Research Article

Novel Method of Evaluating the Purity of Multiwall Carbon Nanotubes Using Raman Spectroscopy

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We propose the quantitative method of evaluating the purity of multiwall carbon nanotubes (MWCNTs) using Raman spectroscopy. High purity MWCNTs were prepared by chemical vapor deposition (CVD) to be used as a reference material with 100% purity. Since the intensity and wavenumber of D'' -band located at around 1500 cm^{-1} were found to be independent of the excitation wavelength of a laser, the purity of MWCNTs was measured by comparing the intensity ratio of D'' -band to G-band ($I_{D''}/I_G$) of the sample with that of a reference material. The established method was verified by testing the mixture of amorphous carbon particles and reference MWCNTs.

1. Introduction

Since multiwall carbon nanotubes (MWCNTs) possess high electrical conductivity, high thermal conductivity, and excellent mechanical properties [1–3], they have been extensively studied for being used in the electrical, thermal, and mechanical applications [4–7]. In order to achieve better characteristics of application products, the advancement in the synthesis technology has been tried to improve the properties of MWCNTs, including crystallinity, dispersibility, and purity [8–10]. Among these characteristics, purity is one of the most important properties from the viewpoint of better performance of application products. In addition, since higher purity means that a smaller amount of CNTs is required to achieve targeted properties, it is very important for industrial applications to use high purity MWCNTs in terms of low cost. Many researchers have used thermogravimetric analysis (TGA) [11–13] and D -band to G-band intensity ratio of Raman spectrum (I_D/I_G) [14] to measure the purity of MWCNTs. However, TGA represents the whole carbon content in the sample because measuring the weight

loss with increasing temperature does not distinguish carbon nanotubes from other carbon species. Meanwhile, apart from the fact that the intensity and position of D -band peak are varied with the excitation wavelength of a laser to a great extent [15], D -band originates from not only amorphous carbon particles but also nanotube-related aspects including defects in the curved graphene sheets, tube ends, and finite size of crystalline domains of the tubes [16]. Thus, the measurement of (I_D/I_G) is not useful for evaluating the purity of MWCNTs using various wavelengths of laser. In contrast to D -band, the intensity and position of D'' band are not varied with the wavelength of laser. Moreover, D'' -band originates from only amorphous carbons [17]. Therefore, we propose here the quantitative method evaluating the purity of MWCNTs using the D'' -band Raman spectrum of MWCNTs as a signal for amorphous carbon particles.

As-synthesized MWCNTs are in general composed of the nanotubes, catalyst particles, and amorphous carbonaceous particles. Since the crystallinity of MWCNTs observed from Raman spectroscopy is clearly distinguishable from that of amorphous carbons, we used the comparison of Raman peaks

FIGURE 1: (a) SEM image of reference MWCNTs with 100% purity. Inset shows the HRTEM image of reference MWCNTs. (b) Raman spectrum of reference MWCNTs.

observed from MWCNTs and amorphous carbons for evaluating the purity of MWCNTs. A high purity MWCNT-sample was prepared and then used as a reference material. The purity was evaluated from comparing D'' -band to G-band intensity ratio ($I_{D''}/I_G$) of sample with $I_{D''}/I_G$ of reference materials. MWCNTs have been synthesized by either arc-discharge [18, 19] or chemical vapor deposition (CVD) [1–10]. Since the MWCNTs synthesized by arc-discharge have higher crystallinity, D'' -band is scarcely seen in the Raman spectrum. Therefore, the method to be introduced in this report is useful for only CVD-grown MWCNTs. But, the MWCNTs synthesized by arc-discharge are not used in the practical applications due to the impossibility of mass production. Therefore, it is still worthy of developing the method have evaluating the purity of CVD-grown MWCNTs that are unexceptionally shown D'' -band in the Raman spectrum. We will provide the detailed protocols for determining the purity of CVD-grown MWCNTs, which are confirmed by testing the mixture of high purity MWCNTs and amorphous carbon particles.

2. Experimental

In order to synthesize MWCNTs, Fe/Mo/Al₂O₃ particles were prepared using combustion method. Fe/Mo particles were used as catalysts and Al₂O₃ was supporting the catalysts. Metal-organic precursors of iron nitrate, molybdenum acetate, and aluminum nitrate were dissolved in deionized water, and then the prepared solution was transformed into catalyst powder by thermal treatment at 450°C for 30 min in air ambient. The quartz boat having the catalyst powder was placed inside a quartz tube reactor. After heating the reactor to 700°C in Ar atmosphere, a gas mixture of C₂H₄/H₂ (1:1) was fed into the reactor with a pressure of 1 atm for the synthesis, followed by cooling to room temperature under Ar atmosphere.

