Exfoliation of Single-Walled Carbon Nanotubes Induced by the Structural Effect of Perylene Derivatives and Their Optoelectronic Properties

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We designed an innovative and effective dispersion system for single-walled carbon nanotubes (SWCNTs) by introducing an exfoliation concept. Perylene derivatives were used as organic additives for dispersion of the SWCNTs. The SWCNT solutions were characterized with UV-vis-NIR absorption spectroscopy and transmission electron microscopy. Our newly designed dispersion system improved the degree of dispersion of the SWCNTs more than 10% and showed much better dispersion stability, compared to a conventional dispersion system. Furthermore, from the optoelectronic properties, we found that our designed dispersion system reduced the sheet resistance by about 50% at similar transmittance. Our analysis demonstrated that our designed dispersion system could provide a well-dispersed SWCNTs solution with long-term dispersion stability even under an extremely low dispersant concentration for dispersion of SWCNTs (weight ratio of CNTs/organic additive = 1, concentration of organic additives = 0.1 g/L, sonic treatment = 6 h).

Introduction

The extraordinary electrical, physical, and thermal properties of carbon nanotubes (CNTs) make them good candidates for many applications.1 In particular, because of their excellent conductivities, CNTs are likely to be among the most reliable materials used in flexible optoelectronic devices in the future. However, their use in such applications has been hindered by difficulties associated with their dispersion,2 since the aggregation of CNTs causes deterioration of their exceptional conductivities and optical properties. The dispersion of CNTs is necessary a priori in addition to the improvement of the CNT’s conductivity by using postchemical doping.3–5 It has been shown that the electrical properties of CNT films are mainly related to their percolation threshold. This threshold is affected by the aspect ratio, dispersion property, and alignment.6 Consequently, enhancement of the electronic properties of nanotubes through an improvement in their dispersion properties is desirable for electronic device applications.

The dispersion of CNTs can be classified into solubilization, where they can be bundled but dissolved in a solvent, and nanodispersion, where CNTs are individually dissolved in the solvent. The dispersion of single-walled carbon nanotubes (SWCNTs) in solution generally consists of three steps: (i) wetting between the nanotube aggregates and the solvent, (ii) debundling of the wet aggregates, and (iii) stabilization of dispersion to prevent the debundled nanotubes from reaggregating. Among these processes, debundling is regarded as critical to achieve nanodispersion of nanotubes. Debundling CNTs, thus overcoming the substantial van der Waals attractions among CNTs, requires a strong physical approach like ultrasonication. Among the various dispersion methods of CNTs that have been suggested in the literature to date in order to prepare stable and homogeneous dispersions of CNTs, noncovalent functionalizations, mainly based on the physical adsorption of polymers and a surfactant, have been regarded as useful methods for improving the solubility and dispersibility of CNTs without any degradation of their intrinsic properties.7,8 Deoxyribonucleic acid (DNA) has been useful in creating nanodispersion of CNTs in water.9 In our previous investigations, we reported that the dispersion properties of SWCNTs were mainly affected by the conformation and chemical structure of the dispersant.7,10 However, these conventional dispersion methods do not satisfactorily meet the debundling process condition of nanotubes; that is, the polymer or surfactant may be physically adsorbed on bundled nanotubes instead being adsorbed on the sufficiently debundled nanotubes, prohibiting nanotubes from being efficiently nanodispersed. This situation should be alleviated to improve the degree of dispersion of SWCNTs.

In this investigation, we designed an innovative and effective dispersion system for SWCNTs by introducing an exfoliation concept for organic or inorganic layered materials. This system reduces the sheet resistance by about 50% at a similar transmittance as well as improves the degree of nanodispersion of SWCNTs by more than 10% (measured from optical absorption). This system shows much better dispersion stability compared to the conventional dispersion system. To exfoliate inorganic layered materials with strong van der Waals attractive forces between layers, these layers must first be intercalated by molecules to increase the distance between layers.11 For organic layered materials, graphite, an alkali metal, was used to intercalate the graphene layer.12 The intercalant...
must be small enough to effectively intercalate between layers. Considering this strategic concept, if intercalants effectively intercalate nanotubes to increase the intertube spacing, allowing a dispersant to easily penetrate between nanotubes, the degree of dispersion of CNTs is expected to be maximized resulting in improving the electrical properties of transparent conducting films (TCFs). Therefore, we designed the new dispersion system for SWCNTs using the intercalation effect and investigated how much the degree of dispersion can be improved. 3,4,9,10-Perylene tetracarboxylic dianhydride (PTCDA) was used as an intercalant. Because of its flatness and aromaticity, PTCDA can effectively intercalate between the intertube spacing as well as strongly interact with the surfaces of CNTs. Moreover, a dispersant, preventing the debundled SWCNTs from being reaggregated through steric effects, was synthesized from the intercalant materials. Polymer polyethylene oxide (PEO) was chosen as a tail group to improve the affinity and solubility with N-methyl-2-pyrrolidone (NMP).

