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研究課題名（和文）　走査型トンネル顕微鏡発光分光を用いたプラズモニクスの局限的分析

研究課題名（英文）　One Nanometer Scale Chemical and Structural Analysis of Carbon Nanotubes by STM Tip Enhanced Raman Imaging in Ambient Condition.

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研究成果の概要（和文）：

本研究では、近接場ラマン分光用の走査型トンネル顕微鏡(STM)を構築し、ナノスケールでの構造/ラマンイメージングとラマン信号を用いた化学分析を 行った。探針増強ラマン散乱(TERS)測定用試料としては、明瞭な構造と比較的強いラマン信号を示すカーボンナノチューブを用いた。今回、1.7nm の 空間分解能において、数種のラマンモードからなる TERS 分光イメージングに成功した。ラマン散乱の D バンド信号がナノチューブの局所欠陥によること、共鳴条件のナノチューブ直径依存性、また複数のナノチューブの相互作用が「実空間」で観測出来ることを示し、これは世界初の成果と考えられる。このような高 分解能での化学分析法は、今後、分析化学また分光光学の方法論を大きく変化させる可能性がある。本研究の成果がナノスケールでの物理、化学、生物学分野で さらに発展することが期待される。

研究成果の概要（英文）：

Scanning tunneling microscope (STM) combined with near field Raman spectroscopy is constructed in this research for hybrid imaging and chemical analysis. SWNT is selected as our sample for tip enhanced Raman spectroscopy (TERS) because it has very strong Raman signal and clear morphology. We obtained spectrally resolved TERS images at different Raman modes with 1.7 nm spatial resolution. For the first time, the local defect origin of D band, diameter factor of resonance condition, and tube bundling effect are all visualized in real space. We are so exciting to have such high resolution tool and it may change the views and ways of analytical chemistry as well as optics and spectroscopy. This opens new possibilities to investigate nanoscale physics, chemistry, and biology.

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１．研究開始当初の背景

Two years ago, the original topic was about real space surface plasmon analysis by STM induced light emission. The technique itself was already successfully developed by myself during Ph. D. thesis so that it was less challenging. While setting up the equipment, I devoted myself to a very exciting direction toward STM tip enhanced Raman spectroscopy imaging (TERS). Eventually I succeeded in ultrahigh resolution TERS imaging of multi vibration modes with spatial resolution at 1.7 nm. This is a new milestone in optics, spectroscopy, and nano-scale chemical analysis. Though I changed the research direction, I hope this achievement could justify my two years effort during the supporting period of this budget.

The desire to see the invisibly small world has triggered the development of all kinds of microscopy techniques, including optical microscopy, electron microscopy, and scanning probe microscopy covering the length scale from mm to nm. However, microscopic images do not provide any chemical or energetic information of composing materials. Adding spectroscopic ability to these microscopes for in-situ analysis is the key technology toward understanding and controlling hidden physics and chemistry.

Nowadays, the surface morphology of materials is routinely analyzed by AFM and STM down to sub-nanometer precision. However, it is still difficult to distinguish chemical species simply based on topography of STM or AFM. With the innovation of tip enhanced Raman spectroscopy (TERS) in 2000, it soon becomes a potential tool for nanoscale chemical analysis and imaging with high resolution. TERS imaging has been realized using metallized AFM tip, so far the reported spatial resolution of TERS is in the order of 10 nanometer, which is still one order larger than AFM and STM's resolution.

To improve the lateral resolution of TERS, one way is to employ the spatially confined gap mode plasmon, which could be realized in the STM tunneling junction. A STM tip and its mirror dipole form the gap configuration as in the case of bowtie antenna and nanoparticle pairs. The enhancement due to gap mode is predicted to be 100 times stronger than the enhancement from tip only and the electromagnetic field is more confined. By the help of this budget, a STM based tip enhancement Raman spectroscopy (STM-TERS) system was built toward this target.

２．研究の目的

The purpose of this research is to achieve ultrahigh spatial resolution chemical contrast of different species by STM based TERS imaging as a "chemical nanoscopy". So far, most of reported TERS experiments simply compare the far/near field Raman spectra to prove the tip enhancement, which is far away from the potential capability of the TERS as a tool of chemical imaging.

