Gas sensing properties of polyacrylonitrile/metal oxide nanofibrous mat prepared by electrospinning

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Abstract

Polyacrylonitrile(PAN)/metal oxide(MO) nanocomposite mats with a thickness of 0.12 mm were electrospun by adding 0 to 10 wt% of MO nanoparticles (Fe_2O_3, ZnO, SnO_2, Sb_2O_3-SnO_2) into PAN. Pt electrode was patterned on Al_2O_3 substrate by DC sputtering and then the PAN(/MO) mats on the Pt patterned Al_2O_3 were electrically wired to investigate the CO_2 gas sensing properties. As the MO content rose, the fiber diameter decreased due to the presence of lumps caused by the presence of MOs in the fiber. The PAN/2% ZnO mat revealed a faster response time of 93 s and a relatively short recovery of 54 s with a ΔR of 0.031 MΩ at a CO_2 concentration of 200 ppm. The difference in sensitivity was not observed significantly for the PAN/MO fiber mats in the CO_2 concentration range of 100 to 500 ppm. It can be concluded that an appropriate amount of MO nanoparticles in the PAN backbone leads to improvement of the CO_2 gas sensing properties.

Key Words : polyacrylonitrile(PAN), metal oxides (Fe_2O_3, ZnO, SnO_2, Sb_2O_3-SnO_2), electrospinning, nanofiber, CO_2 gas sensor, sensitivity

1. Introduction

The increased demand for cheap, small, economical and reliable sensors that incorporate the well-known "3S" (sensitivity, selectivity, stability) capabilities in such areas as environmental monitoring, toxic chemical gas detection, biomedical diagnosis, and public security has fueled the development and introduction of polymer-based nanocomposites[1-7]. The electrospinning process has been used to produce polymeric nanofiber membranes for sensing applications. These membranes have unique properties such as a high surface area-to-volume ratio and high porosity[7,8]. Greater porosity is likely to provide pathways for the analyte to permeate through the fiber membrane[5]. In addition, specific functionalization of the polymer backbone can be achieved by the incorporation of metal oxide (MO) nanoparticles into the polymer[5-8].

Among polymers, polyacrylonitrile (PAN), a homopolymer of acrylonitrile (-CH_2-CH(CN)-), is used in this study as the base polymer due to its higher strength compared to polyacrylic acid fibers[9,10]. PAN is a vinyl polymer and a derivative of the acrylate family of polymers. It is known that electrospun fibrous membranes have a surface area approximately one to two orders of magnitude greater than continuous films[6].

Luoh and Hahn[5] reported that higher specific surface area improved the sensitivity due to enhanced gas adsorption. Among polymer/MO (Sb-SnO_2, ZnO, Fe_2O_3) nanocomposites, they demonstrated that Fe_2O_3 doped PAN produced composite mats with improved CO_2 gas sensitivity, as adsorption was found to be a function of the affinity between gas molecules and surface molecules. Although the sensing characteristics of a nanocomposite fiber mat were investigated qualitatively using the Fourier transform infrared spectroscopy (FTIR) absorbance spectra, quantitative studies of electrospun fibers were not studied in detail. Pt electrode was patterned on Al_2O_3 plate by DC sputtering. The PAN/(MO) mats were electrically connected to investigate the gas sensing properties and elucidate the feasibility of polymer based gas sensor.

2. Experimental Procedure

PAN powder (Aldrich Chemical Co., Japan), Fe_2O_3

(5~25 nm, Aldrich Inc., USA), SnO_2 (18.3 nm, Aldrich Inc., USA), Sb_3O_4-SnO_2 (19 nm, Aldrich Inc., USA), ZnO (50-70 nm, Aldrich Inc., USA) and dimethylformamide (DMF, Fisher Scientific, Japan) were used as precursors. This work focuses on the 10 wt% PAN fibers as optimized previously[9,10]. PAN/MO nanocomposites were prepared by adding 0 to 10 wt% of MO nanopowders into PAN. PAN/MO powders were added to the DMF solvent. The mixture was stirred with a magnetic bar until the lumps of PAN powder were broken up and well dispersed.

