

## Dispersion Stability of Single-Walled Carbon Nanotubes Using Nafion in Bisolvent

Jin-Hyon Lee,<sup>†</sup> Ungyu Paik,<sup>\*,†</sup> Jae-Young Choi,<sup>\*,‡</sup> Ki Kang Kim,<sup>§</sup> Seon-Mi Yoon,<sup>‡</sup> Jeonghee Lee,<sup>‡</sup> Byung-Ki Kim,<sup>‡</sup> Jong Min Kim,<sup>‡</sup> Min Ho Park,<sup>||</sup> Cheol Woong Yang,<sup>||</sup> Kay Hyeok An,<sup>§</sup> and Young Hee Lee<sup>\*,§</sup>

*Division of Advanced Materials Science Engineering, Hanyang University, Seoul 133-791, R. O. Korea, Materials Center, Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, R. O. Korea, School of Advanced Materials and Engineering, Sungkyunkwan University, Suwon 440-746, R. O. Korea, and the BK21 Physics Division, Institute of Basic Sciences, Carbon Nanotube Research Laboratory, Center for Nanotubes and Nanostructured Composites, Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, R. O. Korea*

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We have investigated the effect of Nafion and its resulting interaction with single-walled carbon nanotubes (SWCNTs) on the solubility and dispersion properties of SWCNTs in bisolvent. Nafion was used as a polymeric dispersant, providing both electrostatic and steric stabilization in the preparation of a stable and homogeneous suspension of SWCNTs. A correlation was made between solubility and nanodispersion of SWCNTs. Optical spectroscopy showed that the solubility and nanodispersion of SWCNTs increased with the addition of 1-propanol and were greatest at a volume mixture of water/1-propanol of 80/20. We propose a mechanism of improved solubility and nanodispersion of SWCNTs, which is strongly correlated with the adsorption behavior of Nafion on SWCNTs, the surface potential of SWCNTs, and the solubility of Nafion in a liquid medium; amphiphilic Nafion enhances the dispersion of SWCNTs in the mixture of hydrophilic water and relatively hydrophobic 1-propanol.

## Introduction

Carbon nanotubes (CNTs) have been known to exhibit multifunctional properties with superb mechanical strength, high electrical conductivity, and excellent chemical stability.<sup>1</sup> However, their use in practical applications has been impeded by their poor solubility and dispersibility,<sup>2</sup> which have been bottlenecks from a scientific and technological point of view. It is well-known that single-walled carbon nanotubes (SWCNTs) are easily entangled from substantial van der Waals attraction between tubes to form an agglomeration.<sup>3</sup> This agglomeration is barely breakable with conventional physical approaches such as sonication and ball mixing, and the solubility in various solvents is thus expected to be poor. The dispersion of CNTs can be classified into solubilization, where they can be bundled but dissolved in the solvent, and nanodispersion where CNTs are individually dissolved in the solvent. Excellent information on the electronic structure can be extracted through nanodispersion of SWCNTs from optical absorption and fluorescence spectra.<sup>4–6</sup> Nanodispersion is necessary to fabricate individual nanotube transistors.<sup>7</sup> Therefore, nanodispersion is recognized as an important first step toward various potential applications and an indispensable scientific goal for practical applications.

To prepare stable and homogeneous dispersions of carbon nanotubes, several challenges have been suggested through the covalent<sup>8,9</sup> and noncovalent functionalization<sup>10,11</sup> of SWCNTs. The covalent functionalization deteriorates the unique electronic

properties of SWCNTs by the formation of new covalent bonds on the CNT walls.<sup>12</sup> To overcome this disadvantage of covalent modification, noncovalent functionalization mainly based on the physical adsorption of polymers and surfactants was developed. It is well-known that noncovalent functionalization such as surface wrapping of SWCNTs with polymeric chains<sup>10,11</sup> and surface coatings using low molecular surfactants<sup>13</sup> have been shown to be useful for improving solubility and dispersibility without degradation of physical properties. Among various surfactants investigated, sodium dodecylbenzene sulfonate (NaDDBS) is the most commonly used and effective surfactant in water due to the presence of hydrophobic alkyl interaction and  $\pi$ – $\pi$  interaction between NaDDBS and SWCNTs, as well as the electrostatic charging of SWCNTs by sulfonic acid.<sup>14</sup>

In order to achieve better stabilization by wrapping SWCNTs with polymeric chains, the hydrophobic backbone of the polymer or surfactant should be strongly anchored to the hydrophobic nanotube surface with a polymer layer of sufficient thickness, while the hydrophilic parts should be fully ionized to impart sufficient ionic charge to the SWCNT surfaces. For this reason, various polymeric dispersants such as PmPV,<sup>11</sup> starch,<sup>15</sup> and peptide<sup>16</sup> have been used to improve the dispersion stability of SWCNTs by surface wrapping. However, since the backbone of these polymeric dispersants mainly consists of alkyl chains, the interaction energy between the backbone in the polymeric dispersant and the SWCNTs is not sufficient to disperse hydrophobic SWCNTs via hydrophobic interaction. Therefore, it is necessary to improve the interaction energy to achieve better dispersion stability. Fluorinated surfactants, where hydrogen atoms are replaced by fluorine atoms, exhibit higher hydrophobicity compared to hydrocarbon-based surfactants.<sup>17,18</sup> In addition to considering this interaction energy, better stabilization

\* Corresponding authors' e-mail: (U.P.) upaik@hanyang.ac.kr; (J.-Y.C.) jaeyoung88.choi@samsung.com; (Y.H.L.) leeyoung@skku.edu.

