Multiple splitting of *G*-band modes from individual multiwalled carbon nanotubes

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Surface-enhanced Raman scattering spectra of an individual multiwalled carbon nanotube (MWNT) with the innermost diameter ~1 nm, prepared by hydrogen arc discharge, show a single peak of radial breathing mode and multiple splitting of the tangential stretching *G*-band modes. Based on Lorentzian line shape analysis and related theoretical calculations, the *G*-band modes of MWNT are confirmed to be composed of both *G*-band modes (linewidth 4 cm^{-1}) from the innermost tube and graphite-like mode (linewidth ~20 cm^{-1}) from the outer cylinders in MWNT. This observation indicates that MWNTs are unique and possess characteristic Raman spectra different from other sp^2 carbon allotropes. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1502196]

Highly-graphitized multiwalled carbon nanotubes (MWNTs) with very thin innermost diameter of ~1 nm,[1,2] which were prepared by hydrogen arc discharge evaporation, are of interest for both fundamental and applied studies.[3,4] The reported Raman spectra of the MWNTs synthesized by either helium arc discharge evaporation or chemical vapor deposition closely resemble that of graphite,[5–7] due to their wide innermost diameter (>2 nm)[8] and high defect.[6,9] On the other hand, we found the radial breathing modes (RBMs) of MWNTs in the low-frequency region of Raman spectra for H_2-arc MWNTs.[2]

In this letter, we focus our attention on the tangential stretching *G*-band region (1500–1650 cm^{-1}), and show that the surface-enhanced Raman scattering (SERS) spectra of a single H_2-arc MWNT consist of both multiplet of *G*-band modes and a single RBM. The former peaks are composed of both *G*-band modes from the innermost tube and graphite-like mode from the outer cylinders in MWNT. This indicates that MWNTs with the innermost diameter less than 2 nm possess characteristic Raman spectral features.

We produced pristine MWNTs by hydrogen arc discharge,[1] and purified them by infrared irradiation in air.[10] The specimens for SERS were prepared on silver substrates vacuum-evaporated onto glass slides (silver film thickness of 10 nm). Dispersed H_2-arc MWNTs were obtained by sonication of the H_2-arc MWNTs suspended in isopropanol, and sprayed onto the silver surfaces. Atomic force microscopy and scanning electron microscopy (SEM) observations of the surface of SERS specimens reveal that most of the bundles or individual H_2-arc MWNTs are longer than 5 μm and lie straight on the ''rough'' silver surface of the SERS substrates. A typical SEM micrograph of a SERS specimen surface is shown in Fig. 1. The rough silver surface (labeled Ag) and only one straight H_2-arc MWNT bundle (marked by MWNTs) can be observed over the entire area of ~2.5 μm^2.

The SERS spectra were obtained by excitation with an Ar^+ laser (514.5 nm, 2.41 eV) and collected in the backscattering geometry at room temperature using a Raman spectrometer (Jobin Yvon; RAMANOR T64000) equipped with a charge-coupled device. With a 100× objective lens, the incident laser beam spot had a diameter of ~1 μm, resulting in a power density of ~10^6 W/cm^2 in the Raman active area. This setup had a typical resolution of ~2 cm^{-1} and made it possible to confirm the existence and orientation of the H_2-arc MWNT bundles on the surface of SERS specimens.

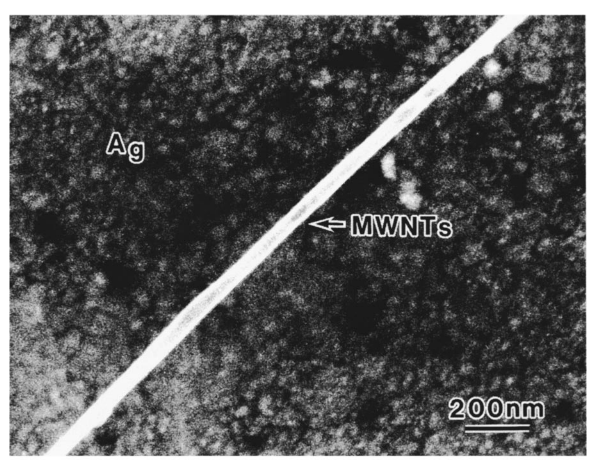

FIG. 1. A typical SEM micrograph of SERS specimens. Rough silver surface (labeled Ag) and only one straight H_2-arc MWNT bundle (marked by MWNTs) can be observed in the area of ~2.5 μm^2.

