PURITY MEASUREMENT OF SINGLE-WALLED CARBON NANOTUBES BY UV-VIS-NIR ABSORPTION SPECTROSCOPY AND THERMOGRAVIMETRIC ANALYSIS

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We measured the content of single-walled carbon nanotubes (SWCNTs) in SWCNT soot within 3.7% error using UV-VIS-NIR absorption spectroscopy. We also propose a better overall evaluation method by combining thermogravimetric analysis with UV-VIS-NIR absorption spectroscopy to analyze the purity of SWCNT providing the accurate assessment of the amounts of...
noncarbonaceous impurity, carbonaceous impurity, and SWCNT each with respect to a highly purified reference.

Keywords: Carbon nanotube; purity measurement; UV-VIS-NIR absorption; thermogravimetric analysis.

1. Introduction

Since its discovery by Iijima in 1991, the carbon nanotube (CNT) has rapidly attracted much attention because of the abundant possibility of micro and macro applications in many fields. The unique features of CNTs’ physical and chemical properties have allowed the possibilities in development of many new functional materials and devices such as various emitters, vacuum fluorescent display (VFD), white light sources, field emission display (FED), contacts in Li ion secondary battery, hydrogen storages, nanowires, AFM/STM tips, single electron transistor, gas sensors, micro parts in medical devices, functional composites, etc. Single-walled CNTs (SWCNTs) are synthesized commonly by arc-discharge, chemical vapor deposition, or laser ablation. There are several manufacturers in current market providing the commercial products of SWCNTs. Yet, each manufacturer uses its own method of evaluating the purity of SWCNTs, and there has been no standard definition or method of purity evaluation globally accepted. This causes unavoidable confusion for consumers. In the research and development aspect, the different evaluation platforms disturb researchers that the consistency of their outcomes is at risk, causing a critical delay in development of new applications and commercialization. Thus, it is an urgent matter that the purity evaluation method of SWCNT should be globally standardized.

The impurities in SWCNT mainly consist of noncarbonaceous impurity and carbonaceous impurity. SWCNT soot synthesized by arc-discharge or laser vaporization may possess a few percent of noncarbonaceous impurity such as the residual metals used in catalysis. The noncarbonaceous impurity can be measured by raising the temperature up to 1000°C in the thermogravimetric analysis (TGA). SWCNT soot may also have a significant amount of carbonaceous impurity such as amorphous carbon and carbon nanoparticles. The impurities in SWCNT can be analyzed qualitatively using transmission electron microscopy (TEM) or scanning electron microscopy (SEM). SEM is more favored because it is relatively easier to operate and requires simpler pre-processing procedures for the sample. Using SEM is a very reliable way of directly observing the presence of carbonaceous impurities in SWCNT. However, the amount of SWCNT that can be detected in a single scanning is only about one trillionth of a gram. This limits SEM from being used for evaluating the purity of a large amount of SWCNT in grams, which most of SWCNT vendors offer.

On the contrary, the optical methods provide a relatively fast way of evaluating a large amount of SWCNT. Among the various optical methods, Raman scattering is used for qualitative evaluation, and absorption spectroscopy is used for quantitative measurement. Previously suggested by Itkis et al. for evaluating the purity of SWCNT, absorption spectroscopy requires very simple sample preparations, and costs only one tenth of SEM. Nevertheless, this method measures the purity of SWCNT from the absorption characteristic of the semiconducting SWCNT only, and may not be reliable for evaluating the purity of SWCNT soot containing both semiconducting and metallic SWCNT. Likewise, another suggestion by Ryabenko et al. is also not reliable either because it measures the absorption of metallic SWCNT only. Landi et al. made an attempt of evaluating the purity of SWCNT by removing the π-plasmon peak from the absorption spectrum following Lorentzian curve-fitting. This method also has a questionable accuracy in a view point that the peak energy of π-plasmon peak, spectral width, and amplitude are estimated using the spectral data only in 4.0–4.25 eV region. Furthermore, the above-mentioned methods can only measure the amount of SWCNT with respect to all the carbon complexes in SWCNT because it uses the absorption data of only carbon complexes. To achieve a more reliable purity evaluation with better accuracy, each amount of noncarbonaceous impurity, carbonaceous impurity, and SWCNT in SWCNT soot should be measured separately followed by calculating the amount of SWCNT with...
respect to all the contents including the noncarbonaceous and carbonaceous impurities.

In our study, we report a new method of evaluating the purity of SWCNT combining absorption spectroscopy and TGA in such a way that the amounts of semiconducting/metallic SWCNT in SWCNT soot are measured by UV-VIS-NIR absorption spectroscopy and the amount of noncarbonaceous impurity is measured by TGA.

