Optical characterization of single-walled carbon nanotubes synthesized by catalytic decomposition of alcohol

Shigeo Maruyama1, Yuhei Miyauchi, Yoichi Murakami and Shohei Chiashi
Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
E-mail: maruyama@photon.t.u-tokyo.ac.jp

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Abstract. Single-walled carbon nanotubes (SWNTs), synthesized by a catalytic decomposition of alcohol (alcohol CVD method, ACCVD), are compared with high-pressure CO (HiPco) SWNT samples through optical spectroscopic measurements such as resonant Raman scattering, optical absorption and near infrared fluorescence. By the ACCVD method, SWNTs were synthesized either on zeolite catalyst-support particles or directly on the surface of a quartz substrate; in the latter case, a simple dip-coating technique was employed for mounting the metal catalyst. Specific morphological characteristics of as-grown SWNTs generated on zeolite support are presented using SEM and TEM, revealing that the SWNTs produced by the proposed method possess the significant quality of being almost free from amorphous carbons or metal particle impurities. The quality and diameter distribution of SWNTs were investigated and discussed through the results of Raman scattering and optical absorption. The average diameter was slightly smaller for SWNTs grown on zeolite particles than for HiPco SWNTs. Finally, fluorescent emission spectra from isolated SWNTs in an aqueous surfactant suspension were measured for various excitation wavelengths to determine the structural \((n, m)\) distribution of the SWNTs. The narrower chirality distribution for ACCVD SWNTs grown on zeolite compared with HiPco SWNTs was demonstrated.

1 Author to whom any correspondence should be addressed.
1. Introduction

The discovery of single-walled carbon nanotubes (SWNTs) [1] has created much research interest because of their unique physical properties [2] and hence remarkable potential as a new material in a wide range of applications. A technique for producing SWNTs in sufficient quantity and quality has long been sought. Following the landmark establishment of a synthesis method producing macroscopic amounts [3, 4], several techniques employing a CVD approach [5]–[18] have been proposed for the improved efficiency or productivity of the bulk synthesis of SWNTs. At present, CVD approaches, including the high-pressure CO (HiPco) technique [8, 12], have become dominant for the mass production of SWNTs.

The current main issue concerning SWNT production, therefore, is the enhancement of the quality that is critical for the reliable performance of proposed SWNT-based applications. Contamination (amorphous carbon or metal particle impurities) often accompanies the products as can readily be seen from pictures in the literature (see [8, 10] and [12]–[16]). As one possible solution for this, we have proposed the use of alcohol, especially ethanol and methanol, for the carbon feedstock [19, 20]. The proposed alcohol catalytic CVD (ACCVD) method can produce SWNTs with fine quality when combined with appropriate catalysts and experimental procedures. Furthermore, it was recently demonstrated that high quality SWNTs could be synthesized on a mesoporous silica coated substrate [21] or directly on a solid substrate such as silicon or quartz [22].

In this report, the quality of SWNTs synthesized from ethanol was investigated both qualitatively and quantitatively through several spectroscopic analyses. Throughout this paper, a pristine HiPco sample supplied from Rice University (batch No.: HPR113.4, using 1 ppm Fe(CO)₅, reaction pressure 30 atm and temperature about 950 °C) was employed as a reference for a comparison. First, the SEM and TEM studies were performed in order to discuss the quality as well as morphological characteristics of SWNTs grown on zeolite support powder. Then, Raman scattering analyses and optical absorption measurements were performed for the quantitative characterization of the ACCVD SWNTs. Finally, the chirality distribution of the SWNTs was determined by measuring fluorescence emitted from isolated SWNTs in aqueous suspension.
2. Experimental procedure and measurement

The detailed preparation of metal supporting zeolite powder was described in our previous reports [19, 20]. We prepared a catalytic powder by impregnating iron acetate \((\text{CH}_3\text{CO}_2)_2\text{Fe}\) and cobalt acetate \((\text{CH}_3\text{CO}_2)_2\text{Co-4H}_2\text{O}\) onto USY-zeolite powder (HSZ-390HUA, over 99% SiO\(_2\)) [23, 24]. The weight concentration of Fe and Co was chosen to be 2.5 wt% each over the catalytic powder. Molybdenum acetate and cobalt acetate were employed for the catalytic loading on to the quartz substrate using a dip-coat technique, the detailed procedure for which was presented in a previous report [22]. The adoption of Mo instead of Fe in the case of quartz is based on knowledge we obtained by preliminary experiments.

