Dispersion of Single-Walled Carbon Nanotube Bundles in Non-Aqueous Solution

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ABSTRACT We report the observation of photoluminescence from SWNTs dispersed in a tetrahydrofuran(THF)/octylamine solution, providing the first clear evidence for individual SWNTs in non-aqueous solution. We also report the effective amine-assisted dispersion of C_{60} and La@C_{82} peapods. This solution phase handling is applicable to the analysis of electronic properties and modification of SWNTs and peapods.

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications.[1] However, practical applications have been hindered by the poor dispersibility and solubility. Therefore, dispersion of bundled SWNTs to individual ones in organic solvents is an important scientific goal, which makes homogeneous chemical reactions possible. It has been suggested that the non-covalent bond formation of SWNTs with polymers[2] and π-conjugated compounds[3] leads to the dispersion of bundled SWNTs in non-aqueous solution without changing their structure and properties. However, no spectroscopic evidence for individual SWNTs in non-aqueous solution has been reported up to now. Here we report the observation of photoluminescence from SWNTs dispersed in a tetrahydrofuran(THF)/octylamine solution, providing the first clear evidence for individual SWNTs in non-aqueous solution. We also report the effective amine-assisted dispersion of C_{60} and La@C_{82} peapods.

Choi et al. have reported, by observing microscopic image, that amines untangle SWNTs in non-aqueous solution.[4,5] In the amidation reaction, we have found that the dispersibility of SWNTs depends on the amount of amines.[6] To provide insight into the dispersion efficiencies, we tested a series of amines with different substituents.[7] The dispersion efficiency obtained by measuring the optical absorption intensity of the dispersion solution of SWNTs (HiPcoTM, Carbon Nanotechnologies)[8] at 1310 nm are summarized in Table 1. A typical dispersion procedure is as follows: 1mg of SWNT was added to 10 mL of a 0.01 M solution of 1-octylamine in tetrahydrofuran (THF) and then sonicated for 1 h at room temperature followed by centrifugation of the suspension to remove non-dispersible SWNTs. The vis-NIR spectrum of a dark transparent supernatant solution showed the characteristic absorption bands of SWNTs,[9] as shown in Figure 1(a). Among the amines investigated, octylamine has the highest dispersion efficiency, as clearly shown in Table 1. Dispersibility decreases in order of a primary, secondary, and tertiary amine, suggesting that the interaction between SWNTs and amines is sensitive to steric hindrance around a nitrogen atom. As is apparent from Table 1, the interaction between SWNTs and amines is correlated with the basicity of the amines. The most likely mechanism is that the amine nitrogen interacts significantly with the SWNTs surface. The binding energy between amines and SWNTs is estimated to be considerably.[10]

Up to now, there is no reliable way to determine the percentage of individually dispersed SWNTs in solution. However, the present spectroscopic data verify that amine converts bundled SWNTs into individual tubes. The observed near-infrared fluorescence from a THF/octylamine solution of SWNTs shows distinct emission transitions of several different semiconducting SWNTs. Figure 2 also shows the contour plots of fluorescence intensities for SWNTs in amine-THF solution, as a function of the wavelengths of excitation and resultant emission. These features are characteristic of individually dispersed SWNTs solutions, which are also found recently with surfactants after a sonication treatment in aqueous solution.[11] The fluorescence absorption spectra overlap fairly with the absorption spectra for individual SWNT suspended in SDS micelles (Figure 1).[11] Meanwhile, the fluorescence absorption spectra shift a little from the absorption spectra in the amine-assisted dispersion solution (Figure 1). This might originate from the different centrifugation conditions. The centrifugation power (122,000g) used for SDS micelles is much stronger than that (20,000g) for amine/THF solution. The weak centrifugation treatment may not be enough to remove SWNT bundles. Consequently, overlapping of the absorption of SWNT bundles with that of individual SWNT results in broadening the absorption spectrum. Atomic force microscopic (AFM) measurements show that SWNTs in a THF/octylamine solution have a length distribution from 300 to 700 nm, with tube diameters ranging from 0.8 to 4 nm. These diameters are close to the values of 0.9-1.3 nm expected for HiPco tubes (Figure 3).

