Green Tea Solution Individually Solubilizes Single-walled Carbon Nanotubes

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We describe the finding that green tea and catechins individually dissolve single-walled carbon nanotubes (SWNTs). UV–visible–near-IR absorption, photoluminescence, Raman spectroscopy, and atomic force microscopy were used to characterize the solubilized aqueous nanotube solutions.

Since the discovery in 1991,[1] carbon nanotubes (CNTs) are nanomaterials of forefront in nanoscience and nanotechnology; however, CNTs are insoluble in solvents because of their strong intertube van der Waals interactions. Therefore, strategic approaches toward the solubilization of CNTs are highly important in wide fields including chemistry, physics, biochemistry, biology, and pharmaceutical and medical science. Our interest focused on the fundamental and applications of carbon nanotubes soluble in aqueous and organic systems.[2] We[3] and others[4] have already described that compounds (including polymers) bearing a condensed polycyclic aromatic moiety such as pyrene, anthracene, porphyrin, or polyimide group dissolve CNTs in water or in organic compounds. Double-[5] and single-stranded[6] DNAs that are biological compounds carrying polycyclic aromatic moieties are also good CNT solubilizers in water.

We present here new CNT solubilizers, that is, green tea, which contains numerous components with antioxidant activity including polyphenols, minerals, and vitamins. Catechins[7] are typical polyphenols that are contained in tea, so we tested catechins to dissolve CNTs. We used single-walled carbon nanotubes (SWNTs) as CNTs since individually dissolved SWNTs show characteristic structural spectral features in the near-IR region due to the interband transition between the mirror image spikes in the density of states (DOS) of the SWNTs.[8]

Commercially available green tea solution (brand name: "Iemon Koime" from Suntory Limited was used as the material. The UV–vis spectrum of the tea solution is provided in the Supporting Information (Figure 1S).[16] As-produced SWNTs (so-called HiPco) were purchased from Carbon Nanotechnologies Inc. and used as received. Typical SWNT solubilization procedures are as follows.[3] A specific amount of the SWNTs (ca. 0.5 mg) was added to an aqueous solution of each beverage (5 mL) and then sonicated with an ultrasonic cleaner (Branson 5510) for 1 h, followed by centrifugation at 60000 *g* with a ultracentrifuge (Hitachi KOKI, CS100GXL) for 1 h. Figure 1 shows the photographs of the original tea solution and the supernatant solution after the centrifugation.

Typical visible–near-IR absorption spectra (JASCO, spectrophotometer, V-570) of the SWNTs dissolved in the green tea solution are shown in Figure 2 together with that in a sodium dodecyl sulphate (SDS) micelle[9] for comparison, in which we see characteristic structural spectral features in the near-IR region, which resemble with those of the SWNTs individually dissolved in aqueous solutions of the solubilizers[3,9,10] including surfactants, polycyclic aromatic compounds, suggesting that the SWNTs are individually dissolved in the tea solution. Peak maxima of the spectrum of the tea solution in the first semiconducting band are shifted to longer wavelength compared to those dissolved in micelles of SDS[9] by 25–40 nm and close to those of the solubilizers carrying a polycyclic aromatic moiety.[3] The shifts are attributed to changes of the dielectric properties in the environments of the SWNTs.[11] The tea/SWNT solution was filtered to obtain solid SWNTs, which were applied to Raman spectral measurements (Renishaw Ramanscope System 1000, excitation wavelength, 514.5 nm of an Ar-ion laser). It was found that the Raman spectrum of thus obtained SWNTs is similar to that of the pristine SWNTs (see the Supporting Information, Figure S2[16]).

Weisman et al.[12] reported that semiconducting SWNTs individually dissolved in an aqueous micelle of SDS show photoluminescence (PL) in the near-IR region. Since their reports, considerable attention has been focused on this unique optical behavior. We could detect PL signal (HORIBA SPEX Nanolog-near-IR spectrofluorometer equipped with a liquid-nitrogen-cooled InGaAs near-IR detector) from the tea solution, indicating that individually dissolved SWNTs exist in the solution. From the 2D-mapping of the PL (excitation and emission wavelengths were 500–900 and 900–1300 nm, respectively) shown in Figure 3, we identified the chirality[12,13] indices of the dissolved SWNTs as (6,5), (7,5), (10,2), (7,6), (9,4), (8,6), and (8,7), whose diameters are: 0.757, 0.829, 0.884, 0.895, 0.916, 0.966, and 1.032 nm, respectively.