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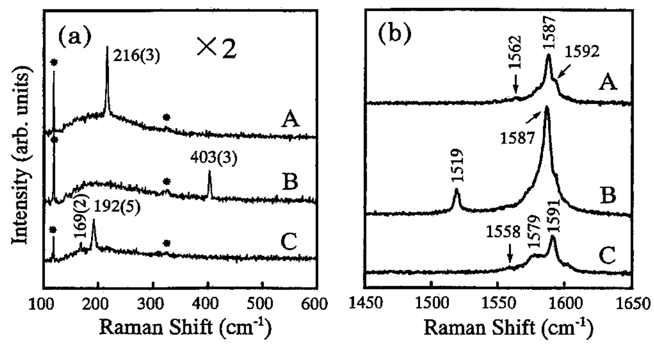

FIG. 2. Three typical SERS spectra from individual H_2-arc MWNTs or thin bundle of H_2-arc MWNTs. (a) Low-frequency region from 100 to 600 cm^{-1}, where only RBMs can be observed. (b) High-frequency region from 1450 to 1650 cm^{-1}, showing the multiple splitting of G-band modes of H_2-arc MWNTs.

We intentionally selected thin H_2-arc MWNT bundles (or an individual H_2-arc MWNT) without neighbors in an area of $\sim 10\,\mu m^2$ to record SERS spectra. Typical SERS spectra of three specimens, A, B, and C, are shown in Figs. 2(a) and 2(b) for the low ($100-600\,cm^{-1}$) and high ($1450-1650\,cm^{-1}$) frequency regions, respectively. On the basis of our study on the low frequency region in the Raman spectra of H_2-arc MWNTs,[2] only the RBM can be observed (the sharp and broad peaks labeled "*" are instrumental artifacts). These RBMs originate from the innermost tubes included in H_2-arc MWNTs, because only the innermost tube is in the similar situation with SWNT rope. The observed RBM frequencies up-shift 5% compared to those of isolated SWNTs, due to interlayer interaction.[2] Therefore, the number of MWNTs within thin H_2-arc MWNT bundles can be determined by the number of RBM peaks in the SERS spectrum. Moreover, the innermost diameter, that is, the diameter of the innermost tube contained in H_2-arc MWNT, can also be identified using the relation[11] $d=223.75/\omega$, where d is the isolated SWNT diameter in nanometer and ω the RBM frequency in wave number.

A single RBM peak can be observed at 216(3) cm^{-1} in SERS spectra A in Fig. 2(a), where the full width at half maximum (FWHM) is given in parentheses. This indicates that SERS spectra A in Figs. 2(a) and 2(b) were recorded from a single H_2-arc MWNT with an innermost diameter of 1.09 nm. Similarly, SERS spectra B in Figs. 2(a) and 2(b) were also obtained from an individual MWNT with an innermost diameter of 0.58 nm because one RBM peak appears at 403(3) cm^{-1}. In SERS spectrum C, two RBMs at 169(2) and 192(5) cm^{-1} can be seen, indicating that this SERS spectrum came from two different H_2-arc MWNTs whose innermost diameters were 1.45 and 1.23 nm, respectively. The observed value of the FWHM ($3\,cm^{-1}$) in RBM is much smaller than those ($5-10\,cm^{-1}$) of individual SWNTs[12,13] and is in good agreement with that ($2.5\,cm^{-1}$) of the purely radial A_{1g} mode in C_{60}. This shows that the innermost tubes protected by outer cylinders in H_2-arc MWNTs have perfect tube structures. The FWHM value in RBM, 3 cm^{-1}, should be the natural width in SWNTs.

