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Fabrication of Ammonia Gas Sensor Based on Polyaniline/Mussel Shell Composite

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Commercial polyaniline/mussel shell (cPANI/MS) and lab-synthesized polyaniline/mussel shell (sPANI/MS) composites were prepared in order to study the sensor performances in ammonia gas detection. Both cPANI/MS and sPANI/MS were characterized using Fourier transform infrared (FTIR) and Ultraviolet-Visible (UV-Vis) spectroscopy techniques. FTIR confirmed the main characteristic peaks of PANI at ~1462 cm^{-1} and ~1599 cm^{-1} which indicates benzenoid and quinoid ring, respectively. Besides that, the peaks in the range of 1417 - 1453 cm^{-1} indicates the presence of calcium carbonate within the PANI matrix. UV-Vis spectra further confirmed both PANI composites are in the doped state by exhibiting the characteristic peak at ~790-820 nm. Sensor performance of cPANI/MS was studied in different concentrations of ammonia gas (10 – 100 ppm). In conclusion, it is possible to prepare waste mussel shells as a composite material with PANI in order to apply it as a gas sensor.

Keywords: conducting polymers; mussel shells; polyaniline; sustainable waste management; gas sensor

I. INTRODUCTION

National Research Council (2008) has identified ammonia (NH_3) as a poisonous compound. It's lethal concentration in the form of gas is at approximately 30 ppm and becomes tremendously toxic above 500 ppm. The increase of NH_3 destructively affects the environment and the public's health. For example, contact or exposure to NH_3 will trigger irritation while at greater concentration can cause temporary blindness and mucous membrane injury (Sambasevam *et al.*, 2015). The agricultural industry is found to be the major source of NH_3 release into the environment (Zhu *et al.*, 2015). Besides, the disposal of domestic wastes which includes seafood shells to the landmines also making a significant contribution to the NH_3 intoxication.

Conducting polymer is a material that has the characteristic of a metal while sustaining the characteristic of a polymer. Polyaniline (PANI) is one of the greatest conducting polymers due to its easy synthesis, environmental stability and unique acid-base chemistry. PANI possesses four oxidation states such as emeraldine salt (ES-green), emeraldine base (EB-blue), pernigraniline (PE-purple) and leucomeraldine (LE-pale yellow) (Feast *et al.*, 1996). PANI will undergo colour changes (Green to Blue) and different oxidation states (ES to EB) upon exposure to NH_3 gas. This unparallel property of a PANI could be used in effective NH_3 gas detection. However, pristine PANI fails to engage and exhibit a constant response in NH_3 gas detection. Hence, fillers were used to strengthen the PANI sensor performances (Song *et al.*, 2019). Among the

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available fillers, mussel shells (MS) from seafood industry has attracted our attention due to the amount of waste that it could generate in the landfills (Martínez-García *et al.*, 2017). MS contains 33% of waste from the entire weight. There is a report stating that over 1 million tons of MS waste are being produced worldwide. Hence, it will contribute to a significant waste problem in the global scale. On the other hand, MS contains abundant of minerals such as calcium carbonate or chitosan (Lv *et al.*, 2015). This has been portrayed in the work undertaken by Song *et al.*, (2019), where they have modified chitosan and polypyrrole and used it as cardiac patch to repair myocardial infarction. In another study, authors demonstrated MS could be a vital filler for the removal of methylene blue from the waste water (Huang *et al.*, 2017).

So far as we concern, there is no report available on the investigation between commercially available PANI (added with MS) and lab synthesized PANI (added with MS) composites as NH_3 gas sensors. In addition, this investigation would set a milestone to understand about the possible interaction between PANI and MS materials. Besides that, the utilization of waste MS would direct this research focus towards sustainable waste management in the seafood industry.

II. MATERIALS AND METHODS

A. Raw Materials

In this research, MS were used as raw materials. The MS were purchased at Pekan Dioh, Kuala Pilah.