<sup>†</sup> Hanyang University.

<sup>‡</sup> SAIT.

<sup>§</sup> BK21 Physics Division, Sungkyunkwan University.

<sup>||</sup> School of Advanced Materials Engineering, Sungkyunkwan University.

of SWCNTs requires additional hydrophilic groups in the tail to be substituted in order to impart ionic charge to the SWCNTs. Some of the most common hydrophilic groups are  $-\text{OH}^-$ ,  $-\text{COO}^-$ ,  $-\text{SO}_3^-$ ,  $-\text{OSO}_3^-$ ,  $-\text{NH}_2^-$ ,  $\text{NH}_4^+$ . Among these groups, sulfonic acid is easily and highly ionized in contact with water.

In this research, Nafion was introduced as a dispersant for the SWCNTs, which is a very good surfactant candidate to meet the aforementioned requirements of polymeric dispersant for hydrophobic SWCNTs. Similar to other polymers which have been used to disperse SWCNTs through noncovalent functionalization,<sup>19</sup> Nafion consists of polar sulfonic acid-terminated perfluorovinyl ether pendants that are regularly spaced along the hydrophobic perfluoroalkyl backbone.<sup>20,21</sup> It was recently discovered that Nafion disperses SWCNTs by protonation, similar to sulfuric acid.<sup>22</sup> However, in this case, commercial Nafion was used without any dilution in order to disperse SWCNTs by protonation. Furthermore, in most previous investigations, the interaction among SWCNTs, Nafion, and the liquid medium was seldom considered from the dispersion point of view; that is, a certain amount of CNTs was simply added to a commercial 5 wt % Nafion solution<sup>22–24</sup> or 1 wt % Nafion solution dissolved in absolute ethanol or a mixture of ethanol and 50 mM phosphate buffer of pH 7.0.<sup>25</sup> It has been reported that in an aqueous medium, Nafion has an intrinsic aggregate about 150 nm in size due to the hydrophobic interaction of the fluoro-backbone.<sup>26</sup> In order to dissolve the hydrophobic backbone, more hydrophobic solvents need to be used.<sup>27</sup> However, the use of more hydrophobic solvents can prevent Nafion from adsorbing on the SWCNT surfaces, which might deteriorate the dispersion of SWCNTs prepared with Nafion. Therefore, in order to achieve the optimum dispersion condition for SWCNTs, particularly, both solubility and conformation of Nafion in the liquid medium must be considered. Bisolvent has been introduced not only to manipulate the solubility and conformation of Nafion but also to prevent the aggregation of nanoparticles during the drying process.<sup>28</sup> The idea of using bisolvent in CNT dispersion with Nafion in our approach implies that the hydrophilic polar group in Nafion interacts strongly with water, whereas the hydrophobic backbone in Nafion interacts with the CNTs. Furthermore, the addition of alcohol partly solubilizes the Nafion backbone, and moreover it prohibits aggregation which leads to conformational changes in the backbone of the Nafion.

In this study, we systematically investigate the influence of Nafion and its resulting interaction with SWCNTs on the solubility and nanodispersion of SWCNTs by controlling the mixing ratio of water/1-propanol. The solubility and nanodispersion of SWCNTs are measured as a function of solvent mixing ratio using UV–vis–NIR spectroscopy. To determine the dispersion mechanism of the SWCNTs, the suspensions are characterized using adsorption isotherms, electrophoretic dynamic mobility, surface tension, and wetting angle measurements. We explain how solubility and nanodispersion of SWCNTs can be improved with bisolvent in conjunction with the interaction within the SWCNT–Nafion–liquid medium as a function of the mixing ratio.

## Experimental Methods

**A. SWCNT Suspension Preparation.** Purified SWCNTs (Grade S-P95-02-Dry) synthesized by a CoMoCAT process<sup>29</sup> were purchased from South West Nanotechnologies and used after a heat treatment for 24 h at 200 °C. We used a Nafion

