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Stable p-type properties of single walled carbon nanotubes with an electrochemical doping

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We report a high stable p-type doping for single walled carbon nanotubes by an electrochemical method. The Raman spectroscopy showed the upshift of G-band when the applied potential increased. Furthermore, carbon core level shifted as much as 0.14 eV in binding energy of XPS measurement, which is an evidence of p-type doping with Fermi level change. The highly doped SWCNTs at applied potential of 1.5 V during electrochemical doping process showed the long time stability as long as 28 days.

Carbon nanotubes (CNTs) have been one of the most commonly mentioned nanomaterials for various applications due to their unique electronic, mechanical, and chemical properties and their tubular structures [1, 2]. The understanding of the doping, injection of charge carriers, into single walled carbon nanotubes (SWCNTs) is important for their application in electronic devices. Electrochemical and chemical doping of carbon nanotubes have been studied to achieve an electronic modulation by many researchers [3-7]. Doping stability, however, has still been a problem to resolve for application in electronic devices [8]. Among several doping techniques, the electrochemical method can allow a precise and well-controlled doping into carbon nanostructures. Recently, a few electrochemical studies of SWCNTs appeared, which confirmed importance of electrochemistry to evaluate the electronic structure of SWCNTs [9,10]. Here, we report on p-type SWCNTs with the ClO_4^- doping for the good electrical properties of SWCNTs using an electrochemical technique.

Highly purified SWCNTs synthesized by the arc discharge method, purchased from Hanwha Nanotech Co., Ltd., were used in this work. The carbon purity estimated by the thermogravimetrical analysis (TGA) of the nanotube material was 93 wt.%. To prepare homogeneous thin SWCNTs films, SWCNTs of 1 mg were added in 50 mL of Dichlorobenzene followed by sonication in a bath type sonicator (Vibra Cell, Sonics) for 20 min at 450 W. This solution was centrifuged (Hanil Science Industrial Co., Ltd., Mega 17R) at 20000 g for 20 min. The SWCNTs films for a working electrode have been prepared by automatic spray coating system on a PET substrate (2 × 2 cm^2) for the electrochemical redox reaction in electrolyte solution. In general, the core of the experimental setup used in electrochemical doping is the typical 3-electrode electrochemical cell. The components of the cell include a working electrode, an auxiliary, or counter electrode, and a reference electrode all submerged in electrolyte solution. Electrochemical experiment was carried out using WPG potentiostats with Pt counter electrode and Ag/AgCl reference electrode. The electrochemical cell was equipped with a common glass beaker. The electrochemical doping was carried out in a 0.1 M $LiClO_4$/Acetonitrile solution, and the amount of adsorption of the ClO_4^- for the doping was controlled using an electric potential between the reference and the working electrode. The applied potential varied from 0.5 V to 1.5 V for 5 min, respectively, and ClO_4^- ions are simultaneously doped on the wall of SWCNTs. The films were rinsed in DI-water and outgassed at 80 °C in a vacuum oven after the electrochemical doping in a solution. The electronic structure was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS spectrometer, VG Scientifics). Raman spectra of the SWCNTs films were measured for excitation of 514.5 nm at room temperature using a Jobin-Yvon HR800UV spectrometer. The peak shift and the intensity change of G-band due to charge transfer were measured as the applied potential increases. Sheet resistance was measured to evaluate the conductivity variation after the doping, and the stability of a highly doped sample was tested for 28 days.

Figure 1(a) shows representative C 1s spectra for SWCNTs doped with increasing potentials. Detailed analysis of the XPS spectra provides clear evidence that the SWCNTs have been chemically modified.

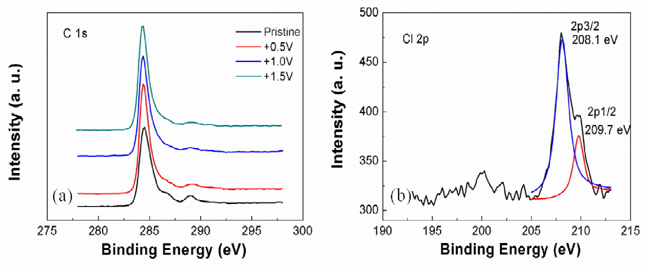

Figure 1. XPS C 1s spectra of SWCNTs doped with ClO4⁻ ion at various potentials (a) and Cl 2p spectra of SWCNTs doped at 1.5 V (b).

