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Preparation of Highly Dispersed Single Walled Carbon Nanotubes on Metal Surface in Solution

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The preparation method of highly dispersed isolated single-walled carbon nanotube (SWNT) on metal surface was optimized to obtain the vibrational information of isolated individual SWNT. The tubes were isolated using a surfactant (sodium dodecyl sulfate) via the formation of the micelle in aqueous solution, and then it was deposited on metal surface. Roughened metal surface gave highly dispersed SWNT. Vibrational information of isolated SWNT on solid surface was obtained using microscopic Raman scattering spectroscopy. Relatively intense scattering was observed when roughed gold metal plate was used as substrates. The optical absorption of roughed gold may contribute to enhance the scattering under near-infrared excitation (785nm). The present observation suggests that roughened gold surface provides the superior substrate to support isolated SWNTs, and causes the enhancement in the scattering. Structural information of isolated individual SWNT on solid surface was successfully obtained via observation of the radial breathing mode.

Key words: single-walled carbon nanotube (SWNT), sodium dodecyl sulfate, confocal micro Raman spectroscopy, radial breathing mode, near-infrared excitation

1. INTRODUCTION

Since the discovery of carbon nanotubes[1], a great deal of efforts has been focused on the developments of their functionalities as a novel nano-scale material[2]. It is known that the tubes are very stable with high mechanical strength, showing very unique chemical and physical characteristics. In particular, the properties of single-walled carbon nanotubes (SWNTs) are quite unique. Their characters can be tuned precisely if one can control their diameter and chirality of the tubes[3]. For the uses of SWNT as a novel well-characterized nano-scale material, we have to develop the techniques to handle isolated SWNTs.

In this report, the methods to prepare highly dispersed SWNT on metal substrates were developed. Several organic solvents and a surfactant were used to prepare highly dispersed solution containing SWNTs. These solutions were deposited onto solid surfaces. After dry up the solvents, structural information about the tubes on the surface was obtained using atomic force microscopy. Vibrational information was also obtained from microscopic near-infrared Raman scattering spectroscopy to evaluate the dispersion of the tubes on the surfaces.

2. EXPERIMENT

For the preparation of highly dispersed SWNT (Carbolex Co., AP-Grade, purity 50-70%) solutions, several solvents (toluene, isopropyl alcohol, methanol and water) without surfactant were examined. Mixture of each solvent (1.0 ml) and SWNT (0.8 mg) was sonicated for 15 min. to prepare the dispersions. Effect of the addition of a surfactant (sodium dodecyl sulfate, SDS) was also examined using water as a solvent. The dispersion containing SDS were prepared according to the method reported by O'Connell et al.[4] Briefly, commercially available SWNT was dispersed in 1 wt % sodium dodecyl sulfate (SDS) surfactant aqueous solution. These dispersions were sonicated for 10 min. Immediately after the ultra-sonication, these dispersions were centrifuged at 12,000 rpm for 15 min., and were then decanted to obtain the highly dispersion.

Adsorption of SWNT onto a cleaned and mirror-finished polycrystalline Au surface was carried out by dropped these dispersions. The polycrystalline Au plate was cleaned by immersing into hot acid (H_2SO_4:HNO_3 = 2:1) for 15min. The Au plate was then polished to optical flatness using a 0.06 μm Al_2O_3 paste for the final finish. Treatment using HCl was also adopted after cleaned-up procedure to introduce roughness on to the Au plate. After drying deposited solution containing SWNT onto these Au plates, the electrode was sonicated in ultra-pure water to remove excess tubes and impurities contained in as received sample.

Confocal resonance near-infrared (NIR) Raman measurements carried out using commercial Raman microprobe spectrometer (Ramanscope System-2000, Renishaw) with a solid-state continuous-wave diode laser for 785 nm (E_{ex} = 1.58 eV) excitation. The expanded NIR beam is focused onto the sample using an water-immersion objective lens with 100x

Table I. The dispersion of SWNT in several solvents.

solvent	after sonication	after centrifugal separation following sonication	on Au surface
Toluene	Good	NG	NG (aggregate)
2-ProOH	NG	NG	NG (aggregate)
Et-OH	NG	NG	NG (aggregate)
H_2O	NG	NG	NG (aggregate)
H_2O with SDS	Good	Good (brown)	Highly dispersed

magnifications and a numerical aperture of 1.0 (Olympus). Estimated spot size of irradiation is 1 μm, with the output intensity of 1 mW.

