Application of pani/metal oxide composite as an active material of liquified petroleum gas sensors

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Polyaniline (PANI) and metal oxides are two materials that have various applications, including active sensors. PANI provides several benefits over other conductive polymers, including ease of synthesis, affordability, and high conductivity. Depending on the benefits of PANI, here we report the fabrication of PANI/metal oxide composites as an active material for gas sensors, especially LPG. By oxidatively polymerizing aniline at room temperature, PANI was formed. PANI/metal oxide composites were produced by using an in-situ polymerization technique. The PANI/MgO and PANI/ZnO nanocomposites were successfully fabricated, as shown by FTIR and XRD characterization results. The sensitivity of PANI/metal oxide sensitivity is better than bare-PANI/MgO, which is one of the kinds of metal oxide used. Several concentrations of gas were used at low ppm: 50, 100, and 200 ppm to identify the sensitivity of PANI. The size of the pores with a radius of 285 Å of the PANI/MgO nanocomposite shows that the value sensitivity was improved. The PANI/MgO nanocomposite has the best sensitivity to LPG exposure because it works well at all concentrations.

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1. Introduction

Conductive polymer materials have attracted many researchers because of their potential applications, such as health monitoring and medical devices, energy storage devices, LEDs, active sensor materials, and microwave-absorbing devices [1]. Conductive polymers have undergone rapid development since their invention. Conductive polymers are conjugated organic polymers with single and double-bond structures that quickly decompose naturally compared to inorganic materials [2]. The conductivity of a conductive polymer can be adjusted by doping, changing the structure chemically, or combining it with different doping, i.e., a metal, a semiconductor, an acid, or even a surfactant. Conductive polymers (CP) are suitable for sensor applications because they exhibit changes in properties such as optical, electrical, and even mass changes when interacting with certain chemicals. One of the conductive polymers, Polyaniline (PANI), has good stability compared to other polymeric materials such as Polypyrrole (Ppy), Polyacetylene (PA), Polythiophene (PT), and Polydiasethylene (PdA) [3].

PANI has several advantages, such as being easy to synthesize, low cost, and high conductivity compared to other conductive polymers [4]. Depending on the addition of the doping type in the synthesis process, PANI has three oxidation states that include fully oxidized pernigraniline base (PB), half oxidized emeraldine base (EB), and fully reduced leucomeraldine base (LB) [5]. The EB phase is the only state with an electrical conductivity that can be adjusted from 10^{-10} S/cm to 100 S/cm through doping [6].

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Various types of gas sensors based on conductive polymer materials have been developed in the last few decades. These sensors are used to detect gas leak hazards quantitatively and qualitatively. These measurements require high conductivity, sensitivity capability, stability, response time, and long-term storage [7]. Several studies have stated that the compatibility of PANIs has a weakness. It is less sensitive to several gases, such as H₂, CO, and LPG, because the gas concentration required reaches 5000-25000 ppm [8, 9]. As a result, it is necessary to composite PANI with metal oxide material to improve its performance as a gas sensor.

Metal oxide is an active material for chemical sensors and has more stable properties than sensors from organic chemicals. ZnO and MgO are metal oxide materials that can detect the presence of several gases, including C_2H_5OH , CO, NO₂, NH₃, H₂S, H₂, and LPG [10]. Previous research [11] performed that conductive polymer composites with metal oxides increase the active surface area for sensing reactions. The sensor performance is directly related to the ratio of the surface area of the sensing element. In addition, the PANI/MgO composite, which was applied as an LPG gas sensor, was proven to detect the presence of gas at a lower concentration of 500-2000 ppm. The addition of MgO to PANI can reduce the detection limit. Making the composite morphology have a pore structure that, when exposed to LPG gas, triggers the gas adsorption process on the active surface of the material.

Here, we report the results of PANI/MgO and PANI/ZnO composite fabrication using the in-situ method. Compared to other fabrication methods, the in-situ method is obtained using the easiest methods to fabricate composites. The gas used in this study is Liquefied Petroleum Gas (LPG) because LPG is widely used in everyday life. LPG leakage in the room will seriously impact human health and safety.

2. Materials and method

2.1. Materials

The materials used in this study were 99.5% monomer aniline (Smart-Lab), ammonium peroxydisulfate (APS) as oxidant, MgO (Emsure), and ZnO powder (Smart-Lab) as filler, 37% HCl (Sigma Aldrich) as dopant, acetone, and demineralized water. Simultaneously, the tools needed were magnetic rods, a 50 ml beaker, aluminum foil, a hot-plate magnetic stirrer, filter paper, an ultrasonicator, porcelain mortars, and compacting tools.

