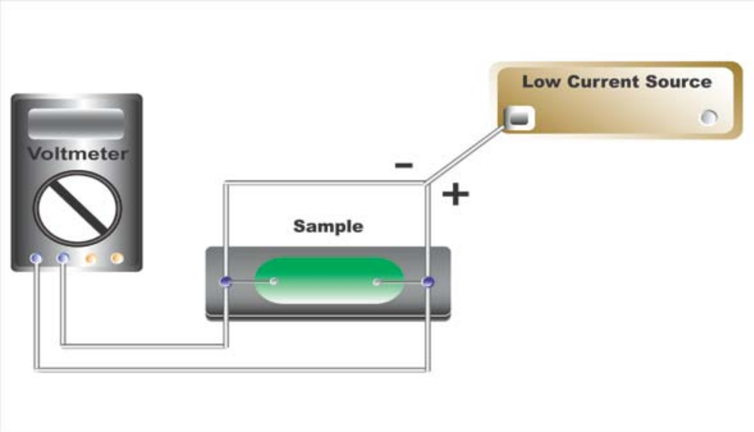


Figure 2. The schematic diagram of the two-probe set-up.

The sensor capability of the *PAni* nanostructure thin films were investigated inside a fabricated box enclosure with a volume of 3358.72 cm^3. Within it, is another box enclosure which is 688 cm^3 in volume as shown in Figure 3. The sample was placed inside the box enclosure with its electrical connections arranged in two-probe method. This is to ensure that other impurities in the air will not interact with the samples. The experimental set-up is shown in Figure 4.

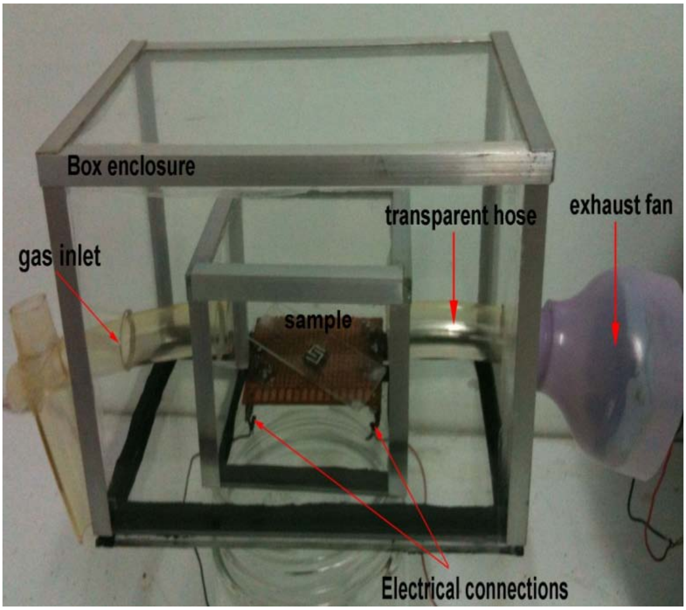


Figure 3. The box enclosure used during NH_3 sensing experiment

Figure 4. The set-up of the resistance measurement and NH_3 sensing experiment

2.3 Gas Sensor Characterization

Ammonia which is a gas at room temperature is a soluble gas and remains in the solution because of its ability to form hydrogen bonds with water. When ammonia is in water in the form of ammonium hydroxide it undergoes some equilibria. When the bottle containing ammonium hydroxide (NH_4OH) is opened, the NH_4OH dissociates to give both ammonia gas and water vapor (Saroch *et al.*, 2008). To facilitate the flow of NH_3 gas into the test chamber, the exhaust fan was turned on to introduce 3,505 ppm of NH_3 from 1 M NH_4OH solution. Two cycles of NH_3 exposure were made for each film, which incurred 30 minutes. To do one cycle of exposure, the operating current which was determined from the I-V curve of each film before NH_3 exposure, was supplied to the sample while the voltage reading was recorded every 5 seconds for the first five minutes. The exhaust fan was then turned on to introduce NH_3 gas to the sample. The length of exposure to NH_3 was 5 minutes with the voltage reading recorded every 5 seconds. The NH_3 supply was then cutoff with the corresponding voltage recorded again for five minutes every 5 seconds. The sample responses or sensitivities with and without the presence of NH_3 were then calculated using the equation:

