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13. ABSTRACT *(Maximum 200 words)*

This project supported a new universal scanning microscope system combining near-field scanning optical microscopy (NSOM), conventional atomic force (AFM) microscopy, and confocal optical microscopy. To build a universal system capable of high resolution topographical imaging concurrently with spectroscopic abilities, we have acquired several independent units and combined them into a custom-designed NSOM/AFM/Raman instrument. We have acquired an atomic force microscope (Multimode, Digital Instruments) and a near-field scanning microscope (Aurora III, Digital Instruments, partially supported by NASA) and a SpectroPro Raman spectrograph from Roper. In addition to these major instruments we acquired a number of supported parts/instruments aiming on the completion of the system and sample preparation, selection, and charactgerization for Raman studies (CCD camera, avalanche detectors, two lasers, optical parts, air table, fluorescence microscope, miniX-ray unit, etc). A post-doctoral Research Associate was in charge of putting all these parts together. We did not go with a single unit from WiTec because actual demonstrations did not show expected sensitivity.

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Acquisition of a Combined Scanning Near-Field Optical and Atomic Force Microscope

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Project objectives

This project supported a new universal scanning microscope system combining *near-field scanning optical* microscopy (NSOM), conventional *atomic force* (AFM) microscopy, and *confocal optical* microscopy. Additional options include polarization and fluorescence modes, UV and Raman spectroscopies. This universal unit is capable of *concurrent (the same scan) collection* of high-resolution data about surface topography and corresponding optical/spectroscopic properties. This unique combination enables the detailed nano-chemical and nano-structural characterization of a range of biomaterial surfaces, micropatterned biohybrid membranes, and biointerfaces.

Major accomplishments

To build a universal system capable of high resolution topographical imaging concurrently with spectroscopic abilities, we have acquired several independent units and combined them into a custom-designed NSOM/AFM/Raman instrument. We have acquired an atomic force microscope (Multimode, Digital Instruments) and a near-field scanning microscope (Aurora III, Digital Instruments, partially supported by NASA) and a SpectraPro Raman spectrograph from Roper. In addition to these major instruments, we acquired a number of supporting parts/instrumnets aiming on the completion of the system and sample preparation, selection, and characterization for Raman studies (CCD camera, avalanche detectors, two lasers, optical parts, air tables, fluorescence microscope, miniX-ray unit, etc). A post-doctoral Research Associate was in charge of putting all these parts together. We did not go with a single unit from WiTec because actual demonstrations did not show expected sensitivity. Below, we present the current design of the instrument and some preliminary results obtained with this instrument to date.

Combined Instrument Description

The schematic of the custom-designed instrument combined in the PI lab is presented in Figure 1. This schematic displays an AFM/NSOM instrument with either AuroraIII or Multimode scanners (top) combined through an optical path with Raman spectrograph (bottom) with a selection of two lasers and two detection schemes. E.g., Nd:YAG laser beam (second harmonic, 532 nm) adjusted to certain power (1-100mW) and beam size (3mm) is guided into the transmission entrance of the Aurora III. The beam is focused onto the sample surface by a high numerical aperture microscope objective (40X/0.65NA).

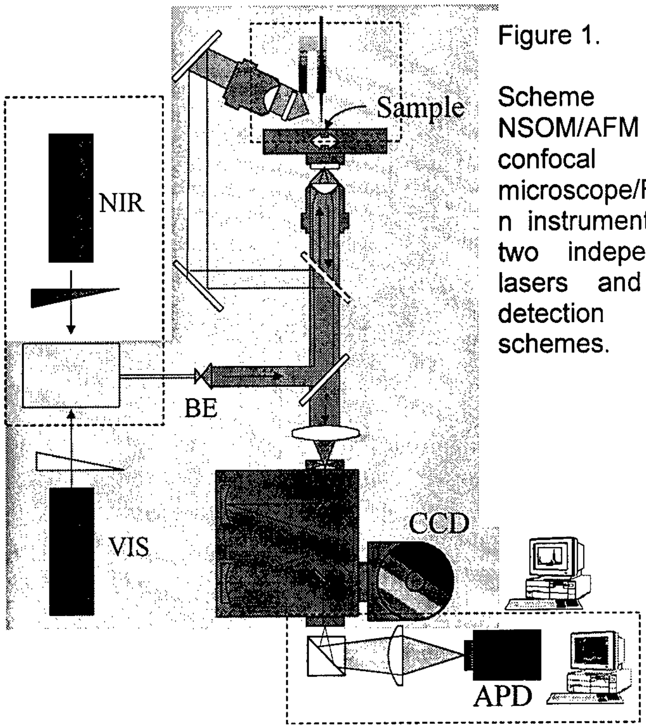

Figure 1.

