

Polyaniline–Nylon 6 Composite Fabric for Ammonia Gas Sensor

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ABSTRACT: Conducting polymers constitute a new class of sensing materials, which can be prepared by a simple oxidative polymerization method. An ammonia gas sensor was prepared by polymerizing aniline on the surface of nylon 6 fabrics and doped with various acids in this study. The fabricated polyaniline (PANI)–nylon 6 composite fabrics showed high sensitivity and fast response for NH₃ gas. In particular, the PANI–nylon 6 composite fabrics doped by monocarboxylic acids (such as formic acid, acrylic acid, and trichloroacetic acid) displayed excellent sensitivity and fast

response. Moreover, no significant changes in the T_m and crystallinity were found in these composite fabrics. Hence the PANI–nylon 6 composite fabrics are attractive alternatives for use in sensing applications because of their excellent sensing ability, low cost, and ease of preparation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 37–42, 2004

Key words: conductive fabric; polyaniline; gas sensor; nylon 6; dopant

INTRODUCTION

Since their discovery, intrinsic conducting polymers (ICPs) have been investigated intensively because of a select group of properties that they exhibit: electronic conduction, environmental stability on the conducting state, reversible redox reactions, electrochromism, and electroluminescence. These properties make possible their use in several practical applications, including batteries, antistatic coatings, electromagnetic interference shields, display, and capacitors, for example.¹

The use of conducting polymers as sensing elements in chemical sensors is an intensive area of research because of their high sensitivity on electrical or optical changes when exposed to diverse types of gases or liquids.² This characteristic holds promise for successful designs of different types of sensor transducers based on conducting polymers. Several reports revealed that conducting polymers as chemical sensors for air-borne volatile organic compounds (especially alcohols, ethers, halocarbons, ammonia, NO₂, and CO₂) have a lower detectable limit in the range of a few tens of parts per millions, and the potential to operate at or near room temperature.^{3–5}

Among organic conducting polymers, polyaniline (PANI) is regarded as one of the most technologically promising conductive polymers because the monomer is inexpensive, the polymer can be easily prepared by

oxidative polymerization with high yield, and products are stable under ambient conditions.⁶ Promising results have also been shown for application in gas sensors. This mechanism is attributed to the π -conjugated system in the conducting polymer chain. The interaction between the organic material and gas molecules results in an increase/decrease of polaron and/or bipolaron densities inside the band gap of the polymer. Therefore their modification implies both electrical and optical property changes in the conducting polymer.^{7,8}

The physical property changes of PANI can be observed at room temperature, when they are exposed to lower concentrations of the chemicals, making them attractive candidates for gas-sensing elements. Because conventional ammonia gas sensors like metal oxide films need high operating temperatures, it is thus not easy to use them under general conditions. Even though PANI chemical sensors have been developed for ammonia, however, they still have some problems in insufficient gas sensitivity and reversibility. Matsuguchi et al.³ found that the sensing characteristics depend on the kind of dopant species, measuring temperature, matrix polymer, and the solvent used for film preparation. Among the sensors under consideration, the PANI, bis(2-ethyl hexyl) hydrogen phosphate (DiOHP) as dopant, and poly(methyl methacrylate) (PMMA) as matrix polymer using toluene as solvent had the best sensing properties. However, it has been reported that the reversibility and especially response time were not sufficient for practical use, so further study is needed.

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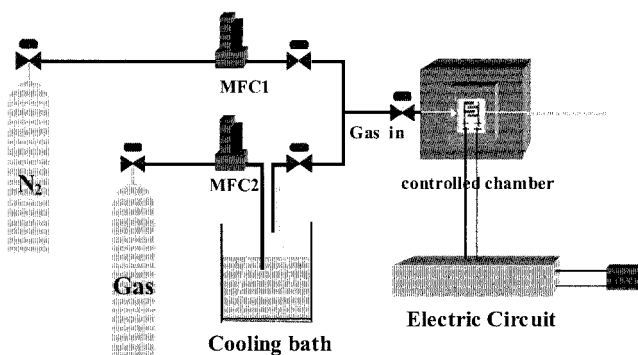


Figure 1 Diagram of gas-sensing measurement system.

