

Effects of centrifugation on the carboxyl modified single-walled carbon nanotubes suspension

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ABSTRACT

The centrifugal method is adopted to investigate the properties of carboxyl-terminated single-walled carbon nanotube (c-SWCNT) suspension. The chemical properties of each supernatant sample are confirmed with the Fourier transform infrared analysis (FTIR) and are not influenced by centrifugal process. The optical properties observed by ultraviolet-visible-near infrared spectroscopy (UV-VIS-NIR) show that the oxidation debris co-existed with c-SWCNTs in supernatant samples is a material creating perturbation at the electronic structure of the c-SWCNT. The G-band in the Raman results displays the red shift toward the low frequency side. The red shift of G-band is estimated because the removal of the oxidation debris by centrifugal method induces the de-doping effect on the electrical structure of SWCNTs.

Keywords: SWCNTs, centrifugation, separation

1 INTRODUCTION

The functionalization techniques have been mentioned as a prerequisite for the realization of SWCNT-applications because the chemical reactivity between chemically modified SWCNTs and bio-chemical molecules holds various utilities. Especially, the soluble-functionalized CNT with specific functional group such as carboxyl group is important to detect the bio and chemical molecules likewise the purpose for dispersion.

Generally, the oxidation by strong acids has been used to attach the carboxyl group on the structure of SWCNTs. The carboxyl group as a functional linker is the most preferred reactive group for the reaction with amino groups. The reactivity between carboxyl and amino groups in liquid state can be applied not only to the combination of both bio-chemical molecules with an amino group and c-SWCNTs, but also to align the c-SWCNTs on the substrate treated with amino group. Furthermore, these reactions have the advantage in terms of low temperature process

technology and the sensitivity of bio and biochemical sensors.

However, the SWCNT suspension containing a carboxyl group has several problems. One of the problems is that the c-SWCNT in suspension coexistence with by-products generated during the functionalization process. To separate the functionalized SWCNT and by-products in prepared suspension, the centrifugation method is introduced. The SWCNT supernatant samples obtained according to the centrifugal method are the subject of study and the characterization about the supernatant samples is carried out about the optical and structural properties.

2 EXPERIMENTAL METHODS

The dispersion of SWCNTs (by arc-discharge method, ILJIN Nanotec., Korea) has been achieved with the mixture of nitric and sulfuric acids. The SWCNTs of 10mg were suspended in 40 mL of a mixture of nitric and sulfuric acids with a volume ratio of 1:3 [1,2]. The mixture was stirred for 48 hours at room temperature, and then sonicated for 10 hours using a Branson water bath sonicator (40kHz, 185W). This reaction mixture was diluted with 200 mL of distilled water. The diluted solution was filtered through a 0.2 μ m pore size under vacuum with an aspirator. The residue formed on the filter membrane was repeatedly washed using 10 mM NaOH solution and distilled water until the pH of the filtrates was 7. The residue mat was immersed in distilled water and was taken out from the filter membrane through sonication (30 min). After stirring for 30 min, the resulting suspension can be maintained a stable, homogeneous dispersion. The centrifugal process was applied to separate the different elements of the resulting suspension. The full experimental procedures for sample preparation are shown in Figure 1.

The characterizations of each sample were presented using the FTIR spectroscopy (Nicolet 6700, Thermo Nicolet), UV-VIS-NIR spectroscopy (Varian Cary 5000 spectrophotometer), and Raman spectroscopy (Thermo Nicolet, Almega XR). The Raman spectra of each sample

were collected using a dispersive Raman spectrometer with 532 nm excitation source.

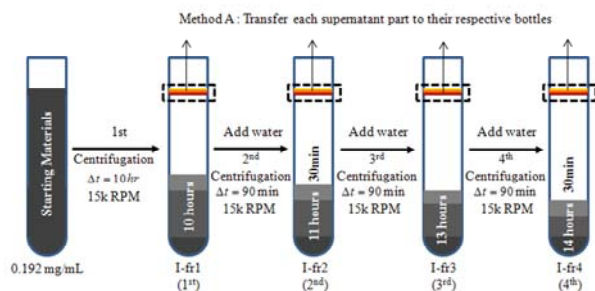


Figure 1: Schematic of the process to separate SWCNT supernatant part generated via centrifugation.

