

Enhancing Conductive Polymer Performance Using Eggshell for Ammonia Sensor

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Abstract: *Polyaniline/eggshell powder composites are proposed as a novel ammonia detecting sensor. The conductive composite is prepared by mixing eggshell powder and polyaniline using polymerisation process, blended in an appropriate solvent. The mixture is deposited on an interdigit electrode. The solvent then evaporates leaving a polyaniline/eggshell powder composite film. The SEM micrograph shows better interfacial adhesion between the eggshell powders with polyaniline. The polyaniline/eggshell powder composite was assumed to process a face centred cubic (FCC) structure. The sensor S-2 with 0.5 g eggshell powder showed better ammonia gas response and selectivity than sensor S-0 without eggshell powder.*

Keywords: eggshell powder, conductive polymer, polyaniline, ammonia gas sensor

1. INTRODUCTION

Polyaniline is a popular conducting polymer due to its easy synthesis, environmental stability and good electrical conductivity.^{1,2} The preparation of polyaniline composite with various materials has received a great attention because of their unique properties and applications, which include various types of sensing devices. In this paper, polymer-eggshell powder composite is proposed as ammonia sensor. Eggshell was selected because it is a waste product with high content of oxides (Mn, Si, Al, Fe, Cr, Cu and Ca) and organic substances. These components of eggshell, when combined with polyaniline, form a better composite with higher conductivity and increased porosity.

Currently, there are many studies related to polyaniline composites. The blend of polyaniline with conventional polymers has been shown to possess relatively high conductivity, excellent electrical and good mechanical properties, and is found to be sensitive to a variety of volatile organic compounds.³⁻⁵

Munoz⁶ also introduced sensor array based on the conductive polymer/carbon black composites used in an electronic nose. It was found that the sensors were very reliable, giving repeatable results and can be reproducibly manufactured. They also did not degrade when exposed to humidity or large temperature fluctuations.⁷

In this paper, we describe a sensor based on polyaniline/eggshell powder composites. The composites have been used as a sensor for ammonia gas. The sensing elements are built from eggshell powder particles dispersed in a polymer matrix.

2. EXPERIMENTAL

2.1 Materials

Polyaniline (emeraldine base) with an approximate Mw~5000 was obtained from Sigma-Aldrich. 1-methyl-2-pyrrolidinone (NPM) with an Mw of 99.13 was supplied by AR Alatan, Alor Star, Kedah, Malaysia. Eggshells were obtained from a local market in Perlis, and activated charcoal powder was supplied by Mega Makmur Sdn. Bhd., Pulau Pinang, Malaysia.

2.2 Sample Preparation

The eggshells were washed and dried in an oven at 105°C to eliminate contaminant and odour. Then, they were grinded into powder form. The form was next sieved using an industrial sieve to obtain the required particle size of 63 µm. The inorganic content in the eggshell powder is shown in Table 1.

Table 1: Inorganic content in eggshell powder measured by using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer.

Elements	%Wt
Al ₂ O ₃	0.001
SiO ₂	0.001
S	0.001
Cl	0.009
CaO	99.83
Cr ₂ O ₃	0.003
MnO	0.001
CuO	0.001
LOI	0.153

2.3 Mixing and Compounding

1-methyl-2-pyrrolidinone (NMP) (10.33 g) was added to 0.25 g of emeraldine base polyaniline and mixed to produce a polyaniline solution. Activated charcoal powder (0.50 g) was then added to the solution and was aliquoted equally in five test tubes. Five different amounts of eggshell filler (0.25 g, 0.50 g, 0.75 g, 1.0 g and 1.25 g) were added into the solution in the test tube, respectively. Table 2 shows the composition of the mixture for the polyaniline/eggshell composites. The weight percentage of eggshell of polyaniline/1-methyl-2-pyrrolidinone (PANI–NMP) was calculated according to the following formulae:

$$\text{Weight \% of ESP} = \frac{ESP}{MA} \times 100\% \quad (1)$$

where ESP is the amount of eggshell powder and MA is the amount of matrix. The final polyaniline mixture was placed into a heating mantle with a controlled temperature of 105°C, which is the boiling point of the solution, for 30 min. The conductive polymer produced was analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Table 2: Composition of the mixture for polyaniline/eggshell powder as a conductive composites.

