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Selective probe of the morphology and local vibrations at carbon nanoasperities

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We introduce a way to selectively probe local vibration modes at nanostructured asperities such as tips of carbon nanohorns. Our observations benefit from signal amplification in surface-enhanced Raman scattering (SERS) at sites near a silver surface. We observe nanohorn tip vibration modes in the range 200–500 cm^{-1}, which are obscured in regular Raman spectra. *Ab initio* density functional calculations assign modes in this frequency range to local vibrations at the nanohorn cap resembling the radial breathing mode of fullerenes. Careful interpretation of our SERS spectra indicates presence of caps with 5 or 6 pentagons, which are chemically the most active sites. Changes in the peak intensities and frequencies with time indicate that exposure to laser irradiation may cause structural rearrangements at the cap. © *2012 American Institute of Physics*. [doi:10.1063/1.3682771]

I. INTRODUCTION

The peculiar morphology of capped graphitic cones called single-wall carbon nanohorns (SWCNHs) (Ref. 1) provides selective adsorption scenarios for specific functionalizations. Ideal SWCNH structures with different cone opening angles are obtained by substituting 1–5 hexagonal carbon rings in the honeycomb lattice of graphene by pentagons, which are chemically the most active sites. The precise morphology near the tip, determined by the distribution of pentagons, plays a crucial role, as it identifies sites with high local curvature that exhibit enhanced chemical reactivity.[2] Since carbon nanohorns may be viewed as a hybrid between fullerenes and nanotubes, information about the equilibrium structure and structural changes at the tip should provide valuable information also about the growth process of fullerenes and nanotubes. Unfortunately, imaging nanohorn tips with atomic resolution is nearly impossible, since nanohorns typically assemble in a close-packed dahlia-flower structure, shown in Fig. 1. A potentially more promising approach to get structural information is to explore local vibration modes at the tip.

Local vibration modes have been successfully probed in isolated nanostructures such as supported single-wall carbon nanotubes (SWCNTs) by a sharp metal tip of a scanning tunneling microscope using inelastic electron tunneling spectroscopy (STM-IETS) under cryogenic conditions.[3] In more complex systems such as free-standing nanohorn assemblies, where STM-IETS cannot be applied, Raman spectroscopy is the most common tool to probe vibration spectra.[4] Whereas

Raman spectroscopy is more convenient as it does not require ultra-low temperatures, its important drawback is that specific vibration modes, including those at the tip, are obscured in the spectrum of the entire sample. Unfortunately, lacking a mechanism to selectively enhance the signal at the tip, the modes of interest are obscured among the majority of other vibration modes.

Here we introduce a way to selectively probe local vibration modes at tips of carbon nanohorns and other nanostructured asperities using surface-enhanced Raman scattering (SERS). Selective amplification of vibration modes localized in the tip region, which are obscured in regular Raman spectra, is achieved by bringing nanohorn tips into close vicinity of a SERS-active metal such as silver. We observe nanohorn vibration modes in the range 200–500 cm^{-1} and use *ab initio* density functional calculations to assign these modes to local vibrations at the nanohorn tip, which resemble the radial breathing mode (RBM) of fullerenes. Careful interpretation of our SERS spectra indicates presence of caps with 5 or 6 pentagons. Changes in the peak intensities and frequencies with time indicate that exposure to laser irradiation may cause structural rearrangements at the cap.

SERS is known to enhance the Raman signal locally by many orders of magnitude[5] in the vicinity of a SERS-active metal such as silver and has been used successfully to characterize defect-related vibration modes in carbon nanostructures.[6,7] Whereas maximum amplification of the SERS signal is achieved by bringing a sharp metal tip close to the nanocarbon region under study, we proceed the opposite way and bring a SERS-active metal close to the sharp nanohorn tips protruding radially from the dahlia-shaped nanohorn assembly, shown in Fig. 1. The enhanced

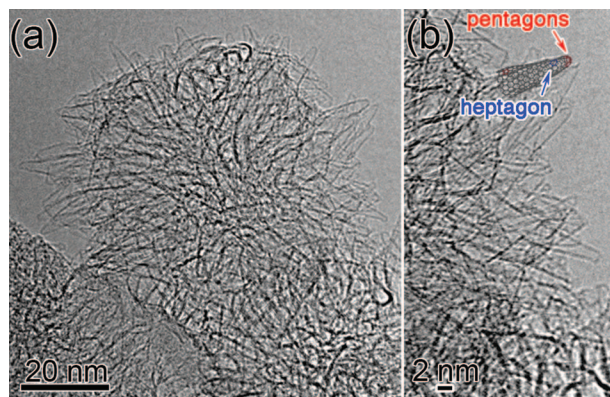a)Electronic mail: kkaneko@shinshu-u.ac.jp.