In this study, we prepared PANI–nylon 6 composite fabrics doped with various acids by oxidative polymerization of aniline monomer. Given that the polymerization is conducted in the presence of a fabric with a high surface area, the entire polymerization occurs on the surface of fabric in a high yield and so the fabric type would be a proper material for a PANI-coated composite. Moreover, nylon 6 is a high modulus and strength fiber among the synthetic fibers and has a relatively good chemical resistance. Moreover, it has amide groups ($-\text{NHCO}-$), which can serve as sites for hydrogen bonds, in its backbone and so the adhesion between substrate and PANI is relatively superior to that of the other synthetic fibers. Through our previous study, we established that *in situ* polymerization of PANI on the surface of nylon 6 fabrics does not require the destruction of the substrate and provides reasonably good conductivity.⁹ To improve the sensing characteristics of the PANI–nylon 6 composite fabrics, we doped polyaniline composite fabrics with various dopant species and then the effect of NH_3 , CO , and C_3H_8 gases on the electrical resistance of PANI–nylon 6 composite fabrics was examined for the purpose of preparing a practical gas sensor of good sensitivity and reversibility.

EXPERIMENTAL

Materials and chemicals

Scoured nylon 6 plain-weave fabrics (70×70 d; 43×30 cm) obtained from KATRI (Korea Apparel Testing and Research Institute) were used as substrates. Aniline (Shiny Pure Chemicals Co., Japan) was distilled under vacuum before use. The other chemicals included ammonium peroxydisulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$] (Junsei Chemical Co., Japan), and acrylic acid ($\text{CH}_2=\text{CHCOOH}$), dodecylbenzene sulfonic acid (DBSA; $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{H}$), formic acid (HCOOH), hydrochloric acid (HCl), maleic acid ($\text{HOOCCH}=\text{CHCOOH}$), oxalic acid ($\text{HOOC}-\text{COOH}$), sulfuric acid (H_2SO_4), and trichloroacetic acid (CCl_3COOH),

all of reagent grade, and obtained from Ducksan Pure Chemical Co., Korea.

Preparation of PANI–nylon 6 composite fabrics

Conductive PANI–nylon 6 composite fabrics were prepared by the DPMB process, which was introduced in our previous study.⁹ Freshly distilled aniline and ammonium peroxydisulfate were dissolved separately in 0.35M HCl aqueous solutions for diffusion and polymerization, respectively.

The nylon 6 fabrics were immersed in an aqueous hydrochloride solution of 0.5M aniline at 40°C for 2.5 h. Successive polymerization was then initiated by mixing the same volume of oxidant solution containing 0.5M ammonium peroxydisulfate and 0.35M HCl in the diffusion bath. Fabrics were polymerized at 5°C for 1 h, after which they were washed with distilled water and dried. After polymerization was completed, the PANI–nylon 6 composite fabrics were dedoped with 0.1M $\text{NH}_3\cdot\text{OH}$ aqueous solution. The samples were then redoped with various dopants by immersing each in a dopant solution (0.3M acid aqueous solution) for 24 h.

Evaluation

The sensing performance of the PANI–nylon 6 composite fabrics was tested by subjecting the treated fabrics to chemical vapors in a closed glass container at room temperature. A diagram of the experimental configuration employed for examining the chemical-sensing characteristics of the composite fabric materials is shown in Figure 1. A voltage-detecting method was used to calculate the sensitivity of the sensor equipped in the measurement circuit, as shown in Figure 2.¹⁰ The percentage sensitivity is defined as $(R_{\text{gas}} - R_{\text{air}})/R_{\text{gas}} \times 100$, where R_{gas} and R_{air} are the electrical resistances in explosive gas to be detected and clean air, respectively.

The conductivity of the composite fabric was measured by four straight lines and equidistant points, taking the thickness as that of the fabric.¹¹ The thermal behavior of the composite fabrics was characterized using differential scanning calorimetry (DSC), per-

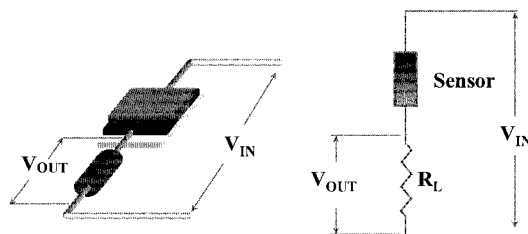


Figure 2 Measurement circuit.

formed on a Du Pont DSC 2100V 4.1C system (Du Pont, Boston, MA) under nitrogen atmosphere with programmed heating of 10°C/min. The X-ray photoelectron spectroscopy (XPS) measurements were performed with an Aries ARSC 10MCD 150 (VSW, UK) spectrometer from Surface Science Instruments. This spectrometer was equipped with an Mg-K α X-ray source, set at 10 kV and 15 mA. The pressure in the analysis chamber was maintained at $\leq 10^{-9}$ Torr during the measurement. All core-level spectra were obtained at a photoelectron takeoff angle of 55° with respect to the sample surface. To compensate for the surface-charging effect, all binding energies were referenced to a C $_{1s}$ neutral carbon peak at 284.5 eV. In peak analysis, the line widths (the width at half-maximum) of the Gaussian peaks were kept constant for the components in a particular spectrum. The surface elemental compositions were determined from the peak area ratios and were accurate to within 1%.

