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Synthesis and fabrication of polyaniline/eggshell composite in ammonia detection

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Abstract

This study focuses on the measurement and performance of bio-filler composite based on polyaniline (PANI)/chicken eggshell (CES). The composite films were prepared via ex-situ polymerisation using DBSA as its dopant. The PANI solution was distributed equally before mixing it with three different ratios of CES powder. Characterisations of the composite films were analysed using Fourier-transform infrared spectroscopy (FTIR) and Ultraviolet-visible spectroscopy (UV-Vis), Scanning electron microscope/energy dispersive x-ray (SEM/EDX) and multimeter. PANI film that contained 20mg CES filler possessed the highest conductivity and the fastest time to achieve 90% of sensitivity. The film was also very selective towards ammonia gas and can be reused up to eight cycles. All data reported in this study proved that PANI film with 20mg CES filler can act as a sensitive sensor with 6 ppm limit of detection.

1. Introduction

About four decades ago, polymer was classified as a poor electrical conductor as it lacked electron movements. However, it had been proven wrong in 1975 by Hideki Shirakawa with his associates Alan MacDiarmid and Alan Heeger where they had discovered electrical conductivity in the polymeric materials [1]. Since then studies related to polymers have caught the attention of many researchers as these polymers carry lots of advantages, such as high resistivity towards corrosion and chemicals, versatile functionality, lighter weight, and inexpensive monomers [2]. The polymers must impersonate the properties of a metal, where the electrons in the polymer must be freely movable and are not bounded to any atom in order to exhibit a certain degree of conductivity [3]. The conjugated pattern in a polymer forms delocalised bonding, enhancing the mobility of the electrons along the chain through a process called doping.

Among all the conducting polymers available, polyaniline (PANI) received most attention due to its highest specific capacitance as a result of its multi-redox reactions, good electronic properties, [4] and low cost of infinite abundance. Moreover, it has better thermal stability and can be easily synthesised by chemical or electrochemical methods, resulting in powder or thin film [5]. PANI can be found in three types of oxidation states, namely pernigraniline (fully oxidised), leucoemeraldine (fully reduced), and emeraldine. Among this three, emeraldine is the most promising and stable state [5]. Polymer composites that use PANI as their matrices have become popular among researchers as their resultant combination with inorganic materials have improved process ability and have good mechanical properties [3,6]. Calcium carbonate ($CaCO_3$) mineral is one of the most highly used inorganic fillers in polymer composites. However, recently, the use of bio compounds as fillers is likely to become more favourable. Polymer blends with bio-fillers that are cheap and sustainable are mainly considered in cultivating environmental-friendly composite which will enhance its properties [7].

Chicken eggshells (CES) are an example of natural resources of $CaCO_3$ compounds. Eggshells have been used in several research as the substitute of commercial $CaCO_3$ due to the abundance of $CaCO_3$ (94%) in CES. Replacing commercial fillers with bio-fillers gives a lot of advantages, such as cost reduction and cultivated improvement compared to commercial fillers. CES are easy to get and widely available as they come in bulk quantity. CES also have lower density compared to $CaCO_3$ mineral [8]. Besides that, CES bio-filler possesses several unique properties, such as easy implementation, low energy consumption, and low abrasive properties [9]. By using CES in a polymer composite, one can minimise the environmental impact of CES as residues and keep the cleanliness of environment.

The aim of this study is to improve the properties of PANI film composite. As far as we are concerned, there are not many research discussing on PANI/CES composite sensors for toxic gas detection. Therefore, in this paper, PANI is used as a matrix, while CES are used as fillers to prepare PANI/CES composites in ammonia gas detection.

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2. Experimental

2.1 Materials

Aniline (Ani) monomer, ammonium peroxydisulfate (APS), and 95% dodecylbenzene sulfonic acid (DBSA) were purchased from Sigma Aldrich. DBSA acted as the dopant. Both 37% hydrochloric acid (HCl) and analytical grade Toluene were purchased from R&M Chemicals. Distilled water was used throughout the research. Ammonium hydroxide (NH_4OH) was purchased from Merck Millipore. CES were obtained from a local supermarket (NutriPlus Omega 3 (Grade AA)) in Kuala Pilah. Cleaned and dried CES was ground and sieved to get a particle size of ~250 μm.