The schematic of our CVD apparatus and the procedure of the CVD were presented in [25] and [20], respectively. In brief, the specimen was placed on a quartz boat and the boat was set in the centre of a quartz tube (internal diameter = 26 mm, length = 1 m). One end of the quartz tube was connected to a rotary pump by two different paths, a 25 mm and a 6 mm diameter tube, to select the pumping power. The central 30 cm of the quartz tube was surrounded with an electric furnace. As the furnace was heated up from room temperature, a flow of about 300 sccm of Ar/H\(_2\) (3% H\(_2\)) was used, with only the smaller evacuation path open, to maintain the inside of the quartz tube at 300 ± 20 Torr. After the electric furnace reached the desired temperature, the Ar/H\(_2\) flow was stopped and the larger evacuation path was opened to bring the inside of the quartz tube to vacuum. Subsequently, ethanol vapour was supplied from an ethanol reservoir at a constant pressure of 10 Torr into the quartz tube. After the CVD reaction, the electric furnace was turned off and brought back to room temperature with a 100 sccm flow of Ar/H\(_2\).

In this report, CVD temperatures of 850 and 800\(^\circ\)C were employed for the zeolite powder and quartz substrate, respectively, because these are the optimum temperatures when ethanol vapour pressure is 10 Torr [20, 22].

The synthesized SWNTs were characterized by FE-SEM (HITACHI, S-900) and TEM (JEOL 2000-EX). For the micro Raman scattering measurements, CHROMEX 501is and ANDOR DV401-FI were used for the spectrometer and CCD system, respectively, with a SEKI TECHNOTRON STR250 optical system. In every Raman scattering measurement the spectrometer was calibrated using naphthalene and sulfur peaks. All Raman spectra presented in this report were an arithmetic average of the measurements at five randomly chosen different locations on the specimen. The VIS–NIR absorption spectra were measured with a HITACHI U-4000. The fluorescence was measured with a JOBIN YVON Fluorolog-311 spectrofluorometer with a liquid nitrogen cooled InGaAs near IR detector.

3. SEM and TEM observations

Figure 1 shows SEM images of ACCVD SWNTs grown on zeolite (figure 1(a)) and HiPco (figure 1(b)) SWNTs taken at several magnifications. The CVD temperature and time for the sample in figure 1(a) is 850 \(^\circ\)C and 60 min, respectively. The low magnification picture of figure 1(a) reveals that zeolite particles of several hundreds of nanometres were integrated by web-like bundles of SWNTs. The surface of the zeolite powders was densely covered with SWNTs bundles with a typical thickness of 10–20 nm. In the highest magnification picture, it was observed that the thinner bundles around/below 10 nm were seen preferably near the surface of the powder particle, and the bundle thickness seems to increase as they extend along the particle, due to van der Waals interactions, on the particle surface. At the outermost surface they
Figure 1. SEM images at various magnifications of (a) ACCVD SWNTs on zeolite particles and (b) HiPco SWNTs. ACCVD SWNTs were synthesized under the conditions of 850 °C and 60 min for CVD temperature and time, respectively.

Finally seem to depart into space, where the bending stiffness of the thereby thickened bundles could exceed the van der Waals forces from the surface. It is notable that our SWNT bundles are relatively straight and these walls are smooth, which is morphologically different from the bundles of HiPco SWNTs (figure 1(b)).

