Doping Effect on Polyaniline|graphite Composite as Formaldehyde Gas Sensor

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Abstract. Here, we report the study about doping effect on composite Polyaniline (PANI) and graphite as the application as the formaldehyde gas sensor. The high conductivity of doping devices using HClO$_4$ if compared to the others. As a more expanded polymeric chain should expose more sites of adsorption, it is acceptable that the expectation of the sensor response will follow the same behavior as the conductivity. The composite doped using all kind of acid presents the band at 1140 cm$^{-1}$. However the band between 1050 – 1140 cm$^{-1}$ on HClO$_4$ and H$_2$SO$_4$ doping appears the peak that assigned to υ(S=O) and υ(Cl-O), then υ(N=O) stretching also appears on the band at 1380 cm$^{-1}$. The present of H$_2$SO$_4$, HClO$_4$, and HNO$_3$ doping on FT-IR are accepted that they have a multiplying effect on the change of the PANI polymeric conformation, from a compact coil to an expanded coil form, and consequently, the conductivity is increased.

1. Introduction

Food does not last long to store, especially food ingredients that contain high moisture content. Relatively short food storage certainly harms the food producer or industry. This triggers producers of small and medium enterprises and home industries to use additional ingredients such as preservatives [1,3,4]. Food additives are ingredients that are added intentionally into small amounts of food to improve appearance, flavor, texture, increase nutritional value and extend shelf life. The use of additional ingredients is prohibited if it aims to cover low quality and hide improper processing. But formalin is often misused, although based on the Republic of Indonesia Health Minister Regulation No.033 of 2012 formalin is prohibited from being used as food additives. Formalin is widely used as a food preservative by home industries or small and medium industries because the price is relatively more affordable compared to using chemicals included in the ADI (Acceptable Daily Intake) group such as benzoic acid and salt [5].

So far, there are number types of techniques available with the proper observing and monitoring of formaldehyde gas-based on solid-state sensors, high-performance liquid chromatography, amperometry, enzyme electrodes, voltammetry, ion chromatography, and spectroscopy [2,6]. A large number of these strategies required the formaldehyde to be caught/moved into a fluid arrangement or on a layer before the investigation and thus are unsatisfactory for constant checking. Also, a few strategies rely upon
costly instrumentation, depend on qualified faculty, are moderate, and not compact/field-deployable. In Indonesian, a lot of ways as a natural alternative to detect the presence of formaldehyde such as turmeric, dragon fruit, and several flower extract. The detection method is very economical but not accurate because its detection level only serves as a control of the presence or absence of formalin (positive and negative) [9]. Therefore, this issue needs to get another method to detect the percent of formaldehyde which is economical, low cost, easy operable.

PANI was concerned as a sensing material because of its high stability at room temperature, relatively good conductivity, and a natural doping process compared to other conducting polymers. The several applications of PANI as gas sensors have been reported. Because of the study about PANI|graphite films still little research developing for formaldehyde gas sensor. In this paper, we provided a survey about the chemoresistive sensors for formaldehyde detection base on composite PANI|graphite films with the effect of acid doping.

2. Methodology

The aniline monomer (Sigma Aldrich) was distilled under vacuum graphite, ammonium peroxydisulfate (APS), hydrochloric acid (HCl), hydrobromic acid (HBr), perchloric acid (HClO₄), sulfuric acid (H₂SO₄), nitric acid (HNO₃), ammonia (NH₃·H₂O), deionized water, acetone, dimethylsulfoxide (DMSO), formaldehyde (HCHO) and Whatman filter paper No. 42.

The PANI was synthesis by electrochemical polymerization of aniline at 0.7 V at room temperature in the mixed solution containing 0.40 mol dm⁻³ aniline, graphite, ethanol, and 1.0 mol dm⁻³ strong acid. The electrolytic cell consisted a saturated Ag/AgCl as a reference electrode on Gamry Reference 3000 electroanalysis instrument. A graphite sheet (GS) was used as a working electrode and a platinum plate as a counter electrode, respectively. All potentials given here are referred to an Ag/AgCl [10].

PANI synthesis was characterized by voltammetry technique at room temperature. This process used three-electrode cell that connected with Gamry Reference 3000 potentiostat. Platinum (Pt) metal as the counter electrode, Ag/AgCl in KCl saturated solution as the reference electrode, and PANI as working electrode. Scanning was done on 15 cycles in the potential range from -0.2 V to 0.8 V. 50 mV/s scanning speed was used for this treatment [12]. Furthermore, Fourier transforms infrared (FTIR) spectra of the material in KBr pellets were recorded using Bruker Alpha FTIR, with a range of 4000 - 550 cm⁻¹ and the number of scans 16 times. The PANI/KBr mixture was pressed to form PANI pellets within the KBr matrix.