To obtain a direct image of the individually dissolved SWNTs, we measured atomic force microscopic (AFM) images (Veeco, NanoScope® IIIa). A mica substrate was dipped in the green tea solution for a few seconds, followed by rinsing with water and then by drying under vacuum. A typical AFM image is demonstrated in Figure 4. From the height distribution histogram of the AFM image, the diameters of the nanotubes were in the range of 1–2 nm.

What are the important compounds in tea to dissolve the SWNTs? Catechins are expected to be candidates since they are polycyclic aromatic compounds. Thus far, we tested the ability of catechin to solubilize the SWNTs. In this study, (–)-epigallocatechin gallate (TCI, 0.8 mg/mL water), whose mean content is 50–60% in green tea leaves,[14,15] was used. The solubilization procedures were similar to those of the tea solutions. The visible–near-IR absorption spectrum of the SWNTs/(–)-epigallocatechin gallate solution is shown in Figure 5 (see UV–vis spectrum of (–)-epigallocatechin gallate, Figure 3S[16]). It was found that used catechin, (–)-epigallocatechin gallate, was able to dissolve/disperse the SWNTs. It is evident that catechin plays an important role for the solubilization/dispersion of the SWNTs.

In conclusion, we found that green tea solution is able to

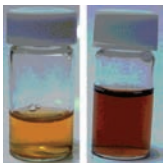

Figure 1. Photographs of a green tea solution (left) and the solution after the centrifugation (right).

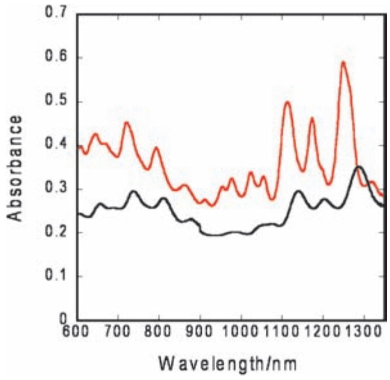

Figure 2. Visible–near-IR spectra of the SWNTs dissolved in aqueous solutions of green tea (black) and SDS (red). Optical cell length, 1 cm.

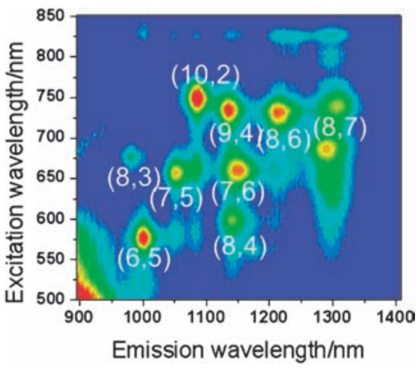

Figure 3. 2D-mapping of PL for the green tea/SWNT solution.

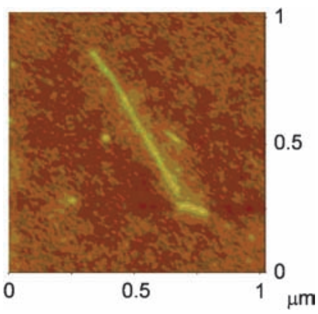

Figure 4. Typical AFM image of the green tea/SWNT solution on mica.

solubilize SWNTs individually. Green teas are inexpensive and safe materials and would be applicable to dissolve different kind of carbon nanotubes. Biological activities of nanotubes/teas (catechins) might be interesting since the solubilizers contain polyphenols, which are known to possess antioxidant activities.

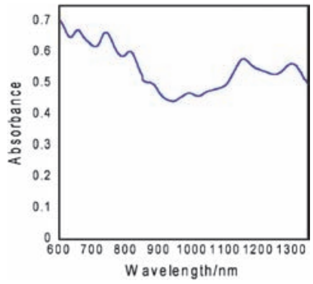

Figure 5. Visible–near-IR absorption spectrum of the SWNTs dissolved/dispersed in an aqueous solution of (−)-epigallocatechin gallate. Optical cell length, 1 cm.

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16 Supporting Information is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/index.html.

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