B. Chemicals

Chemicals that were purchased from Sigma-Aldrich are commercial PANI (ES) with a molecular weight (Mw) of 5000 g/mol and 4-Dodecylbenzenesulfonic acid (DBSA) with 97% purity. Hydrochloric acid (HCl) 37% and ammonium persulfate (APS) powder were purchased from R&M Chemicals. For the lab-synthesized PANI, aniline (Ani) monomer of ≥99.5% purity was used. Toluene was used in the preparation of the PANI/MS composites as solvent where it was purchased from Bendosen. Ammonia solution (NH_3) (28%) was purchased from QReC. Distilled water was used throughout this study.

C. Shell Preparation

According to Shankar and Jambulingam (2017), the MS were undergoing physical washing with distilled water followed by a boiling process for 20 minutes in order to remove the internal membranes. The boiled MS were kept in an oven at 80^{o}C for 24 hrs. Then, MS were blended into fine powder by using a blender (Tefal) followed by sieving process using a shaker sieve with a pore size of 250 µm.

D. Synthesis and Preparation of Lab-synthesized PANI/Mussel Shell (sPANI/MS)

According to Sambasevam *et al.* (2015), sPANI was synthesized *via* chemical oxidation method. Typically, 15 mmol of aniline was dissolved in 100ml of 1 M HCl and it was stirred for 1 hour at 200 rpm. The whole reaction medium was placed in an ice bath. Next, 15 mmol of APS was dissolved in 33 ml of HCl solution and placed in refrigerator prior to use. After 1 hour, the solution of pre-cooled APS solution was added slowly into the mixture of Ani/HCl solutions for 1 hour under constant stirring. The flask was left for 24 hours for the polymerization to occur. The colour of the mixture changed into dark green and sPANI precipitate was formed at the bottom of the flask. The sPANI precipitate was filtered and washed using distilled water for several times. Then, the sPANI precipitate was dried at ambient air.

Next, sPANI was stirred in 100ml 1M of NH_3 solution for overnight under 200 rpm. Separately, an amount of 21 mmol of DBSA was sonicated into 100ml toluene for 6 hours. Next, PANI that dispersed in NH_3 solution was filtered and washed using distilled water before being dissolved in the toluene/DBSA mixture. This process will ensure, sPANI contains uniform doping at its backbone and it can be processed in the solution form. Then, 1.0 g of MS in the molar ratio of 1:1, was added into the test tube of sPANI solution and sonicated for 3 hours. The resulting sample was labelled as sPANI/MS.

E. Preparation of Commercial PANI/MS

Commercial PANI (cPANI) was already in the emeraldine salt (ES) form. Thus, 0.5 g of cPANI was dispersed in 1M of NH_3 solution overnight and was dedoped. The resulted precipitates were washed with distilled water and dissolved in 10.33 g of DBSA/toluene mixture under constant stirring. Then, 1.0 g of MS in the molar ratio of 1:1, was added into

the test tube of cPANI solution and sonicated for 3 hours. The sample labelled as cPANI/MS.

F. Characterizations of cPANI/MS and sPANI/MS

In general, cPANI/MS and sPANI/MS composites were characterized by using attenuated total reflectance (ATR)-FTIR, UV-Vis and digital multimeter. ATR-FTIR Spectrometer (model: Spectrum 100 FTIR Spectrometer, brand: Perkin Elmer) was used in the wavenumber range of 650-2000 cm^{-1}. UV-Vis (model: T80+ UV/VIS Spectrometer, brand: PG Instruments Ltd) was used in the wavelength range of 400-900 nm. A digital multimeter (Fluke) is an electronic instrument that can measure two or more electrical values such as principally voltage (volts), current (amps) and resistance (ohms). In this analysis, the multimeter is used to measure the resistance of cPANI/MS and sPANI/MS films and the conductivity was determined.

G. Thin Film Preparation and Sensor Measurement

Both cPANI/MS and sPANI/MS composites were coated on a glass substrate by drop-coating technique and were dried for 30 minutes in an oven at 70 °C. The cPANI/MS and sPANI/MS composite films were tested as a gas sensor by using NH_3 vapour in various concentrations (10 – 100 ppm) in a home-made gas chamber (Figure 1). The sensor measurement on % of sensitivity (%S) was recorded by using equation 1, where R_i = initial resistance and R_f = final resistance.

$$\%S = \frac{R_f - R_i}{R_i} \, x \, 100 \qquad (1)$$

Typically, NH_3 solution of desired concentration was heated at 50 °C (Supri & Heah, 2010) to produce NH_3 vapour. The resistance with stable value was recorded. Generally, all the measurements took approximately, 5 min to give a stable resistance reading regardless of NH_3 concentration. Thus, 5 min was fixed as the response time in this study.