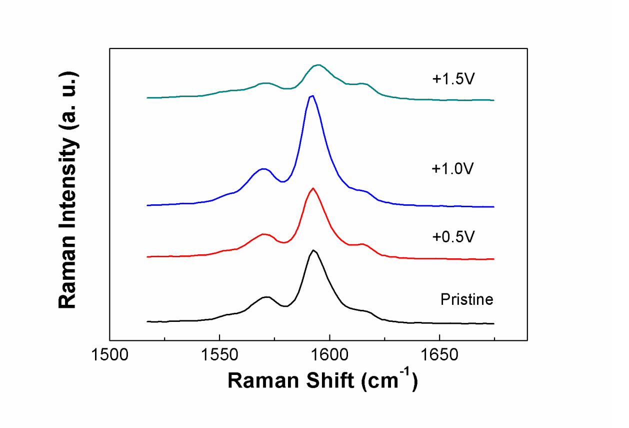

Figure 2. Raman spectra of SWCNTs doped with ClO4$^-$ ion according to increasing potential.

The peak position at 284.7 eV for the pristine SWCNTs without immersing in electrolyte (0.0 V) is very close to the value for the pure sp^2 C-C bonding in the pristine highly oriented pyrolytic graphite (HOPG), indicating that carbon atoms are almost exclusively sp^2 hybridized in non-doped CNTs [11]. The downshift of carbon core level of 0.14 eV in the binding energy for SWCNTs doped at 1.5 V evidences the p-type doping with the Fermi level change as ClO_4^- ion concentration increases [12, 13]. The chlorine Cl 2p core level spectrum in SWCNTs doped at 1.5 V, depicted in Figure 1(b), reveals two inequivalent chlorine sites. The core level binding energies appear as doublets associated with 3/2 and 1/2 levels, which are separated by 1.6 eV due to spin-orbit coupling. The more intense Cl 2p component with a core level binding energy of 209.7 eV is typical chlorine participating in organic C-Cl bonds. The less intense component with a lower binding energy of 208.1 eV can be assigned to chloride ions which are ionically bonded to the nanotube surface [12, 14].

Raman spectroscopy results for SWCNTs shown in Figure 2 provide further evidence for chemical modification of the nanotubes with the increasing concentration of ClO_4^-. The G band of the pristine SWCNTs appeared at 1594 cm^{-1} and shows the G-band splitting in both of pristine and doped samples. The G-band corresponds to Raman active optical phonons at the Γ-point. Two dominant peaks (G+~1594 cm^{-1} and G– ~ 1560 cm^{-1}) are usually shown in SWCNTs [15]. In semiconducting SWCNTs, the G+ mode corresponds to a longitudinal optical (LO), and the G– mode, asymmetry on the low frequency side of the G band at 1560 cm^{-1}, corresponds to a transverse optical (TO) phonon. This asymmetry is related to the interaction of phonon excitations with the continuum electronic excitations and is called the Breit-Wigner-Fano (BWF) resonance. This effect is characteristic of metallic systems and therefore commonly attributed to metallic tubes [16]. The G+ mode at ~1594 cm^{-1} is due to displacements along the tube axis and its frequency G+ is sensitive to charge transfer from dopant additions to SWCNTs, and the diameter-dependent G- mode at ~ 1560 cm^{-1} is due to displacements along the tube circumference [15]. The peak positions of the G-band were shifted appreciably at a high doping concentration of Cl up to 3.2 at. % and were shifted to higher energy regions markedly by about 2.56 cm^{-1} at a high concentration. This shift, which is indicative of an electron transfer from carbon to the adsorbate, is consistent with the previous report of the phonon stiffening effect by p-type doping [7,17].

