

*TERS-6, The 6<sup>th</sup> International Conference on Tip-Enhanced Raman Spectroscopy  
Aug. 16-18, 2017, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.*

# Abstracts

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# Invited

**INVITED**

## **Nanoscale Chemical Imaging with UHV and EC-TERS**

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### **Abstract**

I will focus in on two recent projects in ultrahigh vacuum (UHV) and electrochemical (EC) TERS which illustrate the power of this emerging technique. First, new insights into the nature of a dynamic phase boundary involved in the room temperature (RT), UHV-TERS of the Ag tip/ N-N'-bis(2,6-diisopropylphenyl)-1,7-(4'-t-butylphenoxy)perylene-3,4:9,10-bis(dicarboximide) (PPDI)/Ag(100) system will be described.[1] We have unraveled the orientation of PPDI molecules at the dynamic molecular domain boundary with ~4 nm spatial resolution by UHV-TERS mapping. TERS provides access to molecular adsorption geometries when STM provides no topographical information. Next, Angstrom-scale spatial resolution in TERS has been achieved.[2] At room temperature, the strong adsorbate-substrate interaction between the meso-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H<sub>2</sub>TBPP) and the underlying Cu(111) substrate leads to the formation of the bowl up/down conformations. Through simultaneous UHV-TERS and STM analysis on the neighboring conformational isomers, we have observed ~15 cm<sup>-1</sup> spectral shift in one of the porphyrin-ring Raman modes and analyzed the origin of this shift using DFT calculations. Finally, I will discuss EC-TERS highlighting single molecule electrochemistry and the imaging of electrochemical reactions on the nanometer length scale.[3,4]

### References:

- [1] N. Jiang, N. Chiang, L. R. Madison, E. A. Pozzi, M. R. Wasielewski, T. Seideman, M. A. Ratner, M. C. Hersam, G. C. Schatz, and R. P. Van Duyne, "Nanoscale Chemical Imaging of a Dynamic Molecular Phase Boundary with Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **16**, 3898-3904 (2016).
- [2] N. Chiang, D. Chulhai, G. Goubert, X. Chen, E. Pozzi, N. Jiang, M. Hersam, T. Seideman, L. Jensen, and R. P. Van Duyne, "Conformational Contrast of Surface-Mediated Molecular Switches Yields Angstrom-Scale Spatial Resolution in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **16**, 7774-7778 (2016).
- [3] D. Kurouski, M. Mattei, and R. P. Van Duyne, "Probing Redox Reactions at the Nanoscale with Electrochemical Tip-Enhanced Raman Spectroscopy," *Nano Letters*, **15**, 7956-7962 (2015).
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**INVITED**

## **Single Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy**

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### **Abstract**

Advances in tip-enhanced Raman spectroscopy (TERS) have demonstrated ultra-high spatial resolution so that the vibrational modes of individual molecules can be visualized. The spatial resolution of TERS is determined by the confinement of the plasmon-induced field in the junction; however, the conditions necessary for achieving the high spatial confinement required for imaging individual molecules are not fully understood. Here, we present our recent work on modeling TERS imaging of single molecules. We will discuss the breakdown of the traditional Raman selection rules in these experiments due to the highly confined near field.

Reference:

- [1] P. Liu, D. V. Chulhai, L. Jensen, "Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy", *ACS Nano*, **11**, 5094-5102, (2017)

## INVITED

# Tip-enhanced Raman Spectroscopy for Nanoscale Characterization of Surface Reaction and Dynamics

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## Abstract

Tip-enhanced Raman spectroscopy (TERS) can not only obtain the topological but also vibrational information of a sample at the nanometer resolution. It is a very promising nanospectroscopy. In this talk, we used TERS to spatially resolve the site-specific electronic and catalytic properties of an atomically well-defined Pd/Au(111) bimetallic model catalyst at 3 nm resolution with molecular fingerprints. Benefiting from this high spatial resolution, we can directly visualize the distinct chemical (electronic) and physical (plasmonic) properties of the Pd island edges compared with the Pd terrace sites on a Au(111) surface. We also extended the study to Pt islands on Au(111) surface. Most of previous TERS studies were performed in air or UHV. If TERS study can be performed in the electrochemical environment, the electronic properties of the surface can be well controlled so that the interaction of the molecules with the substrate and the configuration of the molecules on the surface can be well controlled. We designed a special spectroelectro-chemical cell to eliminate largely the distortion of the liquid layer to the optical path and have been able to obtain TER spectra of reasonably good signal to noise ratio for surface adsorbed molecules under electrochemical potential control. Furthermore, we are able to synergistically control the reaction by both electrode potential and laser power, and characterize the reaction with nanometer spatial resolution. We further extended EC-TERS to 2D materials.