We applied the effective amine-assisted dispersion method to peapods. Peapods[12] (SWNTs encapsulating fullerenes) are currently of great interest as a new form of SWNTs-based materials that may apply for nanometer-sized devices. Figure 4 shows the absorption spectra of Metro-SWNTs, C_{60}@Metro-SWNTs, and La@C_{82}@Metro-SWNTs[13] in a THF/octylamine solution. The absorption bands corresponding to first van Hove transition of semiconducting tubes of C_{60}@Metro-SWNTs (1500-1750 nm) and La@C_{82}@Metro-SWNTs (1500-2200 nm) change in comparison with that of Metro-SWNTs. Theoretical[14] and experimental[15,16] studies show that the structure and electronic properties of SWNTs are changed significantly upon encapsulating fullerenes and endohedral metallofullerenes. In this context, the difference in the absorption spectra of peapod can be explained by the structural deformation of SWNT and charge transfer between SWNTs and C_{60} or La@C_{82}.

In conclusion, individual SWNTs in a THF/amine solution are for the first time verified by spectroscopic data and this solution phase handling is also applicable to the analysis of electronic properties and modification of peapods.

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Supporting Information Available: Vis-NIR spectra of SWNTs and AFM and TEM images of the C_{60} and La@C_{82} peapod provided by casting a THF solution with 1-octhylamine. This material is available free of charge via the Internet at http://pubs.acs.org

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Figure Captions:

Figure 1. Vis-NIR and emission spectra of SWNTs in THF solution with 1-octylamine at 720 nm (red), 650 nm (blue) and 570 nm (green) excitation.

Figure 2. Contour plots of fluorescence intensities for SWNTs in octylamine-THF solution

Figure 3. Tapping-mode AFM height image of SWNTs prepared by casting a THF solution with 1-octyl amine on mica and cross-section profiles indicated by lines.

Figure 4. Vis-NIR spectra of Metro-SWNTs (black), C_{60}@Metro-SWNTs (red) and La@C_{82}@Metro-SWNTs (blue).

Table 1. Absorption intensity ratio ($\lambda_{1310\ \mathrm{nm}}$) of SWNTs in THF solution with amine.

compounds	$\lambda_{1310\ \mathrm{nm}}$	compounds	$\lambda_{1310\ \mathrm{nm}}$
1-octhylamine	7.4	1-octadecylamine	3.6
N-methyl-propylamine	7.0	tripropylamine	3.2
1-dodecylamine	6.7	1-methylpiperidine	2.1
piperidine	6.2	pyridine	1.6
isopropylamine	6.2	aniline	~1
1-propylamine	5.8	DMF	~1
1-methylpropylamine	5.0	propionamide	~1
dipropylamine	4.6	none	1.0
cyclohexylamine	3.9		

Figure 1/ Y. Maeda, et al.

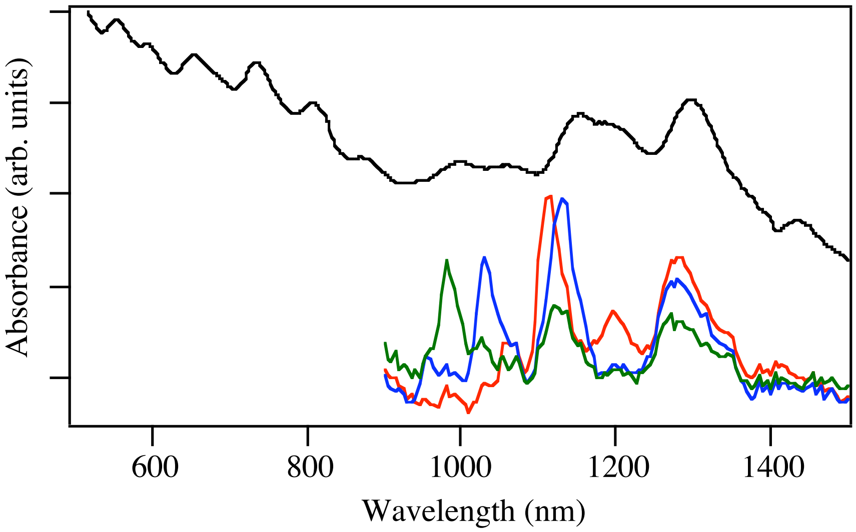
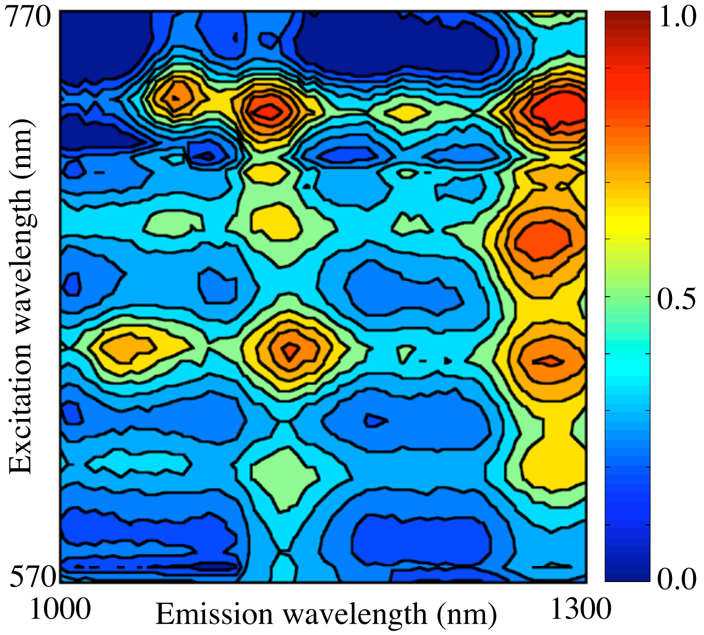