**Experimental Work**

We newly synthesized the dispersant from PTCDA. The chemical structure for the synthesized dispersant was characterized at a 600 MHz ¹H observation frequency using a Bruker Avance 600 spectrometer and Fourier transform infrared (FT-IR) spectroscopy (Thermo Nicolet 4700 FT-IR, Thermo Electron Co., Waltham, MA). Details about the intercalant and dispersant are given in Table 1 and Figure 1. ¹H NMR (600 MHz) of the synthesized dispersant in CDCl₃ gave the following results (Figure 1A): δ 3.37 (s, 6H), 3.54 (m, 4H), 3.63 (m, 40H), 3.64 (t, 4H), 3.87 (t, 4H), 4.46 (t, 4H), 8.39 (bs, 4H), 8.52 (bs, 4H). The FT-IR spectra of intercalant and dispersant were characterized, respectively, as shown in Figure 1B: 3122 cm⁻¹ (C–H stretch); 1768, 1691, and 1658 cm⁻¹ (C=O stretch); 1103 cm⁻¹ (C–O stretch).

Purified SWCNTs (grade S-P95-02-Dry), synthesized by the CoMoCAT process, were purchased from South West Nanotechnologies and used without any heat treatment. For the solubilization of SWCNTs, a purified SWCNT sample (2 mg) was added to the NMP solution (20 mL) of organic additives. The weight ratio of CNTs to organic additives was 1:1. The prepared SWCNT solutions were then treated in a bath-type sonicator (RK 106, Bandelin Electronic, Berlin, Germany) for 6 h at a power level of 240 W. Immediately after ultrasonication, samples were centrifuged (4239R-V4, ALC International Srl, Italy) at 10 000 rpm for 10 min. The systematic process flowchart of our dispersion method in this investigation is shown in the Supporting Information S1. The upper 50% of the resulting supernatant, a stable solution with well-dispersed individual nanotubes, was carefully removed for characterization. UV–vis–NIR absorption measurements were taken using a Cary 5000 spectrophotometer (Varian, CA). All of the measurements were made at room temperature. All of the spectra were corrected by background offset. In order to observe the data reproducibility for our designed dispersion system, error bars were introduced using the calculated standard deviation for the experimental data. We acquired high-resolution transmission electron microscopy (HRTEM) images using an electron microscope from JEOL at 300 kV. For the purpose of preparation of SWCNT films, we adopted a vacuum filtration method originally developed by de Heer et al. The detailed information...

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**TABLE 1: Structure of the Organic Additives Used in This Investigation**

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Molecular Weight (g/mol)</th>
<th>Chemical Structure</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,4,9,10-pylene tetracarboxylic dianhydride</td>
<td>392.32</td>
<td><img src="image" alt="PTCDA" /></td>
<td>Intercalant</td>
</tr>
<tr>
<td>N,N-di(PEO)-3,4,9,10-pylene tetracarboxylic diimide</td>
<td>1035.14</td>
<td><img src="image" alt="Dispersant" /></td>
<td>Dispersant</td>
</tr>
</tbody>
</table>

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Figure 1. (A) NMR data of the dispersant and (B) infrared detection of the intercalant and dispersant, respectively.
for preparation of SWCNTs films is well described in the literature.\textsuperscript{16} No removal process was performed to remove the residual organic additives. Measurements of the sheet resistance were carried out by a four-point probe method (Keithley 2000) at room temperature. The sheet transmittance was measured at 600 nm. Raman spectroscopy (Renishaw RM100-Invia) with excitation energy at 633 nm was used for characterizing the crystallinity of SWCNT films. The prepared conducting films were also used for X-ray photoelectron spectroscopy (XPS) with a mono Al Kα (1486.6 eV) line.