FIG. 1. (a) Transmission electron micrograph of a closely packed single-wall carbon nanohorn aggregate resembling a dahlia-flower. (b) Magnified image near the surface, showing the nanohorn tips protruding outward. An inset in (b) shows a model structure of the nanohorn tip composed of five pentagons and one heptagon.
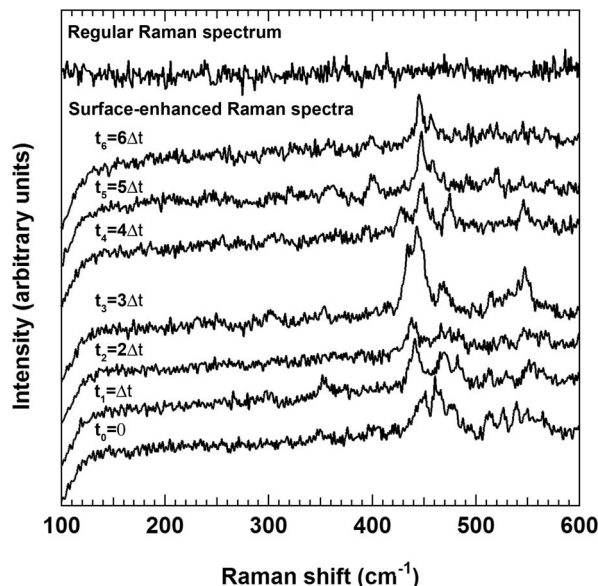

FIG. 2. Comparison between a regular Raman spectrum and a time sequence of SERS spectra of SWCNHs. All SERS spectra were obtained at the same probing position with a time interval $\Delta t \sim 10$ s.

SERS signal strength in the tip region, coupled with Raman selection rules, is expected to provide unprecedented information about the local vibration modes, the symmetry and the structure of the tip. Changes in the local vibrational spectra occurring during the SERS observation will provide microscopic information about structural rearrangements.

II. EXPERIMENTAL

SWCNHs were produced by laser ablation of pure graphite and their morphology was characterized using transmission electron microscopy (TEM). Our TEM images in Fig. 1 indicate that the nanohorns are rather narrow, irregular in shape, and are terminated by caps $\sim$0.5–1.0 nm in diameter. Ideal nanohorns closest to the observed structures contain 5 pentagons at the apex and have an opening angle of 19.2°.[8] Other apex structures may contain at least one pentagon-heptagon pair, in which case the nanohorn may be terminated by a short SWCNT segment terminated by six pentagons.

Our SERS measurements were performed using a silver foil (99.95% purity, 0.015 mm thickness, Wako Pure Chemical Industries, Ltd.) as the SERS-active metal. We first dispersed the SWCNHs in toluene solution and subsequently deposited a droplet of the SWCNH suspension onto the silver surface. The silver foil covered by SWCNHs was first pretreated under 2 mPa vacuum at 423 K in an *in situ* Raman cell. Subsequent SERS measurements were carried out with a single-monochromator micro-Raman spectrometer (JASCO NRS-3100) under 2 mPa vacuum at ambient temperature. SERS spectra were acquired during a $\sim$10 s collection time using the 532.0 nm excitation line of a Nd:YAG laser operated at $\sim10^8$–10^9 W m^{-2} laser power density. The diameter of the laser spot was $\sim$4 μm. A regular Raman spectrum of an SWCNH powder was acquired during a 600 s collection time using the 532.0 nm laser excitation line at the power density of $\sim10^7$–10^8 W m^{-2}.

