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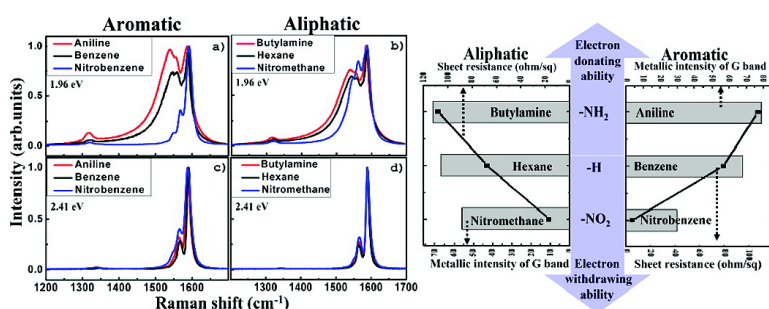
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Tailoring Electronic Structures of Carbon Nanotubes by Solvent with Electron-Donating and -Withdrawing Groups

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Abstract: Various electron-donating and -withdrawing groups in aromatic and aliphatic backbones of solvent have been introduced to tailor the electronic structures of single-walled carbon nanotubes (SWCNTs). In the case of solvent with a withdrawing group, electrons were extracted mainly from metallic SWCNTs, whereas small charge transfer was also observed in semiconducting SWCNTs. On the other hand, in the case of solvent with a donating group, electrons were donated to both metallic and semiconducting SWCNTs. This effect was less prominent in solvent with an aliphatic backbone than that with an aromatic backbone. The strong correlation between the sheet resistance and electronic structures of nanotubes is further discussed in conjunction with a modulation of Schottky barrier height.

Introduction

Various dispersants and solvents have been used to disperse carbon nanotubes. However, this often involves serious modification of their electronic structures.[1,2] For example, sodium dodecyl sulfate (SDS) and polythiophene are good dispersants, but they also modify the electronic structures.[3,4] Despite this, there have been few studies on the effect of the solvent on the electronic structures of carbon nanotubes. In general, donating and withdrawing groups in a π-system of the solvent are well-known (see the Supporting Information S1).[5] The presence of functional groups might induce a permanent or induced dipole moment in a molecular solvent. This presumably involves charge transfer between the adsorbates and carbon nanotubes, which modifies the electronic structures of carbon nanotubes. Furthermore, the effect of functional groups in the solvent has often been disguised by the use of dispersants. In order to tailor the electronic structures of carbon nanotubes to a desired direction, it is necessary to determine the effect of the solvent exclusively without dispersants.

Various electron-donating and -withdrawing groups in solvents with various aromatic and aliphatic backbones were

introduced in an attempt to tailor the electronic structures of single-walled carbon nanotubes (SWCNTs). In the case of a solvent with a withdrawing group, the electrons were extracted mainly from metallic SWCNTs, whereas a small amount of charge transfer has also been observed in semiconducting SWCNTs. On the other hand, in the case of a solvent with a donating group, the electrons are donated to both metallic and semiconducting SWCNTs. This effect is less prominent in a solvent with an aliphatic backbone than that with an aromatic backbone. The change of the sheet resistance of the SWCNT film under various solvent treatments was explained by the modulation of Schottky barrier height at the junction between metallic and semiconducting carbon nanotubes that resulted from the modification of electronic structures of nanotube networks by solvent.

Sample Preparation and Experimental Methods

The SWCNTs were synthesized by arc discharge and purchased from Iljin Nanotech Co. Ltd. The diameters of SWCNTs ranged around 1.4–1.6 nm determined from Raman spectra with several excitation energies. The sample contained 3.54 wt % of metal impurity, which was determined from thermogravimetric method. One milligram of the SWCNTs was immersed in 10 mL of each solvent (Aldrich) and sonicated in a bath type sonicator (Bandelin Electronic GMBH & CO.KG, Sonorex Super: RK106) for 10 h. This solution was further filtered through an anodisc filter (Anodisc 47, Whatman) with a pore size of 0.1 μm to form a bucky paper. The CNTs film was dried at room temperature for 24 h. The sheet resistance at room temperature was measured using a four-point probe method (ChangMin, LTD, CMT-SR2000N). The CNT films were characterized by micro-Raman spectroscopy (Renishaw RM1000-Invia). Two excitation energies of 2.41 eV (514 nm, Ar+ ion laser) and 1.96 eV (632.8 nm, He–Ne laser) with a Rayleigh line rejection filter, which accepts a spectral range of