dispersant with an average molecular weight of 70 000–120 000 which was purchased from Dupont de Nemours & Co. in the form of a solution that contains 5 wt % of Nafion, 50 wt % 1-propanol, and 45 wt % of water. For the preparation of the SWCNT solution as a function of the mixing ratio of water (measured resistivity = 18.1 M $\Omega$  cm)/1-propanol (Aldrich), we first prepared 20 mL of bisolvent with different mixing ratios of water/1-propanol in a 25  $\times$  95 mm<sup>3</sup> vial. The commercial 5 wt % Nafion solution of 0.4 g was then added to the 20 mL of prepared bisolvent. Two milligrams of SWCNTs were finally added to the bisolvent. The weight ratio of CNTs to dispersant was 1:10. Because only 0.4 g of commercial Nafion solution was added to 20 mL of buffer bisolvent, the change in the content of buffer bisolvent was negligible. The prepared SWCNT solutions were then treated in a bath-type sonicator (RK 106, Bandelin Electronic, Berlin, Germany) for 8 h at a power level of 240 W. Immediately after ultrasonication, the samples were centrifuged (4239R-V4, ALC International Srl, Italy) at 10 000 rpm for 10 min. The upper 50% of the resulting supernatant, a stable solution with well-dispersed individual nanotubes, was carefully removed for characterization.

**B. Measurements.** UV–vis–NIR absorption measurements were taken using a Cary 5000 spectrophotometer (Varian, CA). The optical characteristics of the SWCNTs in solution were monitored by the absorbance in the wavelength range of 400–1400 nm. D<sub>2</sub>O was used to measure the absorption spectra of SWCNTs in the range of UV–vis–NIR because the H<sub>2</sub>O bands at 760 and 1000 nm overlap with those of the SWCNTs, where these peaks are shifted to approximately 1000 and 1300 nm in D<sub>2</sub>O, respectively. All the measurements were taken at room temperature, and all the spectra were corrected by a background offset. All samples used H<sub>2</sub>O except the absorption measurements.

To fully understand how Nafion disperses hydrophobic CNTs, adsorption isotherms for Nafion on SWCNTs were determined at 25  $\pm$  1 °C via the solution-depletion method using an inductively coupled plasma emission spectrometer (ICP) analyzer (ICPS-1000, Shimadzu Corp., Kyoto, Japan) as a function of water/1-propanol mixing ratio. A fixed amount of purified SWCNTs (0.1 mg/mL) was added to 20 mL of Nafion solution of known initial concentration as a function of mixing ratio of water/1-propanol. After 8 h of sonication, the samples were centrifuged at 40 000 rpm for 10 min. The resulting clear supernatant was carefully removed using a microfilter with 0.1  $\mu$ m pore size. The concentration of the residual sulfur in the clear supernatant was determined using the ICP analyzer. To calculate the amount of adsorbed surfactant (Nafion) on the CNTs, we subtracted the free surfactant concentration from the total added surfactant concentration. The percentage values of adsorbed Nafion to total Nafion were then calculated. Three rounds of assays were performed for an average. The root-mean-square method was used to combine the uncertainty components (standard deviations) of each data point.

The electrophoretic dynamic mobility of the CNT suspension was determined by photon correlation spectroscopy on a Zetasizer Nano ZS (Malvern Instrument, Malvern, U.K.) as a function of water/1-propanol mixing ratio. Three rounds of assays were performed for an average. All measurements were carried out at 25 °C.

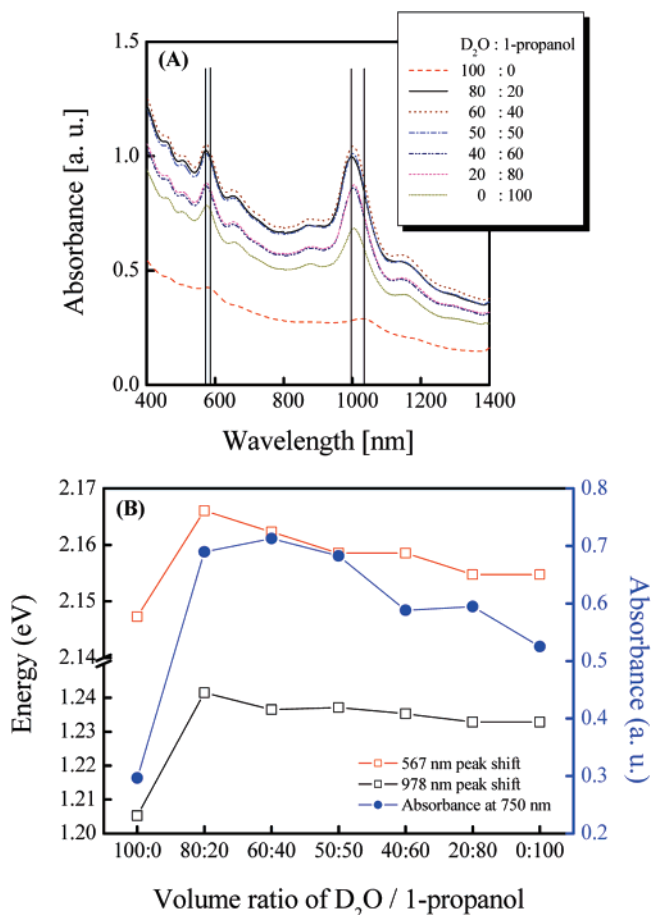
The surface tension as a function of water/1-propanol mixing ratio was measured by a pendant drop analysis (PAT 2P-USB, Sinterface Technologies, Germany) in order to investigate the interfacial tension between Nafion and the bisolvent. All measurements were carried out at 25 °C.