2.2 Synthesis of PANI

PANI was synthesised using ex-situ polymerisation method at 0°C for 24 h. Five mmol of Ani was first added dropwise in 250 ml of 1M HCl solution. After an hour, 5 mmol of pre-cooled APS solution was added dropwise into the mixture. The polymerisation was left for 24 h. Then PANI precipitate was filtered and washed several times using distilled water prior to drying in the oven for 3 h. Dried PANI was then dissolved in 1M of NH_4OH overnight. The precipitates were again filtered and washed before being immersed into toluene/DBSA solution to ensure a uniform redoping at the PANI backbone.

2.3 PANI/CES film

The PANI solution obtained was divided and allocated into four portions, namely PANI/DBSA without CES as a control and PANI with CES of 20 mg, 40 mg, and 60 mg. The PANI/CES solution was sonicated to completely dissolve the filler into the polymer. After that, the composite solution was deposited uniformly onto a clean glass substrate before it was dried in an oven at 60°C to remove any remaining solvent. The film thickness was measured by using digital micrometre whereby the thickness was 1-2 μm.

2.4 Characterisations

All PANI/CES films were characterised by using instruments, such as Fourier- transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 100 FT-IR ATR Spectrometer) within the range of 600-4000 cm^{-1} and were ultraviolet-visible (PG Instruments Ltd. T80+ UV/VIS Spectrometer) within the range of 300-900 nm. The scanning electron microscopy (SEM) micrographs of Pristine PANI and PANI/20 mg CES were recorded by Hitachi S3500N (Model: SU-70) at 5000× magnifications. The sample solutions were uniformly coated onto a clean FTO glass substrate by casting technique prior to SEM analysis. Then the FTO substrate with the sample was mounted on a conductive double-sided adhesive tape on microscope specimen stub. Two-point probe multimetre (Fluke, 15B Digital Multimetre) was used to measure the resistance. Then the conductivity was calculated by employing equation (1);

$$\sigma = \frac{L}{R \times A} \quad (1)$$

Where σ is the conductivity in $S \cdot cm^{-1}$, L is the distance between two-point probe, R is the film resistance that will directly record from the multimetre, and A is the average area of pristine PANI or PANI/ CES film composites.

2.5 Experimental setup for sensing properties

The sensor film was tested in a home-made gas chamber. PANI/CES film were exposed to different concentrations (20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm) of ammonia vapour for the dedoping process and the resistance was recorded. Then PANI/ CES films were let in contact with 'dry' air for redoping process before proceeding with the next concentration of ammonia vapour. The measurements were done in triplicates before and after exposure with ammonia vapour based on equation (2) and the standard deviations were reported in terms of error bars.

$$\text{Sensitivity (\%)} = \frac{\text{final resistance } (\Omega) - \text{initial resistance } (\Omega)}{\text{Initial resistance } (\Omega)} \times 100\% \quad (2)$$

3. Results and discussion

3.1 FTIR Analysis

FTIR Spectra of pristine PANI and PANI/CES composite films are illustrated in Figure 1. In general, both pristine PANI and PANI/CES films exhibited similar characteristic peaks. Typically, the earlier peaks at 689 cm^{-1} and 830 cm^{-1} were assigned to the stretching deformation of the aromatic ring and the out-of-plane bending vibration of the C-H band of the para-disubstituted benzene ring, respectively [10,11]. The characteristic bands that corresponded to $CaCO_3$ were seen at 800 and 1100 cm^{-1}. The intense band which were observed in the range of 1210 cm^{-1} was assigned to the C-N stretching of the secondary amine in the PANI backbone [12], while the band at 1170 cm^{-1} indicated the symmetric and asymmetric stretching of S=O group [12] present from DBSA dopant. Besides that, the vibration band of benzenoid and quinoid appears at 1462 cm^{-1} and 1524 cm^{-1}, respectively [10]. The peaks at ~1760 cm^{-1} showed a positive change towards its intensity ratio where the intensity of the peak increases with the increasing amount of CES filler. This was also shown in asymmetric stretch C-O band of $CaCO_3$ group (1485 cm^{-1}) where the peak slowly became sharp when comparing with PANI film

