Development of NH₃ Gas Sensors at Room Temperature Based on Modified Carbon Nanotubes

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Multiwalled carbon nanotubes (CNTs) were modified with the Hummers method and coated onto Pt electrodes patterned on SiO₂/Si(001) surface to fabricate chemical sensors. The modified CNTs showed a different structure and increased number of defects compared with pristine CNTs, these properties facilitated the adsorption of NH₃ gas molecules on the CNT surfaces. NH₃ gas sensing results indicate that the sensor exhibited an enhanced response to gas at room temperature. The response of the modified CNT-based sensor was 10 times higher than that of pristine CNT-based sensors. [doi:10.2320/matertrans.MT-MN2019005]

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1. Introduction

Our environment currently faces the problem of pollution and toxic chemical gases that are harmful to human life and health. Ammonia (NH₃) gas, a primary product of agricultural and industrial processes, poses a direct threat to humans. At low concentrations of a few tens of part per million (ppm), NH₃ can cause irritation to the eyes, skin, and respiratory system. At high concentrations, NH₃ causes throat irritation, coughing, and even fainting.^{1,2)} Therefore, environmental sensing based on passive sensors with low cost and low power consumption and operation at room temperature has attracted considerable attention.

Carbon nanotubes (CNTs) have become a promising replacement material for gas sensing applications after the first study on the use of single-walled CNTs to fabricate chemical sensors.³⁾ Studies have reported the possibility of using CNT-based sensors for NH₃, NO₂, H₂, and CH₄ gas detection.^{4–6)} Pristine CNTs exhibit a low interaction or activeness with gas molecules due to the configuration of strong sp² bonding.⁷⁾ Previous studies showed the remarkably low response of pristine CNT-based sensors in the case of NH₃.^{8,9)} Substantial efforts have led to the development of versatile methods to functionalize CNTs to expand their efficiency and attractive features. A wide range of structures, such as noble metallic nanoparticles,^{10–13)} and semiconductor metal oxide (SMO) nanostructures have been introduced to CNTs;^{14–16)} composites of polymer/CNTs or SMO/CNTs have also been presented.^{17,18)} In this study, multiwalled CNTs modified by using the Hummers method were used as a material to fabricate a chemical sensor for NH₃ gas detection. The sensor's responses were measured at room temperature.

2. Experimental Procedure

Commercial MWCNTs were purchased from Shenzhen Nanotech Port Co. Ltd. (NTP). The CNTs had about 60–

100 nm in diameter and 1–2 μm in length. The MWCNTs were functionalized through the Hummers method. First, 0.1 g MWCNTs and 0.1 g NaNO₃ were placed in 4.8 mL condensed H₂SO₄ (98%) and 0.5 mL H₃PO₄ (85%). Mixing was conducted at temperatures of as low as 0°C–5°C. The mixture was stirred continuously for 15 min. Second, 0.6 g KMnO₄ was introduced to the mixture and stirred continuously for 90 min at the above-mentioned temperature range. Thereafter, the mixture was stirred continuously for 120 min at room temperature. Third, 40 mL distilled water (DW) was added to the mixture during stirring. Lastly, H₂O₂ solution was added slowly to dissolve any residual MnO₄ and MnO₂ in the solution. Modified CNTs in a dark black color were obtained after three times of cleaning, filtering, and centrifugation at 3000 rpm.

The modified CNTs were dispersed in alcohol and coated on interdigitated Pt electrodes patterned on SiO₂/Si surfaces by using a spinner for use as a gas-sensitive material. At the end of the process, the sample was annealed at 60°C for 2 h for solvent evaporation. The structural and morphological properties of the pristine and modified CNTs were characterized through field emission scanning electron microscopy (FESEM). The vibrational modes of molecules and functional groups of two types of CNTs were measured using Raman and Fourier transform infrared (FTIR) spectroscopies. The modified CNT-based sensors were investigated under NH₃ gas, which was introduced to a 30 L sealed chamber to determine the sensitivity of the sensors. The sensing properties of the sensors were analyzed by changing the sensors' resistance with a static measurement system equipped with a Keithley 6487 picometer/voltage source. The humidity of the measuring medium at room temperature was approximately 50%, and the temperature was approximately 27°C.

