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Novel flexible chemical gas sensor based on poly(3,4-ethylenedioxythiophene) nanotube membrane

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) nanotubes (PEDOT NTs) flexible membrane was successfully fabricated by vapor deposition polymerization (VDP) mediated electrospinning for ammonia gas detection. PVA nanofibers (NFs) were electrospun as a core part and polyvinyl alcohol (PVA)/PEDOT coaxial nanocables (NCs) were prepared by VDP method via EDOT monomer adsorption onto the electrospun PVA NFs as templates. To obtain the PEDOT NTs membrane, the PVA NFs were removed from PVA/PEDOT coaxial NCs with distilled water. PVA/PEDOT coaxial NCs and PEDOT NTs had the conductivities of 71 and 61 S cm^{-1} and were applied as a transducer for ammonia gas detection in the range of 1–100 parts per million (ppm) of NH_3 gas. They exhibited the minimum detectable level of *ca.* 5 parts per million (ppm) and fast response time (less than 1 s) towards ammonia gas. In a recovery time, the PEDOT NTs membrane sensor was *ca.* 30 s and shorter compared to that of the membrane sensor based on the PVA/PEDOT NCs (*ca.* 50 s). In addition, sensor performance of PEDOT NTs membrane was also undertaken as a function of membrane thickness. Thick membrane sensor (30 μm) had the enhanced sensitivity and the sensitivity on the membrane thickness was in the order of 30 μm > 20 μm > 10 μm at 60 ppm of NH_3 gas.

1. Introduction

Significant advance in conducting polymers (CPs) has promoted the development of devices such as organic light-emitting diodes, solar cells, memories, field-effect transistors, biomedical science, and chemical sensors [1–8]. As alternatives to inorganic semiconductors or metals, CPs provide great potential to produce low-cost, large-area, lightweight, and flexible devices [9–14]. Recently, many efforts have been directed toward fabricating nanometer-scale CP materials owing to their remarkable physical and chemical characteristics originated from their small dimensions and high surface area [15,16]. In particular, one-dimensional (1D) CP nanomaterials have received considerable attention because of their versatile applications in the state-of-the-art sensor devices [17–20].

To date, the fabrication method of 1D CPs could be classified by soft and hard template method, template-free methods, interfacial polymerization, and electrospinning [21–25]. Especially, electrospinning has been extensively investigated due to the fascinating characteristics including simplicity, accessibility, and possibility for mass production [26–28]. As early noted, it is very difficult to make electrospin the CP directly due to low viscosity of spinning solution during the process. Recently, some research groups have been achieved the electrospinning of conducting polymer by chemical vapor deposition (CVD) mediated electrospinning or incorporating viscous insulating polymer with CP [29–31]. This additional polymer could form the nanofibers of conducting polymer composite or act as a template for the production of core-sheath nanofiber [32]. Although electrospinning method is attractive for flexible sensor applications, the limited information have been reported because an individual nanofibers should be precisely controlled on electrode-based sensors. In addition, formation of bridging films between nanofibers should be prevented to improve the sensitivity and recovery time. Therefore, it is still challenging to develop flexible membrane sensor for chemical species determination.

Rapid and accurate determination of ammonia (NH_3) gas is of practical importance in environmental analyses because ammonia, a colorless gas with a pungent and suffocating odor, is recognized as one of the primary irritants to humans [33]. Therefore, various methods to detect NH_3 gas have been mainly studied using polymeric membranes. In particular, the attention has been given to the utilization of conducting polymers as active layers in chemical sensors (ammonia, NO_2, CO_2), and organic vapors [34,35]. They showed the sensing abilities of high sensitivities and short response time.