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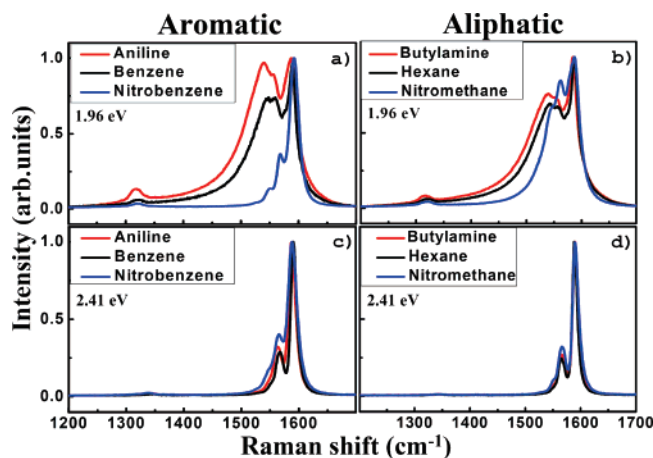
Figure 1. G-band of the Raman spectra for the samples treated in aromatic (a and c) and aliphatic (b and d) solvents with various functional groups backbone at an excitation energy of 1.96 eV (a,b) and 2.41 eV (c,d).

$50-3200$ cm^{-1}, were used in this study. XPS analysis (Quantum 2000, Physical electronics) using a focused monochromatized Al Kα radiation (1486.6 eV) was carried out to check for the presence of residual material and the degree of doping effect.

Results and Discussion

The interaction of solvent with carbon nanotubes relies on both its backbone and functional groups. In this study, solvents with two backbones were chosen: aromatic and aliphatic. Various functional groups in each backbone of solvent were selected according to their electron-donating and electron-withdrawing ability (see the Supporting Information S2). Figure 1 shows the typical G-band of Raman spectra for SWCNTs treated with solvents containing representative functional groups. At an excitation energy of 1.96 eV, the metallic SWCNTs (E_{11}^M) were mostly excited in reference solvent (benzene), as demonstrated by the presence of a large Breit−Wigner−Fano (BWF) line at the lower energy side of the G-band in Figure 1a,b.[6,7] A small portion of the semiconducting nanotubes (E_{33}^S) was also confirmed by the radial breathing mode (RBM) in the Raman spectra (see the Supporting Information S3). In the case of the aromatic backbone (Figure 1a), more BWF components at the lower energy side had developed in electron-donating aniline, compared with benzene. On the other hand, the BWF component was significantly lower in the electron-withdrawing nitrobenzene. The trend of these changes in the aromatic backbone was similar to that in the aliphatic backbone, as shown in Figure 1b. However, the BWF component was changed less prominently in the aliphatic backbone than in the aromatic backbone. This trend of the changes in the aromatic and aliphatic backbones was similar in the other types of solvents used in this study (see the Supporting Information S4). At an excitation energy of 2.41 eV, the semiconducting SWCNTs (E_{33}^S) were excited exclusively (see the Supporting Information S3). In contrast to the Raman spectra at 1.96 eV, there was no significant change in the peak observed in this case, independently of the aliphatic/aromatic backbone and electron-donating/withdrawing group, as shown in Figure 1c,d. This suggests that

the semiconducting nanotubes are relatively inert to solvent treatments, particularly in those with an aliphatic backbone.

Abundant information can be extracted by deconvoluting the G-band into six components: one metallic, one metallic BWF, and four semiconducting components.[6] In the case of the aromatic backbone, the shaded area of the metallic component that appeared at an excitation of 1.96 eV increased to 79% in aniline, and decreased to 30% in nitrobenzene compared with the reference (benzene, 68%) (Figure 2a−c). It should be noted that the metallic BWF component was completely removed in nitrobenzene. In the case of the aliphatic backbone, the metallic component was increased to 71% in butylamine, which revealed a negligible change in nitromethane from the reference (hexane, 67%) (Figure 2d−f). The increase/decrease in the metallic component in the G-band can be attributed to the donation/ withdrawal of electrons to metallic carbon nanotubes from the solvent. Although solvents maintain the general rule of the changes according to their electron-donating/withdrawing ability, as listed in S1, the effect of the solvent is less significant in a solvent with an aliphatic backbone than with an aromatic backbone. This difference between aromatic and aliphatic backbones originates from the interaction between SWCNTs and the adsorbates. The presence of an aromatic backbone in a solvent usually enhances the π-stacking interactions between the hexagons in the backbone and nanotubes, whereas the aliphatic chain interacts relatively weakly with nanotubes through their hydrophobic nature. Therefore, the effect of charge transfer in a solvent with an aliphatic backbone is expected to be weaker than the solvent with an aromatic backbone. It should be emphasized that the effect of the solvent on the CNTs is less significant in semiconducting CNTs than in metallic ones.