Selectivity study was undertaken by testing the cPANI/MS film in the presence of interfering gases such as NH_3, acetone, hexane and ethanol at similar concentrations of 30 ppm. In addition, long term stability of cPANI/MS was carried out by exposing the film to NH_3 gas every day and storing it in an air-tight container filled with silica gel to prevent oxidation of the film.

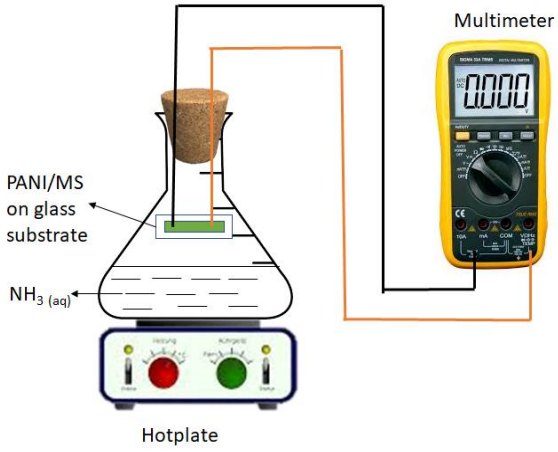

Figure 1. Home-made gas chamber for NH_3 gas detection. Hotplate used to heat up $NH_{3\,(aq)}$ at desired concentration to vaporise and produce NH_3 gas

III. RESULT AND DISCUSSION

A. FTIR Analysis of cPANI/MS and sPANI/MS

Figure 2 shows the FTIR spectra for cPANI/MS and sPANI/MS composites. In general, both spectra exhibited almost similar characteristic peaks with wavelength shifts. The spectra displayed important bands at 1603 – 1649 cm^{-1} and 1445 – 1460 cm^{-1} that corresponds to the quinoid and benzenoid structures of conducting PANI, respectively (Moradian & Nasirian, 2018; Mustapa *et al.*, 2018). In addition, the presence of band at 1417, 870 and 710 cm^{-1} confirms the presence of calcium carbonates fillers from MS in the PANI matrix [incomr1].

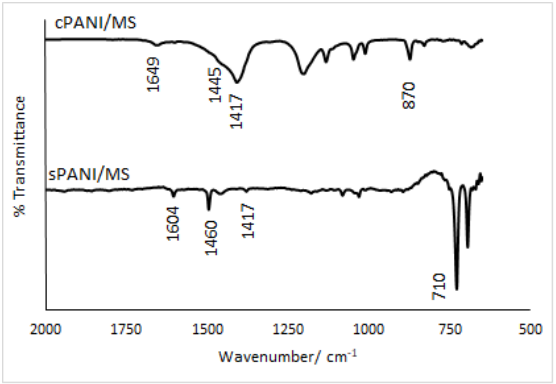

Figure 2. FTIR spectra of cPANI/MS and sPANI/MS

B. UV-Vis Analysis of cPANI/MS and sPANI/MS

Figure 3 depicts UV-Vis spectra of cPANI/MS and sPANI/MS composites in the range of 400–900 nm. Both spectra exhibits two peaks in the range of 420-450 and 750-850 nm which corresponds to π-π* conjugation of the benzenoid structure and π -polaron, respectively (Sambasevam *et al.*, 2017). What is striking in the figure 3 is π -polaron peak of cPANI/MS where it indicates enhanced polaronic character that would be useful in sensor application.