SERS spectra A, B, and C in Fig. 2(b) show multiple splitting of G-band modes in H_2-arc MWNTs. A weak peak at 1562 and a strong peak at 1587 with a shoulder at 1592 cm^{-1} can be seen in the spectrum A in Fig. 2(b). Two peaks can be observed at 1519 and 1587 cm^{-1} in the spectrum B. Three peaks appear at 1558, 1579, and 1591 cm^{-1} in the spectrum C. These multiple splittings of G-band modes were always observed with RBM peaks, and measured for more than twenty SERS spectra.

Figure 3(a) shows the Lorentz fit to the spectrum A in Fig. 2(b) using four Lorentzians with frequencies (FWHMs) of 1562(4), 1584(22), 1588(4), and 1593(3) cm^{-1}. The frequency and line shape of the broad line at 1584(22) cm^{-1} is similar to those of He-arc MWNTs,[5] which have relatively large innermost diameters.[8] Thus, this graphite-like line is attributable to the outer cylinders in this H_2-arc MWNT. The other three sharp lines have a very narrow FWHM of $\sim 4\,cm^{-1}$ and originate from the innermost tube ($d=1.09$ nm) in this H_2-arc MWNT. According to group theory analysis, six modes can be present in the G-band of SWNTs: two A_1 (A_{1g}), two doubly degenerate E_1 (E_{1g}), and two doubly degenerate E_2 (E_{2g}) modes,[14] and three of six modes are seen in this SERS spectrum. For verifying the symmetry assignments of these modes, polarized Raman scattering studies on an individual H_2-arc MWNT would be needed. The sharp FWHM of $\sim 4\,cm^{-1}$ is equal to the natu-

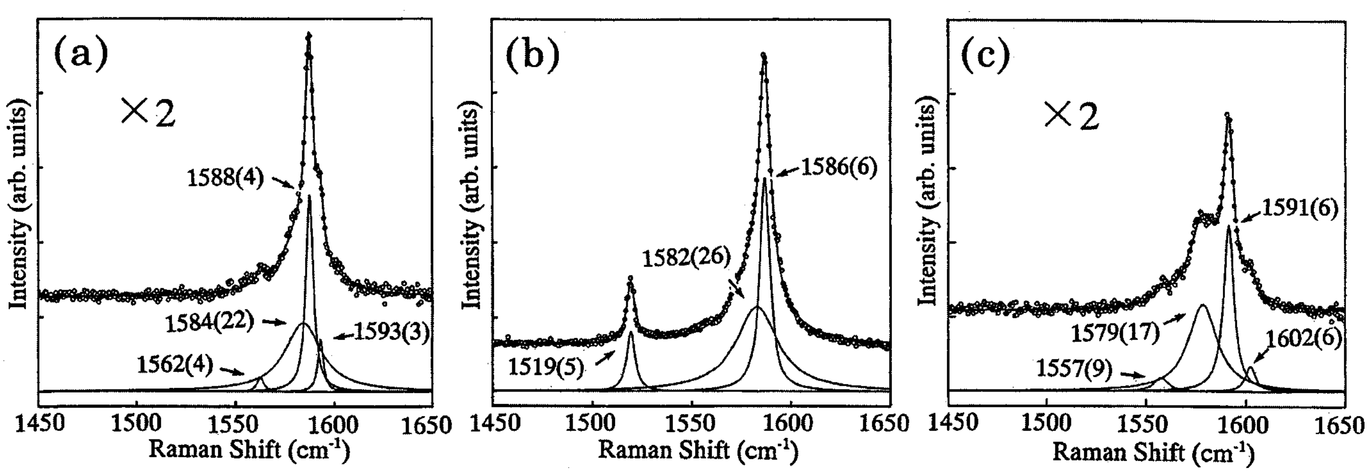

FIG. 3. (a) Result of Lorentzian line shape analysis of the SERS spectrum A in Fig. 2(b). (b) Result of Lorentzian line shape analysis of SERS spectrum B. (c) Result of Lorentzian line shape analysis of SERS spectrum C. The graphitelike line at $\sim 1580\,cm^{-1}$ in each SERS spectrum comes from the outer cylinders in H_2-arc MWNTs.

