

**CATALYTIC CVD GENERATION AND OPTICAL CHARACTERIZATION OF
SINGLE-WALLED CARBON NANOTUBES FROM ALCOHOL**

Shigeo Maruyama, Yoichi Murakami, Yuhei Miyauchi, and Shohei Chiashi

Department of Mechanical Engineering

The University of Tokyo

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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High purity single-walled carbon nanotubes (SWNTs) were synthesized by the alcohol catalytic CVD method (ACCVD method) where ethanol vapor was used as a carbon feedstock [1, 2]. For the bulk synthesis of SWNTs, we employed Fe/Co alloy supported on USY-zeolite powder. Figure 1 shows SEM images of ACCVD SWNTs grown on zeolite in two different magnifications. The temperature and reaction time of the sample in Fig. 1 during CVD were 850 °C and 60 min, respectively. The left panel of Fig. 1 reveals that the zeolite particles of several hundreds of nanometers were integrated by web-like bundles of SWNTs. The surface of the zeolite powders was densely covered with SWNTs bundles with typical thickness of 10 - 20 nm. In higher magnification shown in the right panel, 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 seem to increase as they run around, due to van der Waals interactions, on the particle surface.

The yield of SWNTs grown on zeolite support was estimated by TGA. The yield of SWNTs defined here is chosen as the ratio of weight loss between 500 and 700 °C to the weight remained at 1000 °C [2]. Figure 2 shows the TG results measured for 3 different samples prepared at different CVD reaction times. It is recognized that weight loss between 500 and 700 °C corresponding to SWNTs increases linearly as the CVD time becomes longer. At the reaction time of 120 min, SWNT yield of more than 40 % was achieved over the weight of zeolite support powder with Fe/Co catalyst, which corresponded to more than 800 % yield over the weight of the catalytic metal with assuring as-grown high quality [2].

One feature of the proposed technique lies in its ability to produce abundant amount of SWNTs on a flat substrate such as quartz and Si without using any kind of support or underlayer materials [3, 4]. Figure 3 shows the SEM image of a quartz substrate taken from a tilted angle including broken cross-section of the substrate. The CVD for this sample was performed at 800 °C

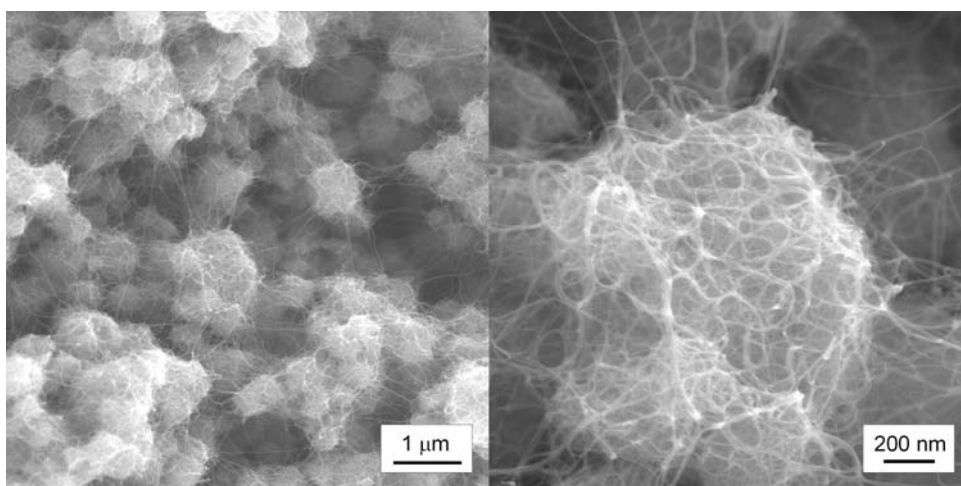


Figure 1: SEM image of ACCVD SWNTs on zeolite particles. The SWNTs were synthesized under the condition of 850 °C and 60 min for CVD temperature and time, respectively.