Scheme of NSOM/AFM and confocal microscope/Raman instrument with two independent lasers and two detection schemes.

A "bird-view" picture of current NSOM-Raman instrument is shown in Figure 2. Presented design includes the combined NSOM unit and a confocal Raman microscope mounted on the optical air-table (TMC 78-23765-01) with a steel honeycomb optical top. The Aurora III base and the spectrograph and CCD camera are control with two synchronized computers. Two monitors are used to observe the video images of specimens obtained with the Aurora optical system. The instrument is located in an isolated dark room.

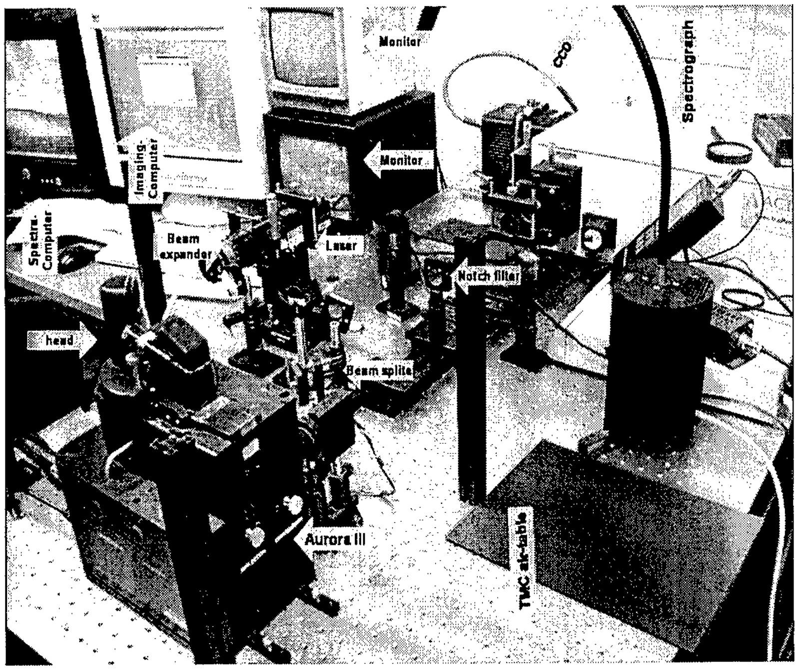

Figure 2. Picture of AFM/NSOM-Raman instrument.

The signal collected from a specimen mounted on the NSOM/AFM scanner passes through a notch filter and is focused on the entrance slit of imaging spectrograph SpectraPro SP-2558-W (Roper Scientific). CCD camera Spec-10:2KB (Roper Scientific) collects the spectra at every point. High-resolution spectra (0.32 cm^{-1}/pixel for 1800 mm^{-1} grating) are used for the selected surface locations. The spectroscope is calibrated by taking the reference spectra (Neon lamp) and using the calibration program from the spectrograph Winspec software. To expand laser spectral range and reduce damaging of biological samples, near infrared (NIR) laser with 785 nm wavelength and 20 mW is purchased from Kaiser Optical System and is installed as an additional source. This rugged laser provides stable laser line with narrow line-width.

We exploit two independent set-ups allowing for transmission Raman data collection for this transparent specimens as well as a backscattering mode of collection for non-transparent and thick specimens (Figure 3). The application of either transmission (for Aurora NSOM scanner) or reflection (Multimode scanner) can be conducted with by guide the laser beam into different objective. CCD camera provides excellent sensitivity and speed. However, as addition option to increase the rate of Raman signal collection and the quality of images, Avalanche photodiode (APD) is attached as an alternative detector to the outer slit of the spectrometer. SPCM-AQ4C detector from *Perkin-Elmer* can detect a single photon in the range of 400 to 1060 nm and its four channels are independent from each other.