Herein, we demonstrated a novel flexible membrane based on poly(3,4-ethylene dioxythiophene) nanotubes (PEDOT NTs) as transducer of ammonia sensor. PEDOT NTs membrane was

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fabricated by vapor deposition polymerization (VDP) mediated electrospinning. Uniform polyvinyl alcohol (PVA)/PEDOT coaxial nanocables (NCs) were prepared onto electrospun PVA nanofibers (NFs) as templates by VDP method and PEDOT NTs membrane was obtained by removing the core PVA NFs after washing with distilled water. The as-prepared PVA/PEDOT coaxial NCs and PEDOT NTs membranes were utilized as transducers of chemical sensor to detect ammonia gas. In the result, the minimum detectable level (MDL) was *ca.* 5 ppm. Moreover, the response and recovery time was *ca.* <1 s and *ca.* <30 s. In comparison with most of the commercially available ammonia sensors based usually on conducting polymer films and polymeric membranes, the sensor made of flexible PEDOT NTs membranes has high sensitivity as well as the advantages of the short response and recovery time; especially, these features are ensured at room temperature. For example, Banerji et al. reported ammonia sensor with the various polymeric membranes based on surface plasmon resonance (SPR) and the MDL was sub-10 ppm [36]. Furthermore, the sensing thickness of the PEDOT NTS membranes were easily controlled by the electrospinning and can be also fabricated with mass production and electroness substrate in the electrical sensor devices.

2. Experimental

2.1. Materials

Poly(3,4-ethylenedioxythiophene) (PEDOT) and high molecular weight poly(vinyl alcohol) (PVA) were purchased from Aldrich Chemical Co. Ferric chloride ($FeCl_3$ Aldrich, 97%) was employed as a oxidizing agent, respectively. Ethanol was used as a chemical solvent of $FeCl_3$. Filter paper from HYUNDAI Micro (90 mm in diameter, 0.05 mm in thickness) was employed as the flexible substrate. The device utilized for fabricating PVA NFs was purchased from *Nano NC* Co. (Korea). The electrical conductivity was measured by monitoring with Keithley 2400 source-meter.

2.2. Fabrication of PVA NFs

Poly(vinyl alcohol) (PVA, M_w = 85,000–146,000 and 124,000–186,000 g/mol) 0.6 g was prepared by dissolving PVA granules in distilled water at 80–90 °C for 3 h with vigorous stirring. When the viscous PVA solution was obtained, this solution was injected into a syringe. The diameter of the needle in the electrospinning was 0.1 mm and the needle was connected to the positive terminal of power supply. The voltage was conducted at 15 kV and the solution was delivered to the syringe by a syringe pump (*KD Scientific, USA*). The flow rate of the syringe pump was fixed at 5 μL/min and the distance between tip and collector was 10 cm.

2.3. Fabrication of PVA/PEDOT coaxial NCs and PEDOT NTs through vapor deposition polymerization (VDP)

In order to fabricate PVA NFs as a core part, PVA solution was electrospun onto collector for 40 min. Then, electrospun PVA NFs were dipped into the 10 wt% $FeCl_3$ solution (40 μL) as the oxidizing agent. The Fe-cations were adsorbed on the surface of PVA NFs. The collected PVA NFs were put in the reactor of a chamber type. The reactor was evacuated at room temperature until the pressure inside reached about 10^{-1} Torr, which put the system under a static vaccum. Then, liquid EDOT monomer (0.2 g) was introduced into the reactor by injection. The monomers were injected inside the reactor at room temperature and completely vaporized by heating the reactor at 60 °C for 3 h. Polymerization of EDOT monomers on the surface of PVA NFs was performed by chemical oxidizing agent. Finally, the uniform PVA/PEDOT coaxial NCs were prepared through VDP method. Moreover, the synthesized PVA/PEDOT coaxial NCs were treated with distilled water for 1 h and the PEDOT NTs membrane with *ca.* 20 μm thickness was finally obtained by removing the core PVA NFs. The conductivities of PVA/PEDOT coaxial NCs and PEDOT NTs were measured using the four-probe method at room temperature and the calculated values were *ca.* 71 S cm^{-1} and 61 S cm^{-1}, respectively. These conductivity values were higher than those of existing PEDOT nanomaterials prepared using $FeCl_3$ as the oxidizing agent (~10^0 S cm^{-1}) [11].