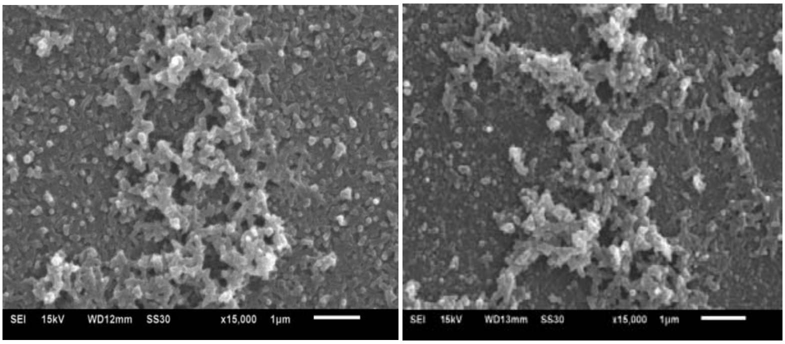
$$S = \frac{R_e - R_{ne}}{R_{ne}} \times 100\ \% \qquad (1)$$

where the ratio of the sum of R_e and R_{ne} with R_{ne} corresponds to the sensitivity of the sample. R_{ne} is the resistance of the sample before it was exposed to the analyte and this corresponds to the operating current of the sample. On the other hand, R_e is the resistance of the sample after it was exposed to the analyte applied to the operating current. In using this equation, sensitivity can reach a value higher than 100% since the fraction of the change in the resistance reading was compared to the resistance of the sample before it was exposed to the analyte (Odarve and Vequizo, 2011).

3. Results and Discussion

3.1 Scanning Electron Microscopy (SEM) Micrographs of Polyaniline Nanostructures

The data obtained from SEM was used to determine the morphology of the films produced in the experiment. The samples were characterized using JEOL JSM-6510LA analytical scanning electron microscope at 15000x magnification. The SEM images of the *PAni* thin films deposited onto the glass substrates are shown in Figure 5 (a) and (b). The nanostructures of hundreds of nanometer in length formed porous interconnected networks of globular formations. The advantage of such porous nanostructure, which is also observed with *PAni* nanofibers is the easy diffusion of NH_3 gas analyte molecules into and out of the film structure, leading to a fast response and high sensitivity.



(a) (b)

Figure 5. The SEM micrographs (15,000x) of *PAni* deposited onto a glass substrate at (a) 2-minute and (b) 8-minute polymerization periods

3.2 Current-Voltage (I-V) Measurements

In Figure 6 (a), the current-voltage (I-V) measurement of the films showed a linear behavior as an indication of the metallic nature of the *PAni* as well as an ohmic contact established between *PAni* and the silver electrode. This, together with the green color of the films, revealed the emeraldine salt oxidation state of the synthesized *PAni*. It was observed that the resistance of the films increased after exposure to NH_3 environment. This indicates that the initial resistance of the *PAni* films was a sensitive parameter in the presence of NH_3 gas. This increase in resistance after the first and second NH_3 gas exposure is shown in Figure 6 (b) and (c) that can be attributed to some structural changes in the polymer and also possibly to the NH_4Cl formation that did not dissociate completely to protons and NH_3 molecules. This further means that the initial resistance of the films was not totally recovered after every exposure to the analyte. In this figure, R_{BE} stands for