The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22-gage metal needle, a grounded collector, and a high-voltage supply source (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with digital current and voltage meters. The solution was placed in a 5 ml BD luer-lok syringe attached to the syringe pump and fed into the metal needle at a flow rate of 1.0 ml/h. A piece of flat aluminum foil was placed 14 cm below the tip of the needle to collect the nanofibers at a voltage of 16 kV[9-11].

The membrane thickness was determined by a laser displacement sensor (Micro-Epsilon, optoNCDT 1700, ILD 1700-100, Germany). The morphology of the nanofibers was evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). The sensing performance of the fiber membranes were evaluated by their Fourier-transform infrared spectrophotometer (FTIR, Simazu Prestage 21, Japan) absorbance spectra in order to clarify the behavior of functional groups in polymer matrix[5].

Pt was patterned on Al_2O_3 plate by DC sputtering. The PAN/MO films were electrically wired to measure the output voltage to evaluate the CO_2 gas sensitivity at room temperature[12]. The concentration of the gas inside the chamber was achieved by injecting a certain amount of the test gas into the chamber pre-filled with air using a mass flow controller and maintained at atmospheric pressure. PAN/MO gas sensor was exposed to different concentrations of CO_2 gases at room temperature.

3. Results and Discussion

Uniform, smooth and continuous fibers with diameter of approximately 300 nm (Fig. 1(a)) were previously found for the 10 wt% PAN fibers at a flow rate of 1.0
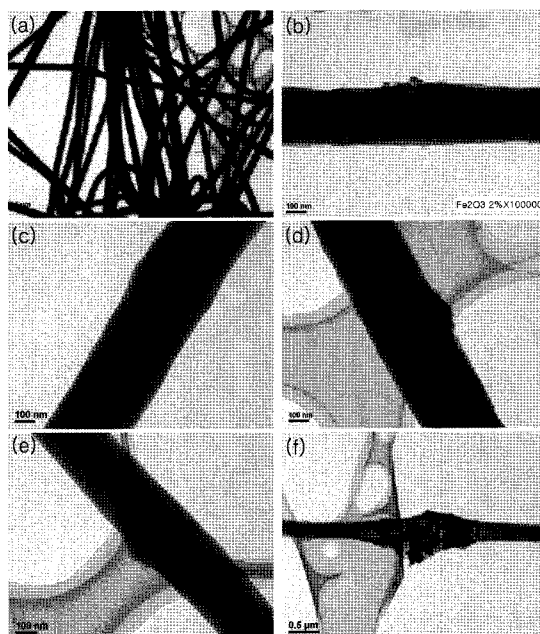

Fig. 1. TEM images of electrospun PAN fibers containing 2 wt% of metal oxide: (a) PAN, (b) PAN/Fe_2O_3, (c) PAN/ZnO, (d) PAN/Sb-SnO_2, (e) PAN/SnO_2 and (f) PAN/ZnO (6 wt%).

ml/h and with an electric field of 0.875 kV/cm, respectively[9-11,13]. TEM images of the electrospun PAN/MO were shown in Fig. 1. It is noted that the fiber diameter is almost uniform when MOs were added by 2 wt%. As the MO content rose, the fiber diameter became smaller due to the presence of lumps caused by the presence of MOs in the fiber, as shown in Fig. 1(f)[13]. The inhomogeneous distribution of MO particles is likely to due to the introduction of mechanical stirring process rather than chemical method. The fibers between the lumps become thinner, implying that the amount of MO is crucial for the morphology of the electrospun fibers. The lump may be attributed to the morphology of the fibers probably due to the inhomogeneous distribution as well as the clusters of MO particles. It is known that MO nanoparticles present inside or on the surface of the fiber may result in enhanced gas adsorption that is most likely due to the higher affinity between gas molecules and surface molecules[1,5,13].