3 RESULTS AND DISCUSSION

3.1 Fourier transform infrared spectra

Figure 2 presents the FTIR spectra of each sample obtained by method depicted in Fig. 1. In Fig. 2, the FTIR spectra do not show any obvious difference among the supernatant samples.

The peak at 3430 cm^{-1} in the frequency range of $3000\text{--}3500\text{ cm}^{-1}$ is due to hydroxyl group (-OH) and surrounded water. The absorption bands in the $1500\text{--}1750\text{ cm}^{-1}$ region can be described as follows. The broad peak at 1630 cm^{-1} reveals the presence of anionic carboxylates by surrounded water and/or aqueous environment. Also the C=O bond as the elements of carboxyl group generally appears near 1710 cm^{-1} [3]. The peak by the C=O bond seem to be included in the broad peak by aqueous environment. Therefore, the results of Fig. 2 indicate that the carboxyl group in each sample do not influence by the centrifugal process.

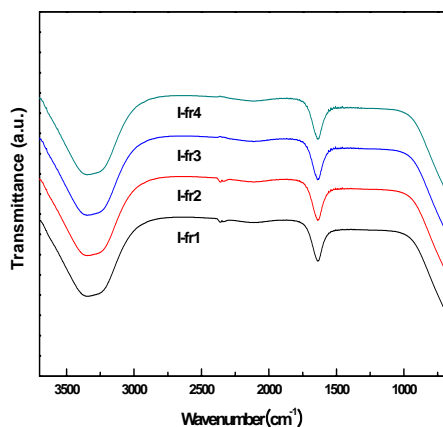
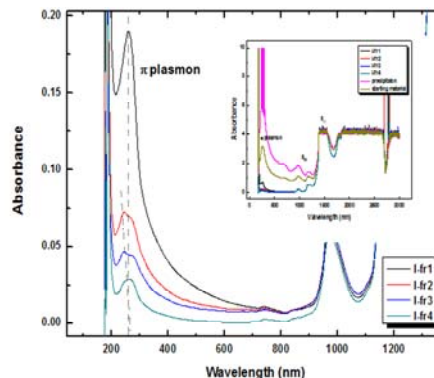


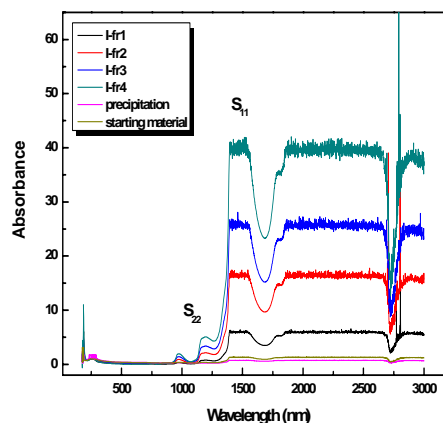
Figure 2: FTIR results of supernatant samples obtained by using the centrifugal method from initial SWCNT suspension.

3.2 UV-VIS-NIR spectra

Figure 3 shows the optical properties of supernatant samples are separated from c-SWCNT suspension. Fig. 3(a) is the enlarged image of the π -plasmon peak. The total absorption spectra are displayed in the insert figure in Fig. 3(a).



(a)



(b)

Figure 3: UV-VIS-NIR absorption spectra of SWCNT supernatant samples. (a) This figure is enlarged image of the π -plasmon peak. The insert figure shows the total absorption spectra. The absorption spectra presented in this figure have been normalized on the most intense band at 1388 nm. (b) The UV-VIS-NIR absorption spectra about S_{11} , S_{22} interband transition. All spectra are normalized with respect to π -plasmon peak.

The UV-VIS-NIR absorption spectra for pristine SWCNTs consist of four bands: metallic interband transition (M_{11}), two kinds of semiconducting interband transition (S_{11} , S_{22}), and π -plasmon [4,5]. However, the absorption spectra, as shown in insert figure (in Fig. 3(a)) consist of three bands. The appearance of absorption spectra in Fig. 3(a) can be ascribed to chemical oxidation of

SWCNTs by the HNO₃/H₂SO₄ mixture [1,2]

The π -network of pristine SWCNTs was destroyed by the chemical oxidation using strong acids. As a result of the oxidation reaction, π -plasmon was generated in SWCNTs suspension. The variation of absorption intensity by π -plasmon as seen in Fig. 3(a) has attributed the cause to the reduction of π -plasmon content in each sample by the centrifugal method.