3. Results and Discussion

The five samples, each with different doping, were tested as a gas sensor interacting with formaldehyde. To perform this measurement, the equipment was calibrated to use dry air intercalated with a preselected mixture of formaldehyde gas and dry air. To compare all devices, the formaldehyde|air relation was set to 10 ppm during the measurements, and the electrical resistance was continuously monitored. As expected, all devices showed a good resistivity in contact with the formaldehyde gas than with dry air. The results extracted of these measurements, such as the average sensitivities, response and recovery time are summarized in Table 1.
Figure 1. Characteristic current intensity versus voltage curve for PANI|G film with various doping using a) HClO$_4$ b) HCl) H$_2$SO$_4$ d) HBr e) HNO$_3$

Moreover, Fig. 1 shows the ohmic behavior of these devices in this voltage range (0.0 $V$ to 1.0 $V$, log-log I x V comparative). Here, it is also possible to notice the high conductivity of doping devices using HClO$_4$ if compared to the others. As a more expanded polymeric chain should expose more sites of adsorption, it is acceptable that the expectation of the sensor response will follow the same behavior as the conductivity. However, the same is not observed at the device's response to formaldehyde, the H$_2$SO$_4$, HClO$_4$, and HNO$_3$ doping does not promote a better sensor response [7,8].

| Doping    | Response (%) | Response Time (s) | Recovery Time (s) |
|-----------|--------------|-------------------|-------------------|
| HCl       | 10.2 ± 1.05  | 38 ± 5            | 155 ± 8           |
| HBr       | 4.24 ± 0.16  | 45 ± 3            | 195 ± 12          |
| HClO$_4$  | 16.85 ± 0.12 | 24 ± 2            | 240 ± 20          |
| HNO$_3$   | 5.53 ± 0.48  | 82 ± 2            | 400 ± 10          |
| H$_2$SO$_4$ | 18.24 ± 0.13 | 78 ± 6           | 253 ± 8           |
The doping using HCl presents the best response when compared to the use of H$_2$SO$_4$, HBr, HClO$_4$, and HNO$_3$ as a dopant. The sensitivity submitted by devices doped using HCl is 1.23 times higher when compared to the sulfuric acid doping, and 1.94 times higher when compared with HBr (Table 1). This result is attributed to the compromise between the polymer conformation and charge transfer achieved by PANI|graphite doped by HCl. An analysis of the FT-IR measurement showed at Fig. 10, can reveal some complementary information to explain the sensor results. The absorption band near 1140 cm$^{-1}$ indicated the $\nu(Q=NH+-B)$ or $\nu(Q-NH\cdash++-B)$ stretching [4,9]. Here, it becomes essential to restate that the typical absorption site to Schiff form on PANI is the secondary or tertiary PANI created by the $\sim$N$\sim$ condensation with formaldehyde [3,11]. The composite doped using all kind of acid presents the band at 1140 cm$^{-1}$. However the band between 1050 – 1140 cm$^{-1}$ on HClO$_4$ and H$_2$SO$_4$ doping appears the peak that assigned to $\nu(S=O)$ and $\nu(Cl-O)$, then $\nu(N=O)$ stretching also appears on the band at 1380 cm$^{-1}$. The present of H$_2$SO$_4$, HClO$_4$, and HNO$_3$ doping on FT-IR are accepted that they have the following effect on the change of the PANI polymeric conformation, from a compact coil to an expanded coil form, and consequently, the conductivity is increased [2].

![FTIR spectra for PANI|graphite (1 wt%) composite on these forms with variation acid doping](image)

**Figure 2.** FTIR spectra for PANI|graphite (1 wt%) composite on these forms with variation acid doping

4. Conclusion
This fact proved to be not useful for sensing a gas since the sensitivity is more affected by the charge location than the polymer conformation. Without a clear site of absorption, the probability that the gas interacts with any free charges on the polymer chain increase. Thus, the possibility of identifying the interaction between the gas and the polymer by an electronic change is reduced. The gas molecule which interacts with a free charge does not represent a significant turn on its electronic configuration, but only cutting on the charges available. So, this fact implies a less intensive change on the electrical properties of the composite when exposed to formaldehyde.

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