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Covalent Attachment of Aromatic Diisocyanate to the Sidewalls of Single- and Double-Walled Carbon Nanotubes

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We carried out covalent functionalization of single- and double-walled carbon nanotubes (SWNTs and DWNTs) comparatively by using isocyanate chemistry. The introduction of aromatic diisocyanate on the sidewalls of the tubes was verified by the strong IR peak around 2272 cm^{-1} arising from the NCO asymmetric stretching mode, by the intensified sp^3 peak at 285.2 eV in the C1s photoemission spectra, and by a typical TEM image of the amorphous-like coating. The suppression of the optical properties in a covalently isocyanate-functionalized SWNT is due to a breakdown of the van Hove singularities, whereas the strong optical activity in a covalently isocyanate-functionalized DWNT originates from the geometrically shielded inner tubes. The chemically active isocyanate groups at the end of the phenyl diisocyanate that are covalently attached to the sidewalls of the DWNTs will allow us to utilize isocyanate chemistry in synthesizing functional organic–inorganic hybrid materials as well as high-performance polymer composites.

Introduction

Single-walled carbon nanotubes (SWNTs) are promising materials in numerous areas, because of their unique electronic structure as well as their excellent electrical, thermal, and mechanical properties.[1] However, such nanotubes are insoluble in water or in an organic solvent because of the hydrophobic nature of their sidewalls, and they are present in a bundle as a result of their van der Waals interactions. Thus, the chemistry of SWNTs has been actively studied in order to solve those problems and then to improve the chemical processibility through two routes of sidewall modification of the tubes (e.g., noncovalent and covalent).[2,3] Noncovalent methods using surfactants allow nanotubes to keep their unique electronic structure,[4] whereas covalent ways (e.g., fluorination, cycloaddition, radical addition, oxidation) provide a high degree of versatility toward utilizing additional nanotube chemistry,[5–8] but such processes also lead to a suppression of the optical properties of the SWNTs because of the covalently introduced chemical moieties on the sidewalls.[9,10] Thus, covalently sidewall-functionalized tubes without loss of their conjugated electronic structure should be developed in order to utilize both the sidewall chemistry and the optical signals of the nanotubes.

Here we suggest that small-diameter double-walled carbon nanotubes (DWNTs) could be a strong candidate for such multifunctional tubes, because it is well known that DWNTs are thermally more stable and mechanically stronger than SWNTs, and furthermore DWNTs exhibit stronger optical signals than those of SWNTs.[11–13] In order to achieve such a target, isocyanate chemistry is chosen, because the isocyanate group with a high chemical reactivity has the ability to react with many types of functional groups (e.g., alcohols, amines, and carboxylic acids).[14] Even though the synthesis of isocyanate-decorated MWNTs was reported previously,[15] there is no systematic study available on the structural and optical characterization of isocyanate-decorated SWNTs and DWNTs. We observed that the chemically active isocyanate in aromatic diisocyanate easily reacts with the hydroxy groups of both acid-treated SWNT and DWNT samples to form an amide bond. However, DWNTs exhibit strong optical activity, whereas SWNTs lose their optical activity. It is expected that the optical activity derived from the geometrically shielded inner tube and the chemically active isocyanate groups on the sidewalls will allow DWNTs to become useful in fabricating high-performance polymer composites, as well as innovative materials.

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Results and Discussion

Our approach is to form amide bonds between the hydroxy groups on the sidewalls of the tubes and aromatic diisocyanate groups by using simple but reactive isocyanate chemistry. Thus, FTIR spectra of both tubes were recorded in order to identify the types of functional groups (Figure 1). Three strong IR peaks are observed at 3440, 1675, and 1182 cm^{-1}, corresponding to OH, C=O, and C–C–O stretching, respectively. In addition, we are able to see a strong peak at 2272 cm^{-1} arising from the isocyanate groups on the sidewalls of both tubes. Interestingly, the intensity of such peaks in DWNTs is two times stronger than that in SWNTs, indicating a higher density of the isocyanate groups on the sidewalls of the DWNTs. Therefore, in order to examine the density (or number) of isocyanate groups introduced onto the sidewalls in a quantitative manner, we carried out XPS measurements on both samples. Figure 2 shows the C1s XPS spectra of the two kinds of tubes. Regarding the pristine tubes, we are able to see the strong peak at 284.3 eV coming from the sp^2-bonded carbon atoms and the broad peak at 285.2 eV coming from the sp^3-bonded carbon atoms.[17,18] It is noteworthy that the isocyanate chemistry intensifies the peaks at 285.2 eV, demonstrating that the isocyanate groups are covalently introduced onto the sidewalls of the tubes. The relatively strong peaks of –COOH, –COO and –C–O– at 290.5, 288.6, and 286.7 eV also show the effects of the isocyanate chemistry. Interestingly, we observed a considerably lower value of sp^2/sp^3 and a three-times higher number of nitrogen atoms in DWNTs as compared with those in SWNTs (see Table 1). Such quantitative results indicate that aromatic diisocyanate groups showed more reactivity toward DWNTs than toward SWNTs, which is consistent with our FTIR study.