In the meantime, the S₂₂ bands in Fig. 3(b) displayed an increasing tendency with proceeding of the centrifugation. The S₂₂ interband transition has been prescribed as a concept for purity estimation with M₁₁, S₁₁ [5]. When the absorption intensity related with the S₂₂ interband transition is characterized by a proportional feature, the movement is recognized to mean the enhancement of purity. From this fact, the purity of each sample can be regarded as showing an enhanced propensity by centrifugation.

The next thing, the S₁₁ interband transition is known as a transition occurred between van Hove singularities (VHS) of SWCNTs [5]. The previous reports demonstrated that the nitric and sulfuric mixture treatment induced the formation of impurity level and holes near the Fermi level of SWCNT [6,7]. As confirmed about the π -plasmon from the analysis of Fig. 3(a), the proportion of oxidation debris involved in SWCNT supernatant samples is going down by the progress of centrifugal time.

From these facts, the reason for variation of absorption intensity shown in Fig. 3(b) is understood to be related with both the rate of oxidation debris and impurity level located near the Fermi level. That is to say, the result of Fig. 3(b) can presume that the variation of absorption intensity occurred due to the effect of oxidation debris inducing the perturbation on the electronic structure of SWCNT supernatant samples.

3.3 Raman spectra

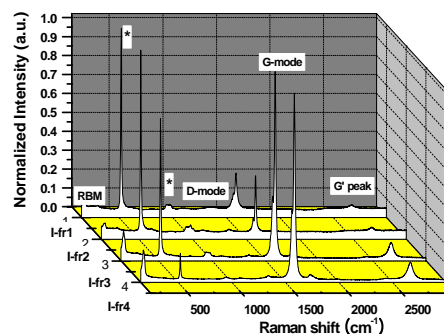
Figure 4 shows the Raman spectra obtained from each sample. The total Raman spectra of each supernatant sample are displayed in Fig. 4(a). Fig. 4(b) shows the CNT tangential mode measured at around 1600 cm⁻¹. The CNT tangential mode is, as it were, called G band derived from a graphite structure. The G band is related to charge transfer in the electronic structure of CNTs by resonant transitions [8]. In Fig. 4(b), the G band presents the peak shift toward the low frequency side. Generally, the shift of G band is divided into two types, red shift and blue shift. The red shift means that the G band moves to lower frequencies for electron-donor dopants, and the blue shift means that the G band moves to higher frequencies for electron-acceptor dopants. Considering the concept of the G band shift, the peak shift toward the low frequency side exhibited in Fig. 4(b) belongs to the red shift.

From the fact that the G band is related to resonant transitions, the red shift of G band is thought to originate from the removal of oxidation debris which is induced the

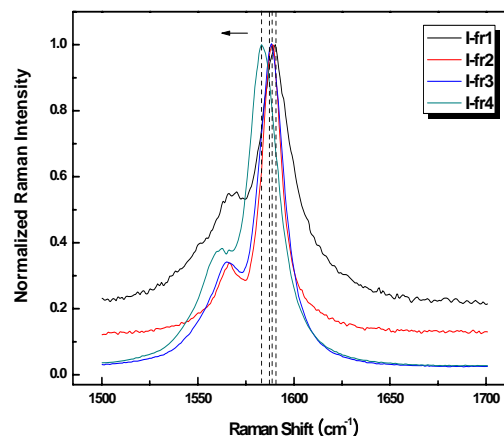
de-doping effects on the electrical structure of SWCNTs by centrifugal method.

4 CONCLUSION

The characteristics of elements existing in c-SWCNT suspension have been investigated after separation by centrifugal method. In FTIR analysis, each centrifugal fraction with carboxyl group is not influenced by centrifugal loading time. From the results of UV-VIS-NIR and Raman spectroscopy, we know that the oxidation debris is a material inducing the perturbation at the electronic structure of SWCNTs and the removal of oxidation debris by centrifugal method is induced the de-doping effects on the electronic structure of SWCNTs.



(a)



(b)

Figure 4: (a) The Raman spectra of the SWCNTs supernatant samples (532 nm). Peaks labelled with an asterisk (*) come from the Si/SiO₂ substrate. (b) The G-band Raman spectra of SWCNT supernatant samples.

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