Sensor	PANI–NMP (M)	ESP (g)	ESP (%)
S-0	0.005	0	0
S-1	0.005	0.25	2.21
S-2	0.005	0.50	4.41
S-3	0.005	0.75	6.62
S-4	0.005	1.00	8.83
S-5	0.005	1.25	11.03

2.4 Scanning Electron Microscope (SEM)

The morphology of the polyaniline/eggshell powder surfaces of conducting polymer was studied using SEM model JOEL JSM-6460LA, Akishima, Japan. Prior to the examination by SEM, the samples were mounted on aluminum stubs and underwent sputtering coating. A thin gold layer of 20 nm was sputter coated on the samples surfaces to avoid electrostatic charge during examination.

2.5 X-ray Diffraction (XRD)

XRD of the polyaniline/eggshell conductive polymer was performed using Shimadzu XRD-6000 Analyzer at an acceleration voltage of 35 kV and 25 mA with Cu K α ($\lambda = 0.15406$ nm). The scans were carried out in the range of 10–80° (2 θ). This analysis was performed at ambient temperature (27°C) with a scanning speed of 5°C min⁻¹. Bragg's Law was used to explain the X-ray interference through crystals and later to study the structures of different materials. Bragg's Law is given by:

$$n\lambda = 2d \sin \theta \quad (2)$$

where d is the distance between atoms, n is the number of order, λ is the wavelength of the incident radiation and θ is the incidence angle.

2.6 Experimental Setup for Sensor Testing

The sensor test system was assembled as shown in Figure 1. Six sensors with different composition mixture of polyaniline/eggshell powder were placed inside the acrylic chamber and connected to NI-6008⁸ for real time data acquisition. The hardware description is given in Table 3. An air pump was used in this experiment to: i) generate bubble, deliver ammonia volatiles, and ii) purge the sensor chamber so that the sensor response will return to the baseline. The detailed sniffing process and parameter setting is given in Table 4.

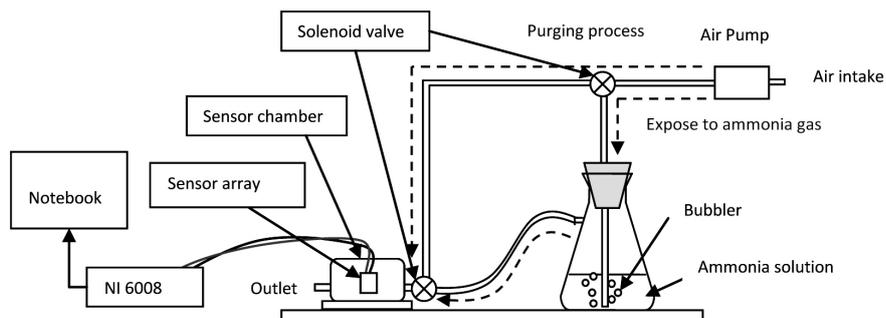


Figure 1: Sensor test setup.

Table 3: Hardware description and setup.

Hardware	Parameter
Sensor Chamber	10 cm (W) × 4cm (H) (Shape: Cylinder) Cylinder Volume = 0.314 L
Air Pump (for bubbler and purging)	12V (Pump speed = 0.5 mL min ⁻¹)
NI USB-6008	Data Acquisition Module from National Instrument
Power Supply	5Vdc supply to sensors. Common ground to both Sensor and NiDAQ. Each cabling was twisted in pair to reduce common mode current leakage.

Table 4: Sniffing process and parameter setting.

Parameter	Setting
Baseline	10 s (60 s during the first starting up)
Sample draw	180 s
Idle	3 s
Sample purge	180 s

3. RESULTS AND DISCUSSION

3.1 Physical Property of Eggshell

The BET analyser showed that the surface area of the eggshell powder was 43.7143 m² g⁻¹, whereas the Langmuir surface was 90.3459 m² g⁻¹. The single point adsorption total pore volume of pores less than 66.2933 nm in width at P/Po = 0.97 was 0.078075 cm³ g⁻¹. The Barret, Joyner and Halenda (BJH) adsorption average pore diameter (4V/A) was 9.9164 nm and the BJH desorption average pore diameter (4V/A) was 14.4322 nm. Traditionally, BET surface area measurement has been used to determine the specific surface area of colloidal inorganic oxides. As far as we are aware, BET studies on conductive polymer based eggshell powder has not been reported. The surface area and porosity values obtained show that the application of eggshell into polyaniline matrix enhanced its composites properties because it created a different phase relative to the matrix materials. These are important characteristics that affect the quality of the polyaniline/eggshell composites. They are important in understanding the structure, formation and conductivity potential, which correspond well to its applications in various fields.