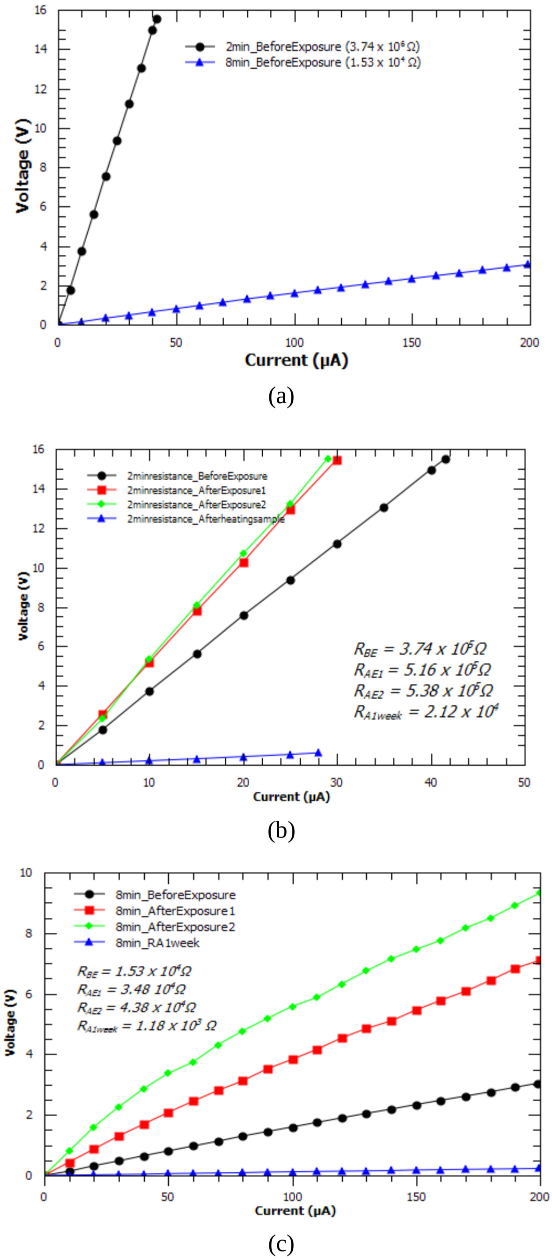


Figure 6. The I-V curve of *PAni* films on glass substrates at (a) 2-min and 8-min before NH_3 exposure, (b) 2-min and (c) 8-min with lines, black: before exposure to NH_3, red: after first exposure to NH_3, green: after second exposure to NH_3, and blue: after one week of exposure to NH_3 .

resistance before exposure, R_{AE1} and R_{AE2} as resistances after the first and second exposure to NH_3. One week after the films were exposed to NH_3 gas and after mild heat treatment at 45°C for 5 minutes, the resistance of each sample was determined again through the two-probe method right after cooling. R_{A1week} represents the resistance after one week time and it was observed to decrease. Thus, it can be inferred that mild heat treatment of the samples was favorable to the crystallization of the doped *PAni*. This can be attributed to the increase in re-protonation, enhanced cross-linking reactions and possible structural rearrangements resulting in a regular and ordered structure.

3.3 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Results

ATR-FTIR spectroscopy in the scanning range of 650-4000 cm^{-1} was used to determine the oxidation states and vibrational modes of the *PAni* films. The spectra of the samples were obtained using the Perkin Elmer Spectrum 100 FT-IR Spectrometer using the ATR technique. The evolution of Fourier Transform Infrared (FTIR) Spectra of the samples that are shown in Figure7 further confirmed the oxidation states of the *PAni* thin films. The spectra of the films in this experiment exhibited two main bands, with maxima situated at peaks 1577 cm^{-1} and 1575 cm^{-1} (quinoid) and 1494 cm^{-1} and 1491 cm^{-1} (benzenoid) for the two-minute and 8-minute deposited films, respectively (Tai *et al.*, 2010). The integrated intensity of peaks Figure (a) and Figure (b) was used to determine the oxidation state of *PAni* films using Equation 2,

$$Degree\ of\ oxidation(\%) = \frac{Aquinoid}{A\ quinoid + A\ benzenoid}\ x\ 100\% \qquad (2)$$

through the QtiPlot software version 9.7.10. In this equation, Aquinoid and Abenzenoid are the respective integrated intensity of the quinoid (peak a) and benzenoid (peak b) rings (Odarve *et al.*, 2011). The calculated oxidation states 43% and 57% for 2 min and 8 min polymerization times, respectively, indicate the nearly equal occurrence of quinoid and benzenoid rings of the emeraldine form of *PAni*. In Figure 7 (c), the spectrum of the 2-minute deposited film, revealed a band at 1309 cm^{-1} assigned to π-electron delocalization induced in the polymer by protonation (Li, *et al.,* 2008) indicating that protonation started at the onset of polymerization of aniline and that *PAni* film was already formed even at this early stage. At 8 minutes,