The PAN/MO fiber membrane at a CO_2 concentration of 2000 ppm was examined to investigate the effect of MO addition on the behavior of functional groups in the polymer by using the FT-IR absorbance spectra[5,10].
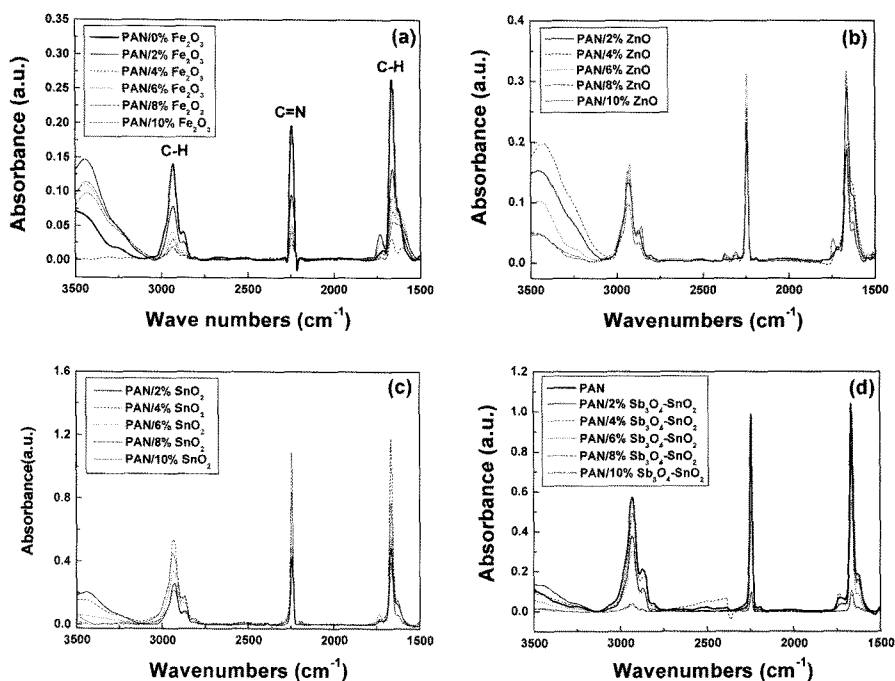
Fig. 2. Absorbance spectra of the nanofibrous PAN membrane with (a) Fe_2O_3, (b) ZnO, (c) SnO_2 and (d) Sb_3O_4-SnO_2 metal oxide nanopowders.

They reported that the PAN/Fe_2O_3 (4 %) mat yielded a 140 % increase in C=O bond intensity in comparison to a PAN mat at a CO_2 concentration of 2000 ppm. Also, it was reported that the addition of Fe_2O_3 nanoparticles to the PAN mat reduced the absorption peak intensity at 2242 cm^{-1} (C≡N bond), but boosted a sharp increase in peak intensity at 2356 cm^{-1} (C=O bond)[13]. Prior to the analysis of the sensing properties of the nanocomposite mat, our air FR-IR results of PAN/MO mat with a thickness of 130 μm, as shown in Fig. 2, revealed that the addition of MO particles led to a decrease in the peak intensity related to C-H and C≡N bonds as expected[13]. The decrease in the C≡N absorbance intensity with the addition of MO was likely due to the reduction of the PAN (-CH$_2$-CH(CN)-) content [5,13]. The appropriate addition of immobilized MO nanoparticles to the PAN backbone may be beneficial to the improvement of the performance of CO_2 gas sensor probably due to the change of functional groups in the membrane [5,13]. Although the CO_2 absorbance spectrum is a viable approach to detect gas, it is not sufficient to draw a concrete conclusion. Detailed CO_2 gas sensor characterization with the measurement of the output

voltage, the subject of this study, is investigated.