without any CES filler. This could be attributed due to the site-selective interaction between the filler and the DBSA dopant. The process might help in enhancing charge transfer between donor and acceptor in the PANI chain [13,14].

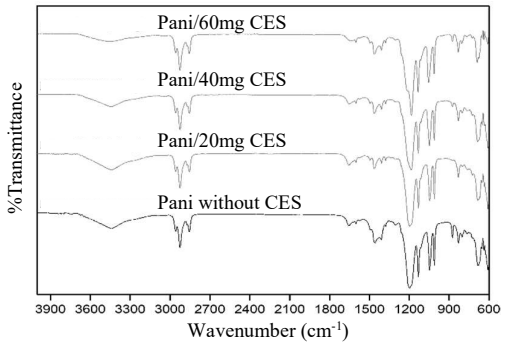

Figure 1. FTIR Spectra of pristine PANI and PANI/ CES films

3.2 UV-Vis analysis

Figure 2 shows UV-Vis absorption spectra of pristine PANI and PANI/CES films. The peak at 345 nm arose due to the π-π* transition in the benzenoid ring, while a peak at 450 nm corresponded to the polaron-π* of quinoid structure within the PANI itself. A prominent peak was observed at 750-800 nm which attributes to the π-polaron peak that is related to the doping level of PANI. The addition of CES fillers caused the π-polaron peaks to shift to a longer wavelength and undergo bathochromic shift (red shift). This happened due to the auxochrome adsorption on the chromosphere that is available on the PANI composite matrix [15]. The auxochrome group, NH_2 has the ability of sharing the non-bonding electrons to extend the conjugation of chromophores, which is broken into a more conjugated double bonds consisting of carbon, nitrogen, and oxygen [16]. Therefore, these active carbon and nitrogen atoms provide sufficient carbon and nitrogen sources for the plasma electrolytic properties [16] that alter both of the wavelength and the intensity of the absorption. In addition, the absorbance intensity decreased with the increasing of CES filler, which is probably due to the traces of undissolved fillers in the polymer matrix. CES is an inorganic matter, thus it can block UV light from scattering and dispersing thoroughly in the PANI film, resulting in low absorbance.

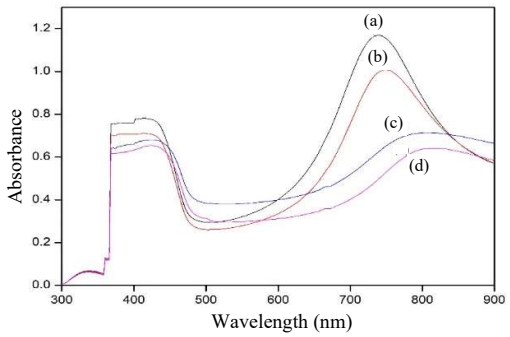

Figure 2. UV-Vis Spectra of PANI Film; (a) PANI without CES; (b) PANI/20mg CES; (c) PANI/40mg CES and (d) PANI/60mg CES.