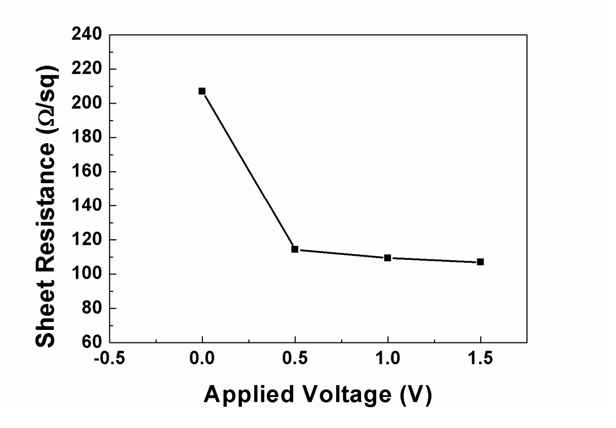

Figure 3. Sheet Resistance of SWCNTs doped with ClO4$^-$ ion according to increasing potential.

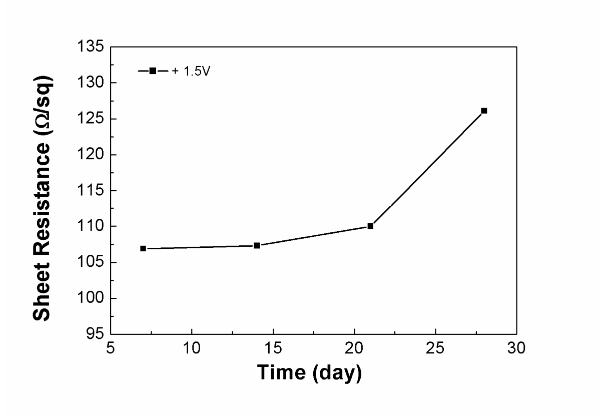

Figure 4. Doping stability of SWCNTs doped at 1.5 V after room-temperature exposing in air ambient.

Figure 3 shows the results of sheet resistance after electrochemical doping. We have repeated a doping/rinsing process according to the applied voltage. Then, resistance measurements were easily repeated for each sample. For the doping mechanism, we suggest that the generated holes through the electrochemical reaction were able to increase the conductivity of SWCNTs as shown in figure 3. Sheet resistance of SWCNTs dropped to 106.6 • /sq after the doping at 1.5 V from 206.5 • /sq of pristine sample. Notably, charge transfer to nanotubes was occurred. As applied voltages increased, the doping contents of ClO_4^- ions on the SWCNT films also increased, which induces the decrease of sheet resistance. However, the doping effect of adsorption was restricted because SWCNTs has two dimensional structures. This means that charge transfer is restricted because the amount of chemical bonding decreases with the increasing voltage over 1.0 V, which leads to the behaviors of saturation of resistance.

We have examined the doping stability after one month exposure to air because the actual operation requires a device working of doped SWCNTs films in air environment. Figure 4 shows the effects of the electrochemical doping with ClO_4^- on the electrical stability versus open air exposure time. As a comparison, the SWCNTs film after the doping at 1.5 V showed a sheet resistance increase of 20 % after being exposed to open air for 28 days. The resistance change of the SWCNTs film has been proven to be highly stable even though the conductivity depends on perchlorate intercalations within the network. We achieved the long time stability of doping into nanotubes compared to the recent work, 25 % increase of resistance for 300 h by *Chen et al.* [8]. In our method, the long time stability

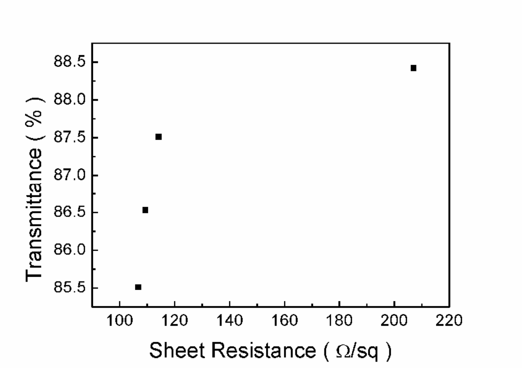

Figure 5. Plot of transmittance (% T at 1000 nm) versus sheet resistance of undoped (207・/sq), and ClO_4^- doped SWCNT films.

means that the bonding between ClO_4^- ions and SWCNTs is very strong, and most of the bondings are chemical adsorption. And then, some of chemical bonds are broken at some part, which make the resistance increase. Therefore, it showed the non-linear increase in Figure 4.