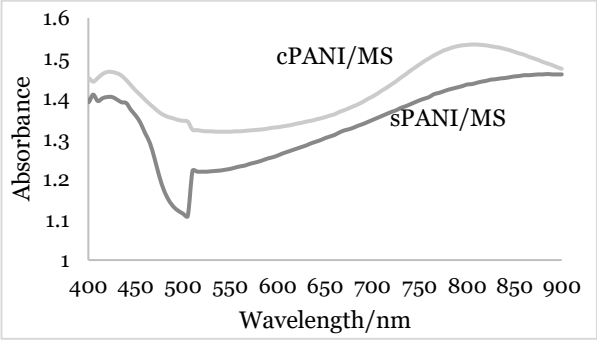

Figure 3. UV-Vis spectra of cPANI/MS and sPANI/MS

C. Conductivity analysis of cPANI/MS and sPANI/MS

This analysis was carried out with the help of a digital multimeter, recorded the conductivity of cPANI/MS and sPANI/MS as 3.72×10^{-7} and 3.59×10^{-8} S/cm, respectively. Obviously, cPANI/MS showed higher conductivity compare to sPANI/MS probably due to the enhanced polaronic factor which was explained in Figure 3. cPANI/MS was prepared from commercially available PANI, thus it might contain defect free sites at the backbone (Jaaoha *et al.,* 2015). Hence, it contributed to the higher conductivity of cPANI/MS composite (Kondawar *et al.,* 2019).

D. SEM/EDX Analysis of cPANI/MS

SEM/EDX analysis was performed for cPANI/MS due to its high conductivity and reported in Figure 4. The SEM exhibited a connected and porous morphology for cPANI/MS composite. The connected and porous nature would enhance the sensing mechanism of cPANI/MS composite. EDX analysis was carried out to further confirm the presence of calcium carbonate from MS in the PANI matrix. For this purpose, cPANI/MS only was selected as it displayed good polaronic character (Figure 3) and higher conductivity compare to sPANI/MS. The EDX analysis of cPANI/MS and it indicates the presence of elements such as C (46.53%), N (14.26), O (18.80%), S (6.06%) and Ca (14.35%). Thus, figure 4 confirms the successful preparation of cPANI/MS.

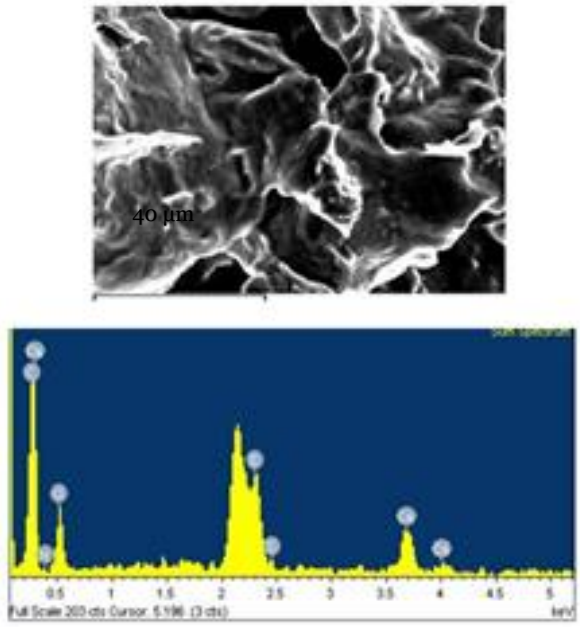

Figure 4. SEM/EDX spectrum of cPANI/MS

E. Sensor Measurement cPANI/MS in NH_3 Gas Detection

Figure 5 shows the sensor measurement of cPANI/MS in various concentrations of NH_3 gas (10 – 100 ppm). The calibration curve for sPANI/MS was not shown here due to its nonlinearity. The % S at different concentrations were recorded at the 5th minute upon the NH_3 gas exposure. From the figure 5, cPANI/MS reports a linear response with R^2 = 0.938 in the increasing concentration of NH_3 gas exposure. Thus, in this study cPANI/MS clearly outperformed sPANI/MS in the NH_3 gas detection. This phenomenon could be related to the polaronic nature of cPANI/MS as shown in Figure 3 and the highest conductivity results in comparison to sPANI/MS (Kumar *et al.*, 2017). In addition, cPANI was the commercially available PANI samples, thus it might be designed with minimal defect sites. On the other hand, sPANI was synthesized in the laboratory scale. An extra care should be given during the synthesis process as this PANI is quite sensitive towards the humidity and the presence of other interfering gases in the atmosphere (Tanushree *et al.,* 2016).

