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# Electrospun Nanofibrous Polyacrylonitrile(PAN)/$Fe_2O_3$ Membrane as $CO_2$ Gas Sensor

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**ABSTRACT**

Polyacrylonitrile (PAN)/$Fe_2O_3$ nanocomposite membranes with a thickness of 0.02 mm were electrospun by adding 0 to 5 wt% of $Fe_2O_3$ into PAN. The surface tension, density, kinematic viscosity and dynamic viscosity of the PAN solution were determined to be 33.8±1 mN/m, 0.9794 g/ml, 1548.6 $mm^2$/sec and 1516.7 cP, respectively. The average diameters of PAN fibers containing 0, 1, 2, 3, and 4 wt% $Fe_2O_3$ particles were 300, 260, 210, 130, and 90 nm, respectively. Fourier-transform infrared spectroscopy results showed that the addition of $Fe_2O_3$ nanoparticles to the PAN mat reduced the absorption peak intensity at 2242 $cm^{-1}$ (C≡N bond) while it caused a sharp increase in the peak intensity at 2356 $cm^{-1}$ (C=O bond). Thus, it appears that an appropriate amount of $Fe_2O_3$ nanoparticles in the PAN backbone leads to an improvement of the performance of the $CO_2$ gas sensor, most likely due to the change of functional groups in the membrane.

***Key words*: *Polyacrylonitrile (PAN), $Fe_2O_3$, Nanofiber, Membrane, $CO_2$ gas sensor***

## 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 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 larger than continuous films.[6] Luoh and Hahn[5] reported that the higher specific surface area improved the sensitivity due to enhanced gas adsorption. Among polymer/metal oxide (Sb-$SnO_2$, ZnO, $Fe_2O_3$) nanocomposites, they demonstrated that an addition of $Fe_2O_3$ to PAN produced composite membranes 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 using the Fourier transform infrared spectroscopy (FTIR) absorbance spectra, no detailed preparatory studies of electrospun fibers was discussed. Characteristics of the fibers, the subject of this study, are evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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## 2. Experimental Procedure

PAN powder (Aldrichi Chemical Co., Japan), $Fe_2O_3$ (5~25 nm, Sigma-Aldrichi Inc., USA) and dimethylformaide (DMF, Fisher Scientific, Japan) were used as precursors. This work focuses on 10 wt% PAN fibers as optimized in an earlier studies.[9,10] PAN/$Fe_2O_3$ nanocomposites were prpared by adding 0 to 5 wt% of $Fe_2O_3$ into PAN. PAN/$Fe_2O_3$ powders were added to the DMF solvent. The mixture was stirred with a magnetic stirrer until the lumps of powder were broken up and well dispersed. The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22-gage