The surface of the Au plate was examined by an atomic force microscope (AFM, NanoScope IIIa, Digital Instruments).

3. RESULTS AND DISCUSSION

Table I shows that the results of the dispersion of SWNT for the solvents. Solutions containing SWNT was prepared using polar (water, methanol and isopropyl alcohol) and non-polar (toluene) solvents. After the sonication, all of suspension showed brown color. This color disappeared after a few minutes via the formation of the precipitations, except for the system of water/SDS and toluene. The results can be explained by the hydrophobicity of SWNT. It is known that polar solvents are not appropriate to disperse SWNT. Importance of non-polar solvent or micelle for the solvation of SWNT was shown in this result of the dispersion in homogeneous systems.

To prepare highly dispersed SWNT solution, the dispersions were centrifuged. Only the system of water/SDS maintained the state of the dispersion. The system of toluene did not contain dispersed SWNT after the centrifugation. The difference may be explained by the stability of the SWNT dispersion. Normally, interaction between the tubes is stronger than those with solvents. This relatively strong interaction prevents the formation of highly dispersed SWNT in solution after the formation of the bundles. The dispersion of SWNT in toluene should be bundles rather than isolated. This bundle may be precipitated after the centrifugation. On the other hand, SWNT aqueous dispersion consists of well-isolated SDS micelles should be more stable than the bundle dispersion in toluene. Relatively strong interaction between hydrophobic groups of SDS molecules and the side-wall of SWNT allows the formation of the micelles contains isolated single SWNT[4]. This strong interaction leads to the formation of the highly-dispersed aqueous solution of SWNT.

In order to prepare highly-dispersed SWNT adsorbed on solid surface, SWNT dispersions were deposited onto the surface of metal substrates. The results using Au substrate were shown in Table I. In the case of water/SDS dispersion system, the SWNT was highly dispersed on the polycrystalline Au plate. Since the surface of cleaned Au substrates is hydrophilic, the polar solvents spread over covering the surface. Furthermore, hydrophilic functional group of SDS at the side of this micelle has a strong interaction with the surface of Au plate. Due to these reasons, the highly dispersed SWNT were adsorbed on Au plate in this system. On the other hand, in the systems of the polar solvent without SDS and non-polar toluene, SWNT was aggregated on Au. It should be noted that SWNT was already aggregated in the system of polar solvent without SDS. Moreover, in the system of toluene,

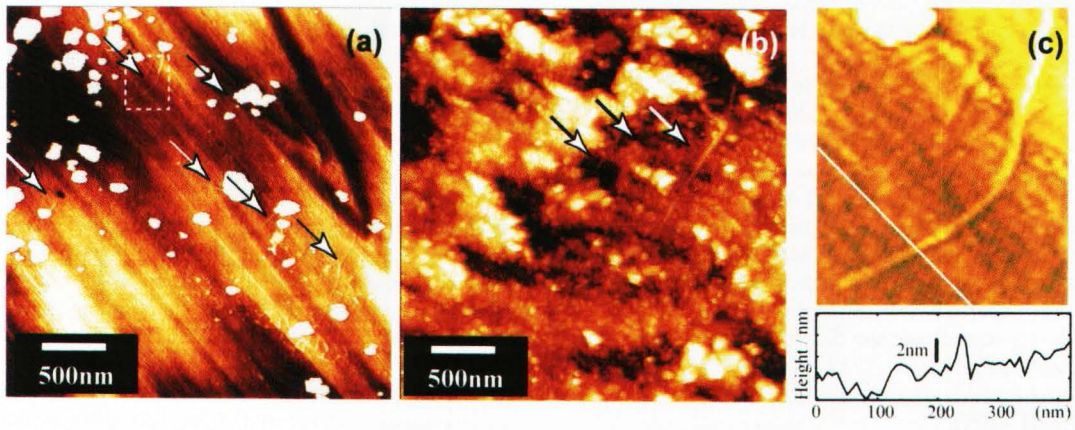

Fig. 1 AFM height images of SWNT adsorbed on polycrystalline Au plate deposited from water/SDS dispersion system: the Au surface was treated with HCl for a few minutes (a) and 10 min. (b) after polished by Al_2O_3. The image (c) is with higher magnification for dotted squared part of the image (a). Vertical sectional view is also shown.

solvent itself cannot spread over Au plate due to the non-polarity, forming aggregation. These results indicate that polarity of the solvent is also important factor to achieve higher dispersion.