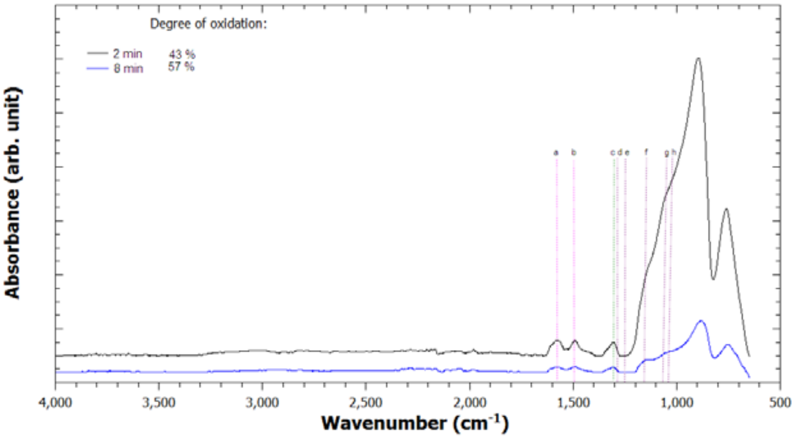
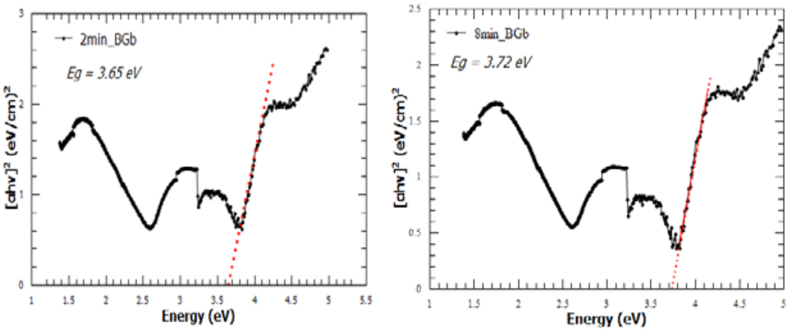


Figure 7. For 2 min at a) 1577 cm^{-1}, b) 1494 cm^{-1} and for both 2 and 8-min at c) 1309 cm$^{-1;}$ for 8 min at a) 1575 cm^{-1}, b) 1491 cm^{-1}, d) 1256 cm$^{-1,}$ e) 1236 cm$^{-1,}$ f) 1145 cm^{-1}, g) 1101 cm^{-1} and h) 1053 cm^{-1}

a number of new peaks were observed. In Figure 7 (d) and Figure (e), the band characteristic of the conducting protonated form interpreted as a C-N$^{+\cdot}$ stretching vibration in the polaron structure was located at 1256 cm^{-1} and 1236 cm^{-1}. The prominent 1145 cm^{-1} in Figure 7(f) band which is assigned to the vibration mode of the –NH$^{\cdot+}$ = structure was formed during protonation of the imine group. In addition, peaks at 1101 cm^{-1} and 1053 cm^{-1} in Figure 7 (g) and (h) indicate that the oxidant was depleted and the pernigraniline was reduced at a faster rate by the residual aniline to the emeraldine form.

3.4 Energy Band Gap Results

The UV- Vis spectra were obtained using the Perkin Elmer Lambda 35 UV/Vis Spectrometer. The obtained transmittance spectra from UV-Vis were used to derive the absorption coefficient and the corresponding band gap of the sample produced. The energy band gap of the *PAni* films was determined using absorption spectra with the help of Tauc relation. Using this relation, the square of ($\alpha h\nu$) versus the photon energy ($h\nu$) was plotted to obtain a straight line (Figure 8). The straight line was then extrapolated to $(\alpha h\nu)^2 = 0$ which gives the value of the band gap (Patidar *et al.*, 2008). The energy band gap of the samples is about 3.65 eV and 3.72 eV belonging to



(a) (b)

Figure 8. Energy band gap values for a) 2-min and b) 8 min deposited *PAni* films.

the semiconductor regime, for the 2-min and 8-min polymerization time, respectively.

