Isolation of Single-wall Carbon Nanotube Bundles Through Gelatin Wrapping and Unwrapping Processes

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The isolation of single-wall carbon nanotube (SWNT) bundles and purification of these SWNTs were investigated by dispersing the SWNTs in an aqueous gelatin solution. TEM images of the SWNTs dispersed in the gelatin solution showed that the interaction between the gelatin molecules and the SWNTs produces a transformation of the SWNT bundles into thin bundles. Raman spectra measurements revealed that dispersing the SWNTs in the gelatin solution is a good purification procedure for the SWNTs.

Since carbon nanotubes were discovered,[1] it has been expected that they would be promising materials for a variety of applications.[2] However, single-wall carbon nanotubes (SWNTs) contain many impurities such as amorphous carbons, fullerenes, and metal catalysts.[3] Moreover, the SWNT bundles are unable to be thoroughly dissolved by any type of solvent,[4] because the cohesive energy between the SWNTs, due to van der Waals interactions, is significantly greater than the solvation energies. The difficulty in isolating and purifying the SWNTs from pristine SWNTs prevents us from developing the best performance of the SWNTs in new molecular devices. Recently, O'Connell et al.[5] studied the solubilization of SWNTs in water by wrapping SWNTs with water soluble linear polymers such as polyvinylpyrrolidone and polystyrenesulfonate under ultrasonic irradiation. It has been shown that the association between the polymers and the SWNTs is robust. Therefore, the solubilization of the SWNTs by polymer wrapping might provide a series of useful techniques from purification to functionalization through more precise manipulation and fractionation of the SWNTs. However, the removal of synthetic polymers, which are used as the dispersing reagent, is difficult, because synthetic polymers cannot be easily decomposed by a chemical reaction. Therefore, the polymer, which is easily decomposed by a chemical reaction (e.g., hydrolysis) is a good reagent for the purification of the SWNTs.

In this study, we developed a new dispersion and purification method for the SWNTs using a biological molecule of gelatin, which is easily decomposed into fragments by hydrolysis, under ultrasonic irradiation.

The SWNTs containing raw soot (40 to 60% purity, obtained from CarboLex Inc.) were purified by a hydrothermal treatment.[6] Gelatin was purchased from Nippi and used without further purification. The SWNT powder and gelatin were first mixed together in water. The hydrothermally-treated SWNTs and gelatin-SWNTs dispersed composites were labelled H-SWNTs and G-SWNTs, respectively. The concentrations of the SWNTs and gelatin in the G-SWNT dispersion were 0.25 and 1.0 mg/ml, respectively. The G-SWNTs were sonicated using an ultrasonic processor equipped with a microtip sonotrode. The ultrasonic processor was intermittently operated at 50 W for 1 h. The gelatin was hydrolyzed using a 6 M alkaline solution for 4 days. The decomposition of the gelatin molecule was examined by the Lowry method. The precipitate produced from the alkaline-treated G-SWNT dispersion was filtered through 3.0 μm diameter pores, and then washed with a 0.1 M HCl aqueous solution and water. The obtained precipitate was called A-SWNTs. The characterization of the A-SWNTs was performed using Raman and FT-IR spectroscopy, and transmission electron microscopy (TEM). The morphology of the SWNTs was observed by TEM (Hitachi, H-9000NAR). The Raman spectra measurement was performed with an ALMEGA laser Raman system (Thermo Nicolet) using an excitation wavelength of 532 nm. The FT-IR spectra were recorded with a Avatar360 spectrometer (Thermo Nicolet) in the ATR mode (Thermo Nicolet, OMNI-sampler) at a resolution of 4 cm^{-1}.

Figure 1 shows the dispersion states for the H-SWNTs, G-SWNTs, and A-SWNTs. The SWNTs in the H-SWNT dispersion were immediately precipitated from the dispersion by aggregation of the SWNTs. On the other hand, the dispersion of the G-SWNTs was stable for one month (Figure 1(b)). Therefore, gelatin is a good stabilizer for the SWNT dispersion. The SWNTs in the dispersion of the G-SWNTs were then slowly precipitated from the dispersion by hydrolysis (Figure 1(c)). This result suggests that most of gelatin was easily removed by hydrolysis.

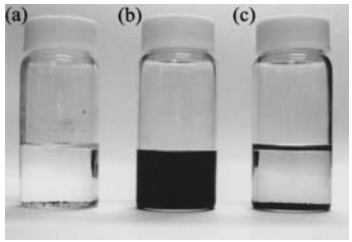

Figure 1. Vials containing the dispersions of (a) the hydrothermally treated SWNTs, (b) gelatin-SWNTs, and (c) gelatin-SWNTs after hydrolysis.