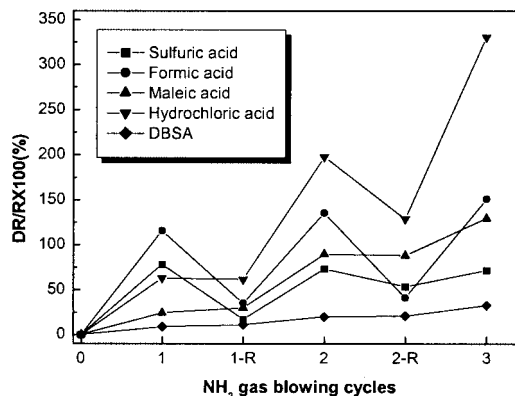
RESULTS AND DISCUSSION

Effect of PANI-nylon 6 composite fabrics for various toxic gases

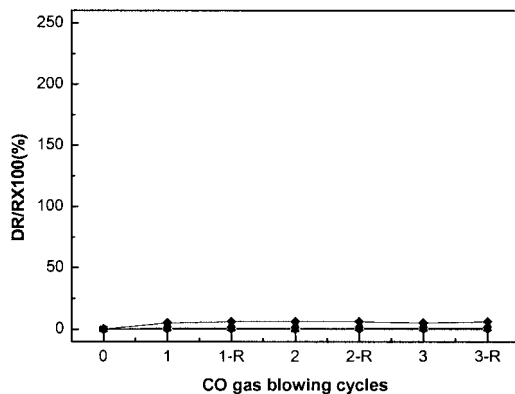
Highly conductive PANI-nylon 6 composite fabrics could be obtained by simple chemical oxidation under optimum polymerization conditions. In this study, we used some strong protonic acids, such as hydrochloric acid and sulfuric acid, and weak carboxylic acids, such as formic acid, maleic acid, and DBSA, as dopants to investigate the influence of dopant on the gas-sensing ability of composite fabrics.

To investigate the gas-sensing ability of the composite fabric, the fabric was placed in a closed chamber and its electrical resistance was measured at 5 min after blowing the gas into the chamber and again at 5 min after removing the gas from the chamber.

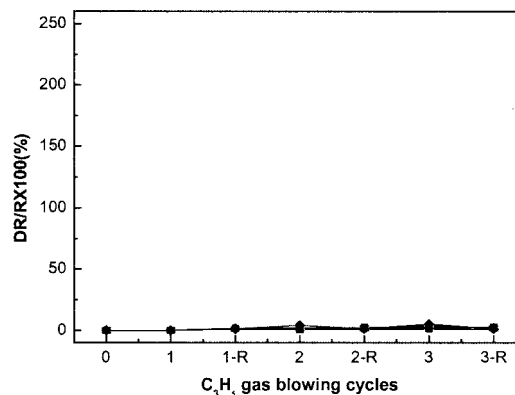
When PANI-nylon 6 composite fabrics were exposed to NH $_3$ gas, they showed rapid response and promising results in electrical resistance (in ohms), as shown in Figure 3(a). Because conductive polymers generally behave in accordance with p-type conductive materials, it is reasonable to expect that NH $_3$, a strong reductant, will result in a decrease of the conductivity because of the elimination of free hole charge carriers. However, CO and C $_3$ H $_8$ gases have no significant effect on the changes of the electrical resistance, as shown in Figure 3(b) and (c). In particular, PANI-nylon 6 composite fabrics doped with formic acid and sulfuric acid showed reasonable sensitivity and reversibility for NH $_3$ gas. Because the excess NH $_3$ molecules being supplied to the composite fabric may take up hydrogen directly from the PANI backbone and form energetically more favorable ammonium NH $_4^+$ (which decomposes back into ammonia, thus leaving out the proton on the adsorption site in the air envi-



(a) NH $_3$ gas



(b) CO gas



(c) C $_3$ H $_8$ gas

Figure 3 Variation of the electrical resistance with blowing (1000 ppm) and removal of gases.