2.4. Fabrication of PEDOT NTs membranes with various thicknesses

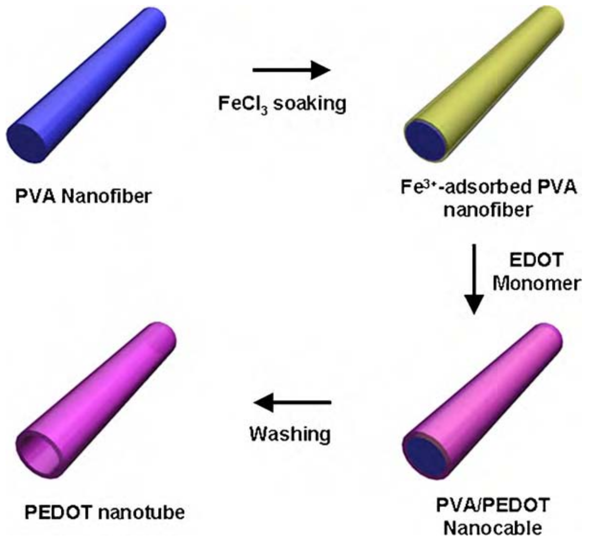
Three kinds of PVA NFs were electrospun onto collector for 20 min, 40 min, and 60 min. PVA NFs also processed under the same experimental method as mentioned above. Electrospun PVA NFs were dipped into the 10 wt% $FeCl_3$ solution. The collected PVA NFs were put in the reactor of a chamber type. Then, liquid EDOT monomer (0.2 g) was introduced into the reactor by injection. Moreover, the PVA/PEDOT coaxial NCs were treated with distilled water for 1 h and the PEDOT NTs was finally obtained by removing the core PVA NFs. Finally, PEDOT NTs membranes with various thicknesses (10 μm, 20 μm, and 30 μm thickness) were easily fabricated through VDP method. The morphology and the surface of the PEDOT NTs membrane with various thicknesses were observed. The inter-nanofiber distance decreased with increasing film thickness, which would result in the aggregated form of the nanofibers during the process of VDP over a critical thickness (see Figure S1 in the Supporting Information).

2.5. The electrical measurement of sensitivities in flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors

The resistance changes of PVA/PEDOT coaxial NCs and PEDOT NTs membranes were monitored with a source-meter connected to a computer. The flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors were placed in a 350 mL vacuum chamber with a vapor inlet/outlet at ~10^0 Torr, and then various NH_3 gas concentrations (1–100 ppm) were injected into the chamber by the Mass Flow Controller (MFC, KNH instruments). The resistance values were recorded in real time at a constant applied current of 10^{-7} A. After PVA/PEDOT coaxial NCs and PEDOT NTs interacted with NH_3 gas concentrations (1–100 ppm) for several minutes, each vapor was replaced by compressed air to remove the NH_3 molecules attached on the backbone of the PECOT nanomaterials. This process was performed repeatedly several times. Vapor/air was supplied at various flow rates of 2–8 SLM and 1–5 SCCM controlled by MFC. The real-time resistance was monitored at a constant applied current of 10^{-7} A (defined as $\Delta R/R_0 = (R - R_0)/R_0$ where R and R_0 are the real-time resistance and the initial resistance, respectively).

2.6. Characterization of PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors

Photographs of transmission electron microscope (TEM) were obtained with a JEOL JEM-200CX. In the sample preparation, nanomaterials diluted in ethanol/methanol were cast onto a copper grid. A JEOL 6700 was used to obtain field-emission scanning electron microscope (FE-SEM) images. The FT-IR spectrum was recorded on a Bomem MB 100 spectroscope (Quebec, Canada) in the absorption mode. The measurement of the electrical conductivity was carried out with a source-meter at ambient temperature by a four-probe method.



Scheme 1. Illustration of reaction steps for fabrication of the flexible sensor platform based on the PEDOT nanotubes membrane.