Some peak shift in the G$^+$-band has been observed in solvents with an aromatic backbone. The upshift by 2 cm^{-1} in nitrobenzene with respect to the reference (benzene) at 1.96 eV is evidence of charge transfer from the CNTs to electron-withdrawing nitrobenzene, whereas the downshift in aniline (Figure 2g) at 2.41 eV contributes to the charge transfer from electron-donating aniline to CNTs. Nevertheless, this trend becomes ambiguous in some cases, particularly in a solvent with an aliphatic backbone (see Table 1). The change in charge transfer was negligible. This concurs with the previous report that intentional doping invoked by charge transfer resulted in a downshift (donor) and upshift (acceptor) of the G-band.[8,9] This suggests that (i) the electron-donating/withdrawing ability determines the amount of charge transfer to metallic nanotubes selectively, without a significant change in the semiconducting nanotubes, and (ii) this effect is less significant in a solvent with an aliphatic backbone due to their weak hydrophobic interaction. More solvents with various aliphatic and aromatic backbones were tested (see the Supporting Information S2). From this point of view, the peak shift in the G$^+$-band effect of charge transfer is less effective than the metallic component of G-band. Therefore, it may not be a good measure of the changes induced by the solvent.

Charge transfer from nanotubes to adsorbates (or vice versa) creates holes (electrons) in the CNT, resulting in the formation of acceptor (donor) levels. This induces a downshift (upshift)

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Aromatic

Aliphatic
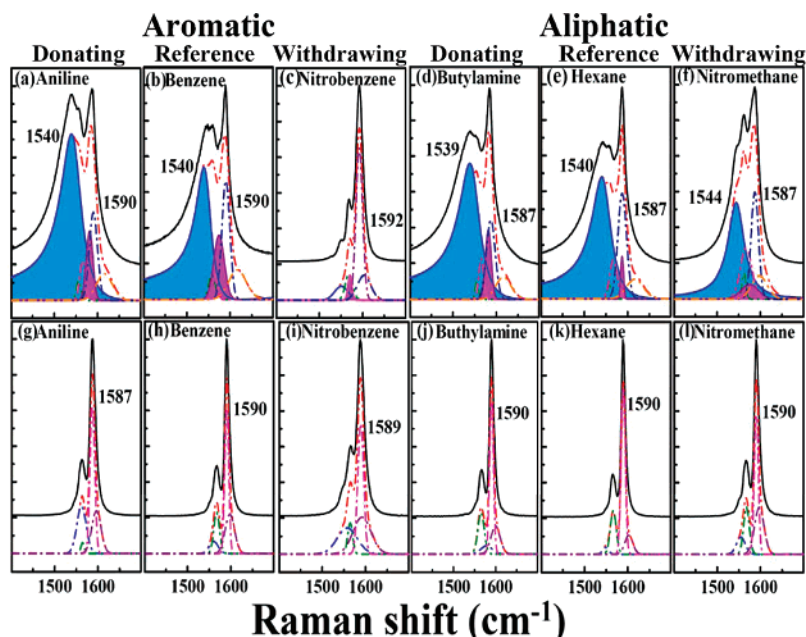
Figure 2. Deconvolution of the G-band into one metallic (shaded area in pink), metallic BWF (shaded area in blue), and four semiconducting (open area) components at an excitation energy of 1.96 eV (upper panel) and 2.41 eV (lower panel). The values on the top-left (bottom-right) in the upper panel indicate the peak positions of the BWF line (G^+ line). The values in the lower panel are the peak positions of semiconducting G^+ line.

Table 1. Various Parameters of the Sheet Resistance (R), G^+ Peak Position in cm^{-1}, BWF, and Metallic Portions (M_{area}) at an Excitation Energy of 1.96 eV, G^+ Peak Position at 2.41 eV Obtained after Deconvoluting the G-Band of the Raman Spectra, the Areal Ratio of sp^3/sp^2 and the Peak Position in the C1s XPS

| backbone | chemical | R, Ω/sq | E_{laser} = 1.96 eV | | | E_{laser} = 2.41 eV | XPS | |
			G^+	BWF_{area} (1545), %	M_{area} (1577), %	G^+	sp^3/sp^2	C1s
aromatic	aniline (D)	109	1590	72	7	1587	0.26	285.1
	benzene (R)	79	1590	57	11	1590	0.30	285.0
	nitrobenzene (W)	5	1592	0	30	1589	0.43	284.8
aliphatic	butylamine (D)	108	1587	65	6	1590	0.33	285.0
	hexane (R)	68	1587	65	2	1590	0.36	285.0
	nitromethane (W)	17	1587	60	6	1590	0.44	285.0

