

Electronic properties control of single-walled carbon nanotube using spontaneous redox process of MnO_4^- and carbon nanotube

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ABSTRACT

Single-walled carbon nanotube (SWCNT) thin film is three dimensional interconnected networks of quantum wires and a large number of factors can affect their optical and electrical properties. In order to obtain the low sheet resistance of SWCNT thin film that has the high transmittance at 550 nm, electronic properties of SWCNTs film are modified through chemical treatment and enhanced carrier injection. We investigated the effectiveness of electronic properties with single-walled carbon nanotube through spontaneous redox-reaction between the metal oxide ion such as MnO_4^- and carbon nanotube. The sheet resistance of SWCNTs film decorated with MnO_2 has lower than that of as-prepared SWCNTs film due to the reduction of MnO_2 particle on the surface of SWCNT. The effect of doping on electronic structure of SWCNTs was investigated by four point probe (FPP), Raman spectroscopy, and UV vis-NIR absorption spectrometer.

Keywords: single-walled carbon nanotube, MnO_2 , transparent conducting film, spontaneous redox-reaction, doping

1 INTRODUCTION

Transparent conducting films (TCFs) fabricated by single-walled carbon nanotube networks with low sheet resistance and high transmittance has been exploited for the wide range of applications, including next generation displays, stretchable and flexible electronic devices, optical devices, sensors [1] and solar cells [2]. However, further improvement in the sheet resistance of SWCNT films is needed to make them an attractive alternative to indium tin oxide (ITO). For improvement of the sheet resistance with transparent conducting films containing SWCNTs resulting from the percolation effect [3] and the heterogeneous contact resistance of the random networks, removal of solubilizer for the dispersion of SWCNTs such as surfactant and organic solvent, chemical doping and enhanced carrier injection have been needed to decrease the contact resistance between the heterogeneous junctions and enhance the percolation effect.

Strategies for doping SWCNT films with n-type and p-type to decrease the contact resistance between the heterogeneous junctions of SWCNT networks were to use

dopants such as alkali metals, alkaline-earth metals, Brønsted acid, and spontaneous redox-reaction between the metal ion (Au and Pt ion) and carbon nanotube. Chemical doping of SWCNT films with several alkali metals, such as Li, K and Cs, and alkaline-earth metals, such as Sr, has resulted in n-type doping behavior [4-8]. In contrast, the decrease of the sheet resistance in SWCNTs films due to the spontaneous reduction of Au and Pt ions on the sidewalls of SWCNTs has been used for p-type doping [9-11]. Similarly, the influence of a Brønsted acid, e.g. H_2SO_4 , HNO_3 , and HCl, in SWCNTs has been used as the dopant for p-type doping [12-15].

In particular, attaching metal nanoparticles to nanotube sidewalls is of interest for obtaining nanotube/nanoparticle hybrid materials with useful properties, for forming metal nanowires on nanotube templates, and for enhancing the conductivity of SWCNTs film. Spontaneous redox-reaction between of metal ions, such as Au and Pt ions, and carbon nanotube can be created Au and Pt nanoparticles on the surface of the SWCNTs and ejected the electrons in SWCNTs as result of the p-type doping. Similarly, decoration of the metal oxide on the surface of SWCNTs due to spontaneous redox-reaction was suggested because the sheet resistance of TCFs containing SWCNTs decreased. Here, we investigated the effectiveness of electronic properties with single-walled carbon nanotube through spontaneous redox-reaction between the metal oxide ion such as MnO_4^- and carbon nanotube. The change of the sheet resistance in TCF containing SWCNTs, bleaching the transition peaks related to van Hove singularities, and the suppression in Raman spectra were checked through the control of the reaction time in the aqueous KMnO_4 solution.

2 EXPERIMENT DETAILS

2.1 Dispersion of SWCNTs

The SWCNTs with a mean diameter of 1.2–1.6 nm and a purity of 90 vol%, which were synthesized by an arc discharge process, were purchased from Hanwha Nanotech. In order to obtain a well-dispersed SWCNTs solution, 10 mg of an SWCNT powder was dispersed in a 1 wt% aqueous solution of sodium dodecylbenzene sulfonate (SDBS) surfactant (10 g of SDBS in 990 ml of deionized water). The mixture was sonicated in a horn-type sonicator (VC 505, Sonics & Materials Inc.), and all sonication

processes were performed in ambient conditions for 10 min. And then, the SWCNTs solution was centrifuged in 12000 *g for 1 h, and 80% of the upper solution was used to this experiments.