3.5 Electronic Levels

The absorbance spectra of samples showed absorption peaks at Figure 9 (a) 296 nm assigned to the benzenoid structure, 362 nm (Figure 9 (b)) indicating principal absorption of the π - π*orbital transitions of the emeraldine form of *PAni* (Zujovic *et al*, 2009). Also, the sharp trough at 477 nm (Figure 9 (c)) can be assigned to the localized polaron which are characteristics of the protonated *PAni*, together with extended tail nearly 758 nm (Figure 9 (d)) representing the conducting emeraldine salt form of the sample (Bavane, *et al.*, 2010).

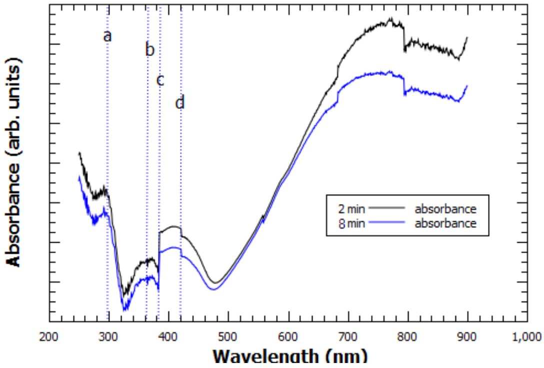


Figure 9. The absorbance spectra of PAni films with peaks at (a) 296 nm, (b) 362 nm, (c) 477, (d) 758 nm

3.6 Temperature Profile and Chemical Reaction during Film Formation

Upon rapidly pouring the oxidant (ammonium peroxydisulfate) solution into the monomer (aniline) solution, a small initial increase in temperature from 29°C to 30°C (Figure 10), due to the heat of mixing was observed during one-minute reaction period. A rapid increase in temperature from 30°C to 43.5°C lasted for five minutes. During this period, the nucleates were expected to convert to initiation centers, starting the subsequent *PAni* chain propagation. This rapid increase in temperature manifested the fast rate of polymerization of aniline, the exothermic formation of brown oligomers being not evident due to their low amount caused by the absence of the induction period. The fast polymerization process can be attributed to the high acidity (pH = 1) of both the monomer and the oxidant solutions, making *PAni* chain growth unconventionally easy and fast. As a result, polymeric products dominated in the reaction mixture (Stejskal *et al.*, 2010).

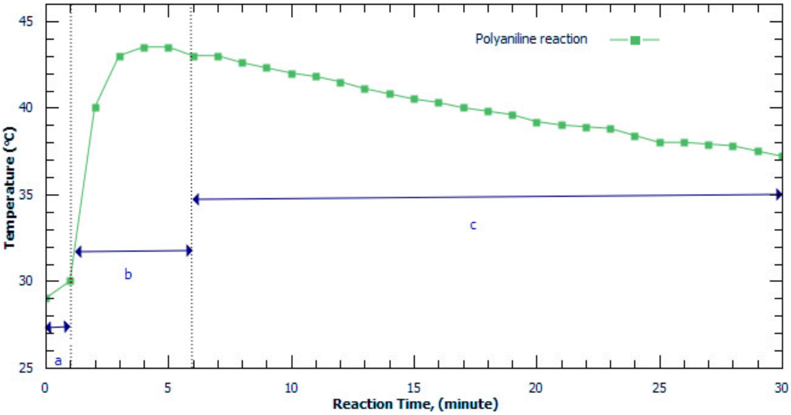


Figure 10. The temperature profile of the polymerization mixture, producing the *PAni* films. (a) Initial increase of temperature, (b) polymerization period, and (c) post-polymerization period.