Wetting angle measurements were made by the sessile drop method at 25 °C with a digital optical contact angle meter (G-10, Krüss, Germany). The wetting angles of solvent on Nafion were measured to evaluate the solubility of Nafion in a liquid medium as a function of the water/1-propanol mixing ratio. In particular, since Nafion is assumed to be present at the interface between SWCNTs and the liquid medium, the wetting behavior of solvent on Nafion is closely related to the conformation of Nafion. This is one critical factor to determining the dispersion properties of SWCNTs. In this investigation, a Nafion film was used as a substrate for wetting angle measurements. The data were obtained from the average of at least three wetting angles. Finally, high-resolution transmission electron microscopy (HRTEM) images were acquired using a Field Emission JEOL 2010F high-resolution TEM at 200 keV. A SWCNT solution prepared with Nafion at a mixing ratio of water/1-propanol of 80/20 was dropped onto a carbon grid and dried at room temperature. The SWCNT solution prepared with Nafion in pure water was used for the comparison.

## Results and Discussion

The purpose of this paper is to examine the dispersion mechanism of negatively charged stable suspensions of SWCNTs prepared with Nafion as a function of the mixing ratio of water/1-propanol. UV-vis-NIR spectra have been widely used to quantify the amount of SWCNTs dissolved in a solution.<sup>30</sup> Figure 1A shows the UV-vis-NIR absorbance of SWCNTs as a function of the mixing ratio of D<sub>2</sub>O/1-propanol in the energy range 400–1400 nm. It is remarkable that the addition of 1-propanol makes the absorption intensities of SWCNTs significantly increase, compared to those in pure D<sub>2</sub>O. The absorption intensity is proportional to the concentration of SWCNTs dissolved in the solution, where SWCNTs do not necessarily have to be nanodispersed.<sup>31</sup> Our data suggest that a volume mixing ratio around 60/40 produces the best solubility. It is also noted that abundant characteristic peaks appeared over the wide range of energies when 1-propanol was added, whereas no such abundant peaks appeared in the case of pure D<sub>2</sub>O except the peaks near 978 nm (1.27 eV) and 567 nm (2.18 eV), which have been reported previously as E<sub>11</sub> and E<sub>22</sub> optical transitions of (6,5) semiconducting nanotubes<sup>30,31</sup> due to the van Hove singularities of SWCNTs. One peak near 511 nm (2.43 eV) is assigned to (7,7) and/or (8,5) metallic tubes and another peak near 462 nm (2.69 eV) may be attributed to (6,6) metallic tubes.<sup>32</sup> These spectral features become more prominent when the SWCNTs are individually dispersed.<sup>33–35</sup> Thus, the appearance of such spectral features has been regarded as an indicator of nanodispersion.<sup>36</sup> The appearance of such spectral features and an increase in absorption intensities exhibited by the bisolvent in Figure 1A simply suggest a significant improvement in solubility and nanodispersion of SWCNTs compared to those of D<sub>2</sub>O.

Figure 1B shows the spectral peak shifts of the two main peaks, 978 nm (1.27 eV) and 567 nm (2.18 eV), and the related peak intensities. As can be clearly seen in Figure 1B, these two peaks are blue-shifted by about 30 meV maximum near a mixing ratio of 80/20 compared to those of pure D<sub>2</sub>O. According to Smalley et al., the debundling of nanotubes causes the spectral peaks to be blue-shifted (or shifted to a higher energy) and narrowed.<sup>6</sup> Another possibility is that the peaks are shifted due to the charge transfer. Since Nafion is composed of fluorine atoms on the backbone and sulfonic acid on the end, it is likely that the charge will be transferred from the nanotubes to adsorbates, making the nanotube an acceptor-type. In such a

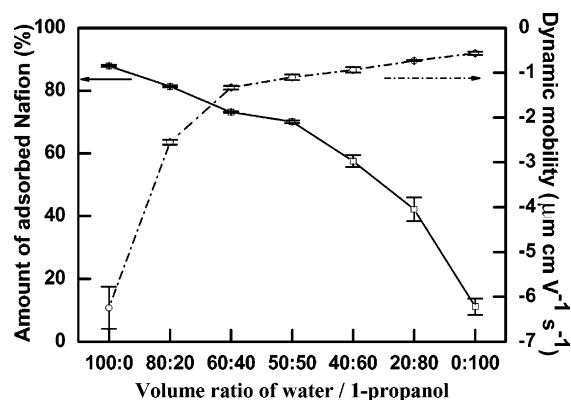


**Figure 1.** UV-vis-NIR absorption of SWCNT prepared with Nafion as a function of D<sub>2</sub>O/1-propanol mixing ratio. Mixing ratios of D<sub>2</sub>O to 1-propanol mixture varied from 100:0 to 0:100 vol %: (A) in the wavelength range of 400–1400 nm (or 0.88–3.1 eV) and (B) the energy of the spectral peaks appearing at 567 nm (2.18 eV) and 978 nm (1.27 eV) and absorbance intensity of SWCNTs at 750 nm. The dotted line depicts the region of peak shift at the spectral peaks of SWCNTs as a function of D<sub>2</sub>O/1-propanol mixing ratio.