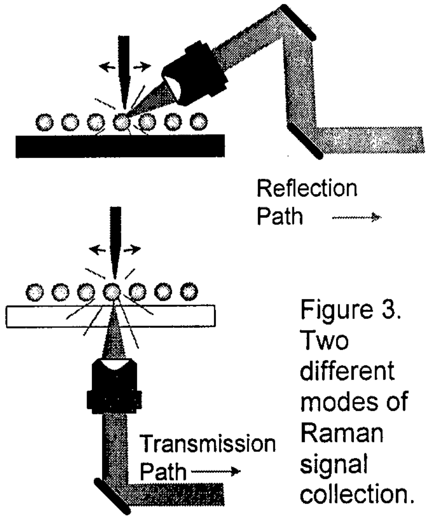

Figure 3. Two different modes of Raman signal collection.

Preliminary results obtained with the instrument

Patterned carbon nanotube arrays.

We used a direct collection of Raman spectra from patterned arrays of bent single wall carbon nanotubes and bundles (3 nm in diameter) with precise localization of the probed area as monitored with this combined instrument (*Appl. Phys. Lett.*, 2004). We used the surface organized arrays of bent and looped nanotube assembled by the patterned microfluidic flow and focused on finding characteristic Raman signatures (Figure 4). We showed that the tangential G-mode on Raman spectra systematically shifts downward upon nanotube bending. This lower frequency shift is attributed to the tensile stress, which results in the loosening of C–C bonds in the outer nanotube walls. Custom designed combined

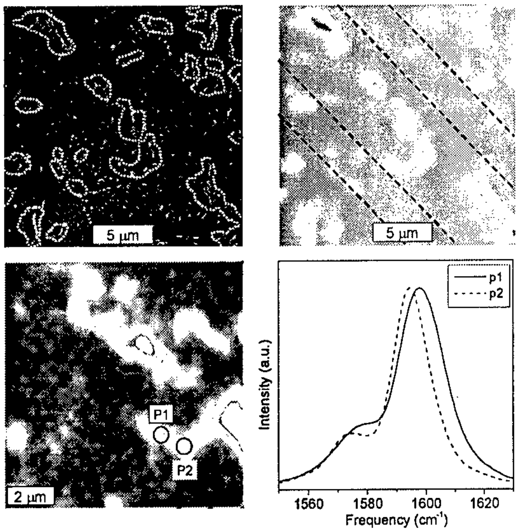

Figure 4. Shear-force AFM (top, left) and Raman (top, right) images of low density nanotube arrays collected for the patterned surface area. High resolution Raman image of the surface area (bottom, left) and Raman G-band at different positions (bottom, right).

AFM-Raman setup based on NSOM Aurora-III was used for Raman mapping and high-resolution Raman spectroscopy from selected locations.

Freely suspended nanomembranes with encapsulated gold nanoparticles.

Freely suspended gold nanoparticle arrays encapsulated into multilayered LbL nanomembranes possessed an anisotropic mechanical response caused by different composite moduli along and perpendicular to the nanoparticles-containing stripes (*Adv. Mater.,* 2005, in print). The presence of gold nanoparticles into the polymeric matrix causes surface enhanced Raman scaterring (SERS) phenomenon with greatly increased (>1000) intensity of selected vibrational bands (Figure 5). The periodic variation of the enhanced Raman scattering across the micropatterned array (*modulated SERS phenomenon*) was found for these micropatterned nanomembranes (Figure 5). We suggest that both phenomena observed for the freely suspended nanomembranes with gold nanoparticles arrays, namely, the anisotropic micromechanical response and modulated optical properties, can be critical for their prospective applications as acoustic sensors with directional sensitivity, tunable optical Raman gratings, and opto-mechanical sensors.