3.3 SEM Analysis

The SEM micrographs of pristine PANI and PANI/ 20 mg CES composites are reported in Figure 3 to study the morphology of CES incorporated PANI. Figure 3(a) showed an almost uniform structure of PANI, while Figure 3(b) exhibited wrinkled surface due to the presence of CES in the PANI matrix. In addition, numerous inter-connections could also be found on the PANI/20 mg CES matrix, which would enhance the mobility of electrons in order to work as an excellent sensor in ammonia gas detection [3,7,8]. In addition, energy dispersive X-ray (EDX) analysis was performed to determine the effective incorporation of CES into PANI matrix (spectrum was not shown). The EDX spectra revealed the presence of C, O, and S elements in both films. Strong intensive peaks with atomic percentage of 82.5% and 72.1% in both spectra correspond to the C atoms, while less intense peaks were observed for O and S. Signal from N was absent in the measured spectra in both films. According to Weder (2009), N atom does not always appear in the PANI EDX spectra due to the low energy of N atom, that is, ~0.40 keV. On the other hand, the presence of weak Si peak in Figure 3(b) is probably due to the impurities that had been accidentally introduced during the sample preparation [12].

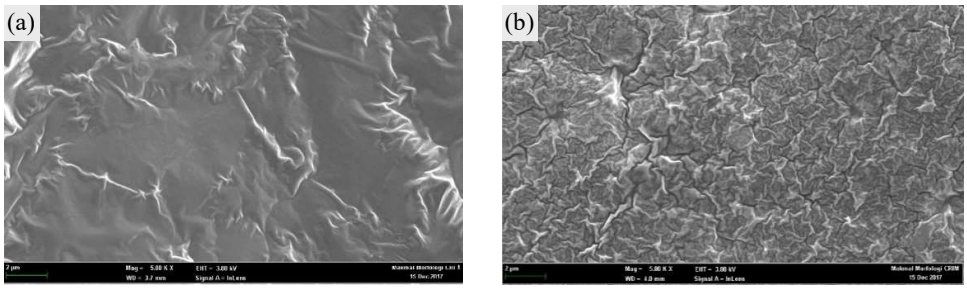

Figure 3. SEM micrographs of (a) pristine PANI and (b) PANI/20 mg CES that recorded at 5000× magnifications.

3.4 Conductivity analysis

Generally, the conductivity of pristine PANI and PANI composites depends on several factors, such as the degree of doping, oxidation state, and its molecular weight [12,17,18]. Conductivity results of pristine PANI and PANI/CES were tabulated in Table 1 below. Based on the table, the conductivities were decreased with the increasing amount of CES bio-fillers. The conductivities of PANI/CES composite films were relatively low compared to the pristine PANI. This is because the CES fillers significantly increase the barrier that obstruct the PANI electron pathways [19]. This fact can be further supported by the UV-Vis spectra as shown in Figure 2. The conductivities of each PANI/CES films dropped significantly with the decreasing of absorbance as the amount of CES fillers increased in the PANI matrix. The CES fillers block both the interchain and intrachain of PANI within the PANI backbone [19], thus decreasing the conductivities. A higher conductivity can be achieved if a spin coating method is used to obtain a uniform film on top of the glass substrate.

Among those three PANI/CES composite films, the film with 20 mg of CES filler exhibited the highest conductivity, that is, 4.709×10^{-6} S·cm^{-1}. The highest conductivity is possessed by 20 mg CES filler as it is the optimum mass for ~30 ml of PANI solution. Too much of filler will make the PANI solution aggregated and too saturated for an electron to move freely [20]. PANI that have good matrix match will give high crystallinity [6], less defect sites [21], and produce high molecular weight polymers that are filled with numerous polarans [22], hence increasing the conductivity.

Table 1. Conductivity value for each PANI/CES film

PANI Film	Conductivity (S·cm^{-1})
Pristine PANI	1.175×10^{-5}
PANI/20mg CES	4.709×10^{-6}
PANI/40mg CES	5.059×10^{-7}
PANI/60mg CES	3.210×10^{-7}