3. Results and discussion

3.1. Fabrication of PVA/PEDOT coaxial NCs and PEDOT NTs membranes

Scheme 1 illustrates the overall procedure for the fabrication of PEDOT NTs membrane by VDP mediated electrospinning. First, PVA was electrospun on the collector at a continuous voltage value. Then, electrospun PVA NFs were dipped into the FeCl$_3$/ethanol solution. In the result, Fe-cations were adsorbed on the surface of PVA NFs due to the charge–charge interaction between Fe^{3+} ions and OH$^-$ group of PVA. Especially, ethanol was selected as a solvent for FeCl$_3$ to prevent dissolution of PVA NFs during soaking process because PVA is a water-soluble material. When Fe-cations were sufficiently adsorbed, PVA/PEDOT coaxial NCs were prepared through VDP with EDOT monomers. The vaporized EDOT monomers can be contacted with Fe-cations onto the surface of the PVA NFs, and then they were polymerized via chemical oxidation polymerization on the surface of the PVA NFs. During polymerization process, the color of product had been gradually changed from yellow to dark green, implying that the uniform PVA/PEDOT coaxial NCs were successfully fabricated by VDP method. VDP method provided a uniform and smooth PEDOT sheath on the electrospun PVA NFs by successive polymerization of vaporized monomers [37–43]. To obtain the PEDOT NTs membrane, PVA core part was removed from PVA/PEDOT coaxial NCs with distilled water.

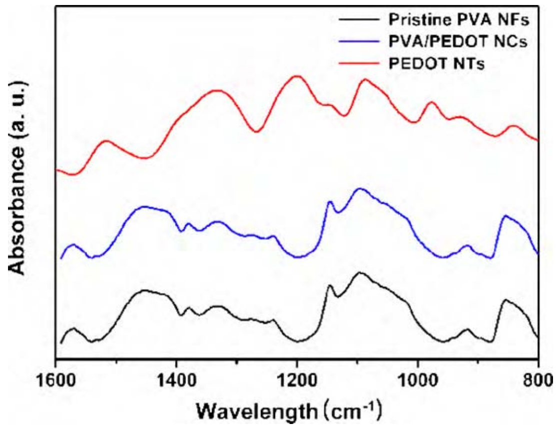


Fig. 2. The FT-IR spectra of pristine PVA nanofibers (NFs), PVA/PEDOT nanocables (NCs) and PEDOT nanotubes (NTs).

3.2. Characterization of PVA/PEDOT coaxial NCs and PEDOT NTs membranes

Fig. 1 displays the FE-SEM and TEM images of PVA NFs, PVA/PEDOT coaxial NCs and PEDOT NTs membranes. As shown in the inset TEM images, the diameter of PVA NFs was *ca.* 100 nm in diameter (Fig. 1a) and the PEDOT sheath thickness of PVA/PEDOT coaxial NCs and PEDOT NTs was *ca.* 20 nm (Fig. 1b and c). The PEDOT sheath was smooth and thin due to the characteristics of VDP including the uniform and smooth coating. PEDOT NTs were fabricated by washing PVA/PEDOT coaxial NCs with distilled water. Moreover, the morphology of PEDOT NTs did not collapse without reduction of outer diameter after washing (Fig. 1c). Furthermore, the conductivities of PVA/PEDOT coaxial NCs and PEDOT NTs membranes were measured by four-probe method at room temperature and were calculated to be *ca.* 71 S cm^{-1} and 61 S cm^{-1}, respectively. These high conductivities can provide PVA/PEDOT coaxial NCs and PEDOT NTs membranes as flexible transducer of chemical sensor.

The successful fabrication of the pristine PVA, PVA/PEDOT coaxial NCs and PEDOT NTs membranes was also confirmed by elemental analysis (EA) and FT-IR spectroscopy. In the case of PVA/PEDOT coaxial NCs, EA data indicated the presence of carbon (32.7%), sulfur (3.4%) and the ratio of C/S was 9.6. On the other hand, the data of PEDOT NTs demonstrated the existence of carbon (44.5%) and sulfur (7.4%) and the ratio of C/S was *ca.* 6. This result was consistent with the ratio of pristine PEDOT. The pristine PVA NFs, PVA/PEDOT coaxial NCs and PEDOT NTs were analyzed by FT-IR spectroscopy (Fig. 2). The band at 1427 cm^{-1} is designated to the CH$_2$ scissoring mode and the peaks at 1375 cm^{-1} and 1331 cm^{-1} are attributed to CH$_2$ deformation. In addition, C–O and C–C stretching vibration peaks appear at 1094 cm^{-1} and 916 cm^{-1}, respectively. The band at 850 cm^{-1} is associated with the CH$_2$ rocking mode of PVA. In the case of PEDOT, the peaks at 942 cm^{-1}, 1083 cm^{-1}, and