2.2. Experimental methods and data analysis

PANI powder was synthesized by oxidative polymerization of aniline at room temperature. To create a homogenous solution, 1 M HCl was dissolved in 0.1 M aniline and stirred using a magnetic stirrer for 15 minutes. After that, 0.1 M ammonium peroxydisulfate (APS) solution was poured into the solution with continuously stirred for 4 hours. Polymerization of the solution was conducted for 12 hours without any disturbance. The dark green precipitate indicated that the polymerization was completed. The precipitate was collected, filtered, and washed with distilled water and acetone 3-4 times and then heated in an oven at 80°C for 16 hours. Finally, the precipitate was crushed using a mortar and compacted to form PANI pellet. PANI/metal oxide composites were synthesized by in-situ polymerization method, with the same steps as the synthesis of PANI powder.

FTIR, XRD, SEM, and EDX characterized the obtained samples. A Fourier transform infrared (FTIR) brand Shimadzu type IR Prestige 21 was used to identify the type of PANI and its composite's functional groups. X-ray diffraction (XRD) system of type XPERT-PRO was observed to identify the phase and crystalline structure with a Cu, 40 kV, 35 mA anode radiation source with a monochromatic wavelength of Cu-ka and a 20 angle of 10°- 90°. The sample's morphological shape was observed using a scanning electron microscopy (SEM) characterization tool, the Inspect-S50 type FEO, operated at 20 kV, 60 μ A, and magnifying 35,000 times. X-ray diffraction (XRD) type XPERT-PRO system was used to figure out the phase and crystalline structure with a Cu, 40 kV, 35 mA anode radiation source at a monochromatic wavelength of Cu-ka and a 20 angle of 10°- 90°. The pore sizes of PANI and its composite were analyzed by Brunauer Emmett Teller (BET) method. Resistance measurement was carried out using a Four Point Probe (FPP) to measure the change in the electrical conductivity of the composite due to exposure to LPG.

2.3. Preparation sensitivity measurement

PANI and nanocomposites PANI/metal oxides that had been compacted in pellets were used in LPG sensor sensing. Figure 1 shows the schematic diagram of the LPG sensor design. The design includes a gas sensing chamber (gas chamber), a portable LPG tube, pellets, a 4-point probe, and a power supply.



Fig. 1. LPG sensor sensing schematic

Fig. 1. shows the sensing process schematic. First, the pellets are inserted into the assembled gas chamber. The gas chamber used for testing the sensor's sensitivity is considered sterile from impurity gas, and the pressure in it is considered constant (1 atm) so that it does not affect the sensor sensitivity measurement process. Furthermore, four probes from the 4-point probe are placed in contact with the sample surface. The four probes are made in a straight line, with the distance between the probes arranged the same distance. After settling the probe distance, the next step is to spray LPG into the gas chamber with a predetermined gas concentration. The measurement of current (I), time (t), and V_{out} values will be stored in the memory card on the 4-point probe device. This step is repeated for different gas concentrations: 50, 100, and 200 ppm.

3. Results and discussion

3.1. Fourier Transform Infra-red (FTIR)

The type of bond formed by the PANI, PANI/MgO, and PANI/ZnO characterization was obtained by FTIR and processed by Origin. The ZnO and MgO materials used were commercial, so the determination of their functional groups adjusted the existing database.



Fig. 2. FTIR spectrum of a) PANI powder, b) PANI/MgO, and c) PANI/ZnO.

The results of the FTIR characterization are shown in Fig. 2., which are observed in the range of 450 - 4000 cm⁻¹. The several peaks in the composite sample occur a slight shift as in the PANI/MgO sample at wave number 1550 cm⁻¹ with the type of C-C bond. This peak shift occurs due to the stretching vibration of the quinoid ring and benzenoid ring. This peak indicates the formation of PANI with the emerald salt phase (ES) [12]. The wave number of 1102 cm⁻¹ is shifted due to the location of the N-H and C-H bonds which are close to each other in the benzenoid ring bound to MgO oxygen [13]. The MgO peak in the composite FTIR spectrum indicates that the MgO particles have been uniformly distributed. The characteristic of the MgO peak appears at a wave number of 3687 cm⁻¹ with H-O-H strain bonds [14] and 569 cm⁻¹ with frequency bonds of MgO vibrations, and 480 cm⁻¹ with MgO vibrational strain bonds [15].