III. RESULTS AND DISCUSSION

Our time-resolved SERS spectra of SWCNHs are presented in Fig. 2 and compared to a regular Raman spectrum of the same sample. All SERS spectra were obtained at the same probing position with a time interval $\Delta t \sim 10$ s between successive measurements. We observe a drastic difference between the featureless regular Raman spectrum and the SERS spectra, which exhibit strong peaks around 400–500 cm^{-1}. The displayed time sequence of SERS spectra exhibits fluctuations in the frequencies and intensities of these peaks, which are commonly referred to as a blinking effect.[9] The likely cause of the blinking are structural rearrangements of topological defects, possibly induced by exposure to the laser beam.[6,7] Same as in fullerenes,[10] such morphological changes most likely involve Stone-Thrower-Wales transformations[11,12] near the tip.

Light-induced changes in the nanohorn structure occur in a complex photochemical process that is not well understood. Absorbed photons excite electrons from their ground-state configuration and lift the system off the Born-Oppenheimer surface. Atomic motion is subjected to a different force field during the period before nonradiative transitions bring the system back to the electronic ground state and excite photons.[13] Since this time scale is longer than atomic vibration periods, rearrangement of atomic bonds occurs in the excited state within a force field that exhibits lower activation barriers and changes constantly during the electronic deexcitation process.

As suggested by the sample morphology in Fig. 1, we expect the closest contact between the SERS-active silver surface and the sample to occur near nanohorn tips. Consequently, vibration modes that are amplified in the SERS spectra should be associated primarily with vibrations in the SWCNH tip region. As a representative of our observations we display in Fig. 3(a) SERS spectra obtained at two different
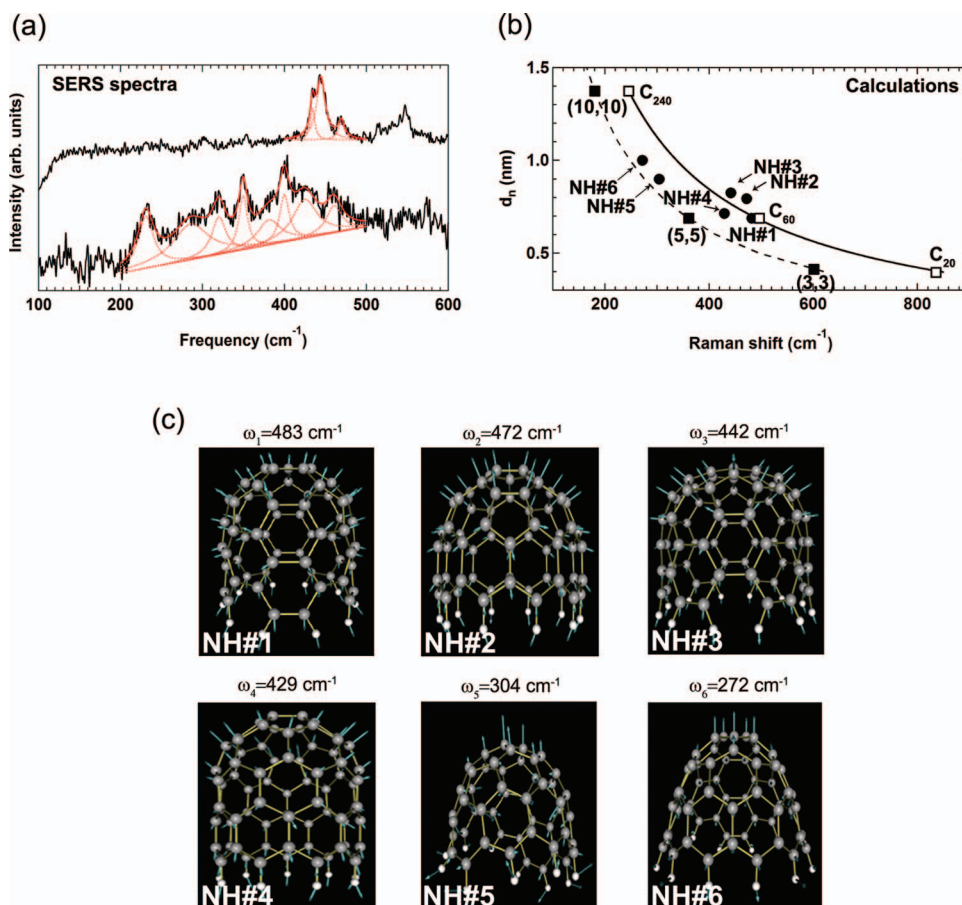
FIG. 3. (a) Representative SERS spectra obtained at two different probing positions of the SWCNH sample along with Lorentzian line fits (dashed lines). (b) Comparison between vibration frequencies of nanohorn structures (solid circles) and RBM frequencies of fullerenes (dotted line connecting open squares) and SWCNTs (dashed line connecting solid squares). d_t denotes the effective diameter of the nanostructure. (c) Calculated vibrational eigenmodes of nanohorn model structures NH#1–NH#6 with a large amplitude at the apex.