2. Sample Preparation and Experimental Details

To measure the absolute amount of SWCNT in SWCNT soot, a reference SWCNT sample with 100% purity is required. Yet, this is practically impossible with current technology. In our study, we prepared a highly purified SWCNT sample by purifying SWCNT soot, and all of our purity measurements were performed with respect to this highly purified reference. It should be noted that the relative purity that we measured here will change when the highly purified reference with even higher purity is available in future.

The reference sample was synthesized by arc-discharge with iron sulfide (FeS), nickel (Ni), and cobalt (Co) catalysts followed by several repetitive procedures of thermal annealing at 350°C for 30 min in the air, nitric acid and hydrochloric acid treatment and centrifugation.

Figure 1(a) shows a SEM image of the highly purified reference SWCNT. The SEM image does not show the presence of carbonaceous impurity, verifying the high purity of the reference.

Figure 1(b) shows UV-VIS-NIR absorption spectrum of the reference. In the figure, semiconducting (S_{11}, S_{22}), metallic (M_{11}), and π-plasmon peaks of SWCNT are clearly visible. The purity indicator calculated from the absorption spectrum curve using the method suggested by Itkis et al. was about 0.23. The reference SWCNT was purified until the amount of noncarbonaceous impurity was 3.3% detected by TGA as shown in Fig. 1(c).

The procedures for preparing a test sample for purity evaluation are described as follows.

A SWCNT sample was heated at 200°C under a flow of nitrogen gas (N\textsubscript{2}: 99.999%) for 12 h to remove the water content. 1 mg of the dried sample was then placed in a 100 mL container. A SWCNT solution was made by filling up the container with 100 mL of N,N-dimethylformamide (DMF: 99.8% with less than 0.005% water). The SWCNT solution was ultrasonicated for 6 h for dispersion. The water level of ultrasonicator was kept higher than that of the SWCNT solution in the 100 mL container. The ultrasonicator was operated at 40 kHz and 240 W. No other apparatus was inside the ultrasonicator,
and water was constantly added during ultrasonification to prevent the temperature change. A series of SWCNT samples were prepared in 10% purity interval from 0% to 100% by adding carbon nanoparticles to the reference accordingly.

Figure 2 shows SEM images for SWCNT samples with different purities to be evaluated. In the figure, one can clearly observe the amount of impurity decreases as the SWCNT purity increases.

TGA was performed with the following parameters: At least 3 mg of SWCNT soot was used in TGA. In order to remove the water content, a flow of highly purified N\textsubscript{2} (99.999\%) was applied at 100 sccm. The SWCNT soot sample in TGA was then heated at 200°C until no change in mass occurs. This mass was recorded as the initial mass. The flowing gas was then changed to highly purified air (99.999\%), and measurements were performed at a rate of 5°C/min up to 1000°C. The average values were taken out of three trials.

Absorption spectroscopy was performed with the following conditions: The reference SWCNT solution and the SWCNT solution of which purity is to be evaluated were placed each in a 1 mm path length spectroscopic quartz cell, and the absorption spectrum was measured using a UV-VIS-NIR spectrophotometer (V-570, JASCO). The SWCNT was placed in the cell prior to addition of the dispersion solution when the solution was mixed. The cell was always capped to minimize the solvent evaporation. The average value was taken out of three trials.

3. Results

Figure 3 shows some guiding lines of calculating the amount of SWCNT in SWCNT soot from the absorption spectrum curve. The absorption spectrum of SWCNT mainly consists of three absorption peaks. (Figure 1(b)) The first peak is at around 0.8 eV ($S_{11}$). The second is at around 1.5 eV ($S_{22}$).
Ryabenko et al. only used the $M_{11}$ peak for evaluating the SWCNT content. More recent researches have been focusing on separation of semiconducting SWCNT and metallic SWCNT. It is well known that the ratio of semiconducting SWCNT and metallic SWCNT takes a variety of different values depending on the synthesizing methods and the chemical processing. Consequently, calculating the amount of SWCNT in SWCNT soot taking only one chirality into account would cause a problem in accuracy.\textsuperscript{7,9,11–17} Landi et al. suggested a method of including both semiconducting and metallic peaks.\textsuperscript{7} This method used the $\pi$-plasmon peak only in 4.0–4.25 eV because the full spectral observation of $\pi$-plasmon peak was difficult due to the absorption in chemical solution. The energy, intensity, and width of the $\pi$-plasmon peak were estimated and then the $\pi$-plasmon peak was removed by nonlinear fitting in calculating the amount of SWCNT. Thus, the purity value varies depending on the fitting parameters even when the fitting agreed with the measurement with 99% accuracy in 4.0–4.25 eV.