Figure 2/ Y. Maeda, et al.



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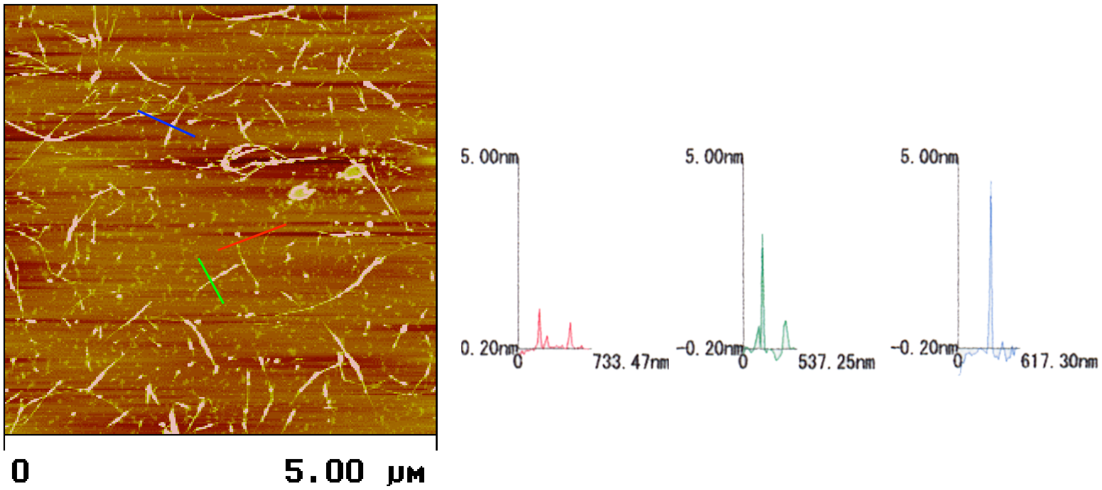
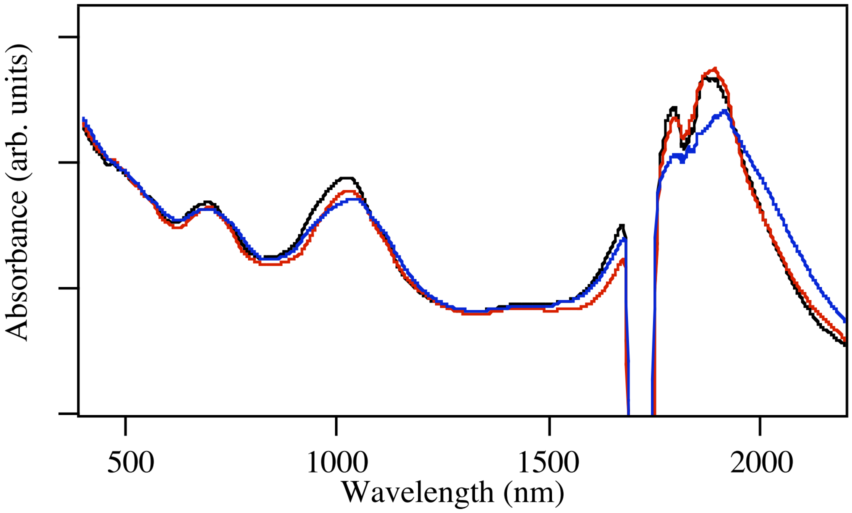


Figure 4/ Y. Maeda, et al.



Abstract: The amine-assisted dispersion of single-walled carbon nanotubes (SWNTs) is investigated. Bundled SWNTs are highly dispersed in tetrahydrofuran by their sonication in the presence of amine. Fluorescence spectroscopy and atomic force microscopy measurements provide the evidence for individual SWNTs.