2.2 Fabrication of TCF containing SWCNTs

The SWCNT film used in this experiment was fabricated on various substrates using a filtration-wet transfer (FWT) method [15-17]. In order to transfer the SWCNT film from the filter to the polyethylene terephthalate (PET) substrate, a conformal contact was first made between the filter and PET. After clipping them together, the filter and PET were placed in deionized water. Initially, lateral wetting occurred at the interface of the filter due to the water flow through the channels in the filter. After complete wetting, the filter was separated from the set and a SWCNT film was formed on the PET substrate. The entire process took only about 80 s. In case of substrates like Si wafer and glass, SWCNTs film was transferred due to the change of the surface energy with Si wafer and glass through the treatment of octadecyl trichlorosilane (OTS) solution for 5 min.

2.3 KMnO₄ solution treatment

SWCNTs film fabricated on various substrates was treated in the aqueous KMnO₄ solution (1 mM) for different treatment time, and all treatment processes were performed in ambient conditions. After the immersion in the aqueous KMnO₄ solution for 1 h to 18 h, MnO₂-doped SWCNTs was rinsed by deionized water for 1 min.

2.4 Analysis of MnO₂-doped SWCNTs

UV-vis-NIR absorption spectroscopy (Shimadzu UV-3600) was used to characterize the change in intensity in the van Hove singularity-related transition peaks, E_{11}^S , E_{22}^S and E_{11}^M through the doping of SWCNT films. Raman spectroscopy (Kaiser Optical System Model RXN 1) was also used to characterize the optical properties of the doped or de-doped SWCNTs. Several excitation energies of 1.96 eV (632.8 nm, helium-neon gas laser) were used. The SWCNT film used for the Raman measurement was fabricated on SiO₂ using a filtration-wet-transfer (FWT) method and the data was collected on numerous spots (five spots) on the sample. All Raman spectra were normalized to the intensity of the G-band to allow a visual comparison between the samples. The change in sheet resistance of the as-prepared SWCNT film and MnO₂-modified SWCNT film were measured by a four-point probe resist meter (AIT CMT-SR1000N).

3 RESULTS AND DISCUSSION

In order to identify the effect of the doping in the reduction of MnO₂ for the decrease in sheet resistance of the SWCNT film immersed in the aqueous KMnO₄ solution,

this study examined the change in sheet resistance of the MnO₂-doped SWCNT film as the treatment of SWCNTs film from 1 h to 18 h. Figure 1 shows a sheet resistance of the as-prepared SWCNT film and MnO₂-doped SWCNTs film as a function of treatment of MnO₂. The sheet resistance of the SWCNT film decreased about 45 % after immersing the as-prepared SWCNTs film in the aqueous KMnO₄ solution for 1 h. The ratio of the change of sheet

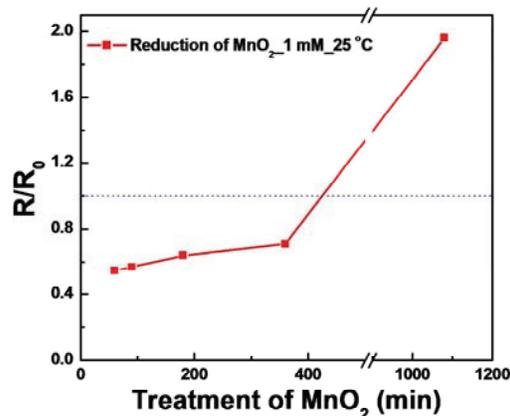


Figure 1. Treatment time of MnO₂ versus sheet resistance for transparent conducting film generated from as-prepared SWCNTs film and MnO₂-doped SWCNTs film as the increase of the treatment time

resistance with the MnO₂-doped SWCNT film decreased with increasing treatment time from 1 h to 18 h, and for 18 h, the sheet resistance of MnO₂-doped SWCNTs film increased by a factor of 2. This indicates that the increase of the contact resistance between heterogeneous junctions due to a number of the creation of the MnO₂ particle on the surface of SWCNT was resulted from the increase of the sheet resistance with MnO₂-doped SWCNTs film. Therefore, we can control the electronic properties of SWCNTs film through the control of the treatment time in the KMnO₄ solution.