The gas sensing properties of PAN/MO mats were measured using a custom-made apparatus. Pt was patterned on Al_2O_3 plate by DC sputtering. The PAN/MO mats were electrically wired to measure the output voltage to evaluate the CO_2 gas sensitivity at room temperature. The output voltage, as depicted in Fig. 3, was determined using the equation (1).

$$V_{out} = [R/(R + R_s)] \times V_{in} \qquad (1)$$

where R_s is the sensor resistance, R the variable resistance, V_{in} input voltage and V_{out} output voltage. Fig. 4
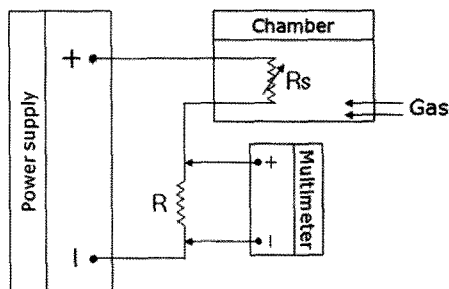

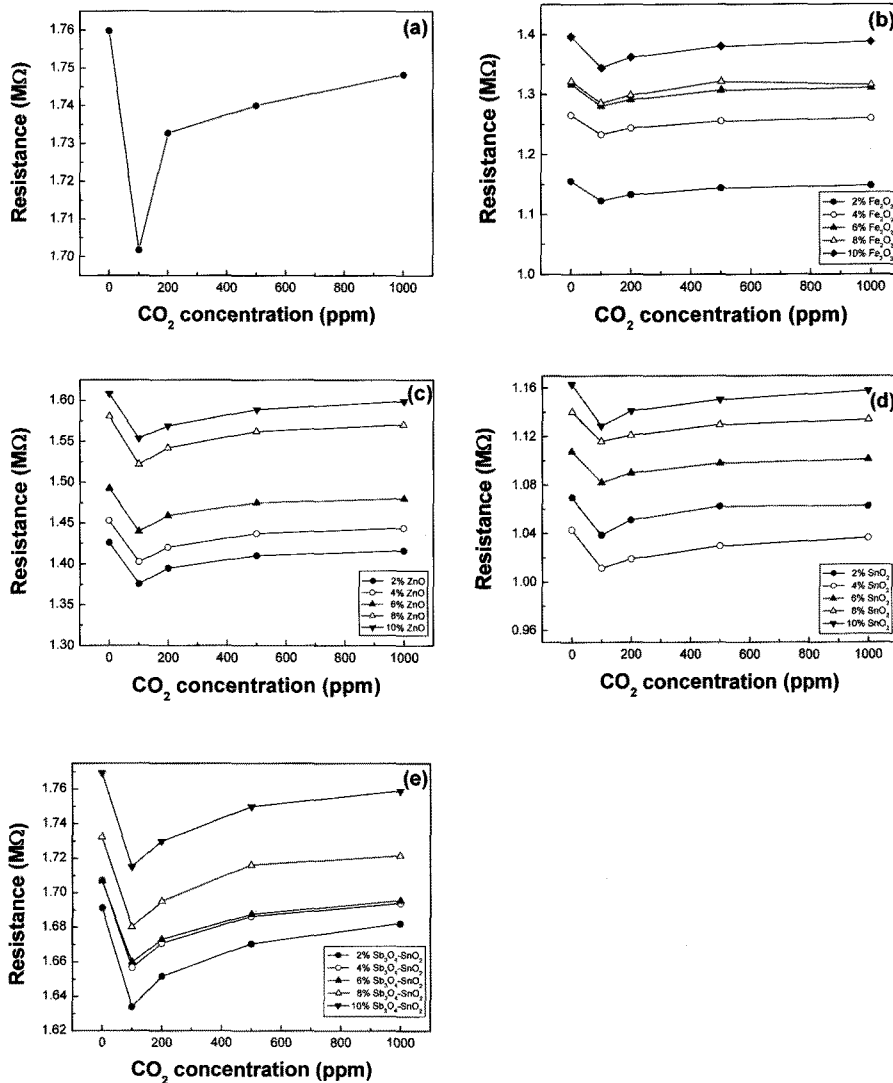Fig. 3. Schematic diagram of the measuring system.