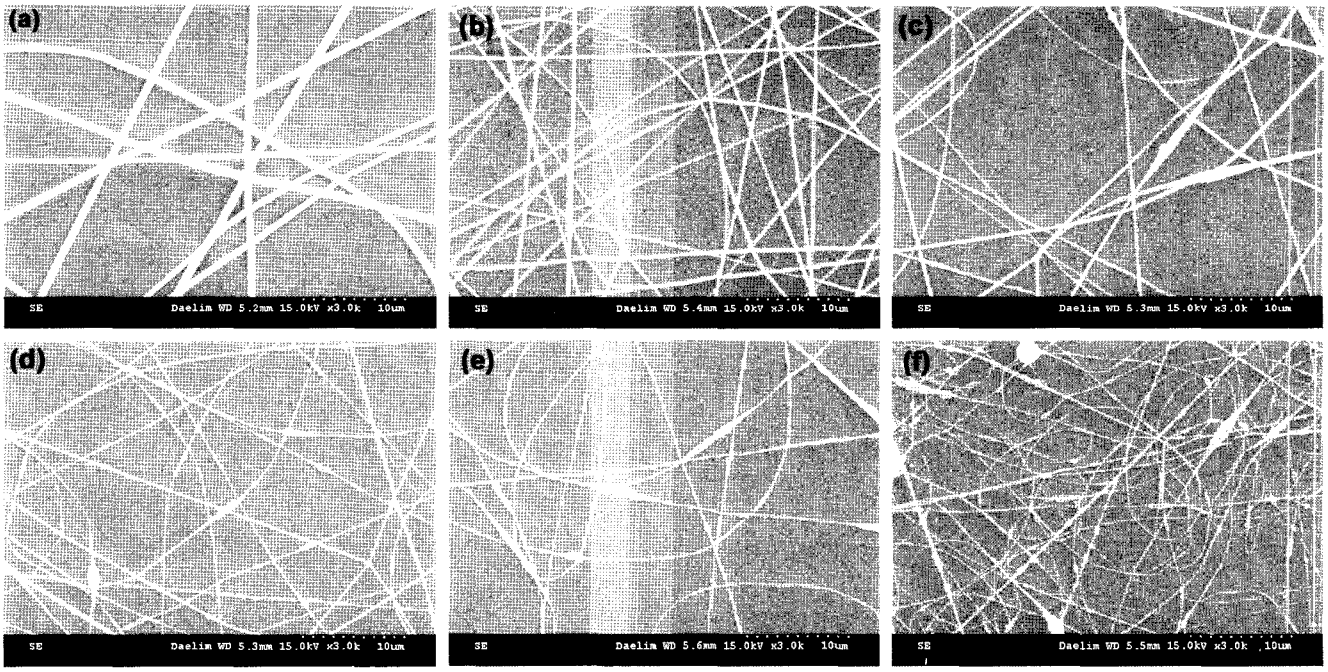


**Fig. 1.** SEM images of electrospun PAN/$Fe_2O_3$ nanocompoite fibers as a function of the $Fe_2O_3$ content; (a) 0%, (b) 1%, (c) 2%, (d) 3%, (e) 4%, and (f) 5%.

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. After spinning 1 or 2 h, the as-spun nanofibers were dried in air for 5 h.

The nanofibers were characterized by measuring the viscosity and fiber morphology. The kinematic viscosity and density of the precursor solution were determined by a Cannon-Fenske viscometer and a pycnometer, respectively. The dynamic viscosity was calculated from the kinematic viscosity and density data. The diameter and the morphology of the nanofibers were evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). All specimens were coated with Au/Pd to ensure higher conductivity. For the SEM observation, the nanofibers were prepared by placing silicon wafers on the aluminum foil during electrospinning. 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]

## 3. Results and Discussion

The surface tension, density, kinematic viscosity and dynamic viscosity of the PAN solution were previously optimized and were determined to be 33.8±1 mN/m, 0.9794 g/ml, 1548.6 $mm^2$/sec and 1516.7 cP, respectively.[9-11] Unform, smooth and continuous fibers with diameters of approximately 300 nm were obtained for the 10 wt% PAN fibers at a flow rate of 1.0 ml/h and with an electric field of 0.875 kV/cm, as shown in Fig. 1(a). TEM images of the electrospun PAN/$Fe_2O_3$ fibers were examined to determine the diameter of the fiber. The average diameters of PAN fibers containing 0, 1, 2, 3, and 4 wt% $Fe_2O_3$ particles were 300, 260, 210, 130, and 90 nm, respectively. Fig. 1 shows that the fiber diameter decreased as the $Fe_2O_3$ content increased, which was most likely due to the presence of lumps caused by the presence of $Fe_2O_3$ particles in the fiber. The fibers between the lumps become thinner, implying that the amount of $Fe_2O_3$ is crucial for the morphology of electrospun fibers. Uniform and straight PAN fibers (Fig. 2(a)) became non-uniform and rough (Fig. 2(c)) as a result of the presence of $Fe_2O_3$, which was in good agreement with the SEM results. The $Fe_2O_3$ particles were nearly spherical and had diameters of less than 25 nm. In addition, lumps were visible due to the higher density of the $Fe_2O_3$ particles inside the fiber, as illustrated in Fig. 2(b). It is evident that the inhomogeneous distribution as well as the clusters (~85 nm) of $Fe_2O_3$ particles may be attributed to the morphology of the electrospun PAN/$Fe_2O_3$ fibers. It is known that metal oxide 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]

PAN/$Fe_2O_3$ fiber membranes with a thickness of 0.02 mm were prepared by electrospinning for 1 h. The membrane thickness was monitored by a laser displacement sensor (Micro-epsilon, ILD1700-100, USA).[2,3,11] The uniform distribution of $Fe_2O_3$ particles was determined by observing the color uniformity of the fiber membrane via the naked eye. as