in the Fermi level.[10,11] This shift in the Fermi level can be observed in the C1s XPS peak. The C1s peak is decomposed into four components, which are identified by sp^2 and sp^3 hybridization, the related carbon oxide, and a $\pi-\pi^*$ plasmon satellite peak (Figure 3).[12] In the case of the aromatic backbone, the Fermi level, which is represented by the main sp^2 peak position, was downshifted (upshifted) by 0.2 eV (0.1 eV) in electron-withdrawing nitrobenzene (electron-donating aniline). However, in the case of the aliphatic backbone, this shift was relatively independent of the electron-donating/withdrawing groups, as listed in Table 1, which is similar to the G^+-band in the Raman spectra.

XPS indicated some correlation with the other properties in the sp^3/sp^2 ratio. The sp^3 represents the presence of defects (D-band in Raman), and sp^2 represents the formation of graphitic carbon (G-band in Raman).[13] Therefore, the areal ratio indicates a measure of the defects formed during treatment. In the case

of the aromatic backbone, the electron-withdrawing nitrobenzene created more defects than the electron-donating aniline. A similar phenomenon was observed in the case of the aliphatic backbone. The generation of D-band strongly suggests that the electron-withdrawing group interacts with the CNTs more strongly than the electron-donating group. This trend may originate from the dominant field effect in the electron-withdrawing group in which the disorder generated by the adsorbate is rather localized at the interacting site, which is in contrast with the resonance effect, in which the disturbed electrons are delocalized instead of creating defects.[5] The difference between the electron-donating and -withdrawing groups was less prominent in the aliphatic backbone (see the Supporting Information S2), which is similar to that observed by Raman spectroscopy.

The sheet resistance of the CNT film was measured in order to further understand the solvent effect on nanotubes (Figure 4). The sheet resistance increased in the donating group, whereas it decreased in the withdrawing group, independent of the backbone. The sheet resistance strongly correlated with the metallic portion of nanotubes that was extracted from the deconvolution of the G-band (see Table 1). Similar trends were observed for the other types of functional groups (see the Supporting Information S5).

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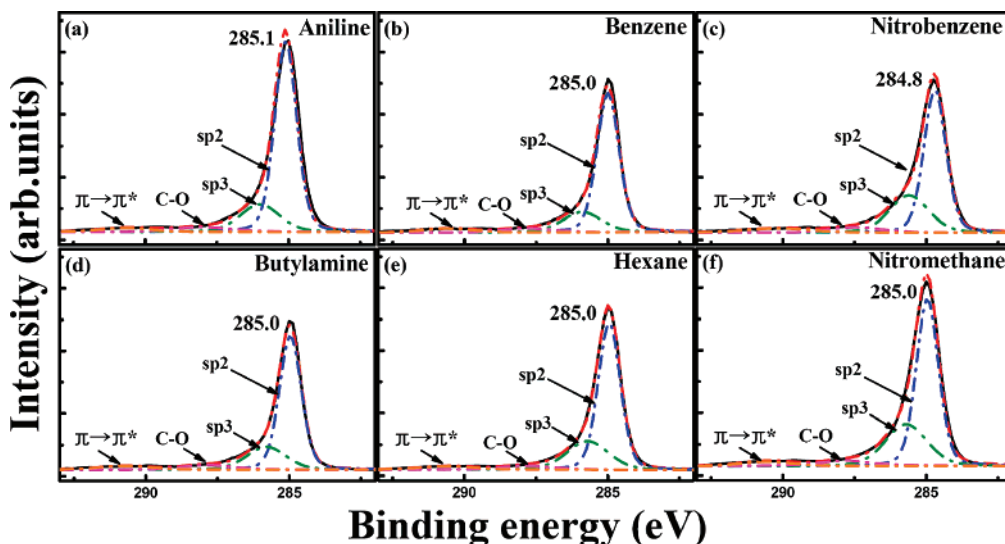
Figure 3. The C1s peak is composed of C=C(sp2), C−C(sp3), C−O, and $\pi-\pi^*$ character. The C1s peak position and its sp3/sp2 ratio were listed in Table 1.
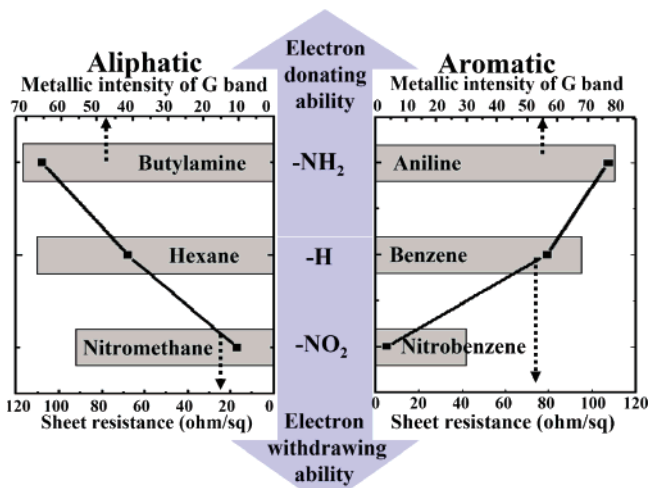