ronment), it is suggested that there should be two energetically different kinds of adsorption sites for ammonia gas on the PANI molecules. Actually, this is congruent with the two different values proposed for

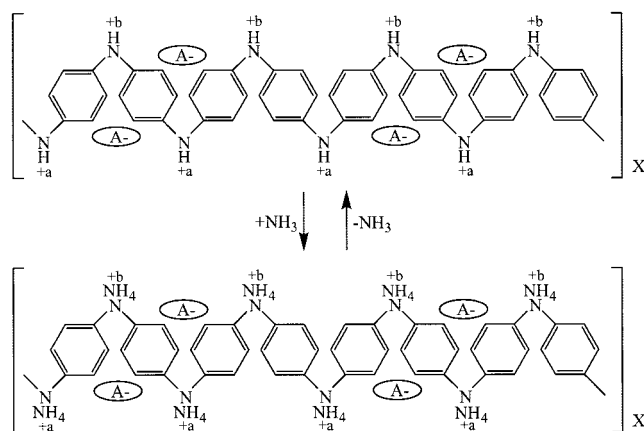


Figure 4 Mechanism of interaction between PANI and NH_3 molecules.¹³

the positive charges on the nitrogen atoms of the polymeric chain in PANI emeraldine salt state. Figure 4 presents the structure of the doped PANI emeraldine salt proposed by McDiarmid et al.¹² and references therein.¹³ From the mechanism of interaction between the NH_3 molecules and PANI–nylon 6 composite fabrics, the adsorption process should be classified as reversible chemisorption. The good fitting of the exponential type of kinetic equation to our adsorption–desorption curves suggests the validity of a molecular and monolayer adsorption in this case.¹⁴

On the other hand, the PANI–nylon 6 composite fabrics doped by formic acid and maleic acid exhibited lower conductivity than that of fabrics doped with HCl, DBSA, and sulfuric acid, as shown in Table I. This is attributed to the carboxylic acid, which dissociates H^+ ions less than other protonic acids, so the PANI backbone doped by carboxylic acid is not sufficiently supplied with polaron and bipolaron to its structure, which was confirmed by the pH values of aqueous doping solutions used in this study. However, the composite fabrics doped by sulfuric acid and DBSA were significantly damaged, as indicated by reduction of the melting point (T_m) compared to that of the other composite fabrics because strong acid deteriorated the nylon substrate relatively well (Fig.

TABLE I
Electrical Conductivities of PANI–Nylon 6 Composite Fabrics Doped with Various Acids and pH Values of the Acid Solutions

Dopant	Conductivity (S/cm)	pH of dopant solution
Hydrochloric acid	3.2×10^{-2}	1.04
Dodecylbenzene sulfonic acid	4.4×10^{-2}	1.65
Formic acid	1.1×10^{-3}	2.45
Sulfuric acid	3.6×10^{-2}	1.21
Maleic acid	7.0×10^{-2}	1.98

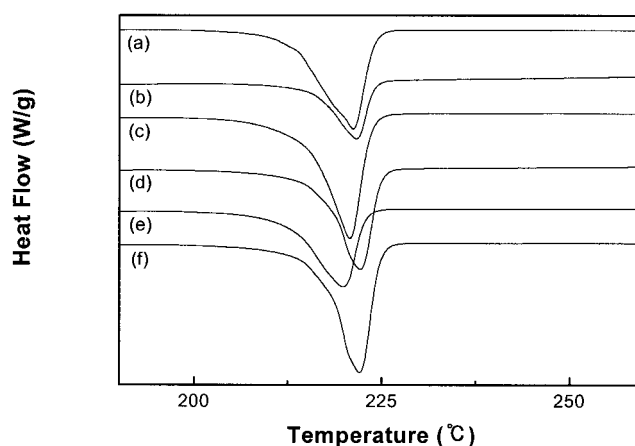


Figure 5 DSC thermograms of untreated nylon 6 fabric and PANI–nylon 6 composite fabrics prepared with various dopants: (a) untreated nylon, (b) hydrochloric acid, (c) dodecylbenzene sulfonic acid (DBSA), (d) formic acid, (e) sulfuric acid, (f) maleic acid.

5). Therefore, we selected various types of monocarboxylic acids to search the effective dopant species for NH_3 gas sensor because they have relatively good sensitivity and reversibility without significantly damaging fabrics.

