EFFECT OF OXYFLUORINATION ON GAS SENSING BEHAVIOR OF POLYANILINE-COATED MULTI-WALLED CARBON NANOTUBES

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Introduction

Recently, carbon nanotubes (CNTs) has attracted great interest owing to its unique physical and chemical properties [1-2]. Previous works have demonstrated that CNT is an ideal candidate for sensing material, and can detect a wide range of gases at near room temperature, such as NO_2 and NH_3 [3]. However, gas sensors based on pristine CNTs have some limitations, such as low sensitivity and lack of selectivity to analytes for which they have low adsorption energy or low affinity [4-5].

Conducting polymers are another type of widely investigated sensing materials. Recent study shows that modifications with the conducting polymers can enhance the sensing properties of CNTs [6]. Polyaniline (PANi) is a potential candidate in sensor applications among the variety of conducting polymers due to its unique electrical properties, environmental stability, and easy fabrication process. However, the poor dispersibility of CNTs would bring some difficulty or extra work in fabrication process. It is still a challenge to introduce easy and low cost fabrication process of gas sensors which retain high sensitivity for application.

In the present paper, polyaniline-coated multi-walled carbon nanotubes (MWCNTs) were prepared by in situ chemical polymerization method. PANi was uniformly coated on MWCNTs, and the thickness of the PANi coatings was controlled by changing the oxyfluorination of MWCNTs. The effects of the thickness of PANi coating on the gas sensing properties were also investigated in detail. The results suggested a potential application of PANi-coated MWCNTs to the fast and sensitive gas sensor.

Experimental

Aniline, ammonium persulfate (APS) and hydrochloride (HCl) were obtained by Aldrich. Aniline was distilled in vacuum before use. MWCNTs (95% purity, diameter 50-80 nm) were obtained from Aldrich.

The surface of MWCNTs was modified by using direct oxyfluorination method. As a pretreatment step, MWCNTs were treated at 120 ℃ for 12 h in order to remove impurities. The oxyfluorination was carried out at 1 bar for 3 min with various oxygen : fluorine gas ratios of 2:8, 5:5, and 8:2. More details were shown in our previous work [17].

Oxyfluorinated MWNTs were coated with PANi in situ polymerization. In typical synthesis process, equal volumes of 1.0 M HCl solutions containing 5mg MWNTs but various weight ratios of aniline monomer were sonicated for 2 h to form uniform suspensions. Then the required amounts of APS (1/1 aniline/APS molar ratio) were dissolved in 5 mL 1.0 M HCl solutions separately, and added slowly into the above suspensions to initiate the polymerization. The resulting reaction mixtures were allowed to react for 4 h at 0-4 ∘C with stirring in order that aniline could be fully polymerized. The PANi coated MWCNTs were filtered and rinsed with deionized water, methanol, and acetone, and then dried at room temperature. The various kinds of oxyfluorinated MWCNTs and PANi coated MWCNTs are classified in Table 1.

Table 1. Classification of oxyfluorinated MWCNTs and PANi coated MWCNTs

Oxyfluorination	MWCNT	PANi coated MWCNTs
None	OF00C	OF00PC
O_2: F_2 = 2 : 8	OF28C	OF28PC
O_2: F_2 = 5 : 5	OF55C	OF55PC
O_2: F_2 = 8 : 2	OF82C	OF82PC

The XPS analysis was carried out with a MultiLab 2000 spectrometer (Thermo Electron Co., England) to evaluate the changes of chemical species on the surface of the MWCNTs before and after oxyfluorination. Al Ka (1485.6 eV) X-rays were used with 14.9 keV anode voltage, 4.6 A filament current, and 20 mA emission current. All samples were treated at 10^{-9} mbar to remove impurities. The survey spectra were obtained with 50 eV pass energy and 0.5 eV step size. Core level spectra were obtained at 20 eV pass energy with 0.05 eV step size.

UV spectrometer (Optizen 2120 UV, Mecasys, Korea) was used to investigate the dispersion of MWCNTs in PVA solution. The measurement was carried out following the general method presented by other groups [18-19]. Measurements were performed at 635 nm during 4 days after sonication for 1 h.