Figure 2 shows the UV-vis-NIR absorption spectra of the as-prepared SWCNT film and doped SWCNT film after immersion in the aqueous KMnO₄ solution for 1 h to 18 h. The van Hove singularities-related transition peaks correspond to the intrinsic excitonic transitions of semiconducting (E_{11}^S , E_{22}^S and E_{33}^S) and metallic (E_{11}^M and E_{22}^M) SWCNTs from the valence band to the conduction band can be observed in these absorption spectra. These peaks were gradually bleached after immersion in the aqueous KMnO₄ solution for 1h to 18 h. Kim *et al* examined SWCNTs doped with various concentrations of AuCl₃ and reported that the van Hove singularity transitions disappeared gradually in the UV-vis-NIR absorption spectra with increasing p-doping concentration and the work function of the SWCNTs increased [9]. In this absorption spectra, the

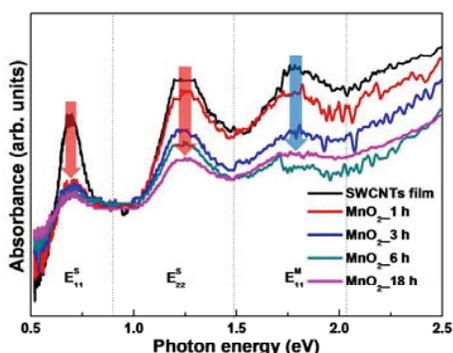


Figure 2. UV-vis-NIR optical absorption spectra with increasing treatment time of MnO_2 . The arrows indicate the suppression of intensity in transition peaks related to van Hove singularity through p-doped SWCNTs. E_{ii}^S and E_{ii}^M indicate the van Hove singularity transitions between the i th energy levels of the semiconducting and metallic SWCNT.

decrease of intensity with transition peaks related to the van Hove singularities, such as the E_{11}^S , E_{22}^S and E_{11}^M bands (red arrow and blue arrow), in the spectra of MnO_2 -doped SWCNT films as the increase of the treatment time suggest that the Fermi level was shifted further down below the first van Hove singularity in the valence band of the semiconductor and metallic nanotube. After the immersion in the aqueous KMnO_4 solution for 1 h, the transition peak of E_{11}^S was almost bleached. In case of the transition peak of E_{22}^S and E_{11}^M , intensity with transition peak was gradually decreased as the increase of the treatment time.

The strong and non-monotonic dependence of the SWCNT Raman spectra on the laser excitation energy E_{laser} demonstrated Raman scattering associated with a resonance

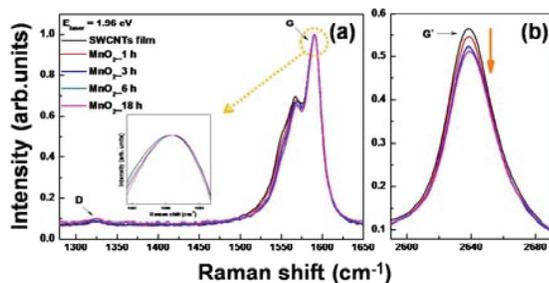


Figure 3. Raman spectra of as-prepared SWCNTs film and MnO_2 -doped SWCNT films at an excitation energy of 1.96 eV. Inset of (a) shows the unchanged peak position in the G band. All Raman spectra were normalized by the G-band intensity. The arrow shows the decrease of G'-band intensity after immersion in the aqueous KMnO_4 solution.

process for the excitation laser energy E_{laser} with the optical transition energy E_{ii} between the van Hove singularities in the valence band and the conduction band [18]. The gradual decrease of intensity in G'-band (figure 3(b)) as the increase of the treatment time was observed due to the transfer of the electrons from the SWCNTs to metal oxide ions. This phenomenon was related to the p-type doping. Inset of figure 3(a) showed the peak position of the G band. Although we can suggest another evidence of p-type doping through the blueshift in G-band, we did not observe the blueshift in the G-band. The non-covalent interaction between the SWCNTs and dopants was attributed to the negligible change in the intensity of the D band.