Fig. 4. The variation of resistance of various PAN/metal oxide nanofibrous mats as a function of CO_2 concentration: (a) PAN, (b) PAN/Fe_2O_3, (c) PAN/ZnO, (d) PAN/SnO_2, and (e) PAN/Sb_3O_4-SnO_2.

shows the resistance variation of the PAN/MO nanofibrous mats as a function of CO_2 concentration at room temperature. Both PAN and PAN/MO fiber mats showed the similar gas sensing properties. The resistance decreased sharply and then showed the minimum resistance values at a CO_2 concentration of 100 ppm. Then it increased gradually and then tended to saturate as the CO_2 concentration rose, as displayed in Fig. 4. It is known that when conducting polymer, polypyrrole (PPy), reacts with gases, its resistance dwindles down initially due to electron transferring and then it is recov-

ered[14]. The CO_2 gas may be adsorbed in the PAN fiber mat regardless of the presence of MO additives. It is reported that two types of adsorption, physical adsorption (up to 27 °C) and chemisorption (27 °C~327 °C), are possible between gas molecules and a solid surface[5]. Traditional MO sensors require elevated temperatures of 150~550 °C to be sensitive to chemisorption[5,15]. Among them, physical adsorption provides the best choice for gas sensor application due to the reproducibility and reliability of sensor performance. It is reported that free moving gas, gas adsorbed on the pol-
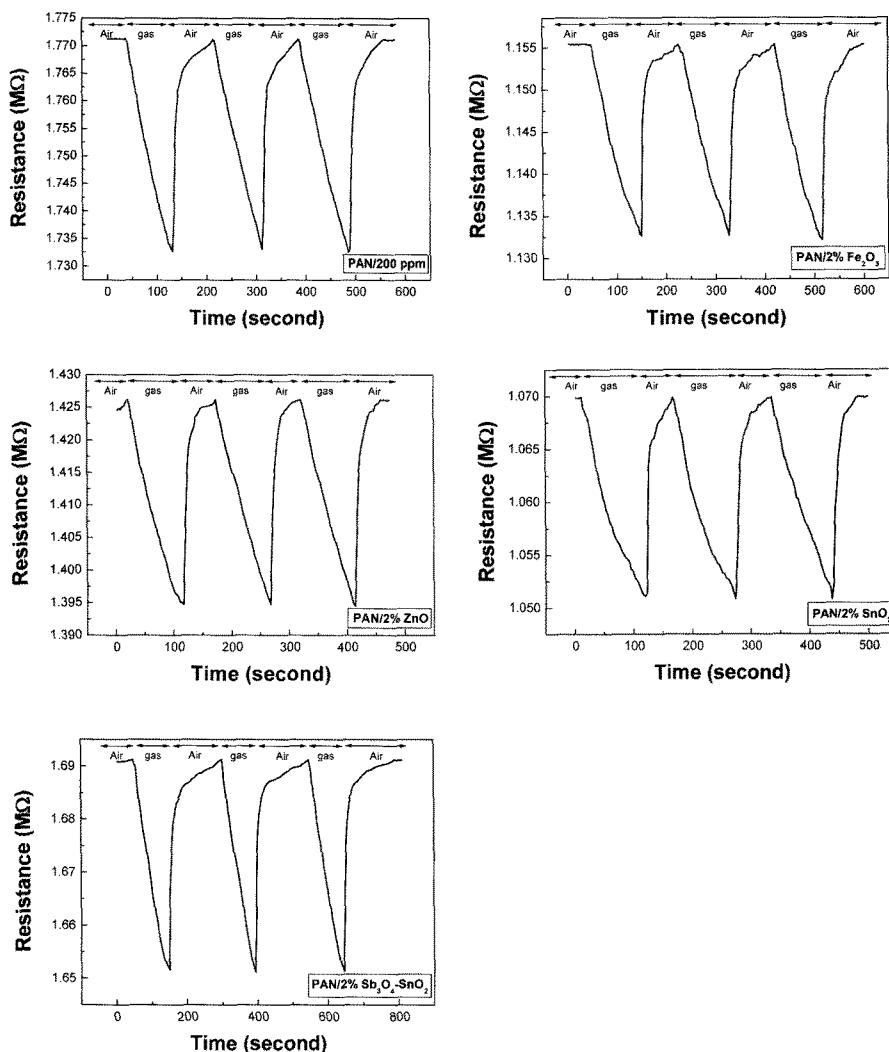
Fig. 5. Dynamic response of resistance plots for the PAN and PAN/MO mats at a CO_2 concentration of 200 ppm.