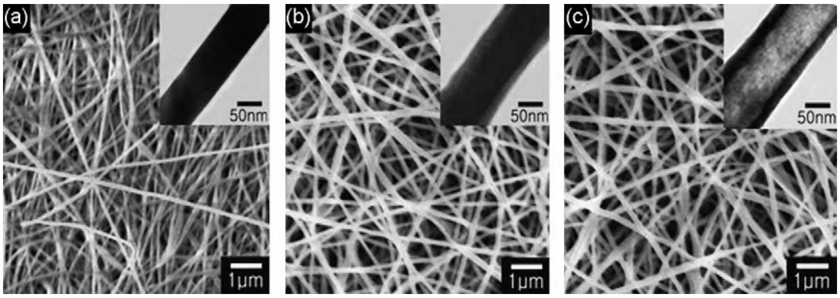


Fig. 1. The SEM and TEM (inset) images of (a) the pristine PVA nanofibers with a diameter of 100 nm, (b) PVA/PEDOT nanocables with a diameter of 140 nm, and (c) PEDOT nanotubes with a diameter of 140 nm.

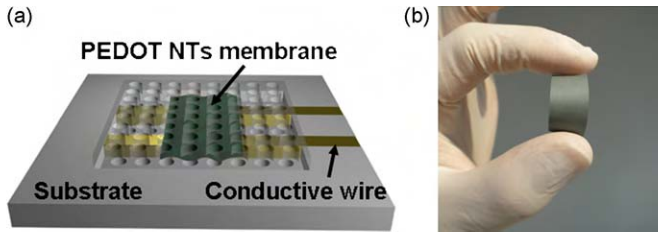


Fig. 3. (a) A schematic representation of the sensor platform based on the PEDOT nanotubes membrane and (b) photograph of bent flexible PEDOT nanotubes membrane.

1384 cm^{-1} are assigned to symmetric C=C, C–S and C–O stretching vibration. Judging from these data, it can be concluded that the pristine PVA NFs, PVA/PEDOT NCs and PEDOT NTs were successfully fabricated by VDP mediated electrospinning method.

3.3. *A flexible sensor based on PEDOT NTs membrane substrate*

Fig. 3 displays the schematic illustration of a sensor platform and flexible membrane based on PEDOT NTs. PEDOT NTs membrane was adopted as a transducer of custom-made sensor device to evaluate the sensing performance owing to high conductivity and surface area. The sensor device was composed of a conductive PEDOT NTs membrane (sensing area: 1 mm × 2 mm) and custom-made device (Fig. 3a). The thickness of PEDOT NTs membrane was fixed at *ca.* 20 μm. PEDOT NTs can induce the formation of conductive pathway between two conductive wires. Furthermore, the sensor platform with PEDOT NTs membrane provided flexibility compared to sensor platforms based on inorganic nanomaterials (Fig. 3b). PEDOT NTs membrane sensor was used as a chemical sensor for detecting ammonia gas vapor and the normalized electrical-resistance change was examined to evaluate their sensitivity at room temperature (defined as $\Delta R/R_0 = (R - R_0)/R_0$ where R and R_0 are the real-time resistance and the initial resistance, respectively).

3.4. *Real-time responses of flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors toward ammonia gas*

To evaluate the sensing capability of the PVA/PEDOT coaxial NCs and PEDOT NTs membranes as signal transducer in chemical sensor application, these membrane sensors were exposed to ammonia gas. The selectivity test was carried out with various VOCs to evaluate the capability of the PEDOT NTs as signal transducers in sensor applications. The normalized resistance change ($\Delta R/R_0$) of the sensor substrate was monitored in real time at room temperature. In the result, each VOCs such as triethylamine, acetonitrile, carbon tetrachloride, chloroform, methanol, ethanol, and diethylether generated a distinctive signal in resistance change, which depend on the response mechanism such as protonation/deprotonation, oxidation/reduction, swelling, and conformational alignment. However, the sensitivity of PEDOT NTs membrane sensor toward the NH_3 was the highest value (see Figure S2 in the Supporting Information). The ammonia gas sensing properties of the PEODT NTs membrane sensor were compared with the literatures in Table 1.