The morphologies of MWCNTs were investigated using scanning electron microscopy (SEM, JEOL JSM 6700F) and

transmission electron microscopy (TEM, FEI Tecnai 20, 200 kV). The amount of catalyst particles included in the synthesized MWCNT samples was investigated by TGA. Amorphous carbon powder was purchased from Aldrich to be used as an impurity material. In order to verify the proposed evaluation method, several intermediate purity samples, having the purity range of 0–100% with 20% interval, were prepared by mixing high purity MWCNTs and amorphous carbon powder, considered as 100% and 0%, respectively. Then, Raman spectroscopy measurement was carried out to evaluate the purity of MWCNTs using a Raman microscope (TRIVIA, Acton).

3. Results and Discussion

Through optimizing the experimental parameters for the synthesis of MWCNTs, we prepared very high purity MWCNTs, as can be seen in Figure 1(a). Despite of a number of observations using SEM, we could not see carbonaceous particles. TEM image (inset figure) clearly shows the synthesized materials are all of MWCNTs with hollow insides. According to TGA analysis, two weight-percent (wt%) of catalyst metal particles is included in the prepared MWCNTs. However, we could hardly see the catalyst particles during both SEM and TEM observations. It is believed that 2 wt% of catalyst particles corresponds to an extremely small *volume* percent that could be negligible, because the bulk density of catalyst particle is much larger than that of MWCNTs. Furthermore, most of the catalyst particles are residing inside MWCNTs after the synthesis [20], which does not affect Raman spectrum. Therefore, this high purity MWCNTs could be considered as a reference material with 100% purity. Figure 1(b) represents the Raman spectrum of a reference MWCNT sample. The spectrum was taken using an excitation wavelength of 633 nm. The Raman spectrum shows a typical feature of MWCNTs: the first ordered D -, G -, and D' -band peaks located at around 1350, 1582, and 1610 cm⁻¹, respectively. G -band peak is assigned to “in plane” displacement of the carbons

FIGURE 2: SEM images of purity-controlled MWCNT samples by mixing amorphous carbon particles and highly pure MWCNTs: (a) 0%, (b) 20%, (c) 40%, (d) 60%, (e) 80%, and (f) 100%.

strongly coupled in the hexagonal sheets [17]. D - and D' -band are found when disorder is introduced into the graphite structure. For this reason, the intensity ratio of D -band to G -band (I_D/I_G) has been used to determine the crystallinity of MWCNTs [15, 20]. However, according to Behler et al. [15], the intensity and position of D -band peak are varied with the excitation wavelength of laser to a great extent. Therefore, the measurement of I_D/I_G cannot be used as a standard method for evaluating the crystallinity of MWCNTs although I_D/I_G is used to compare the crystallinity of carbon nanotubes when the identical wavelength is used. Another broad peak (D'' -band) located at around 1500 cm^{-1} is also found in the Raman spectrum (Figure 1(b)). D'' -band was reported to be associated with amorphous sp^2 -bonded forms of carbon [21, 22]. Unlike I_D/I_G , the intensity ratio of D'' -band to G -band ($I_{D''}/I_G$) was found to be invariable with the excitation wavelength of laser. In addition, D'' -band is associated with only amorphous carbons. Hence, we suggest $I_{D''}/I_G$ instead

of I_D/I_G to be used for representing the crystallinity of carbon nanotubes. $I_{D''}/I_G$ of the reference samples obtained from Figure 1(b) is 0.06. On the other hand, $I_{D''}/I_G$ of amorphous carbon particles that was purchased from Aldrich is 0.37. We suggest that $I_{D''}/I_G$ of the high purity MWCNTs (0.06) and amorphous carbons (0.37) should represent the purities of 100% and 0%, respectively. Therefore, the purity of MWCNTs (P_{MW}) can be simply determined by an equation of

$$P_{MW}(\%) = \left(\frac{AC(D''/G) - MW(D''/G)}{AC(D''/G) - RMW(D''/G)} \right) \times 100, \quad (1)$$

where $AC(D''/G)$, $MW(D''/G)$, and $RMW(D''/G)$ are D''/G ratios of amorphous carbon particles, MWCNTs being tested, and reference MWCNTs, respectively. In order to verify the suggested equation, intermediate purity samples were prepared with 20% purity interval from 0% to 100% by mixing high purity MWCNTs and amorphous carbon particles.