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- [3] X. Wang, J. H. Zhong, M. Zhang, Z. Liu, D. Y. Wu, and B. Ren, *Anal. Chem.*, **88**, 915-921(2016).
- [4] Z. C. Zeng, S. C. Huang, D. Y. Wu, L. Y. Meng, M. H. Li, T. X. Huang, J. H. Zhong, X. Wang, Z. L. Yang, and B. Ren, *J. Am. Chem. Soc.*, **137**, 11928 (2015).
- [5] Z. Liu, S. Y. Ding, Z. B. Chen, X. Wang, J. H. Tian, J. R. Anema, X. S. Zhou, D. Y. Wu, B. W. Mao, X. Xu, B. Ren, and Z. Q. Tian, *Nat. Commun.*, **2**, 305(2011).

INVITED

## 2-Dimensional Polymers studied by TERS

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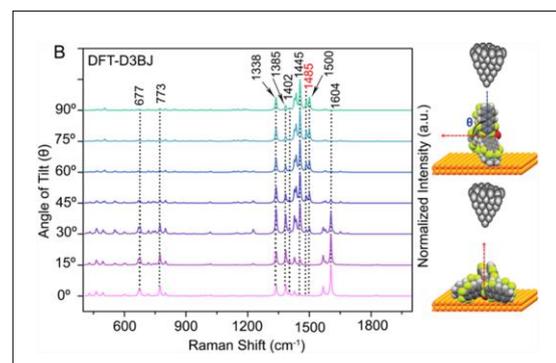
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### Abstract

Monomolecular layers are usually difficult or impossible to characterize in terms of their nanoscale molecular composition. Tip-enhanced Raman Spectroscopy (TERS) not only shows excellent spatial resolution in the low nm range, but is also very useful for rendering monolayers spectroscopically visible. Examples of monomolecular layers where a nanoscale characterization would be highly desirable include self-assembled monolayers (SAMs), Langmuir-Blodgett layers, lipid membranes, and a new class of compounds, 2-dimensional polymers (2DPs). 2DP polymer sheets can be synthesized via the formation of covalent linkages, via  $\pi$ - $\pi$  noncovalent interactions, via transmetallation, and by other means. After polymerization, 2DPs display remarkable mechanical robustness and can be transferred to surfaces and grids. Similar to graphene and its derivatives, 2D polymers with precisely controlled molecular structures and cavities show promise for a range of applications, including energy conversion and storage, gas storage and separation, sensing, and catalysis.



**Figure:** DFT simulation of TERS spectra of a partially fluorinated "carboxy fantrip" monomer that forms 2D polymers via noncovalent  $\pi$ - $\pi$  stacking interactions. The Raman intensities at 1485 and 1604  $\text{cm}^{-1}$  are strongly dependent on the tilt angle, which allows the homogeneity of the 2D polymer layer to be assessed.

In this contribution, TERS studies as well as theoretical calculations to aid the interpretation of the experimental results on several 2DP systems will be presented. TERS maps with pixel sizes as small as 2 nm showed ordered vs. disordered areas, and reacted vs. unreacted monomers.

### References:

- [1] W.-I. Lin et al., *Tip-Enhanced Raman Spectroscopic Imaging Shows Segregation within Binary Self-Assembled Thiol Monolayers at Ambient Conditions*, Anal. Bioanal. Chem. **407**, 8197-8204 (2015).
- [2] W. Dai et al., *Synthesis of a Two-Dimensional Covalent Organic Monolayer through Dynamic Imine Chemistry at the Air/Water Interface*, Angew. Chem. Int. Ed. **55**, 213-217 (2016).
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**INVITED**

## **Semiconducting Nanostructures for Mid-infrared Plasmon-Enhanced Spectroscopy**

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Plasmon-enhanced spectroscopy, in particular surface-enhanced and tip-enhanced Raman scattering (SERS and TERS), can obtain structural information down to even the single molecule level [1,2], due to the large optical field enhancement provided by noble metal nanoparticles. The extension of these concepts to the IR spectral range would enable direct probing of structure through IR vibrational modes, and provide access to additional low energy excitations. Semiconductors are ideal for strong light concentration in the mid-IR spectral range, due to their low plasma frequencies, precise fabrication methods, and robustness. I will discuss the characterization of semiconducting nanostructures, in particular in silicon, fabricated using both top-down and bottom-up fabrication approaches for control of geometry and the spatial distribution of dopants [3]. I address the potential of these structures for mid-infrared plasmonics, taking advantage of the enhanced fields derived from this approach for nano-spectroscopy and surface-enhanced IR absorption.