3. Results and Discussions

Figure 1 shows the FESEM images with different scales (1 μm and 100 nm) of the commercial pristine CNTs (a, b) and modified CNTs (c, d). Unlike the original MWCNTs with

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Fig. 1 FESEM images of pristine-CNTs (a), (b) and modified-CNTs (c), (d) obtained through the Hummers method with different scales. The CNT surfaces were changed due to the effects of chemical agents at the defects on the CNT surface.

Fig. 2 Raman spectra of pristine CNTs (a) and modified CNTs (b). The ratio between D and G band intensities of modified CNTs increased slightly, and the G band was split into two peaks due to impurities and defects.

a hollow cylindrical structure, smooth surface, and porous-arranged CNT layers, the modified CNTs were broken with a round tubular structure and no longer uniform with a flat structure. The modified CNTs presented an average diameter that was larger than the original CNT diameter. This result may be due to the effects of chemical agents at the defects on the CNT surface. This influence may have extended along the length of CNTs to create a dislocation that modified the surface of CNTs.

Figure 2 shows the Raman spectra of CNTs before and after the Hummers chemical treatment. The D-band located at 1327 cm^{-1} , which was present in the Raman spectroscopy sensitive signal, indicated disorder in the sp^2 carbon materials resulting from the defects or disordered structure in the sp^2 bond on the hexagonal surface of CNTs. Meanwhile, the G-band located at nearly 1577 cm^{-1} is attributed to the stretching of the C–C bond in graphitic materials, which

commonly occurs in sp^2 carbon bonding. The second-order two-phonon process of disorder (2D band) and a combined disorder–G band of graphitic structures were observed (Fig. 2(a)) in the Raman spectra.

The ratio between D-peak and G-peak intensities (I_D/I_G) slightly increased from 1.34 for pristine CNTs to 1.39 for modified CNTs (Fig. 2(b)) after treatment. This result means that several sp^2 bonds were broken to form additional defects or to transition to sp^3 structures due to the out-of-plane vibration of carbon atoms with impurities. The G-band split into two peaks (inset at the top right of Fig. 2(b)) due to the impurities and changes in the CNT surface. The G-peak originated from the C–C bonds of the graphitic structure and the D' peak at 1608 cm^{-1} . The main reason was that the localized vibrational modes of the impurities or defects could interact with the graphitic phonon modes of CNTs, resulting in the observed splitting.¹⁹⁾

The pristine and modified CNTs were used as sensing materials to fabricate gas sensors. Our previous study showed that a pristine CNT-based sensor achieves a low response of about 1.5% to 70 ppm NH_3 at room temperature and is more selective to NH_3 gas than to alcohol, acetone, or liquefied petroleum gas.⁸⁾ The pristine MWCNTs were considered p-type semiconductors, and CNT-based sensor responses were assumed to depend on the CNT structures themselves, contacts between CNTs, and contacts between CNTs and metal electrodes (Schottky contacts) to understand the gas-sensing mechanism.²⁰⁾ The difference originated from the CNT treatment in the present case. Therefore, the responses of sensors were mainly affected by the CNTs themselves. Notably, the conductivity of CNTs depends on the change in carrier concentration. Carriers can transfer between CNTs and oxidizing or reducing gas molecules adsorbed on their surface. Exposure to oxidative gases (functioning as p-dopants) increases hole conduction and decreases resistance under ambient conditions. Moreover, exposure to reductive gases (functioning as n-dopants) induces the reverse effect. Therefore, gas molecules interact with the CNT surface, and the resistance of the CNT sensing layer increases when CNTs adsorb NH_3 molecules on their sidewalls. The sensor response is defined as follows: $R(\%) = (R_{\text{gas}} - R_{\text{air}})/R_{\text{air}} \times 100\%$, where R_{gas} and R_{air} are the resistance of the CNT sensing layer with and without gas application, respectively.