Results and Discussion

Figure 2A shows the UV–vis–NIR absorption spectra of the SWCNTs prepared as a function of the types of organic additives in NMP (A and B) and THF (C): (A) raw data, (B) the inverse of the normalized width at the spectral peak near 1300 nm; the inset shows the peak intensity of E\textsubscript{11}\textsuperscript{S} for semiconducting nanotubes (6, 5), and (C) the raw data. The intercalant and dispersant are symbolized as I and D, respectively. Error bars represent the calculated standard deviation for the experimental data.

Figure 2. UV–vis–NIR absorption of the SWCNTs prepared as a function of the types of organic additives in NMP (A and B) and THF (C): (A) raw data, (B) the inverse of the normalized width at the spectral peak near 1300 nm; the inset shows the peak intensity of E\textsubscript{11}\textsuperscript{S} for semiconducting nanotubes (6, 5), and (C) the raw data. The intercalant and dispersant are symbolized as I and D, respectively. Error bars represent the calculated standard deviation for the experimental data.

![Graph showing the UV–vis–NIR absorption spectra of SWCNTs prepared as a function of types of organic additives in NMP (A and B) and THF (C).](image-url)
dominantly achieved by the steric hindrance between side chains adsorbed on the SWCNT surface, it was difficult for the intercalant to impart sufficient dispersion power to SWCNTs. As can be seen in the curves for SWCNTs prepared with intercalant, the absorption behavior was not much different from that in pure NMP. This implied that intercalant might simply play a role in intercalating bundled SWCNTs, rather than imparting dispersion power to SWCNTs. However, the coaddition of the intercalant and dispersant significantly contributed to the nanodispersion of SWCNTs as shown by the new characteristic peak near 1390 nm. Therefore, we inferred that the intercalant might first be adsorbed on the surface of SWCNTs to debundle the bundled SWCNTs. Then, the dispersant may be adsorbed on the SWCNTs which were already debundled by the intercalant. We used a similar dispersion process was used with a conventional surfactant, sodium dodecylbenzene sulfonate (NaDDBS, 1:1 CNT/NaDDBS ratio), for comparison. As shown in the bottom spectra in Figure 2A, the solubility of the resulting materials was poor. In order to investigate the debundling effect caused by the intercalant, we attempted to measure using electron energy loss spectroscopy (EELS) in the TEM and X-ray diffraction (XRD). However, it was not possible to obtain experimental data to clearly support the debundling effect due to the low concentration and extremely small size of the intercalant (the thickness of the intercalant was about 0.142 nm, corresponding to the diameter of a carbon atom).

In order to quantitatively evaluate the nanodispersion of SWCNTs, the inverse of normalized width, defined as the ratio of the peak height to the full width at half-maximum (FWHM) of the peak\(^7,10,15\) was estimated at the spectral peak (6, 5) of a CoMoCAT SWCNT near 1030 nm (Figure 2B). As can be seen, the ratio of the peak height to FWHM of the SWCNTs, prepared with intercalant and dispersant, was seen to increase more than 10%, compared to those with the dispersant; that is, the absorption band became sharper and more intense as the number of suspended individual nanotubes increased. Furthermore, the sharper and more intense absorption peak near 1030 nm indicated a relatively narrow size distribution of nanotubes, with diameters of 0.75 nm. This implied that the degree of nanodispersion of SWCNTs was significantly improved with a narrow size distribution. Error bars were introduced using the calculated standard deviation for the experimental data in order to observe the reproducibility of our designed dispersion system. We found that the dispersion of SWCNT using our designed dispersion system was highly reproducible. Our dispersion concept was also applied to dispersing SWCNTs in tetrahydrofuran (THF), known as a poor solvent for dispersing SWCNTs (Figure 2C). As can be seen, for the SWCNTs prepared with intercalant and dispersant, abundant new characteristic peaks developed even in THF which were assigned to (8, 7), (9, 7), and (9, 5), respectively. This clearly provided evidence that our dispersion concept could provide a highly dispersed SWCNT solution.

The microscopic structure of stable SWCNT dispersions prepared with a combination of intercalant and dispersant was visible using HRTEM as shown in Figure 3. SWCNTs, prepared with intercalant and dispersant (Figure 3D), were highly nanodispersed. This showed that the SWCNTs were separated from each other and exhibited a typical diameter of less than 2

![Figure 3. HRTEM images of the SWCNTs: (A) without any organic additives, (B) prepared with intercalant, (C) prepared with dispersant, and (D) prepared with the intercalant and dispersant.](image-url)
nm compared to those with the dispersant (Figure 3C) or intercalant (Figure 3B). Typically, the crystallinity of CNTs or related carbon materials is identified by the peak intensity ratio of the D-band and G-band ($I_D/I_G$) in the Raman spectra.22,23 In Figure 4, the $I_D/I_G$ of the dispersed samples was similar to that of the pristine sample. With these results we noticed that the individual SWCNTs were not attacked during treatment but maintained the long lengths of the nanotubes. Therefore, the presence of long CNTs with the current dispersion process is advantageous for several applications in achieving high conductance of CNT films.