Single wall carbon nanotube (SWNT) was selected as our sample because of its small diameter at 1-2 nm scale. SWNT has been extensively studied by AFM-TERS. The reported spatial resolution so far is all > 10 nm, which is one order larger than the diameter of SWNT. This means that the observed TERS signal is still the average of > 10 nm length of SWNT for detail analysis. It is essential to achieve the lateral resolution compatible with the diameter of SWNTs at 1-2 nm. During these two years, this goal is realized. 1.7 nm resolution STM-TERS imaging of individual phonon mode is visualized in real space.

３．研究の方法

3.1 STM-TERS system and Raman detection.

The TERS experiment is performed on a small STM designed and built by myself under ambient condition shown in Fig. 1. An environmental enclosure is applied for increasing the stability of STM by exchanging air to dry nitrogen. The STM scanner is designed to perform sample scan rather than tip scan to ensure constant scattering background and optical alignment.

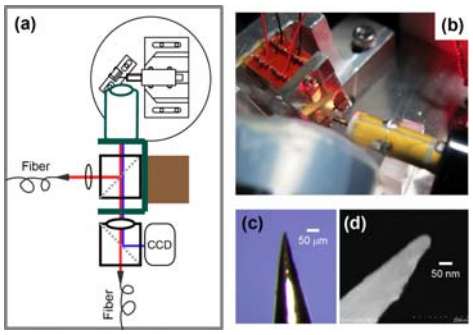

Fig. 1. (a) STM-TERS system inside an environmental enclosure. The illumination/detection optical paths are both fiber coupled. **(b)** Tip and sample junction illuminated by 633 nm laser through the objective lens. **(c)** STM tip under optical microscope. **(d)** SEM image of the tip with diameter ~ 40 nm.

The Z feedback pizo is tilt to have the tip approach at ~ 10° angle from sample surface

normal to open up larger solid angle for photon collection. The incident laser (633 nm, Neoarc, Japan) is focused by a long working distance objective lens at 50° angle from the sample surface, which results in a 1.4 μm focus spot in the long axis of ellipse. The incident laser power is 1mW measured at the sample position. The objective lens, filters, and collection fiber optics are integrated into one unit which can be precisely controlled by piezo motors. The polarization of incident light is parallel to the tip. Scattered Raman photon is collected by the same objective lens and then detected by a charge coupled device after a spectrometer.

3.2 Sample and substrate preparation.

SWNT was purchased from Meijo Nano Carbon (Nagoya, Japan) and used without further purification. The SWNT is specified as 99% metallic with 1.4 nm typical diameter. Experimentally about 80% of SWNT shows 1.2-1.4 nm in diameter determined by STM topographic height at low bias voltage. 20% of SWNT has diameter ranges from 1.5 nm to 2.2 nm. Atomically flat gold substrate was made by thermal deposition of pure gold onto freshly cleaved mica surface at 450°C. Dispersed SWNT solution in dichloroethane (0.5 mg/ ml) was spin casted onto the gold substrate and further dried inside an oven at 220°C for 2 hours. Sharp gold tips were made by electrochemical etching method with diluted HCl solution. The diameter of tip apex diameter ranges from 30 to 80 nm when monitored by a scanning electron microscope.

4．研究成果

Metallic SWNT is selected for TERS experiment because its band gap matches the laser energy at 1.95 eV. Before approach the tip, the resonance Raman scattering was observed in the far field (Fig. 2a). After approaching, TERS signal was found to be stronger than the far field background and showed clear Raman peaks of sp^2 carbon. Fig. 2d-2f shows the TERS imaging at three Raman modes taken simultaneously with topographic scan (Fig. 2c). The TERS signal is spatially confined on the SWNT with very good spatial resolution compatible to the resolution of its corresponding topography.

The diameter of each SWNT is measured by the height of linecut profile in topography. CNT-3 is 2.0 nm in diameter and appears as an isolated single tube. The diameter of CNT-1 is measured as 1.25 nm in the middle but change to 1.7 nm in the upper left corner. CNT-2 is found to have very similar diameter as CNT-1 around 1.25 nm. The planar bundle of CNT-1 and CNT-2 is not possible to be resolved by AFM topography in ambient condition. Better topographic resolution is one advantage of STM-TERS.