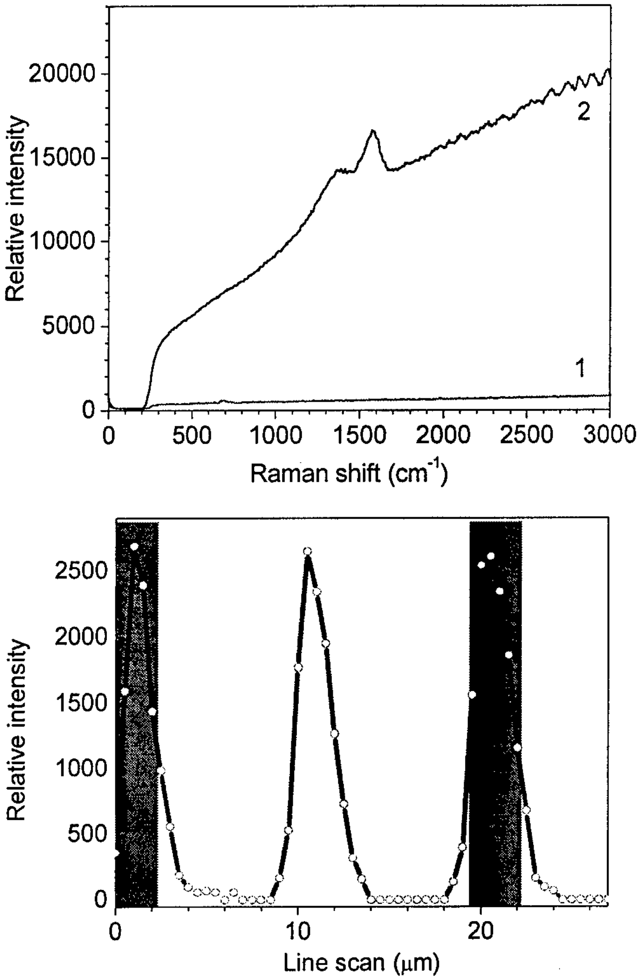

Figure 5. Top: Raman spectra of the 9G*9 nanomembrane with the focal position between (1) and on (2, SERS effect) the gold-nanoparticle stripes; b) the intensity variation at 1590 cm^{-1} peak across several stripes of the gold nanoparticle array. The stripes are marked as background. *Adv. Mater.*, in print

Several other studies which expoited the instrument designed in the PI in the course of DURIP project include the analysis of internal microstructural reorganization of free-suspended nanocomposite membranes in the course of their deflection and SERS phenomena in nanomembranes (see a list of papers submitted).

Peer-reviewed publications resulted from AFOSR-DURIP project (2003-2004).

H. Ko, Y. Pikus, C. Jiang, A. Jauss, O. Hollricher, V. V. Tsukruk, High Resolution Raman microscopy of curled carbon nanotubes, *Appl. Phys. Lett.,* **2004**, *85,* 2598-2600.

C. Jiang, S. Markutsya, H. Shulha, V. V. Tsukruk, Freely Suspended Gold Nanoparticles Arrays, *Adv. Mater.*, **2005**, in print

C. Jiang, W. Y. Lio, V. V. Tsukruk, In-situ Observation of Chain Bridging in Deflecting Free-suspended Multilayered Nanomembranes with Surface Enhanced Raman Spectroscopy, *PRL*, submitted

C. Jiang, H. Ko, V. V. Tsukruk, Strain Sensitive Raman Modes of Carbon Nanotubes in Deflecting Freely Suspended Nanomembranes, *Angew. Chemie*, submitted

H. Ko, C. Jiang, H. Shulha, V. V. Tsukruk, Carbon nanotube arrays encapsulated into freely suspended flexible films, *Chem. Mater.*, submitted

Further activities and impact

1. Three graduate students and two post-doctoral Research Associates from the PI group were trained and conduct measurement on this instrument.
2. One graduate student and a faculty member from MSE department were trained to use this instrument and conduct their independent studies for a nominal fee.
3. Prospective usage of this instrument for peptide-nanoparticle assemblies was discussed with Dr. R. Naik, AFRL.
4. The instrument is used for Raman studies of adsorbed protein molecules and free-standing nanomembranes in the framework of current AFOSR project F49620-02-0205 “Design of Bio-Hybrid Surface Assemblies At Engineering Interfaces”
5. The instrument will be used for surface-enhanced Raman studies of biometallization in the framework of new AFOSR Project “Flex Biohybrid Nanomembranes as a Platform For Multifunctional Microscopic Sensors”, which is scheduled to start in May 2005
6. The instrument is exploited in current AFOSR-STTR project (with Agiltron Corp) to verify chemical composition of thermal sensors
7. Several pending proposals to DARPA, NSF, NIH, and DOE include prospective intense use of the instrumentation designed in the PI lab.