Effect of Molecular Adsorption on SWCNT using Surface-Enhanced Raman Scattering

Toshihiko Fujimori,[1,2] Tomonori Ohba,[1] Hirofumi Kanoh,[1] and Katsumi Kaneko[1, 2]

Graduate School of Science, Chiba University, 1-33 Inage, Yayoi, Chiba, 263-8522, Japan[1]
Institute of Carbon Science & Technology, Shinshu University, 4-17-1 Wakasato, Nagano-city, 380-8553, Japan[2]

Introduction

Single-wall carbon nanotubes (SWCNTs) ideally comprise of hexagonal arrangements of carbon atoms. However, pentagon and heptagon are inevitably present in the SWCNT structure. The non-hexagonal arrangements, which are referred as topological defects, may perturb ideal physical and chemical properties of SWCNTs [1], so that it is necessary to elucidate defect-associated properties of actual SWCNTs. Though presence of topological defects has been revealed mainly by microscopic techniques (e.g., transmission electron microscopy [2]), experimental environments are restricted to ultra-high vacuum conditions. We have evidenced that surface-enhanced Raman scattering (SERS), which is a potential technique to probe a very small amount of matter due to its ultra-high sensitivity, provides information of vibrations associated with topological defects [3, 4]. Since Raman measurements are not restricted to vacuum conditions, it offers a new insight of defect-associated vibrational properties, for example, an effect of molecular adsorption on topological defects. In this context, we will discuss SERS spectra of SWCNT under vacuum and several gas-induced atmospheres.

Experimental

An as-grown SWCNT sample produced by laser ablation method was purified by the following method; refluxing under 15% aqueous H_2O_2 solution at 373 K for 5 h, then subsequently adding 1 M aqueous HCl solution, stirring the mixture for 20 h. After filtration of the solution, the purified SWCNT sample was dried under ambient conditions. The resultant purified-SWCNT sample was used as the specimen (denoted as closed-SWCNT, hereafter). Cap-removed SWCNT sample was prepared by oxidation at 783 K under O_2 gas flow for closed-SWCNT (open-SWCNT).

A silver foil (purity 99.95%, 0.015 mm thickness) was purchased from Wako Pure Chemical Industries, Ltd., and used as the SERS-active metal. The surface geometry of the silver foil has partially a step and terrace structure with an interval of ~100 nm.

Gold nanoparticles were also used as the SERS active metal. An 50 ml of an ice-cooled aqueous $HAuCl_4$ solution (5×10^{-3} M) was mixed with an 150 ml of ice-cooled aqueous $NaBH_4$ solution (2×10^{-3} M). After stirring for 1 h, a color of the mixture became dark purple. In order to remove impurity ions, the gold colloidal solution was dialyzed for 1 day. Fig. 1 shows an extinction spectrum of the dialyzed gold colloidal

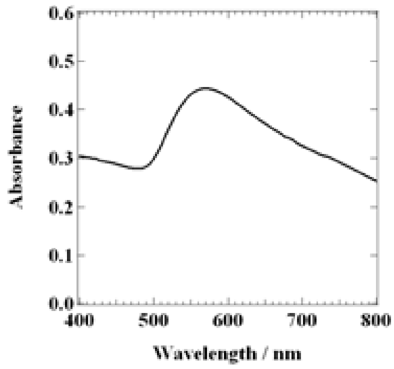

Fig. 1 Optical absorption spectrum of the dialyzed gold colloidal solution.

solution. The broad band starting from 500 nm can be assigned to the surface plasmon absorption. Since the wavelength of the absorption band is close to the excitation wavelength for Raman measurements (532 nm), it gives rise to strong enhancement of Raman scattering intensity due to the SERS effect. The dialysed gold colloidal solution was then dropped onto a glass plate, subsequently heating at 150℃ under 10^4 Pa for removing the solvent. The glass plate depositing gold nanoparticles was used as the SERS active substrate.

A droplet of the closed-SWCNT dispersed 1,2-dichloroethane solution was dropped onto the silver foil, which was precedently washed in ethanol by sonication. The closed-SWCNT dispersed silver foil was then pretreated at 423 K under 2 mPa for removing the solvent. SERS measurements were carried out at ambient temperature under 2 mPa.

A droplet of the open-SWCNT dispersed 1,2-dichloroethane solution was dropped onto the glass plate depositing gold nanoparticles. After sealing the substrate surface with thin glass plate, the substrate was then pretreated at 423 K under 2 mPa. SERS measurements were carried out at ambient temperature under 2 mPa, Ar, and O_2 gases induced atmospheres. The pressures were kept at 10^5 Pa both for Ar and O_2.

Every SERS measurement was carried out with a single-monochromator micro-Raman spectrometer using back-scattering configuration (JASCO NRS-3100). An excitation wavelength was 532 nm (Nd:YAG laser) and the laser power was ~3 mW at the sampling points. A collection time was 5-10 sec for each SERS measurement.

Results and Discussion

When the probe laser light was scanned over the SERS-active metal surfaces, two types of SERS spectra were obtained; (1) one similar to the non-SERS spectrum, resulting from a high-crystallinity region of SWCNTs, and (2) SERS spectra with additional peaks which are absent in the non-SERS spectrum. Some of the additional peaks observed in the SERS spectra (2) are assigned to specific pentagon-heptagon pairs known as a Stone-Thrower-Wales defect (denoted as STW defect, hereafter) [4-6].