Figure 4. The relationship between the metallic component of the G band intensity and the sheet resistance for electron-donating and electron-withdrawing groups on the aliphatic and aromatic solvents.

Since the film is composed of randomly oriented SWCNT networks, the conduction through these networks can be understood as follows. The sheet resistance of the film is a sum of the resistance of the intrinsic SWCNTs and the junction resistance between nanotubes.[14] Nanotubes in ambient conditions usually show a *p*-type behavior due to the presence of oxidating adsorbates.[15] The influence of these adsorbates from the reference solvent, such as hexane and benzene, may be negligible or at least not appreciable compared with the influence

from strong donating and withdrawing groups. Therefore, it is reasonable to assume that the intrinsic SWCNTs still remain in the *p*-doped state similar to the reference. The work function is typically 4.5−5 eV for metallic SWCNT, and 4.8−5.3 eV for semiconducting SWCNT with a diameter ranging from 1−2 nm.[16]

Figure 5 shows a schematic diagram of the junction between the metal and lightly *p*-doped semiconducting SWCNTs, where the Schottky barrier (E_{Sb}) is formed at the junction. When this nanotube is exposed to a solvent with an electron-donating group, extra electrons are provided to the semiconducting SWCNT. This compensates for the *p*-doping effect, i.e., dedoping effect. This will recover an intrinsic level or a conversion to *n*-doping in a solvent with a highly donating functional group. In this case, the Schottky barrier height is increased. The number of hole carriers was reduced with dedoping, which increases the resistance of the intrinsic SWCNTs. Since the film resistance is governed by the exponential dependence of the Schottky barrier height,[17−19] the Schottky barrier height plays an important role in increasing the sheet resistance. In the case of a solvent with electron-withdrawing groups, more holes are generated in semiconducting SWCNTs, which reduce the sheet resistance, and the Fermi level is shifted toward the valence band. In this case, electrons are also extracted from the metallic ones and a pseudo band gap is opened, as shown in Figure 5c. This phenomenon is similar to the diazonium effect.[20] Although this increases the resistance of the intrinsic SWCNTs, the Schottky barrier height is lowered compared with the reference. As a consequence, the sheet resistance is decreased.
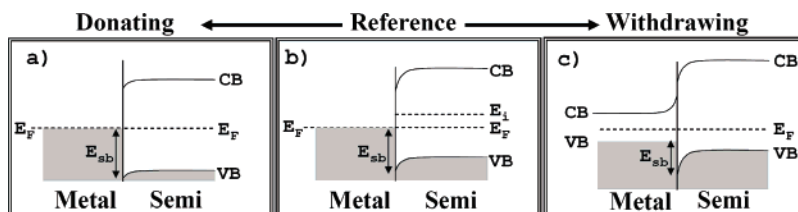
Figure 5. Schematic diagram of junction formation between the metallic and semiconducting nanotubes in the solvent with (a) donating group, (b) reference group, and (c) withdrawing group. The CB, VB, E_i, E_F, and E_{sb} indicate the conduction band, valence band, intrinsic Fermi level, Fermi level after treatment, and Schottky barrier, respectively.

Conclusions

These results present the first experimental demonstration that the electronic structures of SWCNTs can be modified by a solvent treatment. The electronic structures of the SWCNTs can be tailored systematically through the choice of the backbones of solvent molecule and electron-donating and -withdrawing groups. This effect is more obvious with the aromatic backbone than with the aliphatic backbone. An efficient way of modifying the electronic structures of CNTs with various dispersants or adsorbates can be realized by the appropriate choice of solvent. For example, one could achieve *p*-type doping by choosing electron-withdrawing dispersants or adsorbates in an electron-withdrawing solvent with an aromatic backbone.

Supporting Information Available: Experimental procedures, Tables S1 and S2, and Figures S3–S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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