To directly compare the long-term dispersion stability of SWCNTs, Figure 5, we present photographs of SWCNT solutions prepared in the NMP with various additives after 1 month of incubation at room temperature: (A) without any organic additives, (B) prepared with the intercalant, (C) prepared with the dispersant, and (D) prepared with the intercalant and dispersant.

Figure 5. Photographs of the SWCNT solution in NMP after 1 month of incubation at room temperature: (A) without any organic additives, (B) prepared with the intercalant, (C) prepared with the dispersant, and (D) prepared with the intercalant and dispersant.

Figure 4. Raman spectra for the sample of the pristine SWCNTs and SWCNTs prepared with a combination of intercalant and dispersant at excitation energies of 1.96 eV. The intercalant and dispersant are symbolized as I and D, respectively.

In this case, the ratio for CNT to NaDDBS was 1:10 and the SWCNT solutions were sonicated for 24 h. Therefore, even though it was difficult to directly compare the dispersion efficiency between SWCNT solutions prepared with NaDDBS and those with our new dispersion system, considering the conditions for the preparation of a SWCNT solution using NaDDBS7 and our obtained the optical absorption spectra (see Figure 2A), our dispersion system is expected to be advantageous for dispersion stability of SWCNTs.

To understand the effect of charge transfer, the CNT films with organic additives were subjected to XPS analysis. Figure 6 shows the XPS spectra of the CNT films prepared as a function of the types of organic additives. We found that no peak shift occurred in C 1s, which indicated that the incorporation of organic additives did not cause any charge transfer to take place. Figure 7 shows the performance of TCFs of SWCNTs. We know that the performance of TCFs is dependent on the dispersibility, doping level, and metallicity of the nanotubes.24,25 In this work, we assumed that the performance of TCFs was only affected by the dispersibility of nanotubes, because in our dispersion system, we confirmed that no charge transfer occurred in the XPS experiment and no chiral separation had taken place. It is noticeable that the TCFs prepared with intercalant and dispersant showed excellent TCFs properties compared to the others. This results from the improved dispersion properties of the SWCNTs prepared with both intercalant and dispersant. We analyzed the average bundle size distribution from the scanning electron microscopy (SEM) images (not shown here), as shown in Figure 8. Since a bundling effect was caused by capillary force during the
dry process, nanotubes were easily aggregated. However, we found that the films prepared with intercalant and dispersant were less aggregated and had relatively smaller bundle size. (The diameter of the CNT bundle was enlarged due to the presence of intercalant and dispersant.)

We clearly demonstrated that our effective dispersion concept results in significantly improving the dispersion properties of CNTs compared to the conventional dispersion concept. This improvement is evidenced by UV-vis-NIR absorption spectra and the sheet resistance of CNT films (see Table 2) even with an extremely low dispersant concentration and much shorter sonic treatment time for the dispersion of SWCNTs (weight ratio of CNTs/organic additives = 1, concentration of organic additives = 0.1 g/L, sonic treatment = 6 h).

Conclusions

We designed an effective and innovative dispersion system for the dispersion of SWCNTs by using the structural effect of intercalant and dispersant introducing an exfoliation concept. Perylene derivatives were used as organic additives. From the UV-vis-NIR absorption spectra, we found that our dispersion system using an intercalant and dispersant contributed to the improvement of the degree of nanodispersion of the SWCNTs by more than 10% as well as showing a new characteristic peak near 1390 nm leading to reducing the sheet resistance by about 50%. Furthermore, our new dispersion system provides much better dispersion stability for SWCNTs compared to those with a conventional dispersion system. We demonstrated that it was possible to prepare a highly dispersed SWCNTs solution with long-term dispersion stability using our designed dispersion system under an extremely low dispersant concentration for dispersion of SWCNTs (the weight ratio of CNTs/organic additives = 1, concentration of organic additives = 0.1 g/L, sonic treatment = 6 h).

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Supporting Information Available: Systematic process flowchart for dispersion of SWCNTs using our designed dispersion system. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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