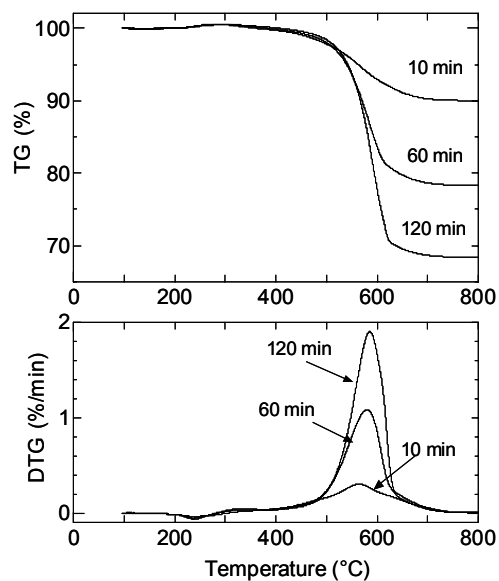


Figure 2: TG curves of ‘as-grown’ SWNT-synthesized zeolite powder for the CVD reaction times of 10, 60, and 120 minutes and its derivative DTG (bottom).

for 1 h using Ar/H₂ (3% H₂) in the heating-up in the CVD process. The substrate was blackened and a uniform ‘mat’ of SWNTs with a thickness of a few hundred nanometers was formed on the both sides of the quartz substrate. Since the optical properties of thereby produced ‘as-grown’ SWNT mat is readily measured, this technique is considered to open-up a new application of SWNTs toward novel optical devices. As an example, a short-pulse mode-lock laser using this sample utilizing saturable absorption of SWNTs [5] is demonstrated. In addition to the quartz and Si, we can

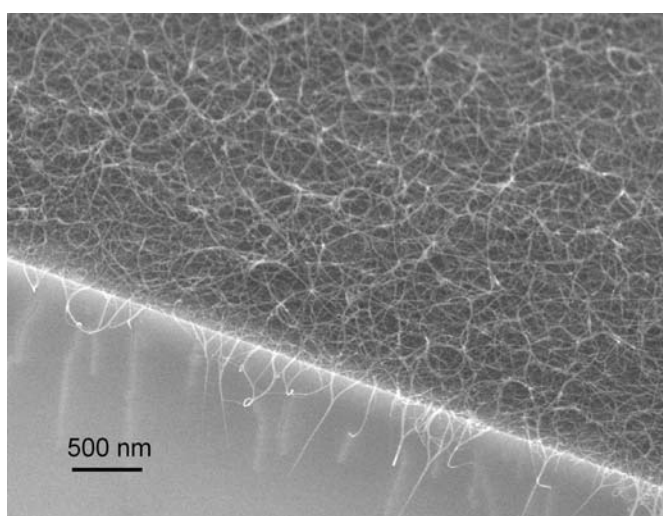


Figure 3: SEM image of SWNTs directly synthesized on a quartz substrate taken from tilted angle including broken cross-section of the substrate.

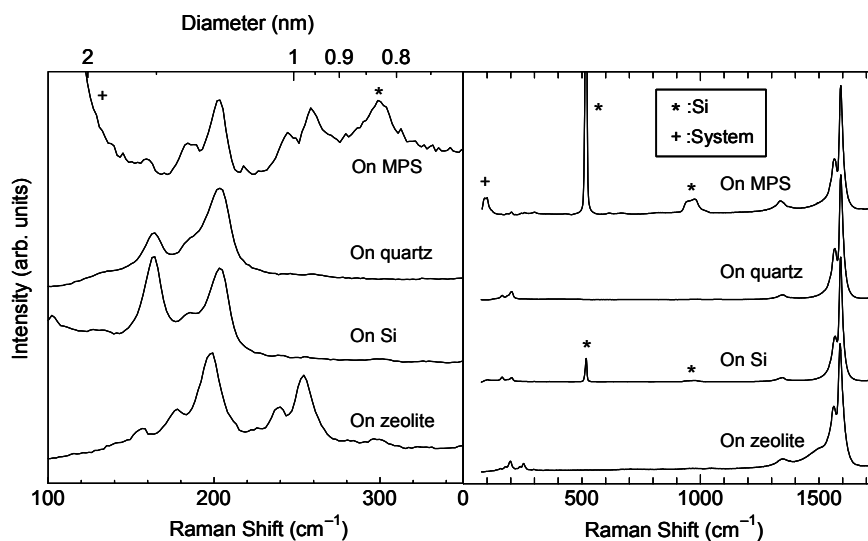


Figure 4: Raman spectra of SWNTs grown on USY-zeolite, Si and quartz substrates, and MPS thin film coated on Si wafer, measured by 488 nm laser. The lower wave number region (left panel) exhibits their RBM spectra, from which the diameter distribution for each case is estimated.

generate SWNTs from SBA-16 type mesoporous silica (MPS) thin film formed on Si substrate for the purpose of more spatially controlled growth of SWNTs [6].