Fig. 2 shows the SERS spectrum of closed-SWCNT obtained under vacuo (2 mPa), indicating a high-crystallinity region of the SWCNT [4]. Full width at half maximum (FWHM) of the G^+-band (~1590 cm^{-1}) in the SERS spectrum is narrower than that of the non-SERS spectrum (17 cm^{-1}). It indicates that the SERS spectrum is a consequence of a small number of SWCNTs or down to single SWCNT detection.

Fig. 3 shows the SERS spectrum with characteristic peaks related to a STW defect in closed-SWCNT. The SERS spectrum was obtained under 2 mPa. The bars in Fig. 3 indicate the calculated vibrational frequencies of a STW defect in flat graphene [7]. The SERS spectrum shows fluctuation of peak intensities and frequencies with time. The fluctuations are ascribed to structural rearrangements of a STW defect [4].

The SERS spectra of open-SWCNT at high-crystallinity region obtained under vacuo (<2 mPa), Ar, and O_2 gases atmospheres are shown in Fig. 4. Since the SERS spectra are obtained at ambient temperature, little spectral changes are observed even under O_2 gas atmosphere. An intriguing case that arises from the gas-adsorbed effect on the defect-associated peaks will be discussed at the conference.

Conclusions

The SERS technique can sensitively probe local crystallinity of SWCNT and it is applicable to investigate gas-induced effect on the defect in SWCNT, which is difficult for other microscopic techniques in principle.

Acknowledgment. The authors thank Dr. Takahashi K at the Institute of Research and Innovation (IRI) for providing the SWCNT sample.

References

[1] Charlier J–C. Defects in Carbon Nanotubes. Acc. Chem. Res. 2002;35:1063-1069.

[2] Suenaga K, Wakabayashi H, Koshino M, Sato Y, Urita K, Iijima S. Imaging active topological defects in carbon nanotubes. Nature Nanotechnol. 2007;2:358-360.

[3] Fujimori T, Urita K, Aoki Y, Kanoh H, Ohba T, Yudasaka M, Iijima S, Kaneko K. Fine Nanostructure Analysis of Single-Wall Carbon Nanohorns by Surface-Enhanced Raman Scattering. J. Phys. Chem. C 2008;112:7552-7556.

[4] Fujimori T, Urita K, Ohba T, Kanoh H, Kaneko K. Evidence of Dynamic Pentagon-Heptagon Pairs in Single-Wall Carbon Nanotube using Surface-Enhanced Raman Scattering. J. Am. Chem. Soc. In Press.

[5] Stone AJ, Wales DJ. Theoretical Studies of Icosahedral C60 And Some Related Species. Chem. Phys. Lett. 1986;128:501-503.

[6] Walker Jr. PL, Ed. The Study of Defects in Graphite by Transmission Electron Microscopy. Chemistry and Physics of Carbon vol. 5, Marcel Dekker: New York, 1962. p.262.

[7] Wu G and Dong J. Raman characteristic peaks induced by the topological defects of carbon nanotube intramolecular junctions. Phys. Rev. B 2006;73:245414.

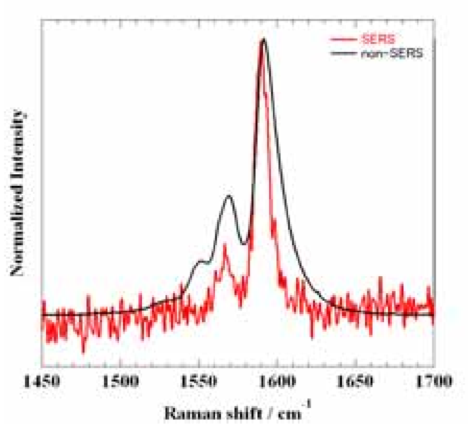

Fig. 2 SERS spectra of closed-SWCNT at high-crystallinity region (under 2 mPa).

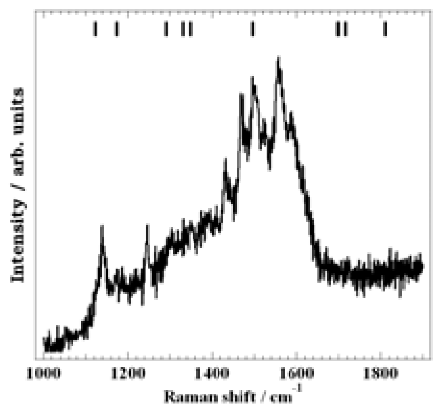

Fig. 3 SERS spectra of closed-SWCNT at defective region (under 2 mPa). Bars indicate vibrational frequencies associated with a STW defect [7].

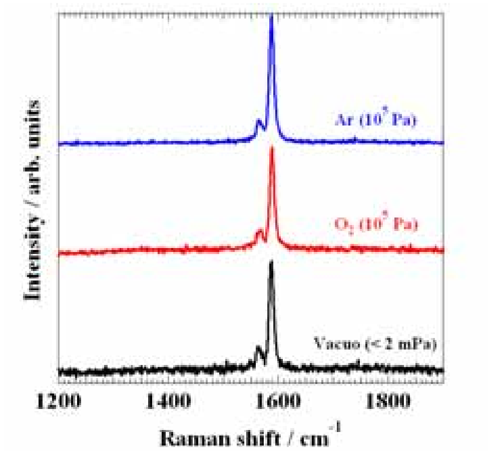

Fig. 4 SERS spectra of open-SWCNT at high-crystallinity region. The SERS spectra were obtained under Vacuo (< 2 mPa), Ar, and O_2 atmospheres.