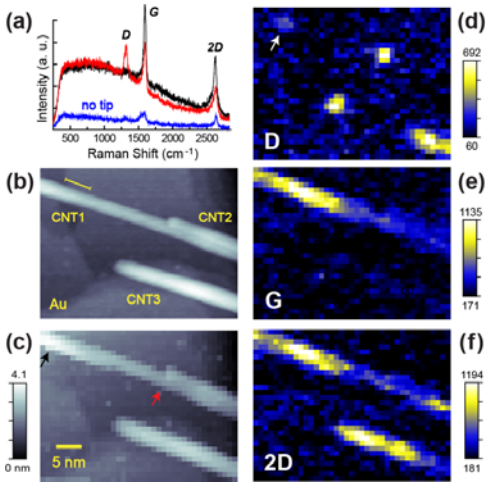

Fig. 2. (a) Far field Raman spectrum (blue, no tip) and TERS spectra (black and red) of two locations taken on the CNT-1 as indicated in (c). Accumulation time of each spectrum is 1 second. **(b)** High resolution STM topography of three labeled SWNTs on Au substrate. The yellow line segment indicates the transition area of diameter change. **(c)** Lower resolution STM topography taken simultaneously with TERS imaging. **(d-f)** TERS images of three Raman bands- D (d), G (e), and 2D (f). The accumulation time at each pixel is 0.1 second. During the experiment, bias voltage is 0.4 V and keep constant tunneling current at 20 pA.

D band intensity is observed to localize at the end of CNT-2 as well as the end of CNT-3 (Fig 2d). From our TERS image, the structural deformation at the ends of SWNT is the active site for D band signal. D band is also observed in the upper left corner of CNT-1 (white arrow, Fig 2d) and it might be related to the transition area of chirality and diameter change. Bottom right hand side of CNT-3 also has D band active site indicating possible localized defect along the tube, which is not observable in the STM topography.

Resonance dependence of individual SWNT is clearly observed in G band's TERS image. Compare to the strong signal from CNT-1, almost no G band could be observed in CNT-3. This could be attributed to the diameter of CNT-3, which is in not good resonance range with 1.96 eV laser excitation. In Fig. 2e, middle of CNT-1 shows strongest G band signal. This region of CNT-1 has a measured diameter at 1.25 nm which is expected to be resonant with the 1.95 eV laser. In the upper left corner is the 1.7 nm region which shows weaker G band. However, G band is also weaken in the overlapped area with CNT-2. Such strong effect of inter-tube interaction will be further discussed in Fig. 3.

Under our experimental condition, 2D band could be observed in most SWNT and distribute relatively uniform along every tube. Concluded

from several experiments with different tips, TERS images of 2D are more similar to its topography rather than D and G band images. D band signal is usually discrete while G band sometimes is missing in case of non-resonant SWNTs. In most far field Raman studies of single SWNT, it is assumed that Raman signal is only from the SWNT which is in good resonance with the incident laser. However, from our data, this is only true for G band. If a far field spectrum is taken in this area, large portion of the observed D and 2D bands is originated from the non-resonant CNT-3.

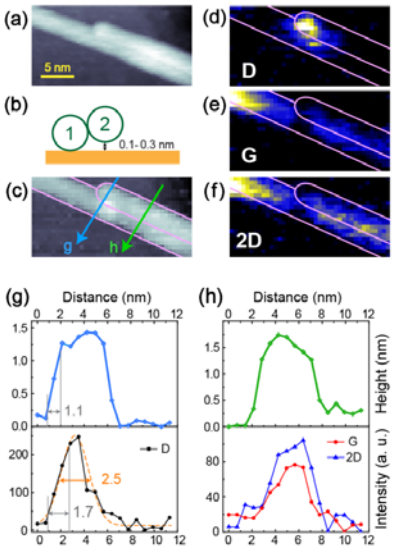

Fig. 3. (a) STM topography of the CNT-2 ending area (24×12 nm, enlarge from Fig. 1b). **(b)** Simple model of the bundling structure of CNT-1 and CNT-2. **(c)** STM topography taken simultaneously with TERS imaging and labeled with the eye-guiding contour and linecuts directions for profiles (j)-(l). **(d-f)** TERS images at three Raman bands- D (d), G (e), and 2D (f). The scanning size is 24 x 12 nm with 40 x 20 pixels. Spectral images are processed the same way as Fig 1. The accumulation time at each pixel is 0.15 second. **(g-h)** Linecut profiles along two different lines- g and h shown in (c). Upper panels are topographic heights and lower panels are Raman intensities. Orange arrows indicate the FWHM width and the grey arrows indicate the 10-90% resolution.