Furthermore, the peak shift also occurred in the PANI/ZnO composite to the lower side at wave numbers 1546 cm⁻¹, 1424 cm⁻¹, and 1103 cm⁻¹ due to the formation of hydrogen bonds between the N-H PANI group and ZnO [16]. The appearance of the ZnO spectrum in the composite is located in the wave number region between 864 cm⁻¹ – 485 cm⁻¹, which shows Zn-O-Zn and Zn-O strains [17].

Wave number (cm ⁻¹)			Bond type		
PANI	PANI/MgO	PANI/ZnO	PANI	PANI/MgO	PANI/ZnO
-	3687	-	-	stretching H-O-H	-
1567	1550	1546	stretching C=N	stretching vibration C-C	stretching C=N
1488	1463	1424	stretching vibration C=C	stretching vibration C=C	stretching vibration C=C
1286	1277	1276	stretching C-N bond at benzenoid	stretching C-N bond at benzenoid	stretching C-N bond at benzenoid
1241	-	1221	stretching C-N bond at benzenoid	-	stretching C-N bond at benzenoid
1126	1102	1103	C-H bending	C-H bending	C-H bending
810	803	865	C-H bending	C-H bending	Zn-O-Zn
-	-	674	-	-	and
578	569	559	C-N-C bond at the aromatic ring	vibration Mg-O	Zn-O
497	480	488	C-N-C bond at the aromatic ring	stretching vibration Mg-O	

Table 1. Wave number and bond types of PANI, PANI/MgO composites, and PANI/ZnO composites.

3.2. X-Ray Diffractometer (XRD)

The structures and crystallinity of the PANI, PANI/MgO, and PANI/ZnO samples were analyzed by XRD Characterization. QualX software was used to determine the diffraction pattern. Each composite sample tended to have a diffraction pattern similar to the PANI sample. The similarity showed that the formation of PANI from the synthesized material was formed successfully. The diffraction pattern of the widening PANI in Fig. 3. (as a black line) shows a partial or semi-crystalline crystal structure. This peak is the initial material before adding some composite (MgO or ZnO). The diffraction pattern appears at the peaks of $2\theta = 20.37^{\circ}$ and 25.18° , which corresponds to hkl (010) and (200) [18].



Fig. 3. XRD patern for PANI, PANI/MgO, and PANI/ZnO.

The green line in Fig. 3 represents the diffraction pattern on the PANI/MgO composite. The presence of PANI in the composite is indicated by the presence of two fairly broad diffraction peaks at $2\theta = 20.86^{\circ}$ (010) and $2\theta = 25.51^{\circ}$ (200). The presence of MgO in the composite indicated by two other peaks appear at $2\theta = 42.36^{\circ}$ (200) and $2\theta = 62.79^{\circ}$ (220). The red line represents the PANI/ZnO composite XRD pattern. The peak where it was formed is quite similar to the PANI XRD pattern but has a higher intensity. The intensity of the hydrogen bond between H-N and oxygen in ZnO is displayed at $2 = 25.7^{\circ}$ (200), suggesting that the PANI/ZnO composite's crystallinity decreased due to the inhibition of ZnO crystallinity in amorphous PANI [19].

3.3. Scanning Electron Microscopy (SEM)

The morphology or surface structure of composite samples can be observed using SEM. Morphological characteristics are related to the shape and size of the particles. SEM analysis was carried out using Image-J software to determine the shape and size of the particles. The morphology of the PANI/MgO and PANI/ZnO composite samples can be seen in Figure 4. Each composite was observed at 35,000 times magnification. Fig. 4a shows that the PANI/MgO sample has a spherical morphology with a pore size of 326 nm. While in Fig. 4b, the PANI/ZnO composite has an ovoidal-shaped shape with a particle diameter of 226 nm. Black areas can be seen in both composite morphological pictures; these correspond to the surface pore structures of the materials. This pore structure functions as the absorbance of gas molecules when the composite is applied as a gas sensor base material. The greater the number of gas adsorption regions on the active surface of the composite, the higher the sensing response of the material [20].



Fig. 4. Morphology of a) nanocompite PANI/MgO and b) nanocomposite PANI/ZnO.