Figure 5 shows a plot of transmittance (% T at 1000 nm) versus sheet resistance for the undoped (207・/sq) and doped films. Like a reported tendency,[18] the resistance decreases with decreasing transparency. S22 (% T at 1000 nm) peaks correspond to the second set of Van Hove singularities in semiconducting SWCNTs. An electron is transferred from the SWCNTs. The decrease of the transmittance and the depletion of electrons from the valence band as ClO_4^- ions are adsorbed mean strong evidence of charge-transfer doping.

Conclusions

We have conducted the ClO_4^- doping into SWCNTs by an electrochemical method. The charge transfer to nanotubes was clearly shown from the red/blue shift in XPS and Raman spectroscopy. The sheet resistance of SWCNTs was decreased as the applied potential increases, and the sheet resistance of SWCNTs doped at 1.5 V showed a remarkable reduction of 50 %. The SWCNTs film after the doping at 1.5 V showed a resistance increase of 20% after being exposed to open air for 28 days. We achieved the long time stability of doping into nanotubes.

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1. P. G. Collins, M. S. Arnold, and P. Avouris, *Science*, 2001, **292**,706.
2. M. R. Falvo, G. J. Clary, R. M. Taylor, V. Chi, F. P. Brooks, S. Washburn, and R. Superfine, *Nature,* 1997, **389**, 582.
3. M. Kalbac, H. Farhat, L. Kavan, J. Kong, K.-I. Sasaki, R. Saito, and M. S. Dresselhaus, *ACS Nano*, 2009, **3**, 706.
4. P. M. Rafailov, C. Thomsen, U. Dettlaff-Weglikowska, and S. Roth, *J. Phys. Chem. B*, 2008, **112**, 5368.
5. S. M. Kim, Y. W. Jo, K. K. Kim, D. L. Duong, H.-J. Shin, J. H. Han, J.-Y. Choi, J. Kong, and Y. H. Lee, *ACS Nano*, 2010, **4**, 6998.
6. K. K. Kim, et al., *J. Ame. Chem. Soc.*, 2008, **130**, 12757.
7. J. Tarabek, L. Kavan, L. Dunsch, and M. Kalbac, *J. Phys. Chem. C*, 2008, **112**, 13856.
8. I. W. P. Chen, L. Richard, Z. Haibo, W. Ben, and Z. Chuck, *Nanotechnology*, 2011, **22**, 485708.
9. L. Kavan and L. Dunsch, *Chem. Phys. Chem.*, 2007, **8**, 974.
10. P. Corio, A. Jorio, N. Demir, and M. S. Dresselhaus, *Chem. Phys. Lett.*, 2004, **392**, 396.
11. S. Maldonado, S. Morin, and K. J. Stevenson, *Carbon*, 2006, **44**, 1429.
12. U. Dettlaff-Weglikowska, et al., *J. Ame. Chem. Soc.*, 2005, **127**, 5125.
13. T. Nagata, et al., *Appl. Phys. Lett.*, 2011, **98**, 232107.
14. İ. Becerık, Ş. Süzer, and F. Kadirgan, J. Electroanal. Chem., 2001, **502**, 118.
15. M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, *Phys. Rep.*, 2005, **409**, 47.
16. S. D. M. Brown, A. Jorio, P. Corio, M. S. Dresselhaus, G. Dresselhaus, R. Saito, and K. Kneipp, *Phys. Rev. B*, 2001, **63**, 155414.
17. A. M. Rao, P. C. Eklund, S. Bandow, A. Thess, and R. E. Smalley, *Nature*, 1997, **388**, 257.
18. B. Chandra, A. Afzali, N. Khare, M. M. El-Ashry, and G. S. Tulevski, *Chem. Materials*, 2010, **22**, 5179.