Figure 3 shows the transient responses of the modified CNT-based sensor after five cycles of on/off exposure to

50 ppm NH_3 gas at room temperature (a) and the on/off cycle response of the sensor (b). The response reached 16.5%, which is more 10 times higher than that of the pristine CNT-based sensor as mentioned above. The sensor showed repeated responses to the NH_3 gas. A single on/off cycle of the response revealed response and recovery times of about 65 and 500 s, respectively. The response and recovery times were similar to those of the pristine CNT-based sensor.

Figure 4(a) shows the modified CNT-based sensor's response versus measurement time at different NH_3 gas concentrations ranging from 2.5 ppm to 110 ppm. Notably, 25 ppm is the low level of NH_3 gas that affects humans. The sensor responded to the gas at room temperature, that is, the sensor became sensitive to the gas after a few tens of seconds during NH_3 adsorption on the CNT surfaces. The response then reached a saturated value at a defined gas concentration. The response of the sensor increased slightly as the gas concentration increased (from 5.8% for 2.5 ppm NH_3 gas to 24.6% for 110 ppm NH_3 gas). By contrast, the response decreased to the initial level after about 400 s when the sensor was exposed to air. Figure 4(b) shows the on/off cycles of gas sensor responses at the above-mentioned NH_3 gas concentrations. The sensor responded well to an injection of NH_3 gas and recovered with exposure to air.

The outer wall of CNTs plays an important role in gas adsorption, which explains the increase in the sensor's response after chemical treatment. Treatment of CNTs using

Fig. 3 Transient responses of the modified CNT-based sensor after five cycles of on/off exposure to 50 ppm NH_3 gas concentration at room temperature (a) and an on/off cycle of the sensor's response (b). The sensor showed good responses to the NH_3 gas and more 10 times higher than that of pristine CNT-based sensor.

Fig. 4 Sensor's response to NH_3 with different gas concentrations ranging from 2.5 ppm to 110 ppm (a) and on/off cycles of sensor responses (b). The sensor responded well to exposure to NH_3 gas.

Fig. 5 FTIR spectra of the pristine and modified CNTs. The appearance of peaks related to the defects and functional groups in modified CNTs demonstrated favorable sites for NH₃ gas adsorption.

strong acids (H₂SO₄ and H₃PO₄) and oxidizing agent (KMnO₄) to produce oxygen functional groups, such as hydroxyl (–OH), carbonyl (–C=O), and carboxylic (–COOH) groups, promotes NH₃ molecule adsorption. Figure 5 shows the FTIR spectra of the pristine and modified CNTs. The spectra revealed intensive bands at 3414 cm^{–1} due to the stretching vibrations of –OH in carboxyl groups. The slight peak shift in the low-wavenumber direction of modified CNTs indicated the presence of strong hydrogen bonds between –OH group.²¹⁾ The band at 2348 cm^{–1} originated from the CO₂ laser source. The bands near 1728 and 1612 cm^{–1} were from the –COOH group and C=C aromatic rings, respectively. The bands located at 1398 and 1234 cm^{–1} were related to C–O stretching and O–H bending vibrations, respectively.²²⁾ The band at 1068 cm^{–1} may be due to O–H deformation, C–O stretching combination, or O–O vibration mode. The increase in the intensity of bands related to the functional groups confirmed that the formation of defects on the CNT surfaces for gas adsorption led to an increase in the sensor's response.

4. Conclusion

MWCNTs modified through the Hummers method can be used as a material for NH₃ gas detection. The response of the modified CNT-based sensor was 10 times higher than that of the pristine CNT-based sensor at room temperature. The sensor's responses increased linearly with increasing NH₃ gas concentration. The increased in sensor response was related to the number of defects and oxygen functional groups on

the CNT side walls formed after chemical treatment, which facilitated the adsorption of NH₃ gas.

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