3.4. Liquified Petroleum Gas Sensing

The sensing response of metal oxide material to LPG is carried out at room temperature. The main parameter for sensing LPG is the change in the electrical resistance of the sample when LPG interacts with it. This resistance change is used to understand the sensing behavior of composite samples using the Four Points Probe. The response and recovery time should be minimal for a suitable sensor. Response time can be defined as the time a sensing material requires to change its resistance to 90% of its maximum value. In comparison, the recovery time is the time the sensing material requires to change its resistance to 10% of its maximum value [21]. Therefore, the current values (I), time (t), and V_{out} that can be obtained are then calculated using the equation [22]:

$$\rho = 2\pi t \frac{Ln2}{V/l} \tag{1}$$

The determination of the conductivity value can be obtained using the following equation:

$$\sigma = \frac{1}{\rho} \tag{2}$$

The electrical conductivity of PANI, PANI/MgO, and PANI/ZnO before LPG sensing are 0.041 S/cm, 0.097 S/cm, and 0.077 S/cm, respectively. After exposure to LPG with a specific concentration, the electrical conductivity of the sample will decrease (Fig. 5. a). The decrease in the linear conductivity value aligns with increasing gas concentration. When exposed to high concentrations of LPG, the conductivity decreases significantly. This study showed that PANI and its composites could detect LPG with a low concentration (50 ppm). This performance was improved compared to earlier research, which could only identify LPG at a concentration of 5000 ppm [8]. The detection ability of LPG is caused by the interaction of gas molecules with the pellet surface. The interaction between molecule gas and pellet causes electron transfer, so when the percentage of pellet nanoparticles is more significant, the conductivity change also increases.

Adding composite to the PANI increases the sensitivity of the PANI as a sensor. This composite addition is indicated by the increased conductivity of the sensor when measuring LPG with different concentrations. Fig. 5. (b) shows the sensitivity of PANI/MgO in detecting LPG gas with various gas concentrations. The sample with the highest sensitivity value is the PANI/MgO composite at 62.19%. The figure shows that the sensitivity value increases along with the rise in the concentration of LPG gas. The increment indicates that the sensitivity of PANI/MgO is directly proportional to the gas concentration. The higher the concentration given, the higher the sensitivity response of PANI.



Fig. 5. (a) Conductivity of PANI and its composite, (b) Graph sensitivity of PANI and its composite.

The Brunauer Emmett Teller (BET) characterization was carried out to determine the pore size of the sample. First, the BET characterization was performed by degassing at 200°C for 5 hours. This process aimed to remove water molecules and impurities from the material's pores. The results of pore measurements on PANI materials and PANI/MgO composites can be seen in Table 2.

Table 2. Surface area and pore radius of PANI and composite PANI/MgO.

No	Sample	Surface area	Pore radius (Å)	Pore volume
		(m^{2}/g)		(cc/g)
1	PANI	36.917	17.023	0.232
2	PANI/MgO	16.415	285.769	0.228

Characterizing BET in surface area testing is essential because it is where adsorption occurs [23]. Samples with a significant surface area have smaller pore sizes than samples with a small surface area. Table 2 shows that adding MgO to PANI makes the mean pores much more significant. The increase in porosity value leads to applying an LPG gas sensor because the gas will be adsorbed onto the active surface of the composite.

The PANI pore size becomes very important because it will affect the characteristics of the pan when used as a sensor. The greater the porosity, the more gas is adsorbed, so the better the sensing carried out by PANI. Table 2 shows that the pore radius of PANI/MgO is more extensive than that of PANI, indicating that the size of pores influences gas absorption during measurement. The higher the pore's diameter, the better the gas absorption and sensitivity of the PANI/MgO. We can prove in Fig. 5.b. that the PANI composite has a higher sensitivity for all concentration variations than the PANI itself. In other words, the porosity's diameter will increase PANI's sensitivity.

Several measurements were made, and the performance of the PANI composite is better than PANI itself. Regarding conductivity and sensitivity, the PANI composite performs better than PANI. This result proves that the addition of composites can improve sensor performance.

4. Conclusion

This research successfully fabricated PANI/metal oxide nanocomposite using the in-situ polymerization method. It has been confirmed by FTIR and XRD characterization results. The diffraction pattern of the widening PANI appears at the peaks of $2\theta = 20.37^{\circ}$ and 25.18. The presence of MgO in the composite indicated by two other peaks appears at $2\theta = 42.36^{\circ}$ (200) and $2\theta = 62.79^{\circ}$ (220), and ZnO appears at $2\theta = 25.7^{\circ}$ (200). PANI/metal oxide nanocomposites have demonstrated more sensitivity than bare-PANI to LPG sensing. The LPG detection limit was achieved at 50 ppm, which is better than the previous studies. In this study, the most functional material for LPG sensors is PANI/MgO nanocomposite because it functions well at all concentrations and has the highest sensitivity. This effective detection capability can be achieved by adding MgO to PANI, which increases the pore radius and improves the gas absorption process.

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