ymer fiber surfaces and gas adsorbed on nanoparticle surfaces may be responsible for gas sensing[5]. The gas is adsorbed in the porous fiber mat, resulting in various forms of adsorption between gaseous molecules and a solid surface. The PAN/MO gas sensor operated at room temperature is likely to be appropriate for CO_2 sensing probably due to physical adsorption[5]. In addition, an appropriate amount of MO nanoparticles in the PAN backbone may be beneficial to the improvement of the gas sensing performance, as shown in Fig. 4.

Fig. 5 shows the resistance variation of the PAN and PAN/MO mats in CO_2. The average time of response (adsorption) and recovery (desorption) of the PAN mat

was 94 s and 84 s with a resistance decrease (ΔR) of 0.038 MΩ at a CO_2 concentration of 200 ppm, while the PAN/2 % Fe_2O_3 mat exhibited the longer response time (102 s) but a shorter recovery time of 75 s with a lower change of ΔR (0.023 MΩ). The PAN/SnO_2 sensor in CO_2 showed the response (105 s) and recovery (64 s) behavior with a ΔR of 0.019 MΩ. The PAN/ZnO mat revealed a faster response time of 93 s and a relatively short recovery of 54 s with a ΔR of 0.031 MΩ. On the other hand, the PAN/Sb_3O_4-SnO_2 sensor responded in 93 s and had longer recovery time of 153 s with amplitude (ΔR) of 0.039 MΩ. Overall results suggest that the adsorption process is quite fast, making prompt detec-
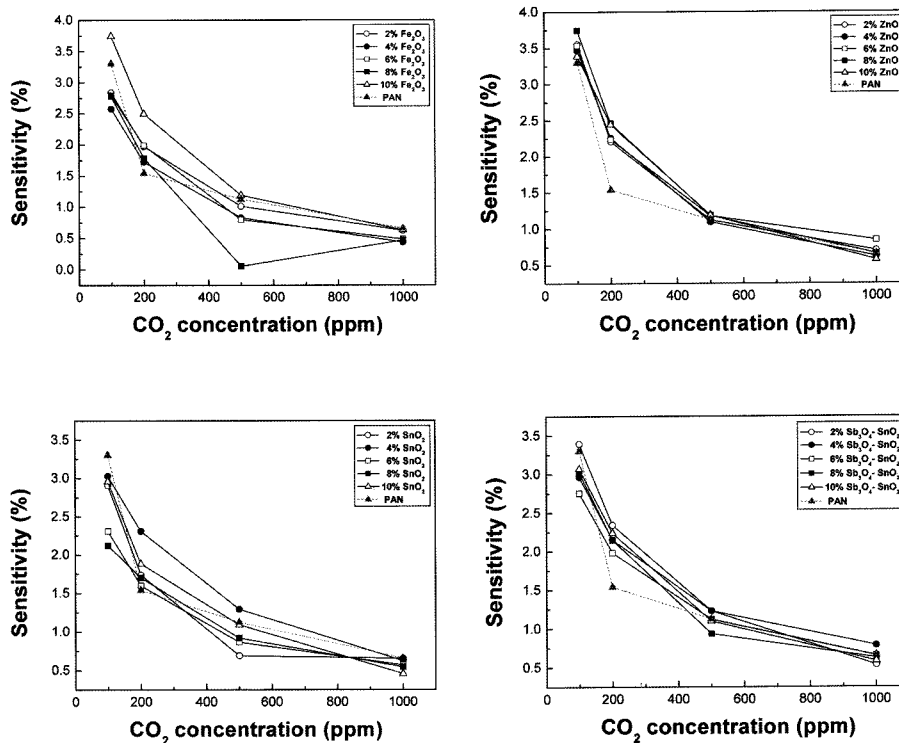
Fig. 6. Sensitivity curves of the PAN and PAN/2 % MO fiber mat as a function of CO_2 concentration at room temperature.