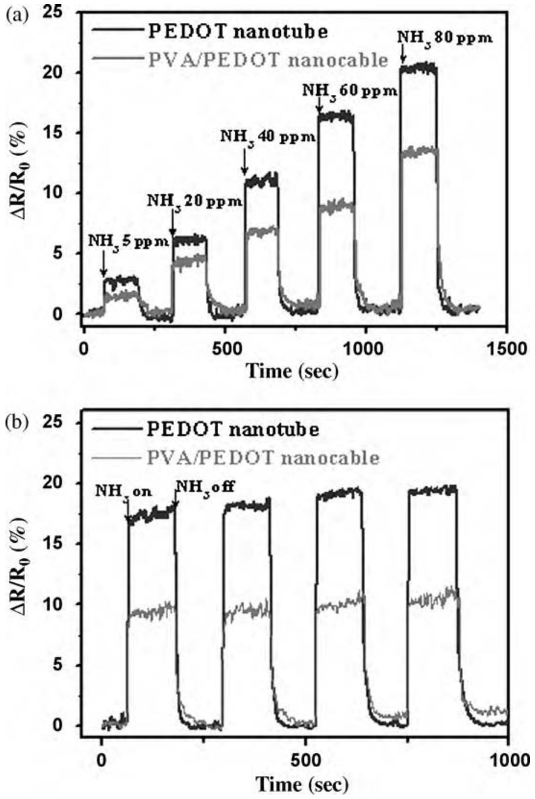


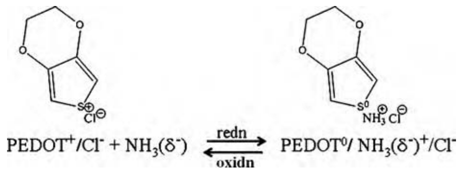
Fig. 4. The reversible and reproducible responseses of PVA/PEDOT nanocables and PEDOT nanotubes membrane sensors upon (a) sequential exposure to vaious NH_3 vapor concentrations and (b) periodic exposure to NH_3 vapor of 60 ppm (R_0 values of the PEDOT NTs and PEDOT NCs are 3×10^3 Ω and 3×10^3 Ω).

Fig. 4 displays the sensitivities (defined as the normalized resistance change) of the flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors as a function of various NH_3 vapor concentrations (there are the raw sensing data in Figure S4 of the Supporting Information). The sensitivities of the membrane sensors increased with increasing the 1–100 ppm of analyte concentration. It can be explained that the vapor diffusivity strongly depends on the NH_3 concentrations. These membrane sensors also showed the enhanced sensing performances in response and recovery times. The response and recovery times are respectively defined as the times required for sensor signals to reach 90% of the saturation and original values. The response time in NH_3 gas detection was *ca.* 1 s and the recovery time was less then 40 s. Importantly, the recovery time (*ca.* 30 s) of the PEDOT NTs membrane sensor was smaller than that (*ca.* 50 s) of the PVA/PEDOT coaxial NCs membrane sensor owing to the high surface area and rapid diffusivity (see Figure S6(a) in the Supporting Information). Moreover, the MDL of these membrane sensors was founded to be *ca.* 5 ppm of NH_3 concentration. In the electrically conductive state, PEDOT is a p-type semiconductor. As PEODT is exposed to

Table 1
Flexible chemical sensor performance of this work toward ammonia gas compared with the literatures.

Sensing materials	Fabrication method	MDL[a] (ppm)	Response/recovery (s)	Reference
PEDOT nanowire film	AAO template	5	10/10	[48]
PEDOT nanorods	Microemulsion	10	–/70	[11]
PEDOT/SA film	LB technique	10	Fast	[49]
TiO_2/PEDOT nanocable	Electrospun	0.675	900/1800	[50]
PEDOT nanotubes	Electrospun	5	1/30	This work

[a] Minimum detectable level.