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1. Kneipp, K., Wang, Y., Kneipp, H., Perelman, L. T., Itzkan, I., Dasari, R. & Feld, M. S. Single molecule detection using surface-enhanced Raman scattering (SERS). *Phys Rev Lett* 78, 1667-1670 (1997).
2. Neacsu, C. C., Dreyer, J., Behr, N. & Raschke, M. B. Scanning-probe Raman spectroscopy with single-molecule sensitivity. *Physical Review B* 73, 193406 (2006).
3. Christesen, J. D., Pinion, C. W., Zhang, X., McBride, J. R. & Cahoon, J. F. Encoding abrupt and uniform dopant profiles in vapor-liquid-solid nanowires by suppressing the reservoir effect of the liquid catalyst. *ACS Nano* 8, 11790-11798 (2014).

**INVITED**

## Multimodal tip-enhanced spectroscopy

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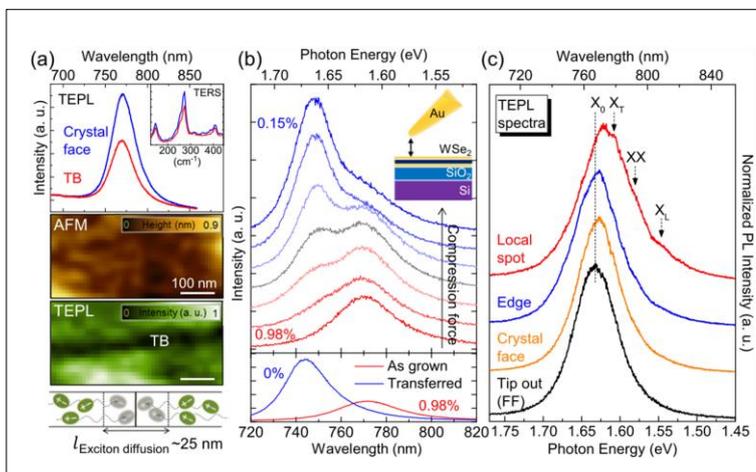
Combining tip-enhanced Raman and photoluminescence with active atomic force tip interaction, I will discuss novel approaches for the study of photo-physical and photo-chemical processes in molecules and nano-solids. As example, we nano-image the exciton behavior and its correlation with defects, grain boundaries, and local strain in different transition metal di-chalcogenides (TMDs). Based on exciton-plamon coupling we achieve a  $10^5$ -fold enhancement of the photoluminescence yield [1].

Further, we are able to achieve TEPL spectroscopy of the otherwise forbidden radiative emission from excitonic dark states

with the optical antenna tip coupling to its out-of-plane transition dipole moment [2]. We achieve room temperature contrast, not possible in conventional approaches, due to the ultrafast radiative dark exciton to the tip-antenna mode with few-nm tip-sample gap localized mode volume induced Purcell factor of  $> 2 \times 10^3$ . With the atomic-force microscope controlled antenna tip we demonstrate correlative nano-opto-mechanical switching and programmable modulation of the dark exciton emission. This hybrid tip-enhanced nano-spectroscopy and -imaging method allows to probe and control neutral-, multi-, localized-, and dark-excitons and their correlation with lattice and electronic structural heterogeneities in 2D materials and molecular systems.

### References:

1. Park, K.-D. et al., "Hybrid tip-enhanced nanospectroscopy and nanoimaging of monolayer WSe<sub>2</sub> with local strain control," *Nano Lett.*, Vol. 16, No. 4, 2621–2627, 2016.
2. Zhou, Y. et al., "Probing dark excitons in atomically thin semiconductors via near-field coupling to surface plasmon polaritons," *arXiv:1701.05938*, 2017.



**Fig. 1.** (a) TEPL spectra and image of the as-grown ML WSe<sub>2</sub> at crystal face and twin boundary regions. (b) Evolution of TEPL spectra with increasing compressive force by the tip, giving rise to a release of the tensile strain of the crystal.