tion possible. Among the sensors, the PAN/ZnO is determined to be the best sensor having the highest sensitivity at a CO_2 concentration of 200 ppm.

The resistance response of each sensor structure was transformed into a sensitivity value using commonly used formular for CO_2 gas[12,15]:

$$S\ (\%)=[(R_g-R_a)/R_a]\times 100 \qquad (2)$$

where R_a and R_g are the resistance of the sensor in the presence of air and gas in air, respectively. The PAN fiber mat can be used as a sensor to detect CO_2 gas, as demonstrated in Figs. 4 and 5. The sensitivity curves of the PAN and PAN/MO fiber mats operated at room temperature are shown in Fig. 6. The sensitivity of the fiber mat decreased gradually with increasing the concentration of CO_2. The addition of various MO nanoparticles up to 10 % enhances the sensitivity at a CO_2 concentration of 200 ppm. However, the sensitivity of the PAN/MO fiber mat became worse than the PAN mat with increasing the CO_2 concentration above 500 ppm, suggesting that the PAN/MO sensor can be used in the CO_2 concentration from 100 to less than 500 ppm. No

CO_2 sensitivity was observed below 100 ppm. The sensitivity of the PAN/MO sensors was not higher than that of the PAN fiber mat in the CO_2 concentration range of 100 to 500 ppm except the PAN/ZnO mat. On the contrary to the previous FT-IR absorbance spectra results[5], an appreciable improvement in sensitivity of the PAN/Fe_2O_3 fiber mat was not found as compared to the PAN mat. The limited improvement of sensitivity at a certain range of CO_2 concentration was only detected for the nanocomposite fiber mat loaded with Fe_2O_3, ZnO, SnO_2 and Sb_3O_4-SnO_2 nanoparticles. Among nanoparticles, ZnO has the largest particle size of 50~70 nm with respect to the others having less than 25 nm. It is noted that the fiber diameter decreases due to the presence of lumps caused by the presence of metal oxides in the fiber, as shown in Fig. 1(f). The fibers between the lumps become thinner, indicating that the porosity tends to increase. The higher porosity of the fiber mat is believed to be effective to the physical gas sensing properties because the gas molecules are adsorbed on the fiber surface as well as nanoparticle surfaces. The higher porosity may provide the pathways for analyte to

permeate through fiber mat easily. However, no significant improvement in sensitivity was noticed.

4. Conclusions

PAN/MO nanocomposite mats with a thickness of 0.12 mm were electrospun by adding 0 to 10 wt% of MO nanoparticles (Fe_2O_3, ZnO, SnO_2, Sb_2O_3-SnO_2) into PAN. Pt electrode was patterned on Al_2O_3 substrate and then the PAN/MO mats were electrically wired to investigate the gas sensing properties. As the MO content rose, the fiber diameter decreased due to the presence of lumps caused by the presence of MOs in the fiber. The PAN/ZnO mat revealed a faster response time of 93 s and a relatively short recovery of 54 s with a ΔR of 0.031 $M\Omega$ at a CO_2 concentration of 200 ppm. The PAN/MO fiber mats can be used as gas sensor in the CO_2 concentration range of 100 to 500 ppm. It can be concluded that an appropriate amount of MO nanoparticles in the PAN backbone leads to improvement of the CO_2 gas sensing properties.

Acknowledgements

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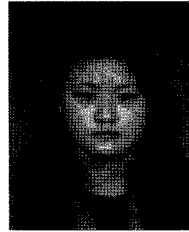
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