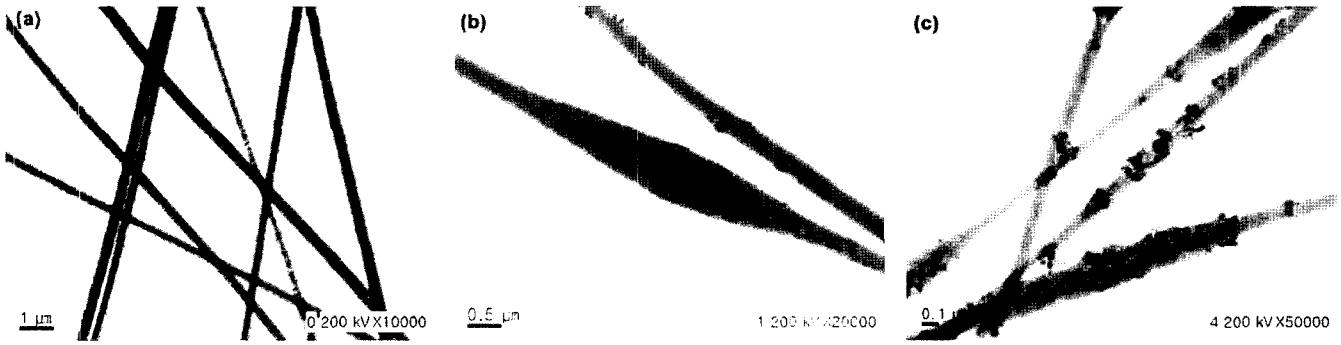


**Fig. 2.** TEM images of electrospun PAN/$Fe_2O_3$ nanocompoite fibers as a function of the $Fe_2O_3$ content; (a) 0%, (b) 1%, and (c) 4%.

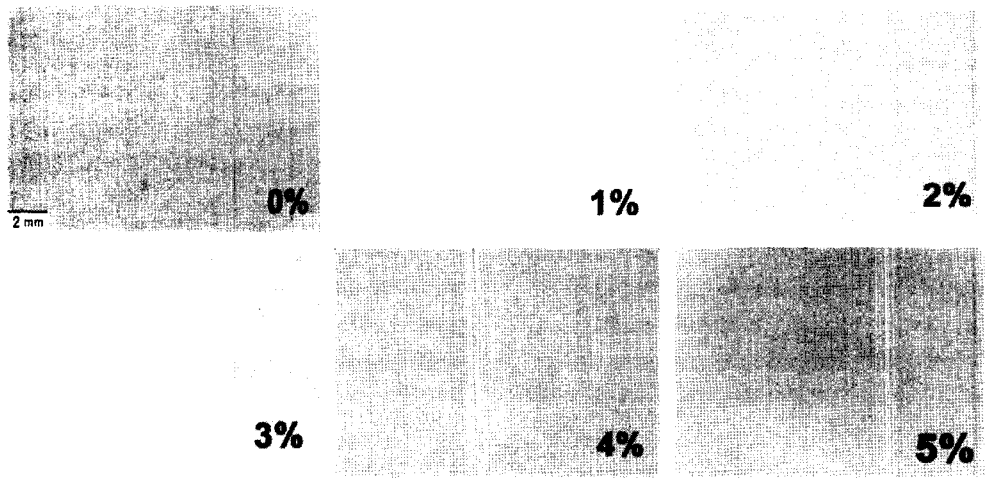


**Fig. 3.** Photographs of the fiber membrane as a function of the $Fe_2O_3$ loading. These images were taken using a digital camera.

shown in Fig. 3 (taken by a digital camera). The color was changed uniformly from white to yellowish-brown as the $Fe_2O_3$ content increased to 4%. The color uniformity was disturbed when more than 5 wt% $Fe_2O_3$ was added. The fiber membrane was examined via the FTIR absorbance spectra in order to evaluate the effect of the $Fe_2O_3$ addition on the behavior of functional groups in the polymer.[5] C-H and C≡N bonds are clearly visible in the absorbance spectra of the PAN membrane, a homopolymer of acrylonitrile (-$CH_2$-CH(CN)-),[12] as shown in Fig. 4. The spectra peaks at 2242 $cm^{-1}$, and 2356 $cm^{-1}$ represent the wave number of the C≡N and C=O bond, respectively. The sudden decrease in the absorbance intensity at 1% $Fe_2O_3$ loading in Fig. 5 was more than 50%. It is noted that a lower height of the peak