Scheme 2. Schematic illustration of working principle between PEDOT nanotubes membrane and ammonia gas.

electron-donating molecules such as NH_3, a redox reaction can occur reversibly as shown in Scheme 2. When the PEDOT one-dimensional (1D) nanomaterials were exposed to NH_3 vapor, a steep increase in resistance was observed. Upon exposure to NH_3 vapor, NH_3 molecules diffused into the PEDOT 1D nanomaterials, and thereafter the dedoping of the PEDOT 1D nanomaterials proceeded rapidly through interaction with the NH_3 molecules. In other words, the introduction of NH_3 into PEDOT 1D nanomaterials led to the formation of a neutral polymer backbone and decrease in charge carriers, which induced in conductivity drop [10,11,44].

It was also observed that the sensitivity of flexible PEDOT NTs membrane sensor was higher than that of the PVA/PEDOT coaxial NCs membrane sensor (Fig. 4a). In general, the sensitivity of conducting polymer increases with increasing the surface area [45]. In order to confirm the sensitivity, the surface area of PVA/PEDOT coaxial NCs and PEDOT NTs membranes was measured by BET analysis and the values were *ca.* 18.1 $m^2\,g^{-1}$ and 31.6 $m^2\,g^{-1}$, respectively. Therefore, PEDOT NTs demonstrated the improved performance compared to PVA/PEDOT coaxial NCs in sensitivity due to high surface area. In the case of the PVA/PEDOT coaxial NCs, it is postulated that the PVA NFs play an role in lowering the sensitivity because PVA NFs are well-known insulating materials and reduce the surface area of transducer by filling the inside of the PEDOT NTs.

To further investigate the applicability of the PVA/PEDOT coaxial NCs and PEDOT NTs membranes, these flexible membranes were exposed periodically to NH_3/air, respectively. In Fig. 4b, the resistance of the membrane sensors almost recovered to the original level when the vapor exposure was terminated, and the cycle test could be performed more than 10 times. As results, it is noteworthy that the responses of the flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors on NH_3 gas exposure are reproducible and reversible. In 60 ppm of NH_3 gas concentration, the recovery times of the flexible PVA/PEDOT coaxial NCs and PEDOT NTs membrane sensors were *ca.* 53 s and 32 s, respectively. These fast recovery values were originated from high aspect ratio of 1D structure [46]. Furthermore, PEDOT nanotube can produce faster diffusion of gas molecules in and out of transducer membrane than that of PVA/PEDOT NCs. Fig. 5 exhibits the sensitivities of the PVA/PEDOT coaxial NCs, PEDOT NTs, and PEDOT bulk films as a function of NH_3 vapor concentration. The sensitivities are determined as the normalized resistance change measured when the saturated values are reached after exposure to ammonium gas. The sensitivity change of PEDOT NTs membrane sensor was observed to linear behavior ($y = 0.2499x$ [ppm] + 0.3835), while the sensitivity values of the PVA/PEDOT coaxial NCs membrane and PEDOT bulk film sensors nearly were represented as non-linear behavior over a wide range of concentrations. In addition, the PEDOT NTs showed enhanced sensitivity than the PVA/PEDOT coaxial NCs and PEDOT bulk films.

3.5. Real-time responses of PEDOT NTs membrane sensors with various membrane thicknesses

The sensitivity of PEDOT NTs membrane sensor can be dependent on the thickness of membrane owing to increasing surface area. The membrane thickness was tuned by collecting time in electrospinning. To confirm the electrical sensing performance of membranes with various thicknesses, reversible and reproducible tests were carried out more than 10 times. Fig. 6 displays the real-time responses of PEDOT NTs membrane sensors as a function of membrane thickness (there are the raw sensing data in Figure S5 of the Supporting Information). The data of reversible and reproducible response indicated that enhanced sensitivity was observed in thicker membrane of PEDOT NTs [47,51]. This can be evident that the surface area of the membrane is strongly affected by the thickness. Moreover, the PDEOT NTs membrane with *ca.* 30 μm in thickness had the optical sensing performance (see Figure S3 in the Supporting Information). In other words, it can be considered that the effective surface area of the membrane increase in the order 10 μm < 20 μm < 30 μm. On the other hand, the 30 μm thickness membrane gave slightly long recovery time compared to other membranes (*ca.* 45 s, see Figure S6(b) in the Supporting Information). The thicker membrane with a higher surface area can interact with a larger amount of NH_3 molecules, in which the NH_3 molecule is conjugated with the sulfur atom of the PEDOT via coulombic charge interaction. Therefore, the thicker membrane allows the trapping of more analyte molecules in the PEDOT NTs, which would result in the longer recovery time.