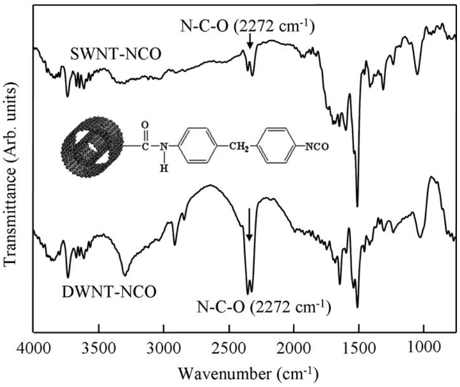

Figure 1. FTIR spectra of the isocyanate-decorated single- and double-walled carbon nanotubes. The image in the inset describes the covalent introduction of the aromatic diisocyanate group onto the sidewall of the outer tube of the DWNT.

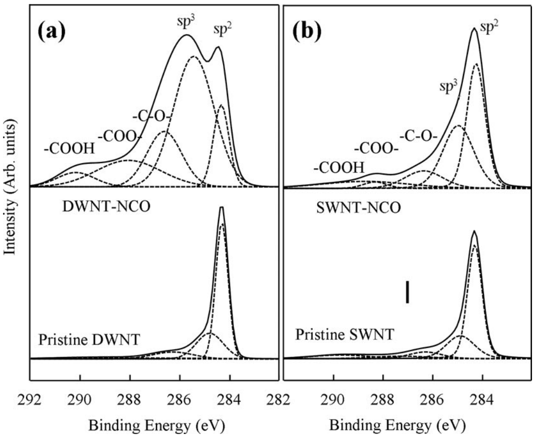

Figure 2. The C 1s XPS spectra of the pristine and isocyanate-decorated tubes: for (a) DWNTs and (b) SWNTs.

Table 1. Atomic composition of pristine and chemically modified SWNT and DWNT samples.

Sample	Carbon [%]	Oxygen [%]	Nitrogen [%]	sp^2/sp^3 [a]
Pristine SWNT	91.01	8.99	0	2.561
SWNT-NCO	65.39	26.63	7.98	1.193
Pristine DWNT	97.93	2.07	0	2.441
DWNT-NCO	58.17	20.51	21.32	0.240

[a] This column lists the integrated intensity of the peak assigned to the sp^2 carbon at 285.2 eV divided by the integrated intensity of the peak assigned to the sp^3 carbon at 284.3 eV.

In order to see the changes in both the visual appearance and the tubular structure, SEM and TEM observations were carried out for both samples. Both pristine tubes are highly bundled and physically entangled [Figure 3 (a, e)] and show clean outer surfaces [Figure 3 (b, f)]. Even though there is no distinctive change in the macromorphology of the functionalized SWNTs [Figure 3 (c)], the functionalized DWNTs exhibit a spaghetti-like structure consisting of long and large-diameter (ca. 100 nm) nanofibers resulting from the large amount of aromatic diisocyanate groups on their sidewalls. Under TEM observation, we found that the isocyanate groups are partially and intermittently attached to the sidewalls of the SWNTs [Figure 3 (d)], but they coat DWNTs homogeneously and completely, which leads to the large increase in diameter from 1.6 nm to 2.6–3.3 nm. The larger amount of isocyanate groups in DWNTs compared to that in SWNTs might be due to the stronger π–π interactions between the large-diameter DWNTs and the two benzene rings in the aromatic diisocyanate groups.