For this reason, we applied the linear fitting method suggested by Itkis et al. to $S_{22}$ and $M_{11}$ peaks including both semiconducting and metallic SWCNT in evaluating the purity.\textsuperscript{7,9}

First, we integrated the $S_{22}$ and $M_{11}$ peaks in absorption spectrum of the reference SWCNT solution (Fig. 3(a)), labeled each integration value as $A_{p_{s}}$ and $A_{p_{m}}$, respectively, and labeled the sum of these two values as $A_{p_{sm}}$. Then, a straight line was drawn between each end point of the $S_{22}$ peak as in Fig. 3(b). The area between the spectrum curve and the straight line was calculated, and labeled as $A'_{s}$. The same procedure was performed for the $M_{11}$ peak, and the area was labeled as $A'_{m}$. The sum of $A'_{s}$ and $A'_{m}$ was then divided by $A_{p_{sm}}$, and the quotient was labeled as $P_{sm}$.

Next, we integrated the $S_{22}$ and $M_{11}$ peaks in absorption spectrum of the SWCNT solution to be evaluated, labeled each value as $A_{t_{s}}$ and $A_{t_{m}}$, respectively, and labeled the sum of these two values as $A_{t_{sm}}$. A straight line was drawn between each end point of the $S_{22}$ peak. The area between the spectrum curve and the straight line was calculated, and labeled as $A'_{t_{s}}$. The same procedure was performed for the $M_{11}$ peak, and the area was labeled as $A'_{t_{m}}$. The sum of $A'_{t_{s}}$ and $A'_{t_{m}}$ was labeled as $A'_{t_{sm}}$. $A'_{t_{sm}}$ was then divided by $A_{t_{sm}}$, and the quotient was labeled as $T_{sm}$.

These two peaks correspond to absorption characteristic of semiconducting SWCNT. The third peak at around 2 eV ($M_{11}$) corresponds to the valence band to conduction band transition of metallic SWCNT. As Itkis and Landi reported, $S_{22}$ peak is very sensitive to the doping condition and environment because it is near Fermi level.\textsuperscript{7,9} So, $S_{22}$ and $M_{11}$ peaks, which are further away from Fermi level, were used in evaluation. A previous method by Itkis et al. calculated the relative purity of SWCNT by comparing the integrated absorbance of $S_{22}$ peak to that of the $S_{22}$ peak of the highly purified reference, assuming the contribution of $\pi$-plasmon was constant throughout all spectral region of interest.\textsuperscript{7}

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**Fig. 3.** Calculation method of relative content of SWCNTs from the absorbance: (a) Integrated spectrum and (b) integrated spectrum by modified baselines for removing the $\pi$-plasmon effect.
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where the confidence value fitting yielded a slope very close to unity, 0.998, and with varying purities from 0% to 100%. The linear from the measurement to the constructed content results are shown in Fig. 4.

We applied the method to the series of SWCNT synthesized by arc-discharge. The average percent error for the whole purity range was 3.7%, which is smaller than 4–6% Landi et al., reported for the calculation of SWCNT content synthesis of our method are shown as triangles in Fig. 4. The percent errors representing the precision results of the SWCNT content are in excellent agreement with the designed values of constructed contents. The percent errors representing the precision content versus constructed content of SWCNTs.

To calculate the content of SWCNT in SWCNT soot, the following formula was applied:

$$\text{Content of the single-walled carbon nanotubes (\%) = } \frac{T_{\text{sm}}}{T_{\text{pm}}} \times 100,$$

where

$$T_{\text{sm}} = \frac{A_{\text{pm}}'}{A_{\text{pm}}} = \frac{A_{\text{p}}'}{A_{\text{p}} + A_{\text{m}}}$$

and

$$P_{\text{sm}} = \frac{A_{\text{p}}'}{A_{\text{pm}}'} = \frac{A_{\text{p}}'}{A_{\text{p}} + A_{\text{m}}}.$$

We applied the method to the series of SWCNT samples with intentionally varied purity, and the results are shown in Fig. 4.