Effect of carboxylic acids on NH_3 gas-sensing ability

Figure 6 shows the response of PANI–nylon 6 composite fabrics doped with various monocarboxylic acids after they were exposed to NH_3 gas. Reversibility in conductivity of PANI has been explained on the basis of the formation of energetically more favorable ammonium ion at the $-\text{N}^+-\text{H}$ adsorption center, indicated by an increase in the resistance when exposed to ammonia. The ammonium ion decomposes back into ammonia, leaving out the proton on the adsorption site in air. As a result, trichloroacetic acid showed the best reversibility and acrylic acid > formic acid in decreasing order. However, in the aspect of sensitivity, which exhibits the degree of resistance change, that order is entirely reversed. It is suspected that this result was caused by electronegative difference in dopants ($\text{Cl}_3\text{C}- > \text{CH}_2=\text{CH}- > \text{H}-$ is the electronegative increasing order). It was assumed that $\text{H}-$ in formic acid withdrew fewer electrons from the carboxylic anion than did $\text{CH}_2=\text{CH}-$ in acrylic acid and $\text{Cl}_3\text{C}-$ in trichloroacetic acid, which means that the carboxylic anion of trichloroacetic acid ($\text{Cl}_3\text{C}-$) is more efficient, in terms of reversibility, than the other carboxylic acids. Therefore the HCOO^- doping state in PANI emeraldine salt can be easily reduced to $\text{HCOO}^- - \text{NH}_4^+$ when exposed in NH_3 gas and cannot be easily reversed after removing NH_3 gas even though its sensitivity is low.

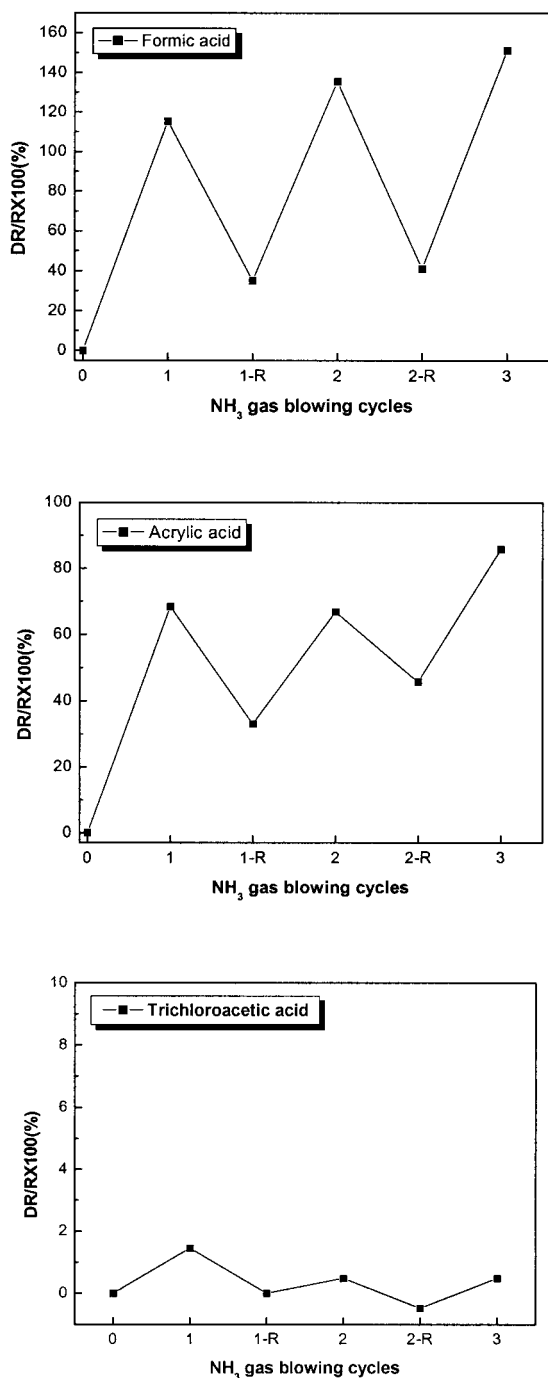


Figure 6 Variation of the electrical resistance of PANI-nylon 6 composite fabrics doped with carboxylic acids with blowing (1000 ppm) and removal of NH₃ gas.

It was presumed that when NH₃ gas was blown onto the sensing fabric, NH₃ molecules can attack at -N⁺-H adsorption sites, which originated from doping during polymerization, such that the resistance of a PANI-based gas sensor is increased and cannot be recovered completely after removing NH₃ gas. For that reason, the reversibility of the sensor was somewhat deteriorated with increasing the number of NH₃

blowing times and with higher electronegativity of doped anion.