We have taken Raman spectra by using a 532 nm laser excitation to understand the change in the vibrational properties of the pristine and functionalized tubes. Two radial breathing modes (RBM) at 260 and 180 cm^{-1} are observed in the low-frequency Raman spectra of the SWNT sample [Figure 4 (a)]. The largely diminished RBM at 260 cm^{-1} in the functionalized SWNTs could be explained by the higher reactivity of the smaller-diameter tubes with regard to aromatic diisocyanate. In addition, the intensified D band (defect-induced mode) at 1350 cm^{-1} also supports the covalent introduction of aromatic diisocyanate groups onto the sidewalls of the SWNTs [Figure 4 (b)]. However, in the case of the functionalized DWNT sample, there is no distinctive change in the low-frequency [Figure 4 (c)] and high-frequency [Figure 4 (d)] Raman spectra, even though the covalent introduction of a large amount of aromatic diiso-

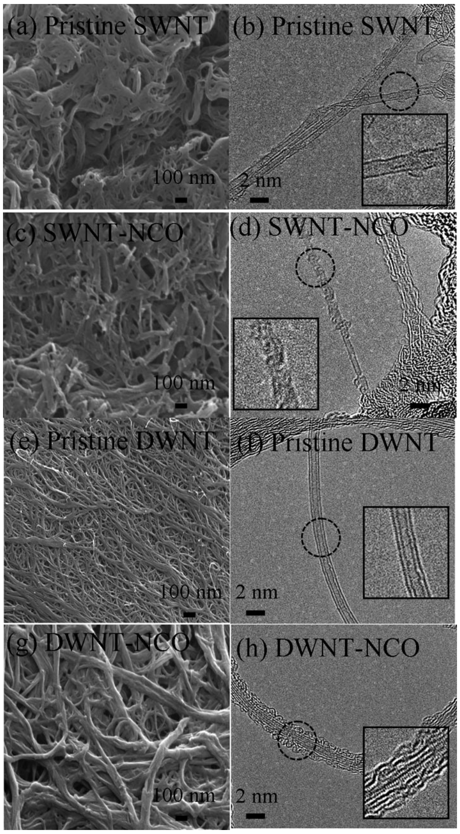

Figure 3. SEM and TEM images of the pristine SWNTs (a, b) and DWNTs (e, f) along with those of the isocyanate-decorated SWNTs (c, d) and DWNTs (g, h), respectively.

cyanate groups onto the sidewalls of the DWNTs is confirmed by using FTIR, XPS, and TEM characterization studies. Such unexpected Raman results from the functionalized DWNT sample can be explained by the coaxial structure of the DWNTs. In other words, the outer tubes in a DWNT act as a protective layer with regard to chemical agents (e.g. fluorine gas), resulting in a completely diminished RBM signal coming from outer tubes, and allow the inner tubes to keep their optical properties, as demonstrated in our previous study.[19] Therefore, we are able to say that both the unchanged RBM at 260 cm^{-1} and G band at 1590 cm^{-1} come from the inner tubes, which are the geometrically shielded by the outer tube containing the covalently introduced aromatic diisocyanate. In addition, the advantage of isocyanate chemistry over fluorine chemistry is its controllability of the covalent sites as well as the variety of the chemistry.

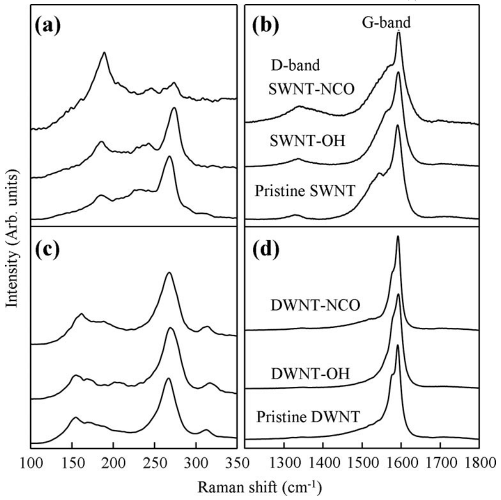

Figure 4. SEM and TEM images of the pristine SWNTs (a, b) and DWNTs (e, f) along with those of the isocyanate-decorated SWNTs (c, d) and DWNTs (g, h), respectively.