probing positions within the SWCNH sample. In the following we will attempt to characterize the prominent vibration modes in these spectra.

Due to their polydispersity, SWCNHs have been much less characterized than SWCNTs and fullerenes. Since the apex of a nanohorn tip resembles a fullerene and the nanohorn cone a SWCNT, we will try to relate the new spectral features to vibrations of fullerenes and nanotubes. We note that the RBM of the C_{60} fullerene at $\omega_{RBM}(C_{60}) = 497$ cm^{-1},[14] and thus also the RBM of a C_{60}-based nanohorn cap, lies well within the frequency range of modes amplified in SERS. A much softer prominent mode at 234 cm^{-1} has been previously identified in STM-IETS spectra near the closed end of a (17, 14) SWCNT with $d_n = 2.1$ nm and also characterized as the RBM of the wide closing cap.[3]

In SWCNTs, which are observed with a wide range of diameters, the RBM decreases with increasing diameter d_n as $\omega_{RBM}(\text{SWCNT}) = 248$ cm$^{-1} \times (1$ nm$/d_n)$,[4] shown by the dashed line in Fig. 3(b). This relationship translates to a frequency range from $\omega_{RBM} = 183$ cm^{-1} for a (10, 10) nanotube with the same diameter $d_n = 1.4$ nm as C_{240} to $\omega_{RBM} = 366$ cm^{-1} for a (5, 5) nanotube with the same diameter $d_n = 0.7$ nm as C_{60}. Similar to nanotubes, also the RBM of fullerenes with full icosahedral symmetry obeys the relationship $\omega_{RBM}(C_n) = 338$ cm$^{-1} \times (1$ nm$/d_n)$, shown by the

dotted line in Fig. 3(b). Calculated RBM frequencies of various fullerenes and nanotubes are displayed in Fig. 3(b) in the frequency range used in Fig. 3(a) for the observed spectra. Since fullerenes are structurally more constrained than nanotubes, the RBM frequencies of fullerenes are also higher than those of nanotubes with the same diameter d_n. The walls of a nanohorn do not contain sufficiently long segments of constant diameter and thus cannot support an RBM. Assuming that our sample of nanohorns with a typical diameter ~2–3 nm contains an admixture of nanotubes with similar width, such impurities should contribute with an RBM in the range 80–120 cm^{-1}, much softer than the observed nanohorn vibrations. We thus conclude that spectral features in Fig. 2 at $\omega \geqq 400$ cm^{-1} are related to the RBM of the fullerene cap at the apex, not the wall of the cone.

To obtain quantitative support for our interpretations, we performed *ab initio* calculations for nanohorn-related structures. We used the spin-polarized local density functional formalism, as implemented in the GAUSSIAN 03 code,[15,16] to determine the equilibrium geometry and Raman-active vibration modes of selected nanohorns and fullerenes. We used the 3-21G basis of atom-centered Gaussian orbitals and the Vosco, Wilk, and Nusair correlation functional.[17] We selected six representative nanohorn structures, labeled NH#1–NH#6 in Fig. 3(c) and Fig. S1(a) in the supplementary material.[16]

Structures NH#1–NH#4 represent nanohorn tips terminated by a short single-wall nanotube segment with a cap containing six pentagons. Structures NH#5 and NH#6 are nanohorns with five pentagons at the terminating cap, taken from Ref. 8. Exposed edges of the finite-size structures have been terminated by hydrogen atoms.