ral FWHM linewidth (4 cm^{-1}) of the *G*-band mode in semiconducting SWNTs.[15] The line shape and positions of three Lorentzians [1562(4), 1588(4), and 1593(3) cm^{-1}] also enable us to assign this innermost tube to be semiconducting.[16,17]

The fit to the spectrum B in Fig. 2(b) using three Lorentzians with frequencies (FWHMs) of 1519(5), 1582(26), and 1586(6) cm^{-1} is shown in Fig. 3(b). The graphite-like line at 1582(26) cm^{-1} is attributable to the outer cylinders, while two lines at 1519(5) and 1586(6) cm^{-1} come from the single innermost tube ($d=0.58$ nm) in this H_2-arc MWNT. It can be seen that the intensity of the line at 1586(6) cm^{-1} is much stronger than that of the graphite-like line at 1582(26) cm^{-1}. The fit to the spectrum C using four Lorentzians with frequencies (FWHMs) of 1557(9), 1579(17), 1591(6), and 1602(6) cm^{-1} is displayed in Fig. 3(c). Except for the graphite-like line at 1579(17) cm^{-1}, the spectral feature is in good agreement with the result for SWNTs published by Corio *et al.*,[17] reconfirming the conclusion that these *G*-band modes originate from the innermost tubes in H_2-arc MWNTs.

In the SERS spectra of an individual H_2-arc MWNT, *G*-band modes from only one single innermost tube appear much stronger compared to the graphite-like line from many outer cylinders. This enables us to easily observe the multiplet of *G*-band modes [see Figs. 3(a) and 3(b)]. The SERS signals can be enhanced by both electromagnetic and chemical SERS effects.[17] Since the electromagnetic SERS effect is expected to be the same for all vibrational modes, we can conclude that the chemical SERS effect plays an important role in generating very strong *G*-band modes of the innermost tubes. The chemical SERS effect depends on the resonance condition between the excitation photons and electronic transitions, which occur between the van Hove singularities in the one-dimensional electronic density of states[18] of the innermost tube in H_2-arc MWNTs, and is modified by interaction with the silver substrate.

In order to clarify the SERS enhancement effect, the Raman experiments of individual H_2-arc MWNTs dispersed on a Si substrate were also performed. The multiple splitting of the *G*-band modes could be observed from individual H_2-arc MWNTs with the intensity of only 1/10 of SERS spectra. On the basis of our resonance Raman study on RBMs of H_2-arc MWNTs,[18] the resonant enhancement is not so strong as that of SWNTs, because the interlayer interaction in a H_2-arc MWNT might smear out one-dimensional van Hove singularity. Nevertheless, it may be possible to record a single RBM with splitting *G*-band modes from an individual H_2-arc MWNT by using normal resonance Raman techniques.

In conclusion, SERS spectra with a single RBM peak and multiplet of *G*-band modes have been obtained from a single H_2-arc MWNT with innermost diameter $\sim$1 nm. The *G*-band modes of MWNT are composed of both the *G*-band modes (linewidth 4 cm^{-1}) from the innermost tube and the graphite-like mode (linewidth $\sim$20 cm^{-1}) from the outer cylinders in MWNT. This shows that highly-graphitized MWNTs with the innermost diameter less than 2 nm possess characteristic Raman spectra different from other sp^2 carbon allotropes. Our study on the vibrational properties of perfect innermost tubes in MWNTs will also provide a standard for the study of individual SWNTs.

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