3.5 Sensor Measurement

The synthesised PANI/CES films were used as a gas sensor in different concentrations (20 ppm, 40 ppm, 60 ppm, 100 ppm) of ammonia vapour. The measurement was done for five minutes for each PANI/CES film. Equation (1) was used to calculate the sensitivity of each PANI film in ammonia vapour. An effective sensor is a sensor that can exhibit 90% of sensitivity [23]. Based on Figure 4, PANI/20mg CES film exhibited higher sensitivity towards ammonia where it achieved 90% of sensitivity faster than other PANI/CES films. Too much CES powder seems to give adverse effect on sensor sensitivity. From Figure 4, the response time decreases with the increasing concentration of ammonia gas. Generally, the resistance of PANI composite film will be increased due to the chemisorption of ammonia with charge transfer [24]. However, after redoping process using 'dry' air, the ammonium ion will convert into ammonia and leave the proton alone, resulting delocalisation of polarons and thus, decrease in resistances [24]. In addition, the incorporation of CES into the PANI matrix enhanced the electrostatic interaction between the amino groups ($-NH_2$) of PANI and carboxylate group of CES. This interaction contributes to the improvement of PANI's gas sensing performance [25]. PANI sensors with the presence of CES powder were highly stable [22,25] compared to pristine PANI when exposed to ambient air. The interactions of pristine PANI with ambient air will lead to the degradation of film due to humidity. Humidity increases the resistance of PANI gradually [27]. The pores that existed in the PANI backbone were filled with water vapour that made the film swell, blocking the electron hopping process [28], thus the resistance of PANI film will increase and the conductivity will decrease. Therefore, it is important to always store and use the film in a tight compartment.

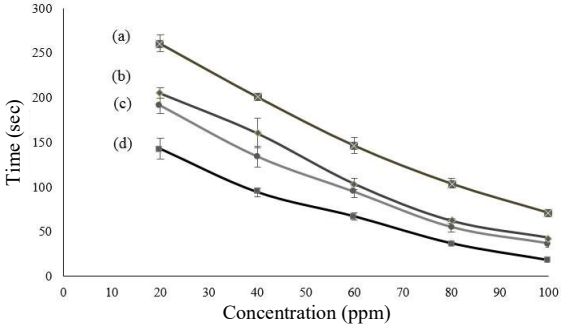

Figure 4. Time taken for (a) PANI/60mg CES, (b) PANI/40mg CES, (c) Pristine PANI and (d) PANI/20mg CES film to achieve 90% sensitivity in ammonia gas.

3.6 Sensor Performance

Figure 5 shows the calibration plot of sensitivity against the concentration of ammonia gas. The correlation of pristine PANI and PANI/CES films is tabulated in Table 2. It was clearly reported that the graph was linearly increased as the concentration of ammonia had been detected. PANI film with 20 mg of CES filler displayed good linear regression equation of $y = 5.6265x+270.49$ with correlation coefficient of 0.9925. The limit of detection (LOD) obtained is 6 ppm, which is much better than PANI without CES filler where it exhibits 0.9858 correlation coefficient and LOD value of 14 ppm. The LOD of PANI/20mg CES film is reliable because it is lower than the threshold value reported for ammonia (50 ppm). It can be further supported by the comparison between PANI/20mg CES film with other PANI composite films that are reported in the literature and were used as

sensor for ammonia detections in Table 3. Interestingly, there were two prior studies which made use of CES as fillers in the PANI matrix [3,25]. Unfortunately, both studies did not reveal the limit of detection which could be used as an important quality criterion for PANI sensor in ammonia gas detection. In addition, Ghani and co-worker [3] PANI/CES sensors exhibited a surprising increase in conductivity upon ammonia gas exposure, which is contrary to the present study. Therefore, the present study was carried out with analytical techniques that include calibration curves and the limit of detection calculations. Among the synthesised PANI composites, PANI/20mg CES film showed the highest sensitivity in ammonia detection, it has been chosen for the selectivity, reusability and long-term stability studies. 50 ppm of concentration was selected throughout this study as it is the threshold value for ammonia gas detection as reported by Occupational, Safety and Health (OSH) act.