The Raman spectra of SWNTs grown on various bases (USY-zeolite, Si, quartz, and MPS) were compared in Fig. 4. The excitation laser wavelength was 488 nm for all cases. Although there are differences in the diameter distributions depending on the types of employed substrates, the radial breathing mode (RBM) peaks of SWNTs were clearly observed and the ratios of G/D peaks were sufficiently high, indicating high quality of produced SWNTs for all cases. Authors believe that the foregoing techniques synthesizing high-quality SWNTs on various types of bases could make a considerable contribution to the development of SWNT-based innovative devices.

Figure 5 compares optical absorption of (a) ACCVD SWNTs grown on quartz substrate, (b) ACCVD SWNTs grown on zeolite support, (c, d) HiPco SWNTs. All samples except Fig. 5(a) were prepared based on the procedure similar to O'Connell et al. [7]. The 'as-grown' sample was dispersed in 1 wt % SDS solution of D₂O by a sonication with a cup-horn sonicator for 1 h at a power density of 460 W/cm². For the samples of Fig. 5(b) and (c), the suspension was further centrifuged at 20,627 g for 24 h and their supernatant rich with isolated SWNTs was used for the measurement. After the centrifugation and decanting of the sonicated HiPco and ACCVD samples, the absorption peaks become sharper. Slight blue shift was observed from Fig. 5(c) to (d), which is explained to be the de-bundling of SWNTs [7]. Comparison of Fig. 5(b) and (c) implies that the ACCVD SWNTs grown on zeolite is thinner than HiPco SWNTs.

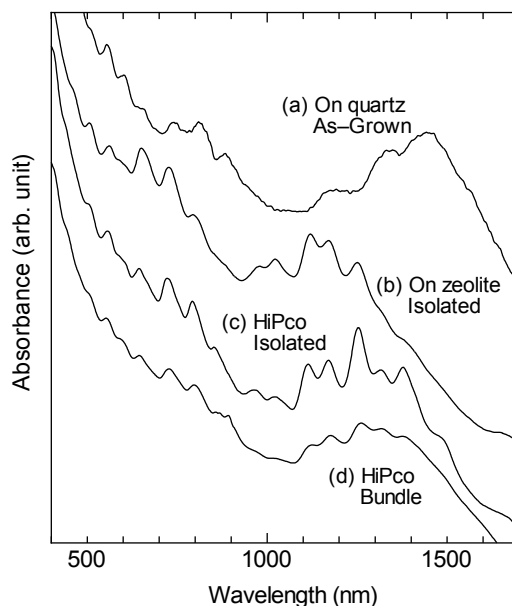


Figure 5: Optical absorption of (a) ACCVD ‘as-grown’ SWNTs directly synthesized on a quartz substrate, (b) ACCVD SWNTs, and (c, d) HiPco SWNTs. As for the samples (b-d), they were sonicated and dispersed in D₂O (1 % SDS). See text for details.

In order for the further characterization of produced SWNTs, we performed a spectrofluorimetric measurement [8], which is a strong tool for the quick determination of SWNT chiral distribution (n, m) recently proposed by Bachilo et al. [9]. The procedure in the sample preparation is the same as that used in Fig. 5. Figures 6(a) and (b) shows the contour plots of fluorescence intensities for ACCVD and HiPco SWNTs, respectively, represented by the wavelengths of excitation (ordinate) and resultant emission (abscissa). The ACCVD SWNTs used in Fig. 6 (and following Fig. 7) were produced on zeolite support powder under the conditions of ‘850 °C, 10 min’ for the CVD temperature and reaction time, respectively. The positions of peaks were almost exactly the same as measurements by Bachilo et al. [9]. Apparently, 2 major peaks of chiral indexes (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 diameter and chiral angle of synthesized SWNTs for both ACCVD and HiPco, where the area of a circle at each chiral point denotes the intensity of the fluorescence measured in Fig. 6. This figure shows a clear difference in the chiral distribution between these two samples. First, ACCVD SWNTs has narrower, at the same time smaller, diameter distribution while HiPco SWNTs has a relatively wider diameter distribution, which coincides with the result in Fig. 5. Second, the SWNTs grown from ethanol has a dominant distribution in higher chiral angle region close to so-called armchair type, while the HiPco SWNTs shows less remarkable dependence of the distribution on the chiral angle [8]. Further investigations to elucidate the origin of this difference in chirality distribution are currently in progress.

