Formation of Single-wall Carbon Nanotubes by Using Porous Glass

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Single-wall carbon nanotubes (SWNTs) were prepared by several kinds of porous glass, with different inner pore size, each of which was prepared by controlling the condition of phase separation. By applying alcohol CCVD technique, it was found that the yield of SWNTs was enhanced when the pore size increases from 6 to 10 nm and 16 nm. On the other hand, the diameter distribution of SWNTs was invariant in all porous glasses under investigation, under the same ambient temperature.

Recently, single-wall carbon nanotubes (SWNTs) were synthesized in good quality by using alcohol catalytic CVD (ACCVD) technique.[1–4] This technique has extensively been used the last few years, since the experimental setup is quite simple in comparison with those of a laser furnace technique or an arc-burning technique, and also, SWNTs with less impurity are easily obtained.

As for the formation mechanism of SWNTs, it is confirmed that the existence of metal particles is necessary in advance. In the typical experimental condition of ACCVD technique, metal particles are generated at first and supported on the limited kinds of porous materials, such as USY zeolite powder[1,2] or home-made porous silica membrane.[3] Then, SWNTs are produced by the reaction of alcohol with these metal particles. In order to purify these SWNTs from the raw sample, it is necessary to get rid of these supported materials as well as the metal particles as themselves. Therefore, recent effort of improving CVD technique, (e.g. dip-coating method[4]) has been made to keep away from using these supported materials. Very recently, the formation of mm-scale bulk material consisting mostly of single-wall carbon nanotubes by using such a kind of modified CVD technique, was reported.[5]

In this letter, SWNTs were made with porous glass particles prepared with a phase separation technique, where borosilicate glass was kept in an oven for several hours. It is known that one can control the inner diameter of the pore size in the glass systematically and accurately by controlling the ambient temperature and the time during phase separation treatments.[6] After heat treatment, porous glass was prepared by etching with chemical treatment. It is interesting to see whether the yield of SWNTs and the diameter distribution of them are influenced or not by using these porous glasses having different inner pore sizes.

Porous glass having several different kinds of pore size (6, 10. 16, 30, 50, and 100 nm in diameter, respectively) were prepared by use of a phase separation technique, which was described elsewhere.[6] SWNTs were prepared on these porous glasses with similar experimental condition for ACCVD technique,[1,2] where cobalt was used as a catalytic metal (supplied as cobalt acetate, 3 wt % against to the weight of porous glass), and the ambient temperature for the reaction of alcohol with the metal particles was kept at 850 °C for 30 min. The quantity of carbon materials containing SWNTs obtained in the typical experimental condition described above is ca. a few wt % or less, against to the weight of porous glass. After the formation of SWNTs, the material was investigated by Raman spectroscopy, using a spectrometer (JOBIN YVON U-1000) with a photo multiplier (HAMAMATSU PHOTONICS R943-02) and an Ar laser (488 nm) for the light source.

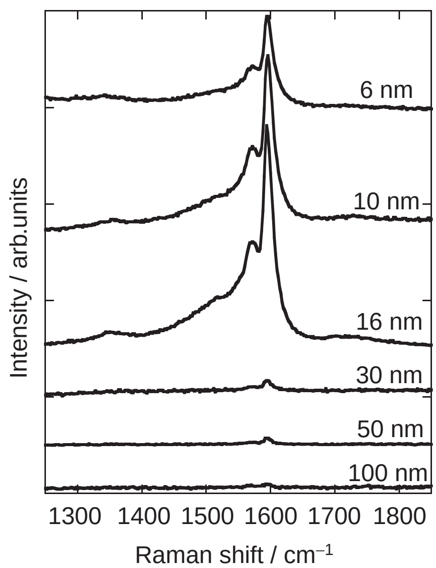

Figure 1. Raman spectra in the higher frequency region (1250–1850 cm^{-1}) of SWNTs prepared by alcohol CCVD technique by using porous glasses of different pore sizes at 850 °C.

Figure 1 summarizes Raman spectra in the higher frequency region (1250–1850 cm^{-1}) of SWNTs prepared by an ACCVD technique by using porous glass of different kinds of pore size. All spectra were obtained with 488-nm laser excitation.