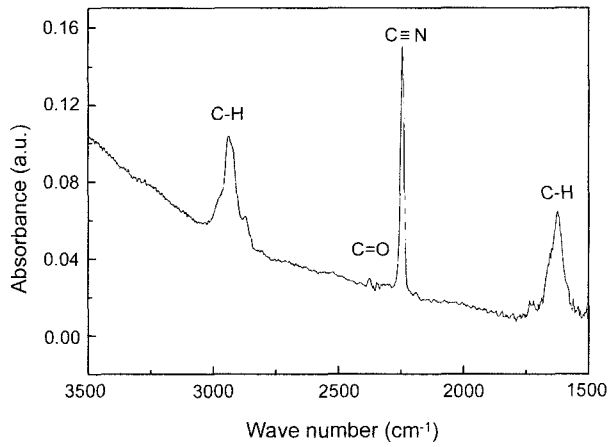


**Fig. 4.** Absorbance spectra of the nanofibrous PAN membrane.

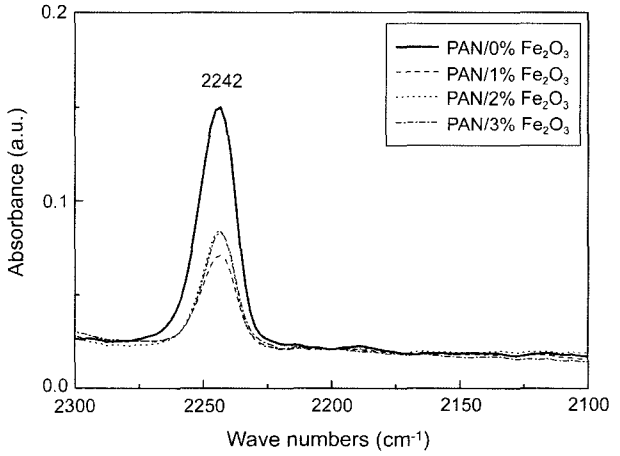


**Fig. 5.** Absorbance spectra at 2242 $cm^{-1}$ of PAN/$Fe_2O_3$ nanocomposite membranes containing various $Fe_2O_3$ amounts in air.

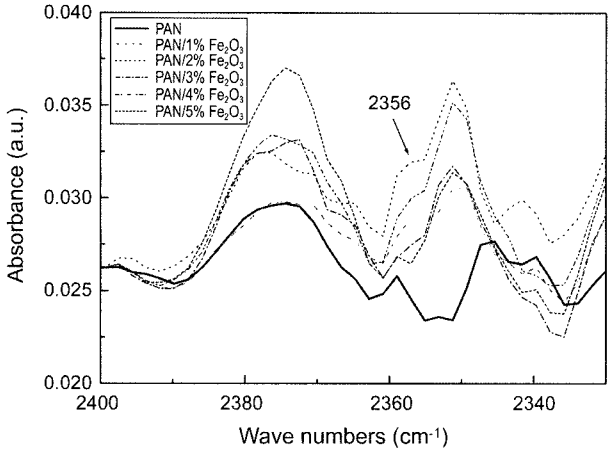


**Fig. 6.** Absorbance spectra at 2356 $cm^{-1}$ of PAN/$Fe_2O_3$ nanocomposite membranes containing various $Fe_2O_3$ amounts in air.

indicates fewer C≡N bonds and thus a smaller amount of PAN in the fiber membrane.[5] The decrease in the C≡N absorbance intensity as the $Fe_2O_3$ content increased was likely due to the decrease in the PAN content. The uniform decrease in the intensity at other wave numbers suggests that the $Fe_2O_3$ particles were well dispersed. This is shown in Fig. 3, and was visible with the naked eye. It was reported that the PAN/$Fe_2O_3$ (4%) membrane yielded a 140% increase in intensity in comparison to a PAN mat at a $CO_2$ concentration of 2000 ppm.[5] Prior to the analysis of the sensing properties of the composite mat, the air FTIR results revealed that the addition of 4% $Fe_2O_3$ nanoparticles to the PAN mat led to a sharp increase in the peak intensity at a wave number of 2356 $cm^{-1}$ (C=O bond), as shown in Fig. 6. Further doping (5%) reduced the peak intensity. Although the experiment was performed in air without $CO_2$ gas, the ionosorption of small amounts of CO over the membrane surfaces in an air atmosphere was inevitable. This implies that the appropriate addition of immobilized $Fe_2O_3$ nanoparticles to the PAN backbone is likely to be beneficial to the improvement of the performance of a $CO_2$ gas sensor due to the change of the functional groups in the membrane. Detailed $CO_2$ gas-sensing characterizations with the measurement of the resistance are in progress and will be presented later.

## 4. Conclusions

PAN/$Fe_2O_3$ nanocomposite membranes with a thickness of 0.02 were electrospun by adding 0 to 5 wt% of $Fe_2O_3$ into PAN. The surface tension, density, kinematic viscosity and dynamic viscosity of the PAN solution were determined to be 33.8±1 mN/m, 0.9794 g/ml, 1548.6 $mm^2$/sec and 1516.7 cP, respectively. The average diameters of PAN fibers containing 0, 1, 2, 3, and 4 wt% $Fe_2O_3$ particles were 300, 260, 210, 130, and 90 nm, respectively. A small addition of $Fe_2O_3$ nanoparticles to the PAN mat reduced the peak intensity at 2242 $cm^{-1}$ (C≡N bond), but produced a sharp increase in the peak intensity at 2356 $cm^{-1}$ (C=O bond). Thus, an appropriate amount of $Fe_2O_3$ nanoparticles in the PAN backbone may be beneficial to the improvement of the performance $CO_2$ gas sensors due to the change of the functional groups in the membrane.

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