Field emission scanning electron microscopy (FE-SEM, Hitachi, S-5500) and field-emission transmission electron microscopy (FE-TEM, Jeol JEM-2100F, Japan) were used to investigate the morphology of PANi coated MWCNTs. Images were taken without prior treatment to ensure the acquisition of accurate images. The samples for measuring the electrical conductivity were prepared by applying the pressure of 1000 psi without using any binder. The sample was pellet type with 10 mm diameter and 2 mm thickness. The pellet type samples were cemented to the platinum leads printed on an alumina plate with the silver paint. The problems of contact resistance could be avoided by these treatments of samples. The pellet resistance was measured with the four-probe method at room temperature using the probe head station (Dasol Eng., Korea) and the ASTM F1529-97 method. The electrical conductivity (σ) was calculated using the following two equations [15].

$$\rho = Rs \times t \ (\Omega cm) \qquad (1)$$

$$\sigma = 1/\rho \ (S/cm) \qquad (2)$$

where ρ, Rs, and t are the bulk resistivity, the surface resistance, and the thickness of sample, respectively.

Thermogravimetric analysis (TGA) was performed in air flow (25 cm^3/min) at a heating rate 10 °C/min with Perkin Elmer TGA5OH thermogravimetric analyzer.

Results and Discussion

The surface morphology of PANi-coated MWCNT was presented in Fig. 1 showing the effects of oxygen content during oxyfluorination. In case of using pristine MWCNT, the aggregated PANi was observed on the surface of MWCNT with approximate size about 0.5 µm. The aggregated PANi was decreased and then it was well distributed on the surface of MWCNT by higher oxygen content during oxyfluorination. This was attributed to the hydrophilic functional groups introduced on the surface of hydrophobic MWCNTs resulting in the improved affinity between PANi and MWCNT.
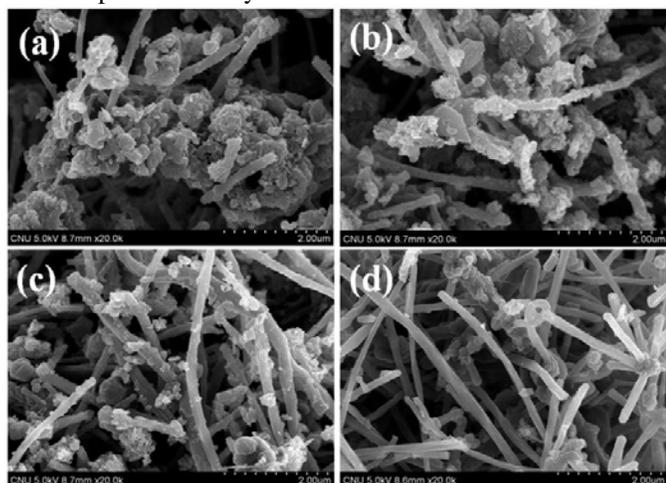
Fig. 1 SEM images of PANi-coated MWCNT (a) OF00PC, (b) OF28PC, (c) OF55PC, and (d) OF82PC.

To investigate the effects of hydrophilic functional groups introduced by oxyflurorination on the surface of MWCNT, TEM images were presented in Fig. 2. The coated PANi on the surface of MWCNT was observed in both cases of OF28PC and OF82PC samples. When comparing them, the thickness of coated PANi decreased significantly from 80 to 10 nm. This phenomenon would result in the decrease of aggregated PANi for the well distributed PANi. Therefore, it was noticed that the hydrophilic functional groups introduced by oxyfluorination played an important role for the well distributed and coated PANi on the hydrophobic surface of MWCNT by improved interface affinity.
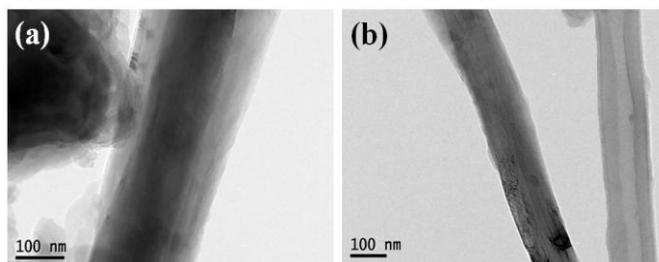
Fig. 2 SEM images of PANi-coated MWCNT (a) OF28PC and (b) OF82PC.

Conclusions

Polyaniline-coated multi-walled carbon nanotubes were prepared by in situ chemical polymerization method. Polyaniline was uniformly coated on multi-walled carbon nanotubes, and the thickness of the polyaniline coatings was controlled by changing the oxyfluorination of multi-walled carbon nanotubes. Sensors were fabricated by spin-coating the polyaniline-coated multi-walled carbon nanotubes onto pre-patterned electrodes. Better response and reproducibility towards ammonia were observed at room temperature. The effects of the thickness of polyaniline coating on the gas sensing properties were also investigated in detail. The results suggested a potential application of polyaniline-coated multi-walled carbon nanotubes to the fast and sensitive gas sensor.

References

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