

Dispersion Behavior and Spectroscopic Properties of Single-walled Carbon Nanotubes in Chitosan Acidic Aqueous Solutions

Teruo Takahashi, Catalin Romeo Luculescu, Katsumi Uchida, Tadahiro Ishii, and Hirofumi Yajima*
Faculty of Science, Department of Applied Chemistry, Tokyo University of Science,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

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We found that the cationic polysaccharide chitosan is an efficient dispersion agent for single-walled carbon nanotubes (SWNTs). The spectroscopic properties of chitosan-SWNTs dispersion are different from sodium dodecyl sulfate (SDS)-SWNTs dispersion in acidic conditions. It has been revealed that chitosan is efficiently protective against the protonation of SWNTs. The dispersion behavior of SWNTs in chitosan solutions will be discussed.

Single-walled carbon nanotubes (SWNTs) have attracted great deal of attention as high performance and multifunctional nanomaterials for extended nanotechnology applications because of their outstanding one-dimensional properties. However, significant drawbacks exist for the practical use of the SWNTs, such as the SWNTs' insolubility in common solvents, facile aggregation in bundles, and usually large amounts of impurities contained. In aqueous solutions, several surfactants¹ and polymers² have been successfully used as dispersing reagents. Isolated SWNTs have been characterized with near-IR photoluminescence and absorption spectroscopy to investigate the interband optical transition of specific chiral SWNTs.³ For SWNTs dispersed in aqueous SDS solutions, Strano et al.⁴ reported that a step decrease in the intensities of the absorption peaks of semiconductive SWNTs, known as hypochromic effect, took place at around pH 5 toward acidic region. This behavior was ascribed to the protonation of the SWNTs. A similar hypochromic effect was reported for DNA-SWNTs dispersion.⁵ Recently, we have developed a new dispersion and purification procedure with some biopolymers, such as gelatin and carboxymethylcellulose.⁶ In our systematic investigation process for the dispersion behavior of SWNTs in some biopolymers solutions, we have found an outstanding solvation of SWNTs in chitosan acidic solutions. In this paper, we are reporting the dispersion characteristics of the chitosan-SWNTs system in comparison with the SDS-SWNTs system, probed by spectroscopic investigations.

The purified HiPco (Carbon Nanotechnologies Inc., 85 wt %), SDS (Nacalai Tesque, 99% purity), chitosan (Kimika Co., $M_r = 150,000$; DDA = 98%), and D₂O (Acros, 99%) were used without further purification. 10 mg/mL SDS solution in D₂O and 10 mg/mL chitosan in 2% acetic acid/D₂O solvent (pH 3.7) were prepared. HiPco SWNTs (0.25 mg/mL) was mixed with either dispersant solution and then treated using an ultrasonic disruptor (Nippon Seiki US300T) equipped with a 3-mm diameter microtip sonotrode. The ultrasonication was constantly operated for 60 min in an ice bath at about 20-W power for each sample. The obtained dispersions were ultracentrifuged at 163,000 g for 60 min (Hitachi CS100GXL) to remove large bundles. After centrifugation, the upper 80% supernatants were carefully collected for further measurements. The SDS-

SWNTs (pH 6) and chitosan-SWNTs (pH 3.7) dispersion liquids were labeled S- and C-SWNTs, respectively. In order to confirm the influence of pH on the absorption spectra of S-SWNTs, the pH of the SDS-SWNTs dispersions was changed with 0.1 M HCl solution after centrifugation. This sample was labeled AS-SWNTs (pH 3). Figure 1 shows the dispersion states for the S-, AS-, and C-SWNTs, including the one for the basic treated C-SWNTs, in which the pH was changed to neutral by aqueous ammonia and for which the gelation is observed. It should be noted that gelation occurs for pH > 6.5.

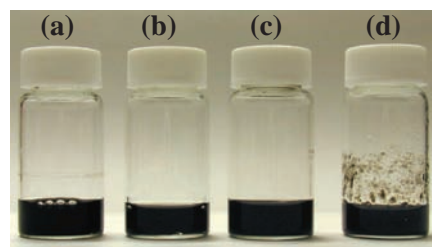


Figure 1. Photograph of SWNTs dispersions (a) S-SWNTs, (b) AS-SWNTs, (c) C-SWNTs, and (d) C-SWNTs after pH was changed to neutral condition.

The UV-vis-NIR absorption spectra were measured in the 200–1800 nm range using JASCO V-570 spectrophotometer. Raman spectra were measured at laser excitation of 532 and 785 nm (JASCO NRS-3000). Emission spectroscopy was performed at room temperature by a laboratory-made system using a Ti:Sapphire laser system for excitation in the 690–830 nm range. Figure 2 shows the UV-vis-NIR absorption and NIR emission spectra of S-, AS-, and C-SWNTs, respectively. A series of sharp and well-resolved peaks were observed for S-SWNTs, which mean sufficient isolation of SWNTs. On the other hand, for AS-SWNTs, the particular peaks in the semiconductor range remarkably disappeared in both absorption and emission spectra for pH ≤ 3. After the basic treatment for AS-SWNTs, dispersion was visually homogeneous and semiconductor range peaks could be observed again. Nevertheless, the C-SWNTs exhibited a similar series of sharp and well-resolved semiconductive SWNTs peaks in the similar manner to that of S-SWNTs even under acidic condition (pH < 5), where for the S-SWNTs, the remarkably hypochromic effect was observed. It is thought that chitosan prevents the protonation of SWNTs. Noteworthy, compared with the S-SWNTs, the absorption peaks for C-SWNTs depicted red shift (up to 25 nm for the semiconductive, and about 5 nm for the metallic nanotubes) accompanied by an increase in the optical densities by about 1.5 factor. It should be noted that C-SWNTs exhibits a larger red shift (up to 31 nm) in the emission spectra in compar-