3.2 Morphology of Conductive Polymer

Figure 2(a) shows the surface morphology of polyaniline film (S-0) without eggshell at 100X magnification. In this morphology, a chain configuration is indicated as the polyaniline chain embedded within its matrix. An expanded coil of the polyaniline structure was also observed.⁹ A major part of the polyaniline is compatible with 1-methyl-2-pyrrolidinone, which makes it soluble in the matrix and hence, a flat surface was observed.

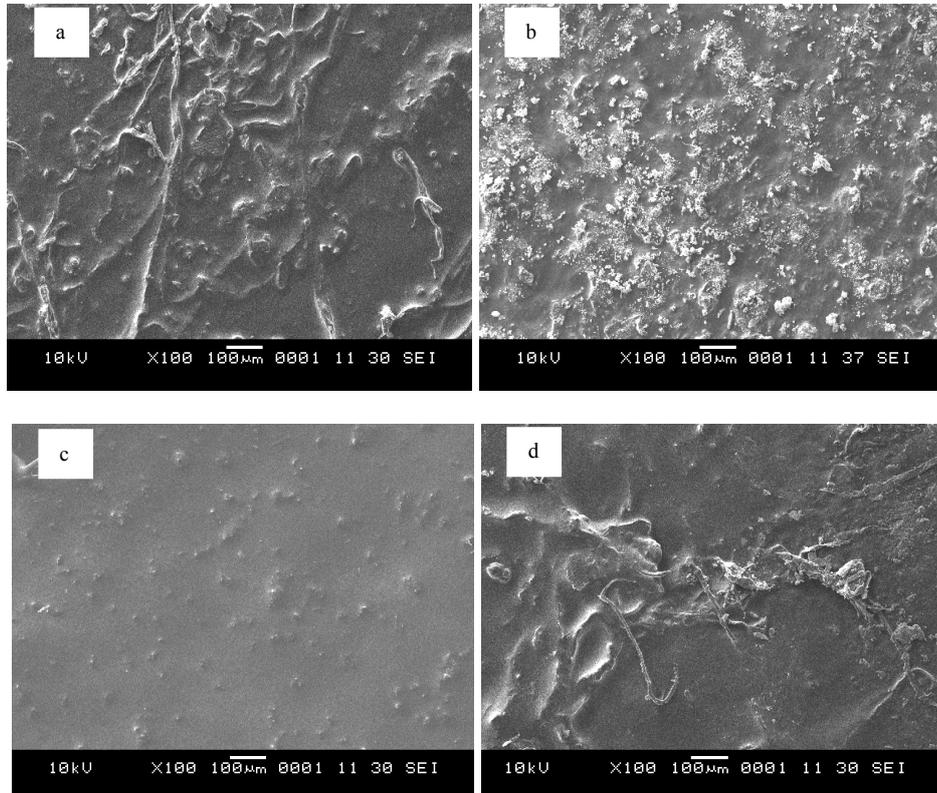


Figure 2: Surface morphology of: (a) film polyaniline [S-0] film conductive composite; (b) polyaniline/eggshell powder [S-6] conductive composite; (c) polyaniline/eggshell [S-2] powder conductive composite before exposed ammonia gas; and (d) polyaniline/eggshell powder [S-2] conductive composite after exposed ammonia gas.

Figure 2(b) shows the surface morphology with a filler of 0.5 g of eggshell powder at 100X magnification. The distribution of the eggshell particle in the polymer matrix is noticeably uniform with agglomerations on the surface of the conductive polymer. Agglomeration in the polyaniline makes the

connection of the conductive path more complete and improves conductivity. A rougher surface was observed as filler loading was increased; the formation of microfiller was found due to difficulties of achieving a homogeneous dispersion of filler at high filler loading.¹⁰ The surface morphologies of the sensor before and after absorption of ammonia gas are shown in Figure 2(c) and (d). It can be seen that the surface of the polyaniline/eggshell composites is smooth. This indicated a good adhesion between the eggshell powder and the matrix [Figure 2(c)]. Figure 2(d) shows the surface morphology of the sensor after absorbing the ammonia gas. The surface morphology of the sensor shows swelling of the conductive polymer film. The optimum eggshell powder concentration at 0.5 g (4.41 wt%) can be correlated with the condition resulting in the effective formation of a porous film.