To further investigate the overlapping effect between CNT-1 and CNT-2 and distinguish the source of Raman signal, higher resolution TERS imaging is required. Here we show STM and TERS images with step precision at 0.6 nm in Fig. 3. Topographic linecut along line-g (Fig. 3g upper panel) shows the spatial resolution of STM at 1.1 nm which is defined by the width of 10% to 90% height transition. Both the finite diameter of SWNT and thermal drift /step precision limit this topographic resolution. From high resolution TERS image of D band, the signal is more confined than its diameter. The profile of D band intensity along line-g gives the 10-90% resolution at 1.7 nm. Five independent experiments with different shapes of gold tips all allows < 2 nm TERS resolution even though every tip is different in TERS enhancement factor. This resolution is one order better than all TERS literature so far. Assuming an averaged 20 nm spatial resolution in the past works, detail information obtained in the whole are of Fig. 3 was averaged and lost fine nanometric physical properties.

In contrast, owing to our 1.7 nm resolution of STM-TERS, the evolution of the physical properties along a single tube is successfully visualized, which represents the inter-tube interactions due to bundling of CNT-1 and CNT-2. Simply from intensity image (Fig. 3e and 3f), both G and 2D band signal mostly concentrate along the boundary of two tubes, which indicate the intensity comes from both CNT-1 and CNT-2. Detail spectral mapping along the CNT-1 and CNT-3 is shown in Fig 4.

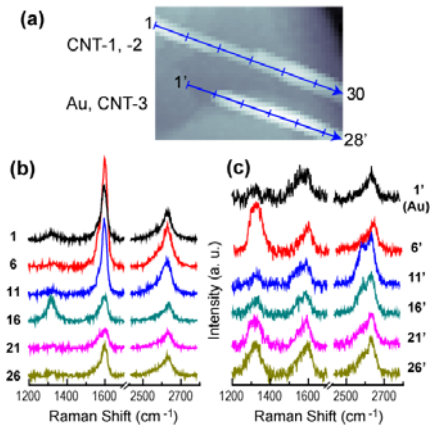

Fig. 4. (a) STM topography labeled with the locations for accumulating spectra on SWNTs. Spectra 1 to 30 are taken on CNT-1 (CNT-2) at 1.5 nm/ step and mixed with the TERS signal of CNT-2 from location 15 to 30. Spectra 1' to 28' are along CNT-3 at 1.3 nm/step. Note that spectra 1' to 4' are taken on Au substrate. **(b)** Six Spectra taken at locations 1, 6, 11, 16, 21, and 26. **(c)** Six Spectra taken along CNT-3. The vertical scale of (c) is half of (b). The integration time of each spectrum is 1 second.

In our TERS spectrum, D band signal shows single Lorentzian lineshape and narrower linewidth than G and 2D bands. The FWHM varies significantly in between different SWNTs. FWHM of D band on CNT-1 (location 1 and 2) is 51 cm^{-1} while the end of CNT-2 (15-17) is 50 cm^{-1}. End of CNT-3 (6'-8') is 79 cm^{-1} and 75-77 cm^{-1} from location 18' to 28'. We can conclude that D band linewidth is not reflecting what kind of local defect it is but only related to the phonon structure of individual SWNT.

Another interesting point in our spectra is the splitting of 2D band. 2D band is composed of two

peaks in our TERS spectra but the 2D$^-$ mode is particularly strong in the middle locations (7'-18') of CNT-3 with clear doublet shape. In our case, we do not have any information about the chirality of CNT-3. However, such change happens locally, not all along CNT-3, so that it is not only determined by phonon structure. Splitting of 2D band has been discussed a lot in case of stacking of a few layers graphene.[12] Basically inter-layer interaction splits the 2D band into multiple peaks. We did not observe any small flakes or carbon network attached to CNT-3 so there must be other reasons for such splitting of 2D band locally.