The spatially resolved STM-IETS spectra of a capped SWCNT (Ref. 3) were dominated by the RBM of the cap at $\omega = 234$ cm^{-1}. For the sake of interpreting our SERS observations, we identified the RBM and related vibration modes with a large amplitude at the cap. These frequencies are highlighted in the calculated spectra of structures NH#1–NH#6, shown in Fig. S1(b) in the supplementary material[16] and shown in Fig. 3(c) along with the mode character. Our results indicate that the RBM of capped nanotube segments NH#1–NH#4 is well defined and extends across the entire cap region. In contrast to these structures, as suggested above, we cannot identify any symmetrical RBMs in the conical structures NH#5 and NH#6. As an alternative to the RBM, we depict for these systems a "jellyfish" vibration mode with a large radial amplitude at the apex and show this mode in Fig. 3(c).

In Fig. 3(b), we compare the vibrational frequencies of nanohorns NH#1–NH#6, indicated by solid circles, to those of fullerenes and nanotubes with a comparable diameter. Since the diameter of a conical nanohorn is not defined, we select the nanostructure diameter at 1 nm from the apex as the effective diameter d_n. Our results in Fig. 3(b) support our previous assessment that the nanohorn vibration modes that should be prominent in SERS spectra are more closely related to the RBM of fullerene caps than to vibrations of the nanohorn wall.

With microscopic information about the character and frequency of relevant vibration modes at hand, we now provide a quantitative guideline for the interpretation of the observed SERS spectra. This is a difficult and complex undertaking due to the nonuniformity of the sample. We have to take into account the fact that due to the finite size of the probing laser beam, each spectrum contains information about many nanohorns with different structure. The time sequence of SERS spectra at one location, shown in Fig. 2, displays prominent feature for $\omega \geq 400$ cm^{-1}. Vibrations in the frequency range from 400–500 cm^{-1} may be assigned to SWCNH tips terminated by a short capped nanotube segment similar to the NH#1–NH#4 structures. Capped SWCNT segments can be seamlessly connected to the mantle of a SWCNH with an opening angle of 19.2° by inserting one heptagon in the honeycomb lattice. Additional peaks in the range from 500 to 550 cm^{-1} may be assigned to fullerene caps with adjacent pentagons that, according to Fig. 3(b), are ∼0.5–0.7 nm in diameter. With progressing time we observe a gradual softening of the modes. A likely explanation is that exposure to the laser beam induces structural changes by redistributing the pentagons at the terminating cap[6] in order to release stress caused by high local curvature.

The SERS spectra taken at two different probing positions, presented in Fig. 3(a) along with their spectral decomposition by Lorentzians, differ significantly in the reported frequency range, indicating different tip morphology distributions in the two regions of the SWCNH sample. An initial stage of SERS spectra obtained at different probing positions is shown in the Fig. S2 in the supplementary material.[16] The upper SERS spectrum in Fig. 3(a) is dominated by peaks at 434, 444, and 470 cm^{-1}, which can be assigned to the RBM of the cap terminating a SWCNT segment at the nanohorn apex, shown in Fig. 3(c) for structures NH#1–NH#4.

Unlike the upper spectrum in Fig. 3(a), which is rather featureless in the frequency range $\omega \geq 400$ cm^{-1}, the lower SERS spectrum exhibits prominent peaks at 285 and 320 cm^{-1}. These frequencies are close to the "jellyfish" vibration modes observed in nanohorn structure NH#5 and NH#6 with only five pentagons at the terminating cap. We expect softer vibration modes with a similar character to occur at dull conical tips, with the five pentagons distributed over a wider fullerene cap.

IV. CONCLUDING REMARKS

In conclusion, we introduce a way to selectively probe local vibration modes at tips of carbon nanohorns and other nanostructured asperities by benefitting from signal amplification in SERS at sites near a silver surface. Nanohorn vibration modes in the range 200–500 cm^{-1}, which are obscured in regular Raman spectra, were interpreted by *ab initio* density functional calculations as local vibration modes at the nanohorn cap. Careful interpretation of our SERS spectra indicates that vibrations at ≥ 400 cm^{-1} are associated with "jellyfish" vibrations of a cone terminated by 5 pentagons, which are chemically the most active sites. Vibrations at $\omega \geq 400$ cm^{-1} resemble the RBM of fullerene caps with 6 pentagons terminating a short nanotube segment near the apex of the nanohorn. Changes in the peak intensities and frequencies with time indicate that exposure to laser irradiation may cause structural rearrangements at the cap aimed at releasing stress.

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