case, a red-shift is expected in the absorption energy.<sup>37</sup> The change in dielectric constant could be another factor in the peak energy shift. The compositional dependence simply follows Vegard's law.<sup>38</sup> The energy shift was negligible when the dielectric constant of the liquid medium nearly exceeded 10.<sup>39</sup> This strongly suggests that the nonlinear peak shifts in Figure 1B are independent of the change in dielectric constant. It may be concluded that at a mixing ratio of 80/20, where the energy shift is highest and the peak widths are narrowed, the SWCNTs are mostly debundled and dispersed into individual ones in the liquid medium. According to Engtrakul et al., it is possible that Nafion disperses SWCNTs by protonation, similar to sulfuric acid.<sup>22</sup> However, the amount of pure Nafion solution used in this investigation was 0.1 wt % compared to the buffer bisolvent. This was too small to change the pH of the bisolvent, which is confirmed by the negligible peak shifts of the G-band in the Raman spectra in our experiments (see Supporting Information S1). Therefore, we conclude that solubility and nanodispersion of SWCNTs prepared with Nafion can be significantly improved by introducing a bisolvent. The mechanism of such dispersions is closely related to the interaction within the SWCNT–Nafion–liquid medium as described in the next section.

In general, both the adsorption behavior of the polymer on solid nanoparticles and the resulting dynamic mobility are critical factors to evaluate the dispersion of nanoparticles.<sup>40</sup> As mentioned previously, Nafion is an amphiphilic polymer,

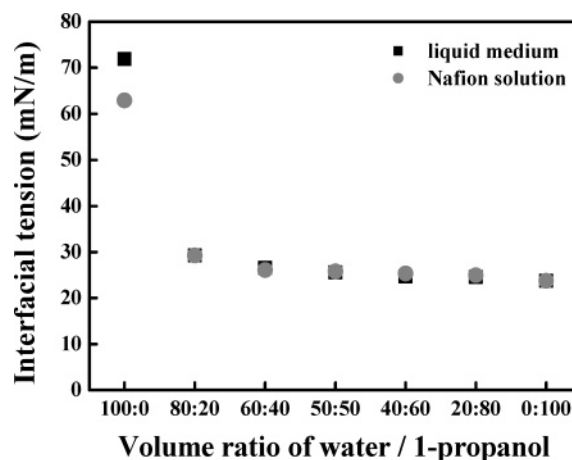




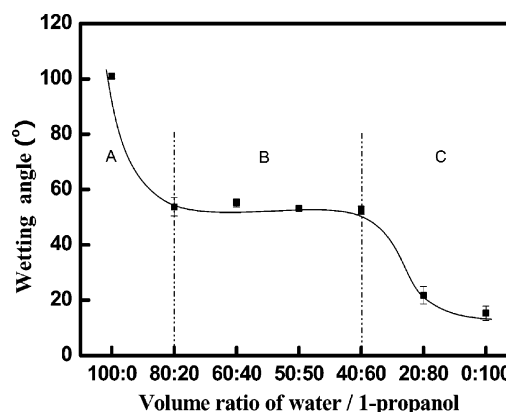
**Figure 2.** Room temperature adsorption isotherms for Nafion on SWCNTs and electrophoretic dynamic mobility of SWCNTs suspensions as a function of water/1-propanol mixing ratio. Error bars represent the calculated standard deviation for the experimental data.

consisting of a hydrophobic fluoro-backbone and a hydrophilic sulfonic acid group.<sup>20,21</sup> Nafion adsorbed on the SWCNT walls has a sulfonic acid group which is readily ionized and negatively charged to impart an electrostatic force on the SWCNTs. Thus we expect a strong correlation to exist between adsorption behavior and dynamic mobility. Figure 2 presents the adsorption isotherms of Nafion on SWCNTs and the dynamic mobility of SWCNTs in the bisolvent as a function of their mixing ratio. Adsorption of Nafion on bare SWCNTs decreases with increasing 1-propanol concentration. This is due to the affinity difference which affects the interaction of Nafion with both the solid phase (SWCNTs) and the liquid medium. Adsorption of Nafion onto SWCNTs is mainly driven by the hydrophobic interaction. It has been reported that not all of the segments of the adsorbed polymer are in direct contact with the solid surface, which is mainly influenced by the solid–polymer–liquid interaction.<sup>41</sup> As the portion of 1-propanol in the mixed solvent increases, the solvent is more and more hydrophobic. This means that the solvent becomes a better solvent (in pure water), considering the interaction between Nafion and the solvent.<sup>41</sup> Therefore, contacts between hydrophobic Nafion and the solvent are preferred, which leads to a decrease in the amount of adsorbed Nafion on the SWCNT surface. This implies that with increasing 1-propanol concentration, the nonadsorbed amount of Nafion increases. Figure 2 also presents the dynamic mobility of SWCNTs as a function of the mixing ratio. The dynamic mobility curve indicates that SWCNTs in the presence of Nafion exhibit a negative potential across the entire solvent mixing ratio. This is attributed to the presence of the sulfonic functional groups within the adsorbed layer of Nafion, which contribute to an effective surface layer charge on the SWCNTs. The absolute dynamic mobility decreases with increasing concentration of 1-propanol, as expected from the smaller dielectric constant of 1-propanol<sup>42</sup> and suppressed ionization of the sulfonic acid group in Nafion.<sup>27</sup> Nevertheless, this does not follow the simple Vegard's law, indicating that some other mechanism plays a role; that is, the adsorbed amount of Nafion on the SWCNTs affects the dynamic mobility of the SWCNTs as well. Less adsorption of Nafion does provide fewer charges on the SWCNT surface, resulting in the reduction of dynamic mobility.