3.3 XRD Analysis

Figure 3 shows the X-ray diffraction pattern of semicrystalline of the polyaniline/eggshell powder (0.5 g). From the XRD diffractogram obtained and the calculation of interparticle spacing, Bravais lattice was found to be followed by a FCC pattern as shown in Table 5. Therefore, the conductive polymer based on polyaniline/eggshell powder was assumed to possess a face centered cubic (FCC) structure. The powders exhibited peaks at two angles, around 20° and 45° (2θ) which indicates that the conductive polymer contains some crystalline domains. The surface morphology structure of polyaniline/eggshell is similar, closed-packed structures, which results in similar conductivity values.¹¹

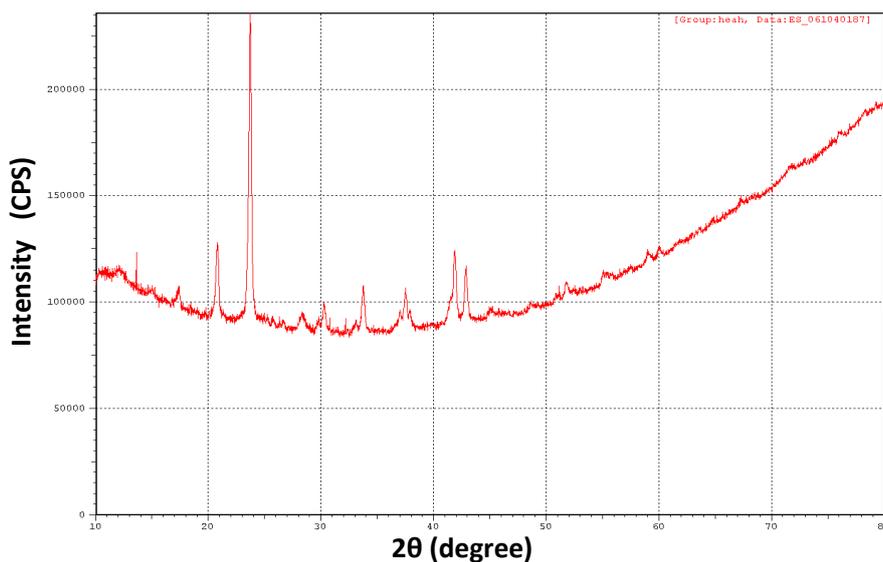


Figure 3: XRD pattern of semicrystalline of the polyaniline/eggshell powder.

Table 5: Calculation of interparticle spacing from the results interpreted from XRD.

Peak	2θ	θ	$\sin^2\theta$	$\frac{\sin^2\theta}{\sin^2\theta_{\min}}$	$\frac{3x\sin^2\theta}{\sin^2\theta_{\min}}$	$h^2 + k^2 + l^2$	hkl	d
A	21.0	10.50	0.03321	1.0000	3.0000	3	111	7.318
B	23.9	11.95	0.04287	1.2909	3.8726	4	200	7.438
C	28.4	14.20	0.06018	1.8121	5.4363	5	210	7.019
D	30.3	15.15	0.0683	2.0566	6.1698	6	211	7.217
E	33.9	16.95	0.08499	2.5592	7.6775	8	220	7.471
F	37.5	18.75	0.10332	3.1111	9.3333	9	300	7.187
G	41.8	20.90	0.12726	3.8320	11.4959	11	311	7.159
H	43.0	21.50	0.13432	4.0446	12.1337	12	222	7.278

Notes:

$\lambda = 1.54 \text{ \AA}$

$n = 1$

$h = 1/x, k = 1/y, l = 1/z$ (from the Miller index)

Bravais lattice is Face-Centered Cubic (FCC)

Average lattice parameter = 7.26071 \AA

3.4 Sensor Response

The response from all six sensors was captured using NiDaQ and save in the MATLAB workspace. These raw data was plot in Figure 4 and 5. Six conducting polymer sensors have a very stable response of baseline (ambient air) shown in Figure 4. However, sensor S-0 has shown some changes when exposed to ambient air. Sensors with the presence of eggshell powder composition are highly stable and do not give much response when exposed to ambient air, compared to the sensor with pure PANI-NMP composition (S-0). Apart from that, all sensors behave normally and there were no drifting observed during the experiment.