Figure 1(a) shows the AFM image of SWNTs on Au plate prepared by the water/SDS dispersion system. An arrow indicates isolated SWNT. The present sample has a concentration of < 1.0 SWNT / μm^2 with tube lengths from 200 nm to 2000 nm on the Au plate. The round dots on the surface are presumed to be excessive SDS. To remove these dot structures completely, prolonged ultrasonic treatment in ultra-pure water was required. From the analysis of the AFM images, the height of these SWNTs was to be in the range between 1 and 4 nm. The images clearly prove successful preparation of highly dispersed SWNT adsorbed on metal.

There were several reports on the methods to obtain highly dispersed SWNT. Typical dispersing method of aggregate SWNTs is to immerse it in the mixed acid (H_2SO_4/HNO_3)[5]. The bundle is separated to small or isolated SWNTs by intercalation of NO_3^- ion to interstice of tubes[6]. Thus, in order to remove intercalated NO_3^-, sufficient washing using alkali and ultra-pure water is required. As compared with this technique, the present method can provide highly dispersed isolated SWNT onto the Au plate much more conventionally using commercially available aggregated SWNT samples.

Furthermore, it was found that a higher dispersed state of isolated SWNT was obtained by using the Au plate treated by HCl for a long time. Figure 1(b) shows the AFM height image of SWNT dispersed on to Au plate treated by HCl for 10 min. The surface of this Au plate was roughened by this treatment. This roughened structure would prevent the aggregation at the evaporation process of the solvents. As mentioned above, the water/SDS dispersion system on polycrystalline Au plate allows the highly dispersed state. Higher dispersion using roughened Au plate is expected to provide the chance of the Raman measurement of isolated individual SWNT on solid surface.

Figure 2 shows the typical NIR-Raman spectrum of the isolated single SWNT on Au plate. Observation of the sample at each spot gave typical Raman spectrum of isolated single SWNT[7], showing radial breathing mode

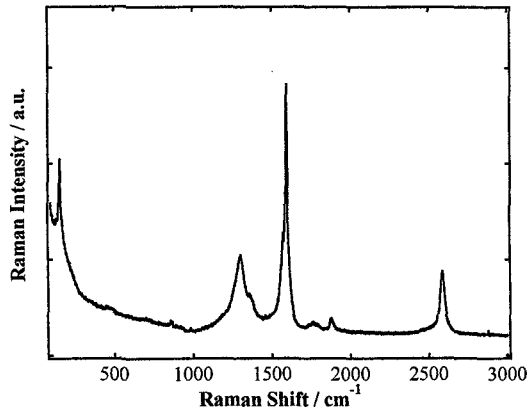

Fig. 2 Typical Raman spectrum of isolated single SWNT adsorbed on Au plate in aqueous solutions.

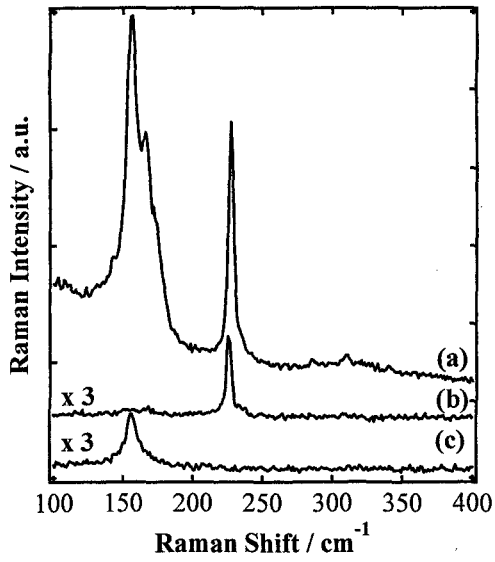

Fig. 3 Raman spectra of bundle SWNT with ω_{RBM} = 156, 166, 172 and 227cm^{-1} (a), isolated single semiconducting tube with ω_{RBM} = 225cm^{-1} (b), and isolated individual metallic tube with ω_{RBM} = 156cm^{-1} (c) on Au plate in aqueous solution, respectively.