So far we have discussed the adsorption behavior of Nafion on SWCNTs and the dynamic mobility of SWCNTs as a function of the mixing ratio. In pure water, Nafion was well adsorbed onto the bare SWCNT surfaces and the dynamic mobility of the SWCNTs was greatest, which is favorable for the dispersion of colloidal particles. However, this is contradic-



**Figure 3.** Surface tensions of Nafion solution and liquid medium as a function of water/1-propanol mixing ratio.

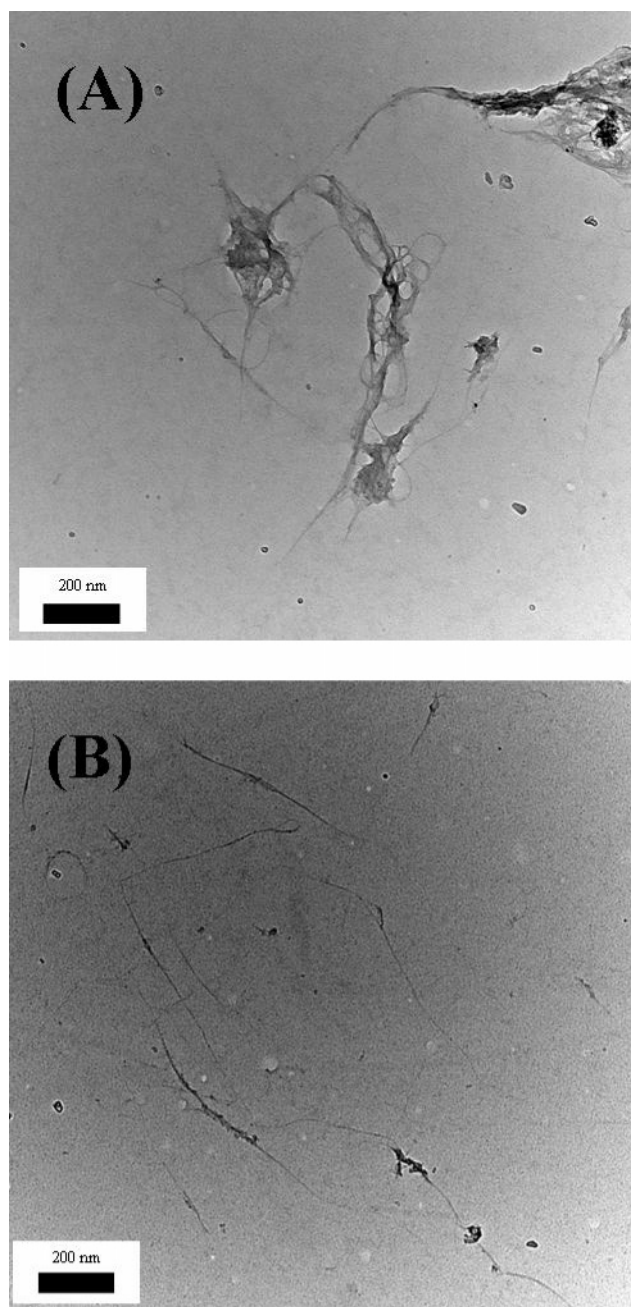


**Figure 4.** Wetting angles for Nafion–liquid medium as a function of water/1-propanol mixing ratio. Error bars represent the calculated standard deviation for the experimental data.