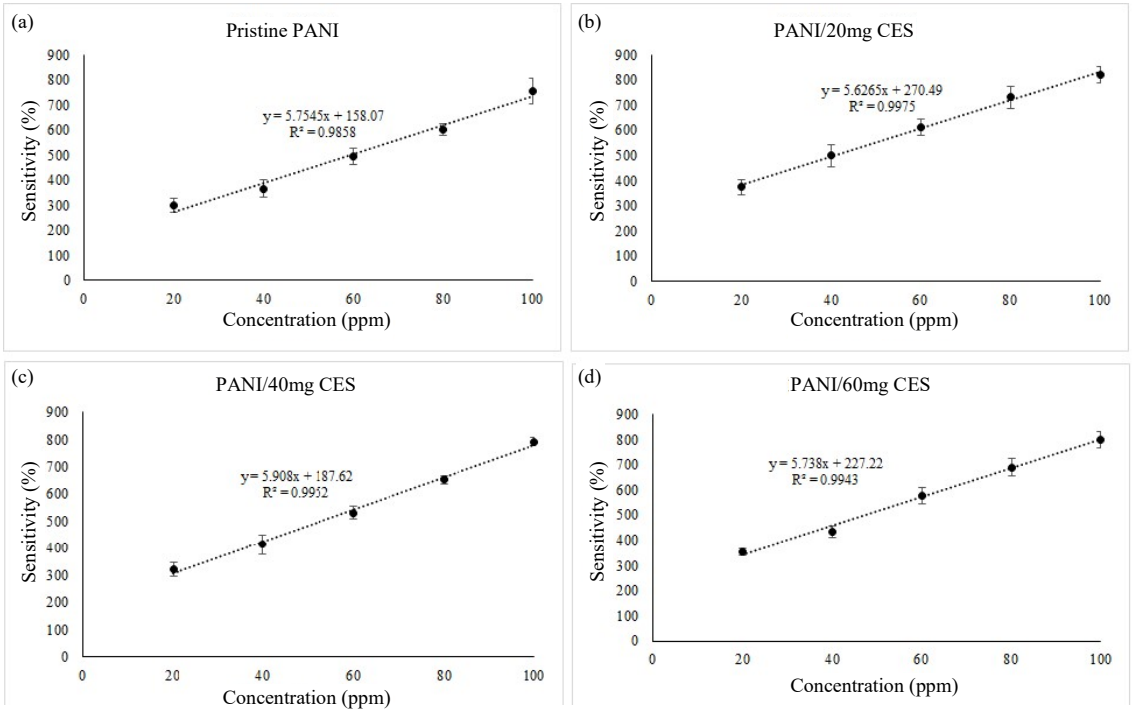

Figure 5. Calibration curve for (a) PANI/20mg CES, (b) PANI/60mg CES, (c) PANI/40mgCES and (d) PANI composite films in ammonia gas detection.

Table 2. Correlation coefficient of each PANI composite films

PANI film	Regression equation	Correlation coefficient (R^2)
Pristine PANI	y = 5.7545x + 158.07	0.9858
PANI/20mg CES	y = 5.6265x + 270.49	0.9975
PANI/40mg CES	y = 5.908x + 187.62	0.9952
PANI/60mg CES	y = 5.738x + 227.22	0.9943

Table 3. Comparison between PANI/20mg CES with other reported sensors.

PANI Composite Film	Method	LOD (ppm)	Ref
PANI/CES	Multimeter	-	[3]
PANI/4.41% CES	NI-6008 National Instruments	-	[26]
PANI/Graphene oxide/ZnO	Spectrometry	23	[33]
PANI/ZnO	Spectrometry	10	[34]
PANI/nanocellulose fibers	Colorimetry	10	[35]
PANI/tungsten oxide (WO_3)	Spectrometry	5	[36]
PANI/20mg CES	Multimeter	6	Present work

Selectivity study is a study of the ability of a chemical sensor to differentiate the targeted species. The PANI/20mg CES film was tested in four different types of vapour gaseous, namely ammonia, HCl, hexane, and methanol. Based on Figure 6, the film depicts high selectivity towards ammonia compare to other gases. This is because the interaction between PANI/CES and ammonia is an ion-dipole interaction [23,28]. Generally, PANI in the conducting state will possess ionic charges at the amine site that could attract the electrons from ammonia gas [29-32]. The mechanism scheme on PANI's interaction with ammonia gas has been illustrated in Scheme 1. While other gases have dipole-induced dipole interaction with PANI/CES which resulted in weaker interaction.