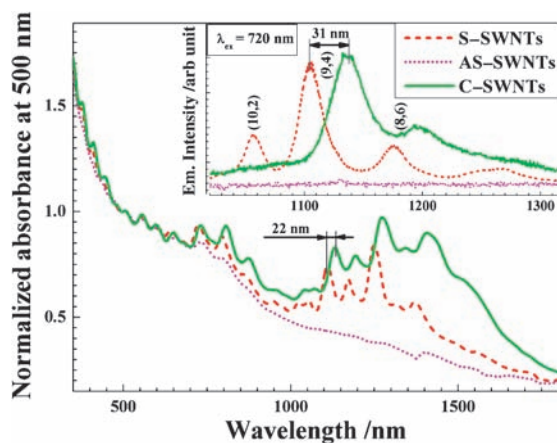


Figure 2. UV-vis-NIR absorption spectra of S-SWNTs (dashed line), AS-SWNTs (dotted line), and C-SWNTs (full line) after ultracentrifugation. The spectra were normalized at 500 nm. The inset shows the emission spectra of the same samples under 720 nm excitation. The emission intensity of S-SWNTs sample was decreased 10 times for clarity.

ison with S-SWNTs.

The band gap shift is suggested to rise from the differences between interaction mechanism of micelle-like surfactant and wrapped polymer with nanotubes. Our preliminary MD calculations show that the chitosan-nanotube interaction which originates intrinsically from CH- π binding is stronger than SDS-nanotube interaction. Another reason for observed red shift could be the difference between average bundle sizes. It suggests that bundle's size is larger in the case of C-SWNTs. This hypothesis is supported by lower fluorescence intensity in C-SWNTs sample by one order of magnitude but is not confirmed by Raman spectra which show the same shift for both samples.

Figure 3 shows the Raman spectra of radial breathing mode (RBM) for pristine HiPco SWNTs (powder), S-SWNTs and C-SWNTs at 532 and 785 nm laser excitations. The former and latter excitations would dominantly be resonant with the metallic and semiconductive SWNTs, respectively. The spectra are offset vertically for clarity. At the 532 nm excitation, the pristine HiPco showed several peaks which are assigned to the (13,1), (9,6), (10,4), and (9,3) SWNTs. For the S- and C-SWNTs, the set of the RBM peaks were shifted about 8 cm^{-1} to higher wavenumbers compared with the solid sample. These results are indicating that the wrapping of polymer or surfactant around SWNTs affects the vibration frequencies.⁷ The blue shift could be also a result of debundling. The dominant peak for S- and C-SWNTs spectra is assigned to the (9,3) SWNTs. The (9,6) and (10,4) SWNTs' peaks remained in the C-SWNTs, but disappeared in the S-SWNTs. On the other hand, at the 785 nm excitation, three dominant peaks assigned to the (12,5), (11,3), and (10,2) SWNTs were observed in the pristine HiPco. Interestingly, for C-SWNTs only (11,3) peak appeared, whereas for the S-SWNTs another dominant peak, (10,2), was observed. It is supposed that the thick (12,5) SWNTs were removed in centrifugation process. As a comparison between the characteristics of the C-SWNTs and S-SWNTs, the thicker component of the (11,3) SWNTs was larger in the C-SWNTs than the S-SWNTs, at the expense of the (10,2) SWNTs. This result is supported by fluorescence spectra in which the (10,2) is appearing only in S-SWNTs

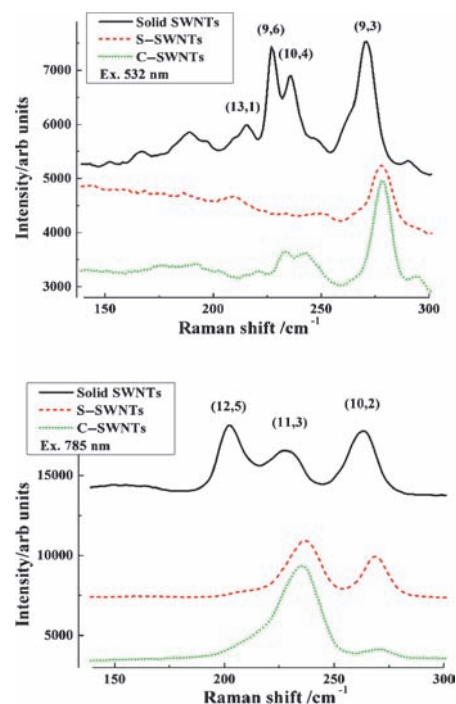


Figure 3. Raman spectra of HiPco SWNTs (full line), S-SWNTs (dashed line), and C-SWNTs (dotted line) at 532 and 785 nm excitation wavelengths.

(see Figure 2). Therefore, it is presumed that chitosan would selectively interact with SWNTs.

In summary, we have found that chitosan is an effective dispersing agent for SWNTs under acidic conditions, and then is efficiently protective for the protonation of SWNTs. Our results led us to the suggestion that chitosan could be a chiral separation agent for SWNTs, similar to DNA. This hypothesis has to be confirmed by further investigations. In addition, in regards of unique characteristics of both chitosan and SWNTs, it is expected that the chitosan-SWNTs composites would be a new promising biomaterial.

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