TEM images of the H-SWNTs, G-SWNTs, and A-SWNTs are shown in Figures 2(a)–(c). The H-SWNTs contained many impurities such as metal particles and amorphous carbons. These common impurities come from the synthetic processes. On the other hand, the black spots of metals decreased in the G-SWNTs, and the bundles of the SWNTs were thinner than that of the H-SWNTs. This thinning mechanism would be explained by the polymer wrapping which has been reported by O'Connell et al.[5] The SWNTs in the A-SWNTs were partly aggregated, however, the bundles were still thinner than that of the H-SWNTs. These results suggest that the gelatin molecules prevented the SWNTs

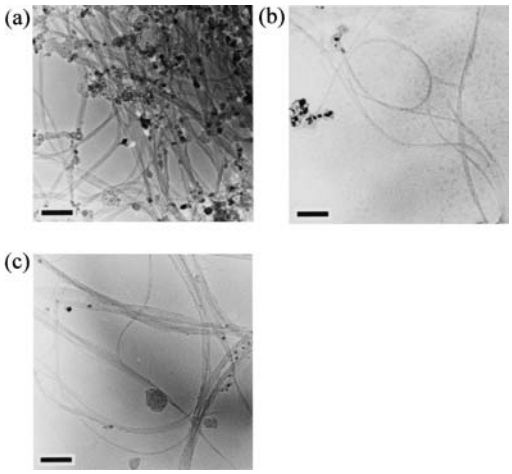

Figure 2. TEM images of (a) the hydrothermally treated SWNTs, (b) gelatin-SWNTs before hydrolysis, and (c) gelatin-SWNTs after hydrolysis. Scale bar, 100 nm.

from aggregating.

The FT-Raman spectra of the H-SWNTs and A-SWNTs are shown in Figure 3. Both samples have almost the same sharp peaks near the high frequency of 1584 cm^{-1} with a shoulder, which are assigned to the tangential modes of the graphite.[7] The peak around 1340 cm^{-1}, which is concerned with amorphous carbons,[8] for the A-SWNTs decreased. This result shows that the amorphous carbons are removed after hydrolysis of the gelatin. The low frequency range of 160–200 cm^{-1} is the radial breathing modes[7] whose frequencies are dependent on the tube diameter. There is no recognizable difference between them. The FT-Raman spectra indicated that the SWNTs were purified by the gelatin treatment. Therefore, the gelatin treatment of the SWNTs with ultrasonication is not only a way to obtain disentangled SWNTs, but also a way to purify them.

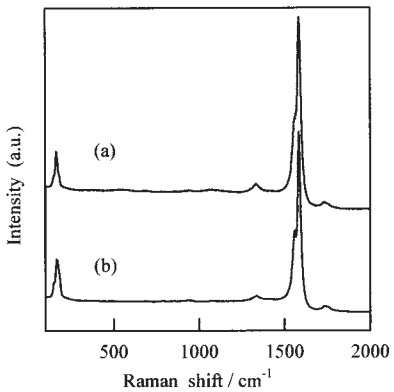

Figure 3. Raman spectra (a) hydrothermally treated SWNTs, and (b) gelatin-SWNTs after hydrolysis.

FTIR-ATR measurements of the H-SWNTs, G-SWNTs, and A-SWNTs are shown in Figures 4(a)–(c). The FTIR-ATR spectrum of the H-SWNTs was almost similar to that previously reported[9] and the G-SWNTs showed only the peaks of the gelatin which are called amide bands. On the other hand, the FTIR-ATR

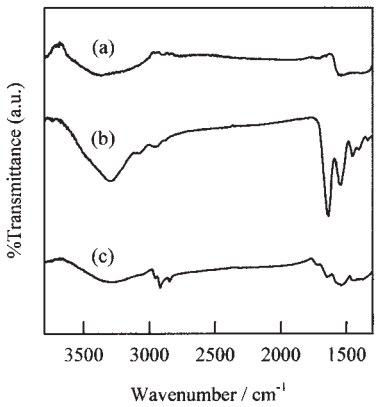

Figure 4. FTIR-ATR spectra of (a) the hydrothermally treated SWNTs, (b) gelatin-SWNTs before hydrolysis, and (c) gelatin-SWNTs after hydrolysis.

spectrum of the A-SWNTs was similar to that of the H-SWNTs, but two composite bands comprising some peaks were observed around 1600 cm^{-1} and 2900 cm^{-1}. The peak at 1716 cm^{-1} is assigned to a C=O bond in the carbonyl groups, and the peaks around 1600 cm^{-1} are related to the amide I and II bands. The other peak bands of 2848, 2916 and 2958 cm^{-1} are assigned to the stretching modes of the C-H bond vibration in the saturated hydrocarbons. The presence of the C-H stretching and the amide band suggests that the decomposed gelatin partially remains on the surface of the SWNTs, or the A-SWNTs are partly comprised of SWNTs which would react with the decomposed components from gelatin by the high-power ultrasonication, as previously reported.[10] The reaction of the SWNTs with the decomposed species is probably avoided by using a homogenizer with saw-edged screws without ultrasonication. This work is now in progress.

Consequently, the gelatin wrapping and unwrapping processes of the SWNT bundles are a useful procedure for the purification and the isolation of the SWNT bundles.

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