(RBM) in the low frequency region around 100-300 cm^{-1}, and D-, G-, and G'- bands in 1200-2600 cm^{-1}. Second-order modes were also observed in 1700-1900cm^{-1}. The RBM frequency, ω_{RBM} [cm^{-1}] is an important signal decided depending on the diameter, d_t [nm] of each SWNT[8,9]. The relation of the RBM frequency and the diameter is expressed with an equation (1).

$$d_t = 248 / \omega_{RBM} \qquad (1)$$

Figure 3 shows the typical RBM Raman spectra of the bundle and isolated individual SWNT. Figure 3(a) is the spectrum of the bundle that consisted at the least three type metallic nanotubes (ω_{RBM} = 156, 166, 172 cm^{-1}) and one type semiconducting nanotube (ω_{RBM} = 227 cm^{-1}). The frequency depends on the diameter of tube. Figure 3(b) and (c) show the RBM spectra of isolated single semiconducting nanotube (ω_{RBM} = 225 cm^{-1}, d_t = 1.1 nm) and isolated single metallic nanotube (ω_{RBM} = 156 cm^{-1}, d_t = 1.6 nm), respectively. These spectra at different spots gave different peaks of RBM. The full width at half maximum (FWHM: Γ_{RBM}) at the RBM peaks of metallic tube around 140-180 cm^{-1} and semiconducting tube around 200-240 cm^{-1} in Figure 3(c), (b) were approximately 11 cm^{-1} and 4 cm^{-1}, respectively. Jorio et al.[10] reported that Γ_{RBM} for isolated single metallic SWNT is in the range of 4 to 15 cm^{-1}, and Γ_{RBM} for isolated single semiconducting SWNT is in the range of 4 to 10 cm^{-1}, respectively. These results of FWHM in Figure 3 agree well with the values of previous report for isolated single SWNT. Thus, from this analysis of FWHM in RBM Raman spectrum, the present preparation method of the water/SDS dispersion system gave the highly dispersed isolated single SWNT on Au

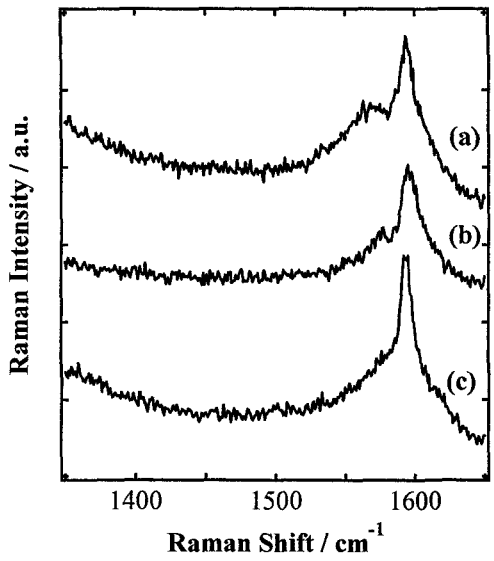

Fig. 4 Breit-Wigner-Fano (BWF) line and G-band Raman spectra of bundle SWNT (a), (b) and isolated single metallic SWNT (c), respectively.

plate.

Apparent feature of asymmetric profile towards lower frequency at G-band, a Breit-Wigner-Fano (BWF) profile[7,10], around 1570 cm^{-1} was examined. Figure 4 shows the G-band and BWF profile Raman spectra of the bundle (a), (b) and isolated single metallic SWNT (c), respectively. In general, the intensity of this broad signal of BWF increases in connection with a number of SWNT which exist in a bundle[11]. Conversely, there is almost no intensity of BWF line at the spectrum of isolated single metallic SWNT in Figure 4(c). And The BWF profiles were not observed at most of the spots for isolated single SWNT, indicating that contribution of bundled tubes and electron-phonon interaction between SWNT and Au substrate is minor in the present system. Thus, it is also suggested that the sample prepared by this water/SDS system provide isolated metallic SWNT on Au plate.