Figure 4 plotted the evaluated content (dots) from the measurement to the constructed content with varying purities from 0% to 100%. The linear fitting yielded a slope very close to unity, 0.998, and the confidence value $R^2$ was 0.994. Thus, our evaluation method considers the amount of ash decreases. As previously mentioned, there are noncarbonaceous impurities in SWCNT soot such as some residuals of metal catalyst. The amount of noncarbonaceous impurity in SWCNT soot should be taken into account for an accurate assessment of the purity. Considering the potential amount of noncarbonaceous impurities in SWCNT soot, the following formula was applied in order to assess the relative purity, $P(\%)$, using the result from TGA:

$$P(\%) = \frac{T_{\text{pm}}}{T_{\text{sm}}} \times C_{\text{m}}(\%)$$

where carbon content $C_{\text{m}}(\%) = 100 - NC_{\text{m}}(\%)$.

The carbon content, $C_{\text{m}}(\%)$, which includes both the SWCNT and carbonaceous impurities, was calculated from the amount of noncarbonaceous impurity, $NC_{\text{m}}(\%)$, in SWCNT soot. The amount of noncarbonaceous impurity, $NC_{\text{m}}(\%)$, can be found from the results of TGA by the following formula:

$$\text{Noncarbonaceous content } NC_{\text{m}}(\%) = \frac{m_{\text{NC}} - (m_p - m_s)}{m_s} \times 100,$$

where $m_{\text{NC}}$ was the minimum mass left during the TGA measurement, $m_p$ was the mass at the maximum peak of the TGA curve, and $m_s$ was the initial mass stabilized from the mass change due to the water content. The parameter $m_s$ was needed for compensating the mass increase due to the oxidation of noncarbonaceous impurity in the SWCNT soot as the temperature increased during TGA and verified by X-ray photoelectron spectroscopy (XPS).

We applied TGA to evaluating the purity of three different SWCNT samples: pristine SWCNT, pristine SWCNT thermally treated at 350°C in the air environment (TH) for 30 min, and TH SWCNT treated with nitric and hydrochloric acid (SP). All three samples were synthesized by arc-discharge method. Figure 5 shows TGA results for these three samples.

As the figure shows, the pristine SWCNT contains about 19.31% of noncarbonaceous impurity, TH contains about 50.46%, and SP contains 9.42%. In TH, the amount of ash increases due to the oxidation of noncarbonaceous impurity, such as Fe, during the thermal treatment. In SP, the acid treatment removes the noncarbonaceous impurity, and the amount of ash decreases.

In case of calculating the SWCNT content using only absorption without using TGA, the results would be same as Fig. 6(a). As we calculated the purity of SWCNT using only absorption spectroscopy suggested by Itkis and Landi, the purity of TH sample was found to be the highest. However, such evaluation method considers the amount of SWCNT with respect to the carbon complexes only, and Fig. 6(a) indicates a relative amount of...
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Fig. 5. TGA results of (a) pristine SWCNT, (b) thermally purified SWCNT (TH), and (c) purified SWCNT by acid (SP).

Fig. 6. (a) Relative content of SWCNTs without noncarbonaceous impurity considered and (b) corrected relative purity of SWCNTs with noncarbonaceous impurity.

SWCNT compared to the SWCNT amount among carbon complexes in the SWCNT soot. To overcome the discrepancy in this type of evaluation method, we included the results from TGA (Fig. 5) in evaluation considering the noncarbonaceous impurity, and we were able to evaluate the content of SWCNT with more accurate purity.

As shown in Fig. 6(b), the relative purities to the reference were more accurately measured as 20.4% for the pristine SWCNT, 43.8% for TH, and 63.8% for SP. These values may be adjusted when the reference with purity even closer to 100% is available in future. In our study, we only used the SWCNT synthesized by arc-discharge method. We believe that our method, which combines UV-VIS-NIR absorption spectroscopy and TGA, would produce similar result with a reasonable purity also for SWCNT synthesized by HiPco or laser vaporization.

4. Conclusion

We have suggested a method of evaluating the content of SWCNT among the carbon complexes in SWCNT soot using UV-VIS-NIR absorption spectroscopy. We have verified that our method can trace the amount of SWCNT in SWCNT soot within an average percent error less than 4% using a series of constructed samples with designed purity, which is the best precision so far for SWCNTs synthesized by arc-discharge. We have also proposed a better evaluation method by combining TGA with UV-VIS-NIR absorption spectroscopy, and were able to evaluate the purity of SWCNT more correctly by providing the accurate assessment of the amounts of noncarbonaceous impurity, carbonaceous impurity, and SWCNT each with respect to a highly purified reference. We believe that our method provides an accurate way to evaluate the purity of SWCNT and may play a key role in investigating the relationship between the purity of SWCNT to its functionality in many applications.

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