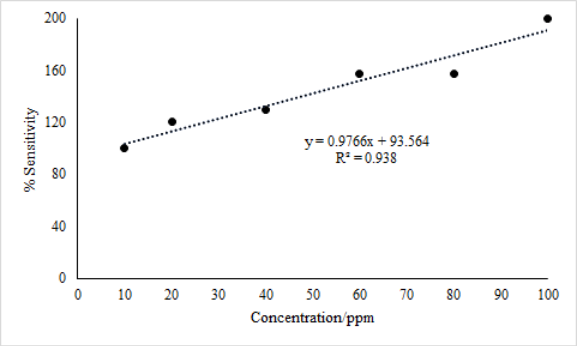

Figure 5. Sensor measurement of cPANI/MS in various concentration of NH_3 gas

F. Selectivity

Figure 6 shows the selectivity study of cPANI/MS in the presence of NH_3, acetone, hexane and ethanol at 30 ppm. cPANI/MS recorded highest sensitivity of 452% in comparison with other target gases as shown in the figure. The reason behind the highest selectivity of cPANI/MS towards NH3 gas is probably due to the stronger ion-dipole interaction compare to other target gases which only had dipole-induced dipole interaction only (Kulkarnia *et al.,* 2019).

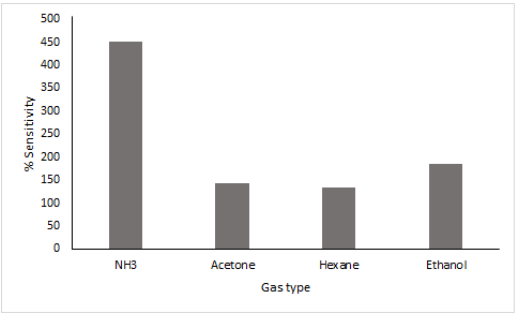

Figure 6. Selectivity study of cPANI/MS in the presence of various target gases at 30 ppm of concentration.

G. Long Term Stability

Figure 7 shows the long-term stability of cPANI/MS in 30 ppm of NH_3 gas detection up to 9 days. The cPANI/MS was carefully stored in a silica gel filled container during the detection period which made the sensor to sustain its sensitivity up to 9 days. However, repeated redoping and dedoping processes that carried out against cPANI.MS film may cause some permanent defect sites at the PANI structure that causes it to lose its sensitivity after 9 days (Li *et al.*, 2019).

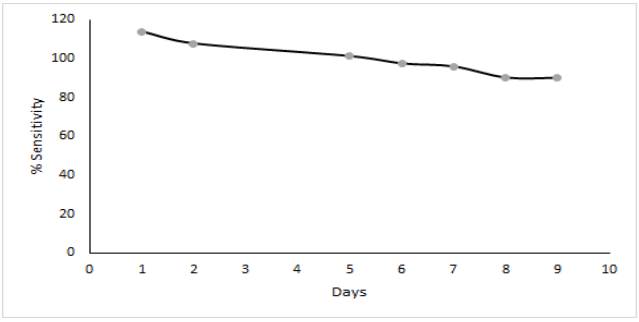

Figure 7. Long term stability of cPANI/MS in NH_3 gas detection

IV. CONCLUSION

In conclusion, the cPANI/MS and sPANI/MS composites were successfully prepared and applied in NH_3 gas detection. The FTIR and UV-Vis analyses have proven the incorporation of MS in the PANI matrix. EDX analysis on cPANI/MS further confirmed the inclusion of MS in PANI. A simple sensor measurement of these composites was performed in NH_3 gas detection. cPANI/MS performed better than sPANI/MS probably due to the internal defects in itself. However, it is the very first-time reporting PANI/MS composites as a potential sensor candidate in the literatures. Thus, this work needs much modification, for instance detailed analysis on the morphology of these PANI in order to understand the defect sites. In addition, sensor measurement requires more sensor performances (interference study and long-term stability) and validation results in order to evaluate the full reliability of the reported cPANI/MS sensor.

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