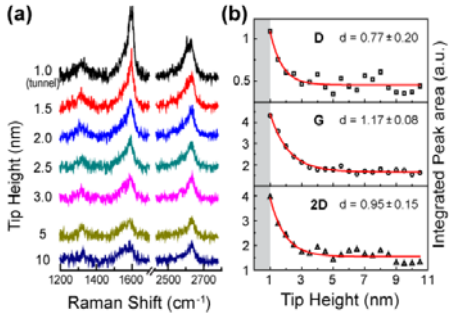

Fig 5. **(a)** Series of spectra taken at location 1 of CNT-1 of Fig. 4a while retracting the tip away from substrate at 0.5 nm/step. The integration time of each spectrum is 1 second. **(b)** Evolution of integrated peak area fitted with single exponential decay versus tip height of three Raman bands.

TERS signal has very strong tip height (z) dependence due to its *evanescent wave* nature in the nanometric tip surface. In case of STM-TERS, the optical field is strongly confined in between the tip dipole and its image dipole (gap mode plasmon) like the cases of optical bowtie antenna and nanoparticle pairs.[14] The distances dependence of EM field enhancement is the key issue in near field optics. The spectral evolution while retracting tip is shown in Fig. 5a. Intensity of all three Raman bands decays quickly within the initial 3 nm and stabilizes after retracting tip more than 4 nm. This indicates a very drastic confined optical field in z direction, which is confirmed by the z dependence curves shown in Figure 5b. The near field Raman signal decays to 1/e when retracting tip by ~1.0 nm. This is one order faster than most cases using AFM-TERS, which greatly improve the spatial resolution of STM-TERS.

The enhancement due to gap mode is predicted to be 100 times stronger than the enhancement from tip only.[7] In our experiment, the calculated *E. F.* are 9.3×10^4, 1.0×10^5, 8.6×10^4 for D, G, and 2D bands, respectively. Note these numbers of *E. F.* have only small deviation as well as similar values in their decay constant within fitting error for each Raman mode. Both clues indicate uniform near field amplification without wavelength variation.

While STM scanning, sometimes it will get the sample molecules attached to the tip. Such a molecule modified tip has dramatic effects in STM imaging such as presenting finer details in topography. In our case, carbon nanotube could be attached to the STM tip sometimes while scanning but very difficult to remove. Such carbon nanotube modified tip shows strong Raman signal originates from the attached carbon nanotube (surface enhanced Raman effect, SERS). When this SWNT-modified tip is used for imaging the surface, a reversed TERS contrast is found (Fig. 6). This is very interesting phenomena and still we are not sure this is simply due to gap distance change or some other reasons. Similarly, reversed contrast also shows good spatial resolution around 2 nm.

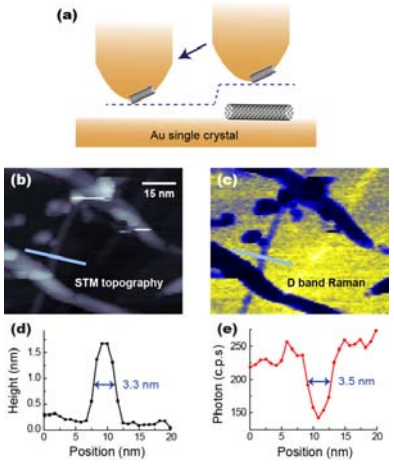

Fig. 6. (Left) STM topography of SWNT and its line cut across a single tube. (Right) Near field Raman imaging shows reversed contrast from usual TERS. The Raman imaging shows high spatial resolution as the STM topography.

In this report, we demonstrate the simultaneous chemical and structural analysis of SWNT by STM-TERS. With 1.7 nm spatial resolution, for the first time, the local defect origin of D band, diameter factor of resonance condition, and tube bundling effect are visualized in real space. TERS is a difficult experiment which requires sophisticated techniques from both optics and scanning probe microscope. However, now it is possible to make it a more practical research tool for chemical recognition and imaging with spatial resolution around 1-2 nm. We are so exciting to have such high resolution tool for investigating nanoscale physics, chemistry, and biology. It may change the views and ways of analytical chemistry as well as optics and spectroscopy. This opens some new possibilities in the nanoscale playground.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 0 件）

〔学会発表〕（計 3 件）

① Sep/2013 (accepted)
Oral presentation (accepted), ICNT-2013, Paris, France.

② Aug/2013
Oral presentation (accepted), Light at the Nanotip, Bonn, Germay.

③ Sep/2012
Poster presentation, VAS-14, Kobe, Japan.
Chi Chen, N. Hayazawa, and S. Kawata,
“Tip Enhanced Raman Spectroscopy Base on A Scanning Tunneling Microscope”

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