FIGURE 3: (a) Raman spectra, taken using an excitation wavelength of 633 nm, of purity-controlled MWCNT samples with purities ranging from 0% to 100% with 20% interval. (b) Purity measured from Raman spectroscopy using 633 nm laser versus constructed content of MWCNTs.

First, we dispersed the MWCNTs and amorphous carbon particles in the dimethylformamide (DMF) separately with 1 mg/100 ml concentration. Then, two solutions were mixed with designed ratios. The mixed solutions were dropped onto glass and Si substrates for the analyses by Raman and SEM, respectively. Figure 2 shows the SEM images of several intermediate purity samples. It can be clearly observed from these figures that the amount of impurity decreases as the purity of MWCNT increases. However, it is hard to define the purity of samples quantitatively by using SEM measurements.

Six different intermediate samples prepared with different purities (0%–100%) were analyzed by Raman spectroscopy. Figure 3(a) shows the Raman spectra, taken using an excitation wavelength of 633 nm, of MWCNTs with various purities. 100% and 0% purity samples show the Raman spectra of reference MWCNTs and amorphous carbons, respectively. Although the deconvoluted peaks of 0% purity sample are not presented here, it was found that the Raman spectrum of 0% purity sample is composed of not only conventional *D*- and *G*-bands but also *D'*-band with a considerable intensity. With increasing the purity of MWCNTs, full width at the half maximum (FWHM) of the peak at 1200–1400 cm^{-1} (*D* + *D'*-bands) decreases because the contribution of *D'*-band is getting smaller. We applied the proposed equation to the series of MWCNT samples with intentionally varied purity, and the results are illustrated in Figure 3(b). Figure 3(b) plots the purity evaluated using the equation to the constructed contents with varying purities from 0% to 100%. The linear fitting yielded a slope close to unity, 0.96, and the confidence value R^2 was 0.95. Thus, the evaluated purities of MWCNTs are in good agreement with the designed values of constructed content. It can be therefore said that the suggested

equation can be simply used for evaluating the purity of MWCNTs.

Various lasers with different excitation wavelengths are used in Raman spectroscopy. Therefore, in order to standardize an evaluation method using Raman spectroscopy, the method should not be dependent upon the excitation wavelength. A number of previous literatures reported the crystallinity of carbon nanotubes determined from the intensity ratio of *D*-band ($\sim 1350 \text{ cm}^{-1}$) to *G*-band (I_D/I_G). However, the measurement of I_D/I_G cannot be used as a standardized evaluation method since the intensity of *D*-band is significantly dependent upon the wavelength of laser [15]. In this study, we measured the purities of several different samples by using the excitation wavelength of not only 633 nm shown in Figure 3(b) but also 532 nm to verify the independency of this method on the wavelength. Generally, 633 nm and 532 nm laser are widely used for the Raman scattering measurement of MWCNTs. Figure 4 represents the purities evaluated from the Raman spectra taken using 532 nm laser as a function of constructed content. $I_{D'}/I_G$, obtained using an excitation wavelength of 532 nm, of high purity reference MWCNTs and amorphous carbon particles was 0.07 and 0.49, respectively. Although $I_{D'}/I_G$ measured using 532 nm laser is slightly different from that obtained using 633 nm laser, the purity measured using an excitation wavelength of 532 nm is also well matched to the constructed content, as can be seen in Figure 4. The linear fitting yielded a slope of 1.03, and the confidence value R^2 was 0.96. Thus, the purities of MWCNTs evaluated using excitation wavelength of 532 nm are also in good agreement with the designed values of constructed content. It can be therefore concluded that evaluating the purity of MWCNTs using $I_{D'}/I_G$ is valid regardless of excitation wavelength of laser.

FIGURE 4: Purity measured from Raman spectroscopy using an excitation wavelength of 532 nm versus constructed content of MWCNTs.

4. Conclusion

A quantitative method for evaluating the purity of MWCNTs using Raman spectroscopy was newly proposed. The purity of MWCNTs was determined by comparing the intensity ratio of D'' -band to G -band ($I_{D''}/I_G$) of MWCNTs being tested with that of the high purity reference material. The established method was verified by testing the mixture of reference MWCNTs of high purity and amorphous carbon particles. Furthermore, it was found that the proposed method was found to be valid regardless of the excitation wavelength of laser.

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