4 CONCLUSIONS

Transparent conducting films containing SWCNTs were fabricated on various substrates using the filtration wet transfer method. Decoration of the metal oxide on the surface of SWCNTs due to spontaneous redox-reaction was suggested because the sheet resistance of TCFs containing SWCNTs decreased. The sheet resistance of the SWCNT film decreased about 45 % after immersing the as-prepared SWCNTs film in the aqueous KMnO_4 solution for 1 h. MnO_2 -doped SWCNTs film chemically doped with an electron acceptor showed the suppression of the van Hove singularity in the UV-vis-NIR absorption spectra and the gradual decrease of intensity in G-band. That is, after treatment of MnO_2 , the Fermi level was shifted further down below the first van Hove singularity with the valence band of the semiconductor and metallic nanotube in the original position on the electronic structure with the as-prepared SWCNTs. In case of 18 h, however, the sheet resistance of MnO_2 -doped SWCNTs film increased by a factor of 2. This indicates that the increase of the contact resistance between heterogeneous junctions due to a number of the creation of the MnO_2 particle on the surface of SWCNT was resulted from the increase of the sheet resistance with MnO_2 -doped SWCNTs film.

REFERENCES

- [1] Cattanaach K, Kulkarni R D, Kozlov M and Manohar S K, *Nanotechnology*, 17, 4123, 2006
- [2] Contreras M A, Barnes T, Lagemaat J, Rumbles G, Coutts T J, Weeks C, Glatkowski P, Levitsky I, Peltola J and Britz D A, *J. Phys. Chem. C*, 111, 14045, 2007
- [3] Hu L, Hecht D S and Gruner G, *Nano Lett.*, 4, 2513, 2004
- [4] Lee R S, Kim H J, Fischer J E, Thess A and Smalley R E, *Nature*, 388, 255, 1997
- [5] Grigorian L, Sumanasekera G U, Loper A L, Fang S, Allen J L and Eklund P C, *Phys. Rev. B* 58, R4195, 1998
- [6] Kong J, Zhou C, Yenilmez E and Dai H, *Appl. Phys.*

- Lett., 77, 3977, 2000
- [7] Chen B, Li B and Chen L, Appl. Phys. Lett., 93, 043104, 2008
- [8] Kim B H, Park T H, Baek T H, Lee D S, Park S J, Kim J S and Park Y W, J. Appl. Phys., 103, 096103, 2008
- [9] Kim K K et al, J. Am. Chem. Soc., 130, 12757, 2008
- [10] Kong B-S, Jung D-H, Oh S-K, Han C-S and Jung H-T, J. Phys. Chem. C, 111, 8377, 2007
- [11] Choi H C, Shim M, Bangsaruntip S, and Dai H, J. Am. Chem. Soc., 124, 9058, 2002
- [12] Sankapal B R, Setyowati K and Chen J, Appl. Phys. Lett., 91, 173103, 2007
- [13] Nascimento G M, Hou T, Kim Y A, Muramatsu H, Hayashi T, Endo M, Akuzawa N and Dresselhaus M S, Nano Lett., 8, 4168, 2008
- [14] Graupner R, Abraham J, Vencelova A, Seyller T, Hennrich F, Kappes M M, Hirsch A and Ley L, Phys. Chem. Chem. Phys., 5, 5472, 2003
- [15] Shin D-W, Lee J H, Kim Y-H, Yu S M, Park S-Y, and Yoo J-B, Nanotechnology, 20, 475703, 2009
- [16] Shin J-H, Shin D W, Patole S P, Lee J H, Park S M and Yoo J B, J. Phys. D: Appl. Phys., 42, 045305, 2009
- [17] Lee J H, Shin D W, Makotchenko V G, Nazarov A S, Fedorov V E, Kim Y H, Choi J-Y, Kim J M and Yoo J B, Adv. Mater. 21, 4383, 2009
- [18] Rao A M, Richter E, Bandow S, Chase B and Eklund P C, Science, 275, 187, 1997