For a more detailed investigation of the structures, TEM images are compared in figure 2. The sample observed in figure 2(a) is same as that in figure 1(a). As expected from the above SEM observation, almost no amorphous carbon or metallic impurities were seen among the produced SWNTs even though this specimen was ‘as-grown’, as was confirmed by TGA [20]. The complete absence of metal particle impurities suggests that the catalytic metals were strongly adhered to the surface of zeolite during the CVD reaction. We ascribe the absence of amorphous carbon to an oxygen atom in the ethanol molecule, which could selectively oxidize carbon atoms with dangling bonds (i.e. a candidate of amorphous carbon) into the form of a more stable species such as CO. On the other hand, the pristine HiPco SWNTs were accompanied by numerous iron particles around 2–5 nm in diameter, as seen in figure 2(b) and as has been well described previously [12, 26]. In figure 2(a), we can find some quite large diameter nanotubes which are not observed in HiPco. For the time being, we suspect that these large diameter nanotubes may come from the fusion process. The total number of such large diameter nanotubes seems to be small,
and they are not observed in the following Raman scattering, absorption and spectrofluorimetric measurements.

4. Raman scattering analyses

Raman analysis is a powerful tool for the characterization of SWNTs [27], from which the quality and diameter distribution can be estimated and metal–semiconductor distinctions are to some extent possible. For the interpretation of the Raman spectra of SWNTs, refer to, for example, [28]. Figure 3 shows Raman spectra of ACCVD SWNTs on a quartz substrate and on zeolite particles, and HiPco SWNTs, measured with the excitation of a 488 nm laser. The CVD conditions of the zeolite and quartz samples were $850 \degree C \times 10 \text{ min}$ and $800 \degree C \times 60 \text{ min}$ for the CVD temperature and time, respectively. These temperatures are the optimum for both the zeolite and quartz cases when Ar/H$_2$ is used during the heating up of the electric furnace. The choice of 10 min for the CVD on zeolite sample is for consistency with the following absorption and spectrofluorimetric measurements. The difference between Raman features in 10 min and 1 h samples is small in any case. In all cases, the height of D-band around $1350 \text{ cm}^{-1}$ is sufficiently small compared with that of the G-band around $1590 \text{ cm}^{-1}$, indicating that the defects in the tube wall are sufficiently small. Note that, however, the G/D ratio is just a quick estimation of SWNT quality and does not always reflect the quality as shown in figures 1 and 2.

Figure 4 shows the radial breathing modes (RBMs) of these SWNTs measured with three different excitation laser wavelengths of 488, 514.5 and 633 nm. Because of the resonance feature of the Raman scattering of SWNTs due to the van Hove singularity of electronic DOS, RBM signals with three excitation energies are compared with the Kataura plot [29] calculated with $\gamma_0 = 2.9 \text{ eV}$ and $a_{c-c} = 0.144 \text{ nm}$ [30, 31] at the top of figure 4. Here, the diameter $d$ (nm) of the SWNTs was estimated from the RBM Raman shift $\nu$ (cm$^{-1}$) using the relationship $d = 248/\nu$ [30, 31]. The change in the resonant condition with 514.5 and 488 nm excitation can be understood from the Kataura plot. However, the resonant condition in this plot is apparently violated in the 633 nm measurements of all three case as denoted by asterisks in figures 4(g)–(i). A probable reason is the resonance condition of the $i$th valence van Hove singularity level to the $(i \pm 1)$th level because the resonance occurs with the light polarized perpendicular to the
Figure 3. Raman spectra of ACCVD SWNTs grown on quartz, ACCVD SWNTs grown on zeolite and HiPco SWNTs measured with 488 nm excitation. CVD conditions of ACCVD SWNTs on zeolite and that on quartz were 850 °C × 10 min and 800 °C × 60 min, respectively.

nanotube axis [32, 33]. Nevertheless, a rough measure of diameter distribution can be obtained by these RBM measurements. While HiPco SWNTs and ACCVD SWNTs on zeolite have a remarkable similar diameter distribution of between 0.9 and 1.5 nm, ACCVD SWNTs grown on a quartz [22] substrate have thicker diameters, between 1.1 and 1.8 nm.

5. Optical absorption

Optical absorption spectra of SWNTs were measured by several different techniques. Kataura et al [29] dispersed SWNTs, obtained by a laser-oven method, in ethanol and sprayed the suspension on to a quartz plate. O’Connell et al [34] suspended HiPco SWNTs in D₂O solution with 1% sodium dodecyl sulfate (SDS) in order to separate the bundled SWNTs into isolated ones. In addition, the absorption properties of ‘as-grown’ SWNTs can be measured by using a technique of synthesizing a SWNT mat directly on to the surface of quartz substrates [22], by which any effects of post-treatments are excluded. From the absorption peaks in the spectra, the electronic state of the produced SWNTs is characterized since each peak corresponds to a band gap of the obtained SWNTs.