However, Chabukswar et al.⁴ recently demonstrated that the resistance of the acrylic acid-doped PANI, which did not undergo the dedoping process with base, was found to decrease when exposed to ammonia vapors. They hypothesized that this response was caused by the reduction in resistance imparted by self-doping in the presence of acrylic acid on exposure to ammonia. In our experiment, however, it was suspected that acrylic acid, which has redoped PANI after dedoping with NH₃-OH, was already ionized and played a dopant role in the polymer backbone so that the resistance of the acrylic acid-doped PANI gas sensor was also increased in ammonia vapors.

Figure 7 shows the N_{1s} core-level spectra of PANI-nylon 6 composite fabrics, which were deconvoluted with specific functional groups, such as N⁺, -NH, and =N-. These core levels were divided by the C_{1s} core-

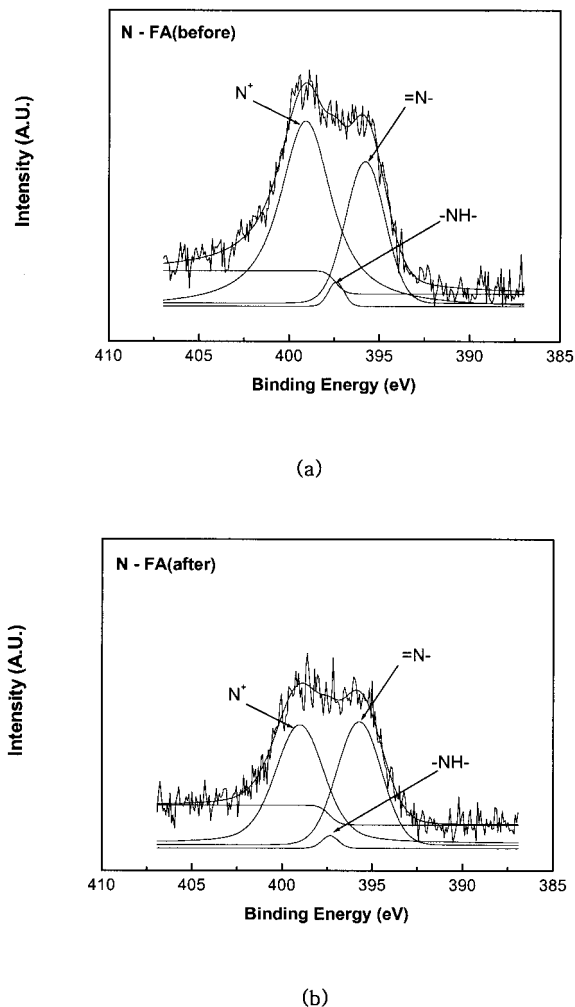


Figure 7 XPS narrow scans of PANI-nylon 6 composite fabrics doped with formic acid (a) before exposure to NH₃ gas and (b) after exposure to NH₃ gas.

level intensity to compare atomic species produced on the surface of PANI–nylon 6 composite fabrics by each treatment. The relative N^{+}/C_{1s} core-level intensity of the PANI–nylon 6 composite fabrics doped by formic acid [Fig. 7(a)] was 0.148 and that dedoped by NH_3 [Fig. 7(b)] was 0.069. However, there were no significant changes in other N_{1s} core-level intensity. From this result, we could confirm that NH_4^{+} reduced the anionized dopant species existing in PANI backbone and thus the backbone was deprotonated.

CONCLUSIONS

Conductive polymer gas sensors were fabricated by a simple chemical polymerization method. Poor processability and poor physical properties of chemically prepared PANI were improved by *in situ* polymerization on the nylon fabrics. The PANI–nylon 6 composite fabrics showed higher sensitivity and faster response for NH_3 gas compared to that for CO and C_3H_8 gases. The electrical resistance of the PANI–nylon 6 composite fabrics was increased when exposed to an ammonia environment but was reversibly recovered after flushing with fresh air. Among the PANI–nylon 6 composite fabrics prepared with various dopants, it was found that formic acid–doped PANI–nylon 6 composite fabrics provided the best sensing properties for NH_3 gas, showing excellent sensitivity and reason-

able reversibility. Hence, the PANI–nylon 6 composite fabrics are attractive alternatives for use in sensing applications because of their excellent sensing ability, low cost, and ease of preparation.

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