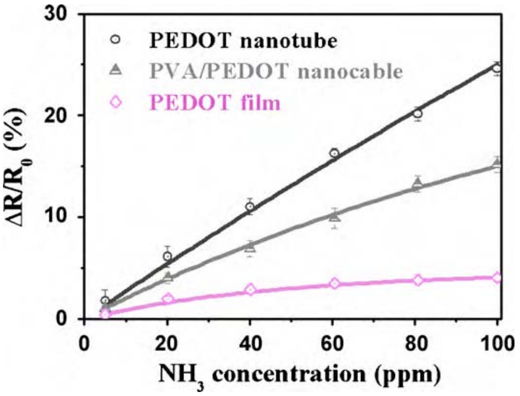


Fig. 5. A calibration curve of bulk PEDOT films, PVA/PEDOT nanocables membrane, and PEDOT nanotubes membrane as a function of NH_3 vapor concentration (R_0 values of the PEDOT NTs and PEDOT NCs are $3 \times 10^3\ \Omega$ and $3 \times 10^3\ \Omega$).

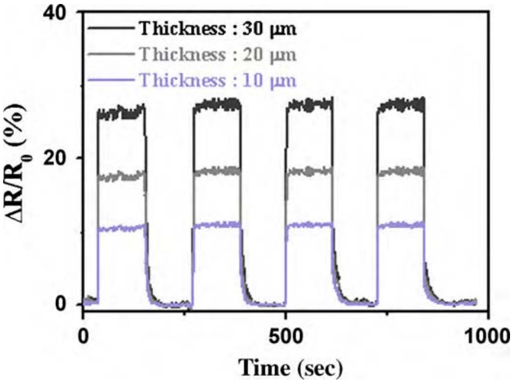


Fig. 6. The reversible and reproducible responses of PEDOT nanotubes membranes with various thicknesses exposure to 60 ppm of NH_3 vapor (R_0 values of the PEDOT NTs with 30 μm, 20 μm and 10 μm in thickness are $2 \times 10^3\ \Omega$, $3 \times 10^3\ \Omega$ and $3 \times 10^3\ \Omega$).

4. Conclusion

In summary, the flexible conducting polymer membrane sensors based on the PVA/PEDOT coaxial NCs and PEDOT NTs membranes were successfully fabricated by VDP mediated electrospinning. The electrospun PVA NFs were adopted as templates for the fabrication of PEDOT membrane. The PVA/PEDOT coaxial NCs and PEDOT NTs have *ca.* 140 nm in diameters and *ca.* 20 nm of the thickness of PEDOT sheath. The conductivities of PVA/PEDOT coaxial NCs and PEDOT NTs membranes were measured to be 71 S cm^{-1} and 61 S cm^{-1} owing to undesirable removal of doping ions during the process of PVA dissolving, respectively. The flexible membrane sensors based on the PVA/PEDOT coaxial NCs and PEDOT NTs demonstrated the enhanced sensitivity, fast response and rapid recovery times. Notably, PEDOT NTs membrane sensor revealed the improved sensitivity compared to PVA/PEDOT coaxial NCs membrane owing to high surface area. Due to the thin wall of PEDOT NTs, rapid response time (*ca.* 1 s) and fast recovery time (*ca.* 30 s) were observed by fast diffusion of NH_3 gas molecules in and out of transducer. These flexible membrane sensors showed measurable values at *ca.* 5 ppm of NH_3 vapor concentration for reversible and reproducible response. Furthermore, the electrical sensitivity in PEDOT NTs membrane sensor increased gradually with increasing membrane thickness owing to enlarged sensing area. Judging from these results, flexible PEDOT NTs membrane sensor demonstrated fast response and recovery times for ammonia gas detection. In addition, this methodology can be expanded to allow the fabrication of various 1D nanomaterials as well as apply for various research fields including chemical/biosensors, separation, and tissue engineering scaffolds.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.06.058.

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