Figure 5 compares optical absorption of (a) ACCVD SWNTs grown on quartz substrate, (b) ACCVD SWNTs grown on zeolite support, and (c) and (d) HiPco SWNTs. All samples except figure 5(a) were prepared using a procedure similar to O’Connell et al [34]. The specimen in the pristine state was dispersed in D₂O (1% SDS), by sonication with an ultrasonic processor (Hielscher GmbH, UP-400S) for 1 h at a power density of 460 W cm⁻². For the samples of
Figure 4. Raman RBM spectra of the samples compared in figure 3, measured with three different excitations of 488, 514.5 and 633 nm. At the top, the Kataura plot calculated with $\gamma_0 = 2.9$ eV and $a_{c-c} = 0.144$ nm is presented with the horizontal lines of the corresponding laser energies.

Since the as-grown SWNTs on quartz in figure 5(a) are in the bundled state and not sonicated/dispersed in liquid at all, the peak separation is most ambiguous. The HiPco SWNTs sonicated and dispersed in D$_2$O (1% SDS) but without centrifugation (figure 5(d)) shows slightly clearer peaks probably because some number of isolated SWNTs exist along with bundled SWNTs. In comparing figures 5(a) and (d), it can be seen that the former has absorption peaks of slightly smaller energy. This coincides with the previous observation regarding figure 4 that SWNTs grown on quartz have larger diameters than those of HiPco SWNTs.

After the centrifugation and decanting of the sonicated HiPco and ACCVD samples, the absorption peaks become sharper, as demonstrated by O’Connell et al [34]. A slight shift towards blue was observed from figure 5(c) to (d), which is due to the de-bundling of SWNTs [34]. Comparison of figures 5(b) and (c) implies that the ACCVD SWNTs grown on zeolite are thinner than HiPco SWNTs, judging from the absence of the peak around 1400 nm (i.e. the thickest peak) in figure 5(c). According to the above sequential comparisons, the diameter order is estimated to be (ACCVD on zeolite) < (HiPco) < (ACCVD on quartz), which coincides with

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Figure 5. Optical absorption of (a) ACCVD ‘as-grown’ SWNTs directly synthesized on a quartz substrate, (b) ACCVD SWNTs, and (c) and (d) HiPco SWNTs. The samples (b)–(d) were sonicated and dispersed in D$_2$O (1% SDS). For ‘isolated’ samples (b) and (c), the suspension was centrifuged under 20 627 g for 24 h and their supernatant used for the exclusion of bundled SWNTs.

the results in figure 4. However, the difference in diameter range between ‘ACCVD on zeolite’ and HiPco may be considerably larger in isolated absorption measurements than the expectation from Raman scattering in figure 4. It is possible that the sonication and centrifugation stages do considerably select easily de-bundled SWNTs. Since bundles in ‘ACCVD on zeolite’ are thicker than HiPco in figure 1, only thinner diameter SWNTs may be easily de-bundled and represent the absorption and following spectrofluorimetric measurements. As a matter of fact, the choice of ‘10 min’ CVD sample rather than ‘1 h’ sample for ACCVD on zeolite was because of this sonication problem. With the latter sample, only weak band-gap absorption was measured by the same preparation procedure.

Comparing with the Kataura plot, the absorption peaks around 1000–1500 nm correspond to the first band of semiconducting SWNTs and peaks around 700–900 nm are considered to correspond to the second band gap.

6. Fluorescence measurement and structural determination

For the further characterization of the produced SWNTs, we performed a spectrofluorimetric measurement, which is a powerful tool for the quick determination of the SWNT chiral distribution ($n,m$) recently proposed by Bachilo et al [35]. The procedure in the sample
Figure 6. Contour plots of fluorescence intensities for (a) ACCVD and (b) HiPco SWNTs, as a function of the wavelength of excitation and resultant emission. ACCVD SWNTs were produced on zeolite support particles under the conditions of 850 °C and 10 min for the CVD temperature and reaction time, respectively.

preparation is the same as that used in figure 5. SWNTs were first dispersed in D_2O (1% SDS) solution using an ultrasonic processor for 1 h, and then the suspension was centrifuged under 20 627 g for 24 h. Here, ACCVD SWNTs with zeolite support were directly used for the initial sonication. The supernatant, including isolated SWNTs, was used for the measurement.