## **INVITED**

# **Electrochemical TERS Elucidates Potential-Induced Molecular Reorientation and Chemical Conversion**

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TERS provides chemical and topographic information of surfaces with high spatial resolution and submonolayer chemical sensitivity. To further the versatility of the TERS approach toward more complex systems such as biological membranes or energy conversion devices, adaptation of the technique to solid/liquid working conditions is essential. In my talk, I discuss our novel side-illumination EC-TERS setup design based on a commercial STM as a versatile, cost-efficient solution for TERS at (electrochemical) solid/liquid interfaces.[1,2] While the STM parameters are found to play a crucial role for solid/liquid TERS sensitivity,[3] the excitation beam aberrations due to the presence of the aqueous phase are small enough not to limit TER signal detection, leading to Raman enhancement factors in the order of 10<sup>5</sup> at  $\mu$ W laser power in the low-bias regime.

To demonstrate the versatility of our approach, we have studied the adsorption geometry and chemical reactivity of adenine/Au(111) as a function of the applied electrode potential.[4] Combining experimental EC-TERS and DFT simulation data, we conclude that protonated physisorbed adenine adopts a tilted orientation at low potentials, whereas it is vertically adsorbed around the potential of zero charge. Further potential increase induces adenine deprotonation and reorientation to a planar configuration. To conclude, by providing the unique possibility to access potential-controlled adsorbate (re)orientation and chemistry on the few-molecule level, EC-TERS holds unprecedented power to gather detailed insight into, for example, electrocatalytic conversion mechanisms or biophysical processes with extreme spatial and chemical resolution.

[1] N. Martín Sabanés, L. Driessen, K.F. Domke\* *Analytical Chemistry* 2016, 88, 7108-7114.

[2] N. Martín Sabanés, K.F. Domke\* *ChemElectroChem* 2017, DOI: 10.1002/celec.201700293

[3] N. Martín Sabanés,\* A. Elizabeth, J.H.K. Pfisterer, K.F. Domke\* *Faraday Discussions "Surface-enhanced Raman scattering"* 2017, DOI: 10.1039/C7FD

[4] N. Martín Sabanés, T. Ohto, D. Andrienko, Y. Nagata, K.F. Domke\* *Angewandte Chemie International Edition* 2017 (VIP paper), DOI: 10.1002/anie.201704460

## INVITED

### Surface-enhanced coherent anti-Stokes Raman scattering

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#### Abstract

Although the Raman effect is a weak light-matter interaction, strong signals can nonetheless be generated with the help of the enhanced optical properties of nano-structured metals. The concentration of the excitation field and the enhancement of radiative rates mediated by the metal's plasmonic modes can raise the otherwise imperceptible Raman signal from single molecules to detectable levels. The amplifying qualities of metallic nano-structures are ideally suited for detecting and identifying molecular species at low concentration, spurring the development of chemical sensors based on surface-enhanced Raman scattering (SERS) into a burgeoning field. Translation of these principles to nonlinear Raman techniques, however, has not been trivial. The different heating kinetics under pulsed illumination, combined with nonlinear optical radiation from the metallic antenna itself, has complicated the realization of clean and reproducible nonlinear Raman experiments. Nonetheless, various efforts have shown potential [1]-[3]. Given the tangible benefits that nonlinear Raman techniques offer, including stronger enhancement of the signal and the ability to time-resolve the molecular response, obtaining a better understanding of nonlinear Raman processes in the vicinity of plasmonic amplifiers is a meaningful endeavor.

In this contribution, we discuss various realizations of surface-enhanced coherent anti-Stokes Raman scattering (SE-CARS) experiments. We start with SE-CARS on flat gold surfaces, followed by experiments on nano-antennas in the single molecule limit. We study the relevant mechanisms at play and discuss the implications for tip-based CARS experiments.

#### Reference:

- [1] C. K. Chen, A. R. B. de Castro, Y. R. Shen, and F. DeMartini, "Surface coherent anti-Stokes Raman spectroscopy," *Phys. Rev. Lett.* **43**, 946–949 (1979).
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# Contributed

## **Optically Tunable Tip Pyramids for TERS**

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### **Abstract**

Reproducibility on fabrication of tip-enhanced Raman spectroscopy (TERS) probes which generates high signal enhancement and spatial resolution beyond 30 nm is the main issue not only to provide reliability on TERS analyses but also to provide tools for the development of TERS metrology. The usage of template-stripe technique on fabrication of TERS probes is the most promising way to solve the fabrication reproducibility issue. However, the pyramidal-like probe produced by this process does not show plasmon confinement on Nano scale and consequently does not support localized surface plasmon (LSP) on the visible spectrum range. Excitation of LSP is crucial to generate high field enhancement on the tip apex vicinity. As we showed in our previous work, an improvement greater than 5 times on signal enhancement is achievable when LSP is excited on the tip apex [1].