The temperature of the reaction mixture dropped to 43°C after five minutes of the reaction time and continued to decrease further until the 30-minute period. The decreasing post-polymerization temperature indicated the decreasing rate of aniline oxidation, although protonation continued until the chemical reaction was terminated.

3.7 Degree of doping [(Cl/N) ratio] and Degree of oxidation of the Films Produced

The degree of doping in the films is associated with the ratio of the Cl atoms with the N atoms in the films. The elemental composition of the films shown in Table 1 was determined using Energy Dispersive X-ray spectroscopy (EDX). The largest percentage of carbon (C) atoms are indicative of the benzene and quinone ring that formed the polymer chain. The existence of the imine and amine nitrogen groups also constituting the polymer chain was detected by the presence of the nitrogen (N) atoms. The trace amounts of chlorine (Cl) atoms can be attributed to the dopants inserted in the polymer backbone. Also, the presence of silicon (Si) and oxygen (O) in the film samples can be attributed to the glass substrates used which are made of silica. On the other hand, from Table 2, it can be observed that the oxidation state increased with polymerization time, but polymerization time is not relative to the degree of doping [$\frac{[Cl]}{[N]}$ ratio]. This means that increasing the polymerization time does not relatively increase the ratio of the Cl^- in the films. On the other hand, the increase in polymerization time corresponds to conductance and sensitivity of the films, with the 8-minute deposited *PAni* gaining a higher conductance and thus a relatively higher sensing response towards NH_3 gas.

Table 1. Elemental composition of PAni samples obtained from Energy Dispersive X-ray Spectroscopy (EDX)

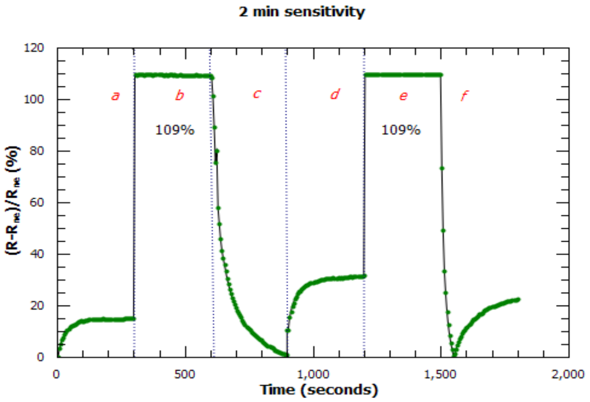
Atom % of Elements						
	C	N	O	S	Cl	Si
2	22.67±0.26	3.94±0.51	39.12±0.22	0.22±0.12	0.54±0.13	22.74±0.10
8	22.87±0.21	3.37±0.41	39.96±0.18	0.21±0.09	0.36±0.11	22.32±0.08

Table 2. The relationship of the increasing polymerization time of PAni to the degree of oxidation, $\frac{[Cl]}{[N]}$ ratio, conductance and its respective NH_3 sensitivity values.

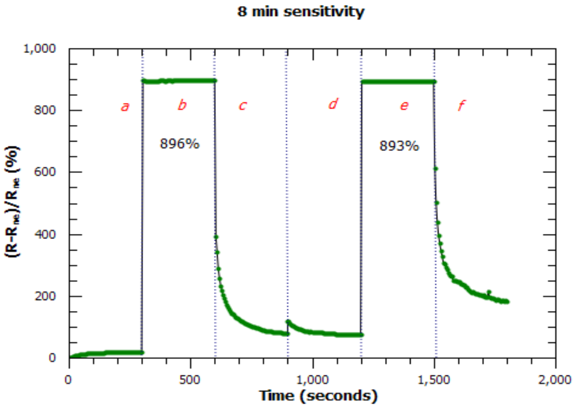
Polymerization time (min), degree of oxidation	$\frac{[Cl]}{[N]}$ ratio	Conductance (S)	Sensitivity (%) (2 cycles)	
			(1st)	(2nd)
2, 43%	0.137	2.67×10^{-6}	109	109
8, 57%	0.107	6.53×10^{-5}	896	893

3.8 Gas Sensor Sensitivity

The response time and the recovery time are defined as the time required for *PAni* film resistance to reach 90% of its saturation value from the starting value on gas exposure, and upon removal of the gas, respectively (Deshpande *et al.*, 2009). In the case of this experiment, the *PAni* films had relatively faster response times ~ 5s, but the recovery times were relatively larger, around 300 s. Figure 11 shows the responding behaviors of the *PAni* sensors toward NH_3 gas.