Figures 6(a) and (b) show the contour plots of fluorescence intensities for ACCVD and HiPco SWNTs, respectively, represented by the wavelength of excitation (ordinate) and resultant emission (abscissa). The fluorescence emitted in the range 900–1300 nm was recorded while the excitation wavelength was scanned from 500 to 900 nm. The ACCVD SWNTs used in figure 6 (and figure 7) were produced on zeolite support powder under the conditions of ‘850 °C, 10 min’ for the CVD temperature and reaction time, respectively. Each distinct peak observed in figure 6 corresponds to fluorescence from a first band gap $E_{11}$ of a semiconducting SWNT excited in a second band gap $E_{22}$ with specific chiral $(n, m)$. The positions of peaks were almost exactly the same as measurements by Bachilo et al [35]. Even though the employed Kataura plot [36] and diameter–RBM frequency relations were inconsistent with those used for our Raman scattering analysis in figure 4, the chirality assignment by Bachilo et al was temporarily adopted in figure 6. Clearly, two major peaks of chiral indices (7, 5) and (7, 6) were prominent for ACCVD SWNTs, while several more peaks were as strong as these peaks for HiPco SWNTs.

Figure 7 shows the distribution of the diameter and chiral angle of synthesized SWNTs for both ACCVD and HiPco, where the area of a circle at each chiral point denotes the strength of the fluorescence measured in figure 6. Since no information of the chirality dependent quantum yield of absorption and emission is known, it is assumed that the strength of fluorescence closely resembled the abundance distribution. This figure shows a clear difference in the chiral distribution between these two samples. First, ACCVD SWNTs have a narrower, and at the same time smaller, diameter distribution while HiPco SWNTs have a relatively wide diameter distribution, which coincides with the result in figure 5. Second, the SWNTs grown from ethanol have a dominant distribution in the higher chiral angle region close to the so-called armchair type, while the HiPco SWNTs shows less noticeable dependence of the distribution on the chiral
angle. Further investigations to elucidate the origin of this difference in chirality distribution are currently in progress by our group.

When this paper was in the final preparation stage, we found that Bachilo et al [37] had measured the chirality distribution of SWNTs generated from the CCVD method of Resasco, which uses the CO-disproportional reaction on a Co/Mo catalyst supported on silica (CoMo). The resultant distribution has major peaks at (6, 5) and (7, 5). The whole distribution was remarkably similar to our ACCVD SWNTs generated at 750 °C as shown in figure 8 in the same fashion as in figures 6 and 7. It is suspected that the chirality distribution tends to be more armchair side when the diameter of the SWNTs is smaller.

7. Conclusion

We have characterized our SWNTs synthesized from ethanol by means of spectroscopic analyses using HiPco SWNTs as a reference specimen. Observations by SEM and TEM exhibited the fine quality of ACCVD SWNTs synthesized on zeolite support powder as well as the morphological difference between those two samples. The resonant Raman analyses with three different excitations 488, 514.5 and 633 nm were performed for ACCVD SWNTs grown on zeolite and quartz substrates, and HiPco SWNTs. It was shown that the ACCVD SWNTs grown on a quartz surface have a larger diameter distribution, in the range of 1.1–1.8 nm, than ACCVD on zeolite and HiPco SWNTs. This was consistent with the optical absorption measurements where a slightly thinner distribution of ACCVD on zeolite compared to HiPco SWNTs was confirmed. The detailed chiral distributions of the latter two specimens were elucidated using spectrofluorimetric analyses. In addition to the fact that the tendency in diameter distributions coincides with the result observed in the optical absorption analyses, it was revealed that the ACCVD SWNTs had a narrower chiral distribution where the tubes with higher chiral angle, i.e. close to armchair type, were dominant among them. This narrower chirality distribution,
observed in the case of ACCVD SWNTs, could contribute to future attempts to synthesize SWNTs with well restricted or even selected chirality.

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