On rough Au surface shown in Figure 1(b), the scattering intensity of these vibrational modes of isolated single SWNT was enhanced strongly. It was suggested that this enhancement is attributable to the surface-enhanced Raman scattering effect (SERS) at the rough surface structure of Au[12,13]. The intensity of RBM was 1-2 order higher in the enhancement as compared with the case of flat Au plate. Thus, roughened Au surface should provide the substrates to achieve much more sensitive detection of highly dispersed isolated on solid surfaces.

4. SUMMARY

In this paper, the preparation method of highly dispersed isolated SWNT on Au plate was established. In this method, SWNT was formed the micelle by using a surfactant (SDS) to stabilize highly dispersed aqueous solution, and it was deposited on polycrystalline Au plate. Moreover, it became clear to take a further dispersed state of isolated SWNT by using roughed Au surface. Thus, it was enabled to obtain the Raman spectrum of isolated single SWNT by this preparation method from the commercial available aggregated SWNT samples.

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References

[1] Iijima, S., *Nature* **354**, 56-58 (1991).
[2] Dai, H. J., Hafner, J. H., Rinzler, A. G., Colbert, D. T. and Smalley, R. E., *Nature* **384**, 147-150 (1996).
[3] Dresselhaus, M. S., Dresselhaus, G. and Eklund, P. C. Science of Fullerenes and Carbon Nanotubes (Academic Press, New York, 1996).
[4] O'Connell, M. J., Bachilo, S. M., Huffman, C., B.Moore, V. C., Strano, M. S., Haroz, E. H., Rialon, K. L., Boul, P. J., Noon, W. H., Kittrell, C., Ma, J. P., Hauge, R. H., Weisman, R. B. and Smalley, R. E., *Science* **297**, 593-596 (2002).
[5] Liu, J., Rinzler, A. G., Dai, H., Hafner, J. H., Bradley, R. K., Boul, P. J., Lu, A., Iverson, T., Shelimov, K., Huffman, C. B., Rodriguez-Macias, F., Shon, Y., Lee, T. R., Colbert, D. T. and Smalley, R. E., *Science* **280**, 1253-1256 (1998).
[6] Bower, C., Kleinhammes, A., Wu, Y. and Zhou, O., *Chem. Phys. Lett.* **288**, 481-486 (1998).
[7] Dresselhaus, M. S., Dresselhaus, G., Jorio, A., Souza, A. G. and Saito, R., *Carbon* **40**, 2043-2061 (2002).
[8] Kataura, H., Kumazawa, Y., Maniwa, Y., Umezu, I., Suzuki, S., Ohtsuka, Y. and Achiba, Y., *Synth. Met.* **103**, 2555-2558 (1999).
[9] Jorio, A., Saito, R., Hafner, J. H., Lieber, C. M., Hunter, M., McClure, T., Dresselhaus, G. and Dresselhaus, M. S., *Phys. Rev. Lett.* **86**, 1118-1121 (2001).
[10] Jorio, A., Fantini, C., Dantas, M. S. S., Pimenta, M. A., Souza, A. G., Samsonidze, G. G., Brar, V. W., Dresselhaus, G., Dresselhaus, M. S., Swan, A. K., Unlu, M. S., Goldberg, B. B. and Saito, R., *Phys. Rev. B* **66**, 115411 (2002).
[11] Jiang, C., Kempa, K., Zhao, J., Schlecht, U., Kolb, U., Basché, T. Burghard, M. and Mews, A., *Phys. Rev. B* **66**, 161404 (2002).
[12] Kneipp, K., Wang, Y., Itzkan, I., Dasari, R. R., and Feld, M. S., *Phys. Rev. Lett.* **76**, 2444-2447 (1996).
[13] Corio, P., Brown, S. D. M., Marucci, A., Pimenta, M. A., Kneipp, K., Dresselhaus, G. and Dresselhaus, M. S., *Phys. Rev. B* **61**, 13202 (2000).

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