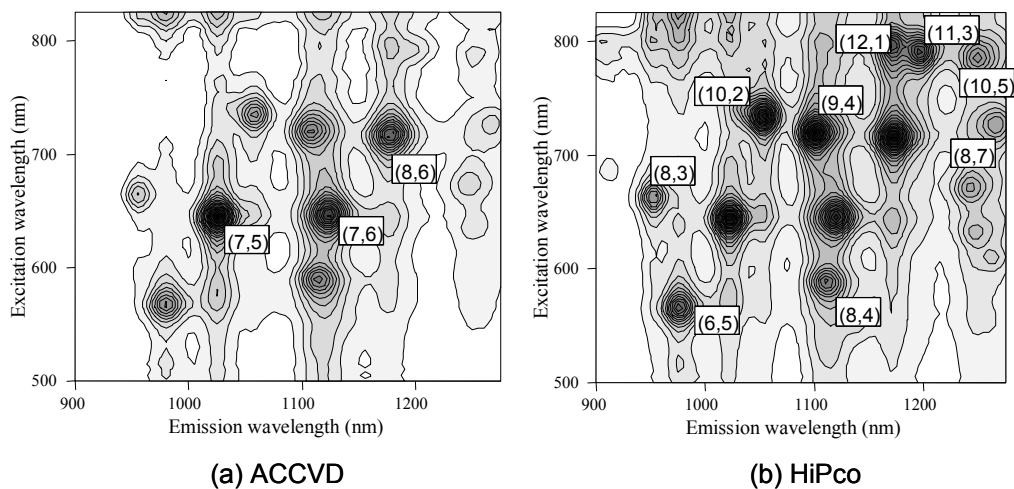


Figure 6: Contour plots of fluorescence intensities for (a) ACCVD and (b) HiPco SWNTs, as a function of the wavelengths of excitation and resultant emission. ACCVD SWNTs were produced on zeolite support particles under the conditions of 850 °C and 10 min for the CVD temperature and reaction time, respectively.

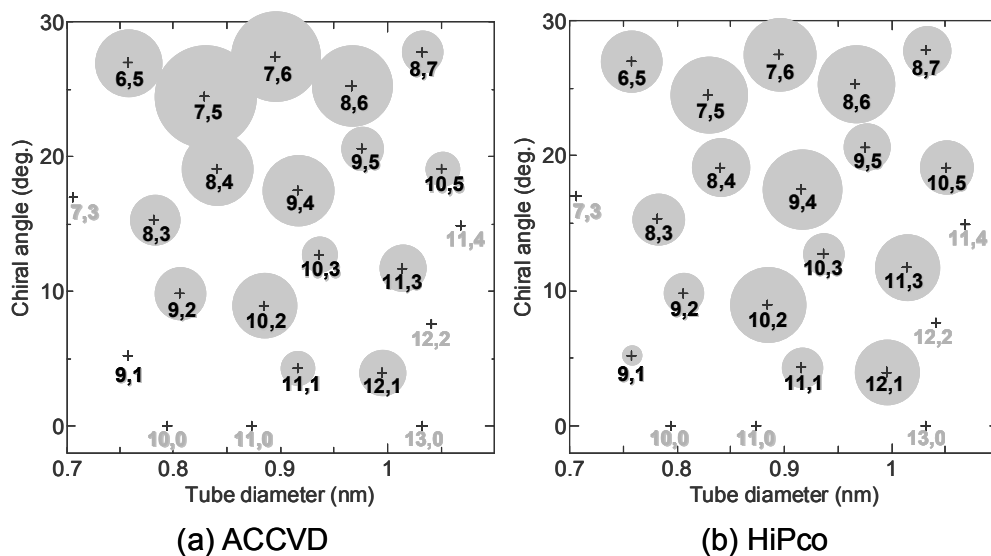


Figure 7: Diameter and chiral angle distribution of (a) ACCVD and (b) HiPco SWNTs where the area of each grayed circle corresponds to the peak intensity observed in Fig. 6.

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