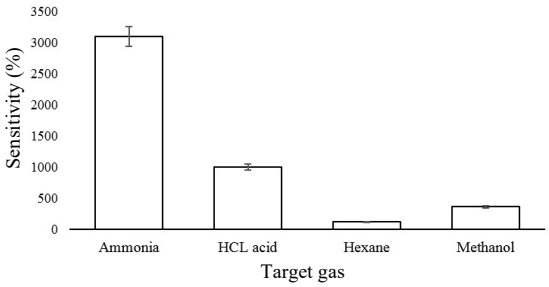

Figure 6. Selectivity of PANI/20mg CES film towards gaseous solution

$$PANI\text{-}H^{+}/CES + NH_3 \rightarrow PANI/CES + NH_4^{+}$$

Scheme 1. The PANI/CES mechanism during the ammonia gas detection.

A reusability study is a study that shows the number of cycles a film is capable of providing good sensor properties. This study was conducted through dedoping and redoping process in 10 cycles. In Figure 7, the trend of the reusable properties of the film fluctuated throughout the 10 cycles. The film started to lose its sensitivity below 90% in the ninth cycle. Since it took more than 5 cycles to lose its sensitivity, this film is considered stable and effective in ammonia gas detection.

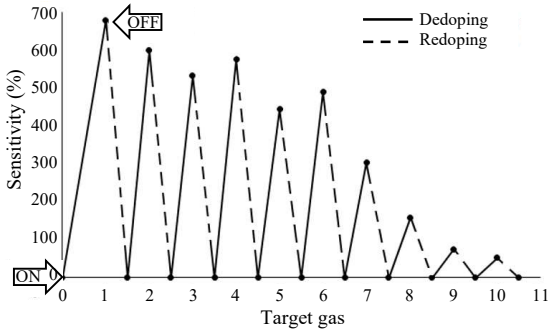

Figure 7. Reusability cycles of PANI/20mg CES film.

Long-term stability determines the number of days the film could be functionalised. The long-term stability study was conducted for 15 days. The PANI/CES film drastically loses its stability on Day 8 (Figure 8). This is due to its sensitivity towards humidity and ambient air. The interactions between PANI/CES film with humidity can lead to degradation of the film.

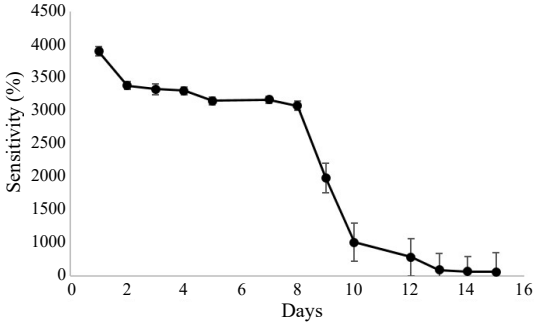

Figure 8. Long-term stability of PANI/20mg CES film.

4. Conclusions

In this analysis, three PANI/CES composite films were successfully made and their sensor measurement and performance were investigated. Based on this, PANI/20 mg CES film showed the best result for both measurement and performance in ammonia detection. The conductivity for this film is 4.709 x 10^{-6} Scm^{-1}. This film also exhibited the best correlation coefficient, that is, 0.9925 among all the PANI films and 6 ppm limit of detection. It was very selective towards ammonia and can be reused up to 9 cycles. The PANI/20 mg CES film was very stable as its long-term stability can reach up to eight days. For future prospect, PANI/CES could be analysed with x-ray diffractometry (XRD) technique to understand the determination of composites phase, and real sample analysis could be added to test the feasibility of the proposed sensor.

5. Acknowledgements

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