

Raman Workshop —

Nanophotonics and Nanospectroscopy

24 June 2011

2:30PM ~ 7:00PM

Chung-Ang University

중앙대학교

창업보육센터 1층 세미나실

주최: 신기능이미징연구소 (중앙대학교)

지원: ANT Co. (NT-MDT Co.)

PROGRAM

24 June, 2011

14:30~15:00 Registration

15:00~15:40 Surface Engineered Micro Gold Shells for Advanced Chemical Analysis based on Surface enhanced Raman Scattering
정택동 교수 (서울대학교)

15:40~16:20 Chemical Imaging by Broadband Coherent Anti-Stokes Raman Scattering (CARS) Microscopy
성지하 교수 (동덕여자대학교)

16:20~16:50 Coffee Break

16:50~17:30 Re-examination of SERS Spectra of 4-aminobenzenethiol: Charge Transfer Enhancements or Photochemical Artifacts?
김지환 교수 (고려대학교)

17:30~18:10 Ultrafast Large Area Imaging of Carbon Nanomaterials using Widefield Raman Spectroscopy
주상용 교수 (연세대학교)

18:10~18:30 Some Key Words in SPM combined with Raman Microscope beyond Diffraction Limit
차호석 박사 (ANT Korea)

19:00~ Dinner

Surface Engineered Micro Gold Shells for Advanced Chemical Analysis based on Surface enhanced Raman Scattering

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Raman scattering has been attracting attention as one of the most promising candidates for *in situ* monitoring of chemical environment during electrochemical reactions or biological events. But it has a critical drawback as well, which is sensitivity. That is why a great amount of efforts have been made to find the way to apply Raman spectroscopy for this purpose by enhancing the light scattering intensity. In this regard, surface enhanced Raman scattering (SERS) has been receiving spotlights. The key factor to accomplish its practical utility as an analytical tool is better substrates. We have been pursuing new SERS substrates based on thin gold shells covering micro polymeric core beads. As a consequence, sophisticatedly engineered micro gold shells were obtained for SERS-based analysis of sub-monolayered molecular species on conducting or non-conducting substrates. Moreover, a single micro gold shell can be used to be an ultramicroelectrode (UME) for scanning electrochemical microscope (SECM). The hybrid probe in this work is expected to provide a new way to monitor the chemical release on local sites of a biological sample, to look into the activity of electrocatalysts, and to analyze the metal or biological molecules by Raman scattering as well as electrochemistry simultaneously. This talk will show how creatively microfluidic technology can be combined with SERS for multiplex analysis, which is the emerging issue of modern analytical chemistry.

Chemical Imaging by Broadband Coherent Anti-Stokes Raman Scattering (CARS) Microscopy

Jiha Sung

Department of Applied Chemistry, Dongduk Women's University

CARS microscopy and microspectroscopy based on the spectral focusing mechanism are demonstrated. Highly chirped broadband pulses from a single Ti:Sapphire laser generate CARS signals at the fingerprint region. Acquisition of the vibrational spectrum is achieved by changing time delay between pump and Stokes laser pulse, which allows rapid and easy frequency switching. Fast modulation of the time delay between laser pulses coupled with lock-in signal detection not only eliminates the non-resonant background but also produces Raman-like CARS signals over $800 - 1700 \text{ cm}^{-1}$ with spectral resolution of 20 cm^{-1} . With IR supercontinuum pulses generated from a photonic crystal fiber, CARS signals at the CH stretching region ($2800 - 3100 \text{ cm}^{-1}$) are obtained with spectral resolution of 30 cm^{-1} . Chemical imaging and micro-spectroscopy of polymer mixture, oil droplets, and biological system such as cell and tissue are demonstrated for both fingerprint region and the region of CH stretching region.

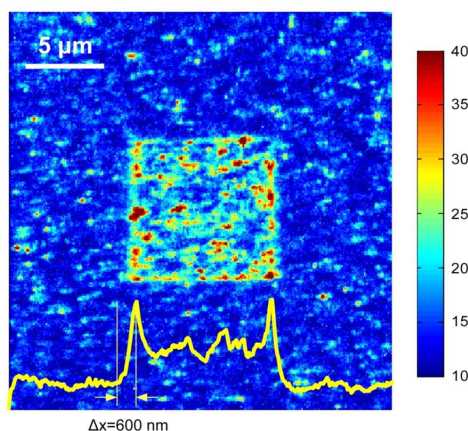
Re-examination of SERS Spectra of 4-aminobenzenethiol: Charge Transfer Enhancements or Photochemical Artifacts?