Furthermore, in order to understand the effect of the covalently introduced isocyanate groups on the sidewalls of SWNTs and DWNTs in detail, we also obtained UV absorption spectra [Figure 5 (a)] and photoluminescence (PL) maps [Figure 5 (b–e)] for both tubes. The absorption spectrum of the pristine SWNT suspension exhibits sharp absorption peaks around 500–800 nm (E^{S}_{11}) and 900–1300 nm (E^{S}_{22}).[2] However, the covalent introduction of the isocyanate groups on the sidewalls of SWNTs leads to a loss of their absorption peaks at full range due to a breakdown of van Hove singularities.[2,6] Such a decay in the transition in SWNTs is additionally confirmed by the absence of a PL signal for the functionalized SWNT suspension [Figure 5 (e)]. The quenched PL in the functionalized SWNT suspension is due to the covalent group sites that act as energy drains. In contrast, the strong absorption peak as well as the PL emission in the covalently functionalized DWNT suspension again supports the concept that the outer tubes effectively protect the inner tubes in DWNTs. For this geometrical reason, DWNTs showed better electrical, thermal, and optical properties than SWNTs.

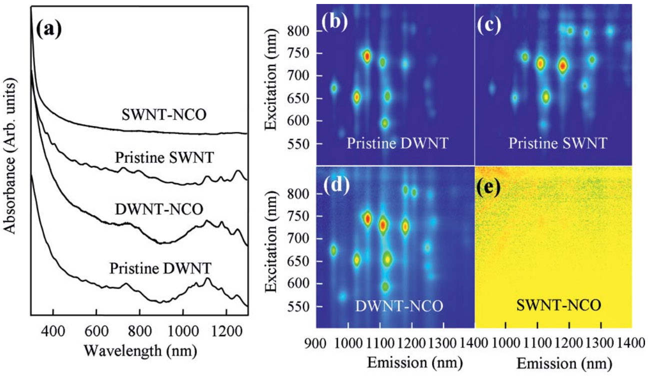

Figure 5. (a) UV absorption spectra of the pristine and the isocyanate-decorated SWNTs and DWNTs and (b–e) their corresponding photoluminescence maps. Note that the SWNTs lose their optical signals due to a covalent reaction, whereas the DWNTs retain their optical properties.

Conclusions

In this study, aromatic diisocyanate is selected as a covalent reacting agent due to its higher chemical reactivity compared to that of aliphatic isocyanate with regard to hydroxy groups on the sidewalls of tubes. We have demonstrated the covalent introduction of highly reactive aromatic diisocyanate onto the sidewalls of SWNTs and of DWNTs by using FTIR and XPS studies. We observed that a thin aromatic diisocyanate layer is coated on the sidewalls of tubes. SWNTs lose their optical properties due to a covalent reaction, whereas DWNTs exhibit strong optical activity arising from their geometrically shielded inner tubes. Thus, optically and chemically active DWNTs will find their use in preparing high-performance polymer composites and synthesizing new functional materials.

Experimental Section

Surface Modification of Tubes: In this study, HiPco-based high-purity SWNTs were purchased, and high-purity DWNTs were prepared by catalytic chemical vapor deposition and by following the oxidative purification process described in ref.[16] In order to increase the density of the hydroxy groups on the sidewalls of the tubes, both the SWNT and DWNT samples (ca. 20 mg) were treated with nitric acid (70%, 20 mL) at 50 °C for 12 h. Then, the acid-treated tubes (ca. 2 mg) were dispersed in dimethylformamide (DMF, 100 mL) under strong ultrasonication. The amidation of the hydroxy groups was achieved by reacting the acid-treated tubes with 4,4′′-methylenebis(phenyl isocyanate) (MDI, 98%, Junsei Chemicals) in a dry argon atmosphere at 50 °C for 24 h. The unreacted MDI was completely removed by washing with acetone three times.

Structural Characterizations: The functional groups of the acid-treated and isocyanate-functionalized tubes were characterized by FTIR spectroscopy (IR Prestige-21, Shimadzu) and X-ray photoemission spectroscopy (apparatus). Raman spectra were obtained by using a Kaiser HoloLab5000 system (532 and 633 laser lines). Then, in order to study the changes in the optical features of isocyanate-decorated SWNT and DWNT samples, absorption spectra and photoluminescence maps were obtained with a UV/Vis/NIR spectrophotometer (Shimadzu soildspec-3700) and a Shimadzu NIR-PL system for the individually dispersed nanotube suspensions with the help of sodium dodecylbenzenesulfonate (SDBS) (0.5 wt.-%) under strong sonication for 1 h at 4 °C and subsequent ultracentrifugation (Optima Max-XP, Beckman Coulter, 240,000 g). The morphological change of the tubes through covalent chemistry was observed by using FE-SEM (JSM6335Fs) and TEM (JEOL2010FEF) instruments.

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