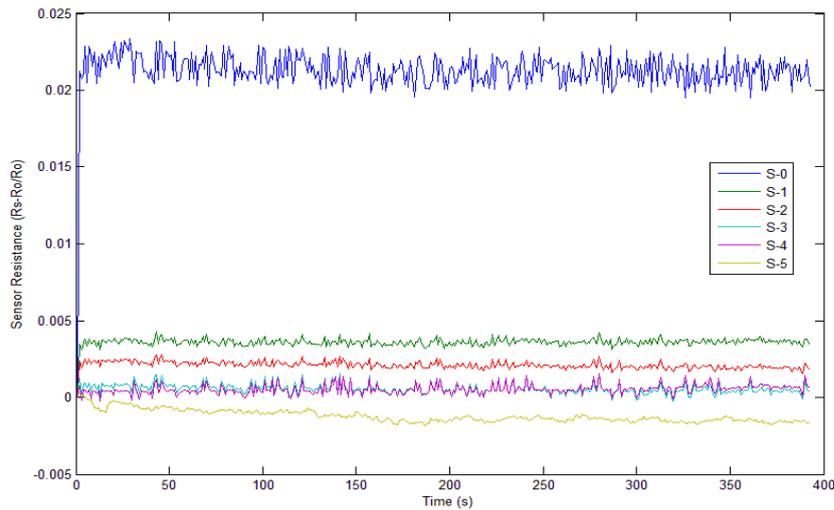


Figure 4: Sensor response when exposed to the ambient air.

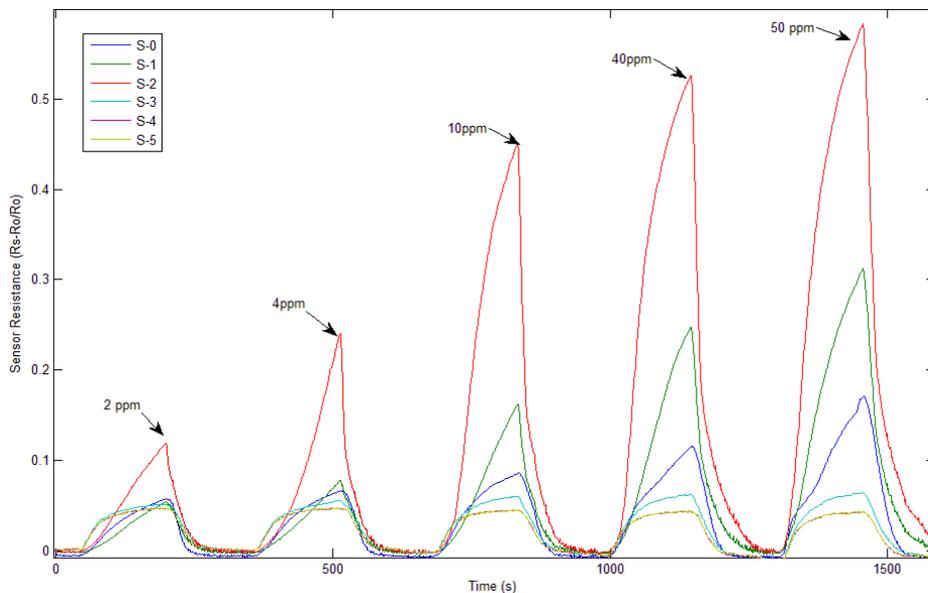


Figure 5: Sensor response when exposed to different concentration of ammonia volatiles.

In Figure 5, 200 mL ammonium solution with different concentration was delivered to six sensors of different composite composition using bubbler method. Five different concentration of ammonia gas was set, starting from 2, 4, 10, 40 and finally 50 ppm. Purging and sniffing time was made 3 min regardless the concentration of ammonia solution used in each experiment. During the purging process, the baseline was also recovered to the original state. There is no

drifting observed during the experiments. Sensor S-2 was observed to deliver the highest response followed by sensor S-1 and sensor S-0. The rest of the sensors seem to deliver insignificant response toward different ammonia concentration.

The ESP improves the sensitivity and increases the selectivity towards ammonia. Too much ESP seems to give adverse effect on sensor sensitivity. Sensor (S-2) with 0.5 g ESP is found to be better than sensor (S-0) with pure PANI-NMP composition. This was due to the eggshell powder contain trace elements of dioxide (Mn, Fe, Al, Cr, Ca, Mg, Na, Zn, Cu) to promote the conductivity of the composites.

4. CONCLUSION

The conductive polymer/eggshell coated interdigitated electrode was successfully applied to sense ammonia. The sensor sensitivity was strongly influenced by the composition of eggshell powder in the composites. The optimum composition ratio of polyaniline/eggshell powder composites was polyaniline-4.41 wt% eggshell powder in sensor 2 (S-2). These physical properties resulted in a sensor that is highly sensitive in the detection of ammonia gas. The sensor can detect ammonia gas of the order of 2 ppm. From the SEM micrograph, the surface morphology of the sensor after exposure to ammonia gas showed significant swelling. This is due to the enhanced absorption/desorption rate as a result of higher porosity and changed in surface morphology of the polyaniline/eggshell composites.

5. ACKNOWLEDGEMENT

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