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The SERS spectra of 4-aminobenzenethiol (ABT) have served as the "probe" molecule, which have helped us to evaluate the electromagnetic (EM) and chemical (CHEM) enhancement mechanisms. In particular, the b_2 -peaks (9b, 3, and 19b) of the SERS spectra of ABT has been known to arise from the vibronic charge-transfer (CT) between Au or Ag surface and the ABT. Quite recently, however, Tian and co-workers claimed that the b_2 -peaks are not the CT-enhanced spectra of ABT. Instead, these peaks arise from the dimercaptoazobenzene (DMAZB) that are produced by the oxidative coupling of two ABTs. Their claim has not yet gained a general consensus thus far, and this issue is under intense debate.

Herein, we present a series of additional evidences that clearly show that the b_2 intensities of ABTs does not arise from the CT-enhancement: (1) the b_2 -intensities can be locally "activated" (i. e. turned on) irreversibly with strong laser radiation; (2) the TOF-SIM mass spectrometry on the activated region show depletion of ABT ions; and finally (3) the spatially resolved FT-IR spectra of the activated region show two pronounced peaks at 1380 cm^{-1} and 1440 cm^{-1} , both of which can be assigned to the stretching mode of N=N bond. While the result does not disprove the existence of CT or CHEM enhancement in general, the result do show that many previous interpretations of the spectra of ABTs should be re-examined.



SERS image of 4-aminobenzenethiols on Ag surface

Ultrafast Large Area Imaging of Carbon Nanomaterials using Widefield Raman Spectroscopy

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Raman spectroscopy has been used extensively to probe carbon nanomaterials. Nanotube chirality, electrical type (metallic and semiconducting), defect or dopant density, and electron-phonon interactions of carbon nanotubes have been extensively studied via Raman spectroscopy. In addition, the numbers of layer, a quality of a few-layered graphene have been studied using this inelastic scattering method. However, due to the size and small contrast of these materials, carbon nanotubes and graphene are often invisible and therefore we need a real-time optical tool to identify and monitor such materials. Here, we present a spectrally-resolved widefield Raman imaging (WRI) technique that images carbon nanotubes and graphene with a speed three orders of magnitude faster than the conventional micro-Raman technique. We combine widefield illumination from an intense (3 W) laser beam with tunable optical filters to image the Raman-scattered bands (D, G, 2D) unique to carbon nanotubes and graphene, providing a diffraction limited image for a large field of view. This enables fast identification of individual carbon nanotubes in seconds, after which high-resolution Raman spectra can be obtained for a region of interest using an imaging spectrometer. The widefield geometry enables large-scale studies of both carbon nanotube and graphene samples, while providing comparable spectral information to that obtainable with micro-Raman imaging. Furthermore, we find that two thirds of the nanotubes are easily visualized in G-band WRI with a single laser line, which suggests that only a few laser lines would be required to image all nanotubes with WRI. We expect that WRI will be a powerful experimental technique for both practical and fundamental studies of carbon nanotubes and graphene.

Some Key Words in SPM combined with Raman Microscope beyond Diffraction Limit.

John Kim¹, Edward Cha^{1,2}

ANT Co., Korea¹, NT-MDT America, USA²

In this talk, we would like to mention some technical steps should be done to make "Hot Spot" to focus incident light beyond diffraction limit on the surface of probing sample. All of these steps are for establishing of reproducibility and stability during measurement of chemical and physical data of sample.

And we will consider some functionality should have to make complimentary data at one shot measurement in SPM integrated with optical system. In Nanoscience, all properties of materials are depending drastically with varying position and distance of inter action particle in nm scale. So, it is very important to do data mining without changing of sample movement between different property measurements.

Finally, we will show how to combine all of these steps and functionality with existing optical system.

장소: 창업보육센터 1층 세미나실 (209동)



찾아오시는 길

- 지하철 7호선: “상도역(중앙대앞)” 5번 출구, 도보 10분 거리,
“상도역(중앙대앞)” 5번 출구 ⇒ 상도터널 방향으로 100미터 도보 ⇒
마을버스 “동작01”로 환승 후 “중앙대 후문” 하차 도보 5분 거리
- 지하철 9호선: “흑석역(중앙대입구)” 4번 출구, 도보 15분 거리

아래의 모든 버스: “명수대현대아파트(중앙대병원입구)” 정류소에서 하차
도보 15분 거리

- 지선버스: 5511, 5517, 5524, 5529, 6411
- 간선버스: 151, 360, 361, 362, 363, 640, 642, 462
- 광역버스: 9408
- 공항버스: 600