(a)



(b)

Figure 11. The response plot (in six regions) of the (a) 2-min and (b) 8-min deposited *PAni* films upon exposure to NH_3 gas from the 1 M NH_4OH (~3,505 ppm of NH_3), first cycle (a) 5-minute before exposure, (b) 5-minute exposure, (c) 5 minutes after exposure and second cycle (d) 5-minute before exposure, (e) 5-minute exposure, (f) 5 minutes after exposure.

From the dynamic ammonia response curves in Figure 11 (a) and (b), it can be inferred that the two *PAni* samples exhibited reproducible responses with high baseline stability to NH_3 gas indicated by the increase in their resistances upon exposure. This occurred because when the conductive emeraldine salt was exposed to NH_3 gas, the dopant was partially dedoped. In Figure 11 (a), the *PAni* film obtained during the 2-min polymerization time reached a 109% response for the first and second cycles. In Figure 11 (b), a dramatic increase in sensing response was achieved by the 8-minute obtained a sample that reached to 896% and 893% for the first and second cycles, respectively This high increase in the *PAni* film's sensing response is attributed to the greater surface area of the porous nanostructures evident in the SEM micrograph, high conductance value and nearly 50% degree of oxidation. Specifically, high surface area brings about faster diffusion of NH_3 molecules into and out of the *PAni* structure, upon introducing and cutting-off NH_3 supply respectively. In addition to the enhanced porosity of the 8-minute deposited sample, results from FTIR analyses showed that protonation was completed in the film produced during this time. This is evidenced by the vibration mode of $–NH^{\cdot\ +}=$ structure present in the spectrum. The re-occurrence of 1309 cm^{-1} band indicates that protonation was completed. This means that just enough Cl^- ions as dopants were inserted into the polymer resulting to the easy abstraction of the Cl^- ions during deprotonation or exposure to NH_3 gas. Thus, the *PAni* film became very reactive with NH_3 gas molecules which resulted in a relatively higher sensitivity.

4. Conclusions and Recommendations

PAni thin films of emeraldine-salt forms were fabricated before the 10-minute optimum polymerization period. As the polymerization period of aniline increases from 2 - 8 minutes, enhancement in optical, morphological, and electrical properties is supported by the results of FTIR and UV-Vis spectra. Meanwhile, SEM of the *PAni* thin films clearly shows network morphology with porous nanostructure, and electrical analysis reveals increasing conductance as polymerization time increases. On the other hand, the NH_3 gas sensitivity measurement shows that *PAni* film sensors have faster response, good sensitivity, and good reproducibility. The result of thermal treatment showed that the loss in conductance after NH_3 gas exposure is mostly reversible although this needs more explanation. Thus, the *PAni* nanostructured thin film sensors produced before 10 minutes of polymerization time are potential candidates for use in NH_3 gas detection, with potential for industrial, environmental, and medical diagnostic applications.

In line with these findings, the following further studies are recommended:

- Although the *PAni* samples achieved very good sensitivities toward NH_3 gas, these were not able to fully recover their original forms. It is therefore recommended to explore more processes to achieve this goal.

- To carry out the oxidative polymerization process of aniline using a stoichiometric oxidant to monomer ratio that is lower and higher than 1.25 could also be explored to verify the possibility of producing *PAni* nanofiber structures which are considered to possess superior characteristics for chemical vapor sensing application.

- Since the resistance of the two samples decreased after mild heat treatment, it is best to test again the sensing responses of the films after one week time to verify enhancement in its properties. This promises an easy way to perfectly recover or even improve the films' NH_3 sensing characteristics.

- For greater accuracy in data recording, the use of a computer that is interfaced with the sensing test is recommended if measurements are to be made in the order of seconds.

6. Acknowledgement

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