tory to the poor absorbance, as seen in the optical spectroscopy (see Figure 1). Figure 1 showed that the addition of the proper amount of 1-propanol into water increased the solubility and the dispersibility of SWCNTs, compared to those in pure water. In order to investigate why the results from Figure 2 do not seem to correlate with the UV absorption data in Figure 1, we evaluate the solubility of Nafion in the liquid medium through the measurement of interfacial tensions (see Figure 3) and wetting angles (Figure 4) between Nafion and the liquid medium as a function of the mixing ratio. The contact angle was measured by dropping liquid on the Nafion surface. In particular, because Nafion is present at the interface between the SWCNTs and the liquid medium, the wetting behavior of the bisolvent on Nafion is closely related to the conformation of Nafion. This is one of the crucial factors in determining the dispersion properties of SWCNTs. As can be seen in Figure 3, in the case of pure water, the surface tension is about 72 mN/m. However, the addition of Nafion reduced the surface tension of water from 72 to 63 mN/m. This is from the hydrophobic properties of Nafion. Furthermore, once 1-propanol was added to pure water, the surface tensions of both the liquid medium and the Nafion solution were significantly decreased compared to pure water. They were almost identical, indicating that the effect of Nafion on the surface tension was negligible in bisolvent. This means that the dominant factor for determining the surface tension or hydrophobicity is the mixing ratio of the liquid medium. Therefore, the addition of 1-propanol will inevitably decrease the surface tension between Nafion and the liquid medium, which may affect the dispersion properties of SWCNTs.

Figure 4 shows the wetting behavior of the liquid medium on Nafion as a function of the mixing ratio. As can be seen in Figure 4, Nafion shows different wetting behaviors with three distinct steps (A, B, and C) as a function of the mixing ratio. Specifically, in step A (no addition of 1-propanol) the wetting angle is about  $100^\circ$ , implying a nonwetting surface. This results from the incompatibility between Nafion and water due to the presence of the hydrophobic fluoro-backbone in Nafion. However, the addition of 1-propanol improves the compatibility between the fluoro-backbone in Nafion and the liquid medium, leading to largely enhanced wettability (from step A to step B). In step B (mixing ratio of 80:20–40:60) the wettability of Nafion in bisolvent is nearly constant. Excessive addition of 1-propanol makes the wettability of Nafion improve even more (from step B to step C). The enhanced wettability results from the improved solubility of Nafion in the liquid medium by the addition of 1-propanol.<sup>27</sup> As mentioned previously, the addition of alcohol improves the solubility of Nafion, which leads to conformational changes in the backbone of Nafion.<sup>27,28</sup> In order to achieve a stable dispersion, the dispersant should be adsorbed strongly onto the solid phase, and simultaneously the conformation of adsorbed polymer on the solid phase should be stretched out to increase the repulsive stabilizing force caused by a loss of configurational entropy. In particular, the solubility of a polymer in the liquid medium mainly affects the conformation of the polymer. Even though the adsorption amount of polymer on the solid phase is greater, the repulsive interaction is not expected to be maximum in the case of an aggregated polymer, deteriorating the dispersion of the solid phase.<sup>40</sup> In step A, Nafion adsorbed on the surface of the SWCNTs in water is not likely to be stretched out due to hydrophobic interaction of the backbone in Nafion.<sup>26,27</sup> Therefore, any possible steric effect of Nafion for the dispersion of SWCNTs cannot be expected. However, in steps B and C, where the solubility of Nafion in the liquid medium is largely improved, the steric effect of Nafion adsorbed on the walls of SWCNTs can be expected due to the change in conformation of the backbone of Nafion caused by the improvement of solubility. Therefore, we simply conclude that the addition of 1-propanol affects the solubility of Nafion in the liquid medium. The improved solubility leads to the conformational change of Nafion adsorbed on the walls of SWCNTs from an aggregated to a stretched-out structure, which is favorable for the dispersion of SWCNTs. Particularly, the conformation of Nafion begins to change from the addition of 20 vol % 1-propanol into the liquid medium.

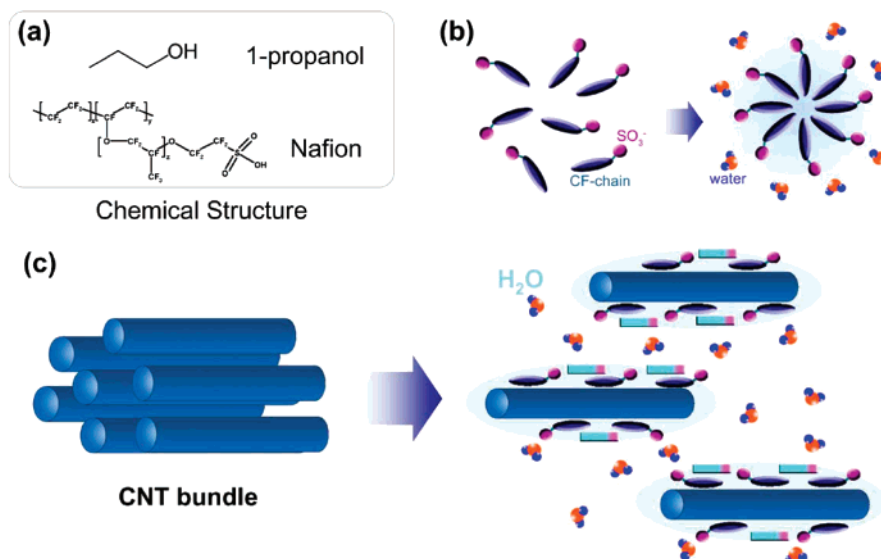
The adsorption isotherm and dynamic mobility data (see Figure 2) show that the large portion of water in the liquid medium seems to be favorable for improving the dispersion of SWCNTs. On the other hand, considering the conformation of Nafion in the liquid medium (Figure 4), the increase of 1-propanol added into the liquid medium is favorable for the dispersion of SWCNTs due to the steric effect of Nafion adsorbed on the walls of the SWCNTs. It is reported that while the hydrophilic sulfonic acid groups in Nafion tend to be dissociated as the water content increases in the mixed solvent, which significantly affects the ionization of the sulfonic acid groups, the incorporation of alcohols makes the polymer solubilize.<sup>26,27</sup> Therefore, it can be expected that, while in pure water, sulfonic acid groups in Nafion are highly ionized, Nafion can easily form aggregation due to poor solubility. Thus, it is difficult to expect any possible steric effect of Nafion for the dispersion of SWCNTs, because the repulsive interaction is not expected to be maximum in the case of an aggregated polymer. On the other hand, the increase of 1-propanol in the mixture