The figure clearly shows the characteristic Raman spectral features of SWNTs, as were seen in the case of ACCVD results obtained with zeolite.[1,2] Furthermore, the figure also shows that the yield of SWNTs is influenced much, depending on the inner pore size of porous glass, i.e., the yield of SWNTs rapidly increases when the pore size increases from 6 to 10 nm and 16 nm, but suddenly drops off above 30 nm. In the present situation, it is not conclusive whether the reason of this sudden decrease simply comes from the difference in the pore size of porous glasses or not, because for those above 30-nm pore size, the shape of each grain was found to have bigger in size than those of having 6–16-nm pore size. Therefore, it is much safer to say that, the yield of SWNTs obtained by porous glasses of 16-nm inner pore size gives the tentative limit of the best yield under investigation. It is interesting to note that the Raman intensity obtained with this porous glass having 16-nm pore size is found to be almost the same as those obtained when zeolite powder was used as reference, with the same apparatus and the same experimental condition.[7]

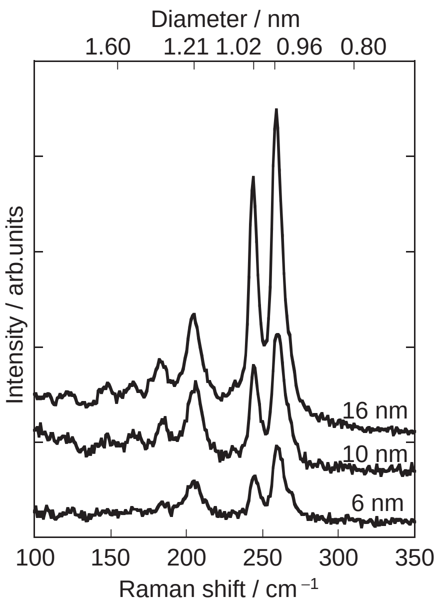

Figure 2. Raman spectra in the lower frequency region (100–350 cm^{-1}) of SWNTs prepared by alcohol CCVD technique by using porous glasses of different pore sizes at 850 °C.

Figure 2 represents Raman spectra in lower frequency region (100–350 cm^{-1}), which correspond to radial breathing mode (RBM) of SWNTs. The Raman peak intensities obtained for the porous glasses having pore size above 30 nm are too weak to be detected (not shown in the figure). The upper horizontal axis shows the diameter of SWNT corresponding to the Raman peak position, assuming that the diameter of each SWNT, d (nm), is given by $d = 248/\omega$,[8,9] where ω (cm^{-1}) indicates the RBM frequency.

Figure 2 declares that the diameter distribution of SWNTs is invariant in all porous glasses having different pore sizes under the same ambient temperature condition. It is well known that the diameter distribution of SWNTs obtained with ACCVD technique with zeolite is, generally speaking, more widely distributed than that obtained with arc discharge or laser furnace technique, and that distribution shifts toward the larger, as the ambient temperature increases.[1] At lower ambient temperature (600–700 °C), the diameter distribution of SWNTs prepared with zeolite gives similar diameter distribution of that prepared with porous glass at 850 °C, as is shown in Figure 2, except the additional features around 300 cm^{-1}, which corresponds to SWNTs having smaller diameters (of around 0.8 nm). In other words, the diameter distribution of SWNTs obtained in this experiment has much sharper distribution than that obtained by usual ACCVD technique with zeolite powder.

In the CVD technique, the generation of SWNTs is usually understood in terms of "VLS (vapor–liquid–solid)" model, where carbon atoms are first dissolved into metal particles and a cylindrical structure of SWNT is considered to grow from these metal–carbon mixtures.[10] Also, it is considered that the size distribution of metal particles is closely related to the diameter distribution of the obtained SWNTs.[11] Actually, the diameter distributions of SWNTs obtained by using CVD technique are very similar to each other, showing rather broad diameter distribution.[1–4,12] It is interesting to see whether the size distribution of metal particles supported by these porous glasses used here is different from others or not, though these metal particles hide inside of or around the pore of these porous glasses.

A preliminary investigation for eliminating supported material with base treatment after the formation of SWNTs indicates that the porous glasses can be easily removed from the raw material, which was confirmed by TEM observation.[7] This TEM image declares that metal particles having diameters less than 16-nm and SWNTs exist in the material, even in the case of porous glass having 16-nm pore size, indicating that SWNTs could be prepared inside the pore of the porous glass. Further study including the investigation of the metal size distribution is now in progress.

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