**Figure 5.** HRTEM images of SWCNTs: (A) prepared in pure water with Nafion and (B) prepared at 80/20 (volume) water/1-propanol mixing ratio.

solvent suppresses the ionization of the sulfonic acid groups, but the solubility of Nafion is improved. This leads to improvement of the steric effect of Nafion adsorbed on the walls of SWCNTs due to the change in conformation of the backbone of Nafion caused by the improvement of solubility. From these results, in order to design the optimum dispersion conditions of SWCNTs using Nafion, it is necessary to determine the optimum mixing ratio of water/1-propanol, where the adsorption of Nafion on SWCNTs and dynamic mobility are sufficiently high, while the adsorbed Nafion is sufficiently stretched out. In this investigation, a volume mixing ratio around 80:20 is the optimum condition for dispersion of SWCNTs through a combination of electrostatic and steric repulsive forces.

The microscopic structures of stable SWCNT dispersion prepared with Nafion in pure water and an 80/20 mixing ratio is visible using HRTEM in Figure 5. The large bundle diameters greater than 10 nm are quite often visible (Figure 5A). On the



**Figure 6.** Schematic diagram of dispersion of SWCNTs in bisolvent with Nafion: (a) chemical structure of 1-propanol and Nafion, (b) dissolution of Nafion in 1-propanol, and (c) dispersion of SWCNTs in bisolvent with Nafion. Ellipsoidal head, cylinder, and rod shapes indicate Nafion, nanotube, and 1-propanol, respectively.

other hand, in a bisolvent with an 80/20 mixing ratio, the most abundant species are well-separated individual nanotubes and small-diameter bundles less than 10 nm shown in Figure 5B, implying partial nanodispersion of SWCNTs. While in pure water (Figure 5A), Nafion was severely aggregated due to its poor solubility, and the addition of 1-propanol prohibited its aggregation (Figure 5B). Some SWCNTs particularly located near the catalyst metal particles (black spots) were still bundled in large diameters. Since metal particles are easily charged, they become hydrophilic. In this case, the amphiphilic group in Nafion does not play a role in dispersing SWCNTs. This again assures that the amphiphilic Nafion in bisolvent enhances nanodispersion. We also noticed that the individual SWCNTs were not attacked during treatment in Figure 5A and B, maintaining long nanotubes, as confirmed by Raman spectroscopy (see Supporting Information S1). This is advantageous in applications with transparent conducting films requiring long CNTs to obtain low film resistance.

Figure 6 presents a schematic diagram of the interaction mechanisms of CNTs with Nafion in bisolvent. The hydrophilic polar group in Nafion dissolves well in water. On the other hand, the hydrophobic backbone in Nafion interacts with the CNTs. This interaction is further enhanced by additional alcohol, which is still hydrophobic compared to the strong hydrophilic water, as shown in the last step of Figure 6. Alcohol not only solubilizes the Nafion backbone but also prohibits Nafion aggregation, which leads to the conformational changes in the backbone of Nafion and enhances interaction with CNTs.

## Conclusions

We have investigated the effect of the solubility of Nafion and its resulting interaction with SWCNTs on the quality of SWCNT dispersion and furthermore the dispersion mechanism of the SWCNTs. We found that the solubility as well as the nanodispersion of SWCNTs prepared with amphiphilic Nafion depends on the interaction within the SWCNT–Nafion–liquid medium as a function of the water/1-propanol mixing ratio. Water promotes the interaction of CNTs with Nafion backbones via a hydrophobic interaction, while 1-propanol provides the steric effect among CNTs by changing the conformation of Nafion. A volume mixing ratio around 80:20 is the optimum

condition for the dispersion of SWCNTs, most likely through a combination of steric and electrostatic repulsive forces. The presence of long CNTs with the current dispersion process is advantageous for several applications requiring highly conductive CNT films.

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**Supporting Information Available:** Raman spectra for samples of pristine SWCNTs, SWCNTs prepared with Nafion in pure water, and those in water and 1-propanol (80:20) at excitation energies of 1.96 eV. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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