Here, we introduce a modified template-stripe technique to fabricate high optical efficiency TERS probes with full reproducibility on its morphology and field enhancement. Herein called Tunable-Tip Pyramid (TTP), the new probe is characterized by having a segmented tip shaft suitable to support and tune LSP on visible/near-IR spectrum range at its apex. In order to characterize the TTP probe plasmon properties we applied electron energy-loss spectroscopy into a transmission electron microscope as well as MNPBEM simulations. As a result we could generate a scale rule connecting the TTP end segment size with the LSP resonance wavelength. In a TERS experiment over exfoliated graphene, we applied TTPs probes with the LSP resonance second mode wavelength matching the incident laser (HeNe) wavelength. We acquired enhancements of the G' Raman band on the range of 16 fold, which is more than 5 times the enhancement produced by a conventional gold pyramid and the higher signal enhancement over graphene sample we found on the literature.

### Reference:

- [1] T. L. Vasconcelos, B. S. Archanjo, B. Fragneaud, B. S. Oliveira, J. Riikonen, C. Li, D. S. Ribeiro, C. Rabelo, W. N. Rodrigues, A. Jorio, C. A. Achete, and L. G. Cançado, "Tuning Localized Surface Plasmon Resonance in Scanning Near-Field Optical Microscopy Probes," *ACS Nano*, 9, 6297-6304 (2015).

## High performance micro/nanofabricated AFM-TERS probes based on a metallic nanocone/nanodisk integrated on a silicon cantilever

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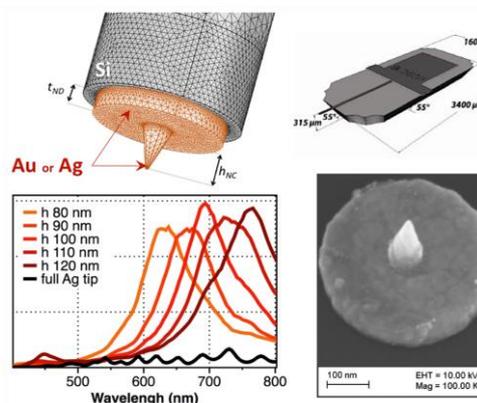
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### Abstract

We present modelling, fabrication and characterization of atomic force microscopy-tip enhanced Raman spectroscopy (AFM-TERS) probes which demonstrate a very high electromagnetic (EM) enhancement due to a novel metallic finite isolated tip antenna combination of a metallic nanocone/nanodisk combination at the tip apex. By element methods, we demonstrate advantages of an antenna precise as a metallic finite isolated tip [1], which greatly improves the EM enhancement with a control of the spectral position of the optical response as a function of dimensions, shape and material composition (Patent Pending n° 1653182). The cantilever-based probes were fabricated using lithography micro/nanotechnology [2] to enable reliable, reproducible batch production. Dark-field microscopy combined with a total internal reflection excitation is in process to characterize the optical properties of the localized EM enhancement in order to compare with the predictions of the calculations [3]. Compatible with a standard AFM cantilever mounting, the TERS nano-antenna integrated on microfabricated probes are novel high-performance optical near-field elements that will enable a powerful optical analysis and imaging technique for high resolution Raman microscopy.



**Fig. 1:** Modelling and fabrication of metal nanodisk-nanocone combination

### References:

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## Tip-Enhanced Hyper-Raman Spectroscopy (TEHRS) for Nanoelectronics

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### Abstract

Tip-enhanced Raman spectroscopy (TERS) is an apertureless near-field scanning microscopy that brings Raman spectroscopy into nanoscale resolution. The near-field optical response generated at the apex of a gold scanning probe in TERS acting as a plasmonic antenna, enhances and confines the interaction of light and matter to few nanometer, thus breaking the diffraction limit of light while preserving the wealth of chemical and structural information from the studied sample [1]. Despite its richness, this approach does not allow the investigation of certain optical phonon modes due to the selection rules. With the possibility to excite the tip with high peak intensity pulses, the way is paved for tip-enhanced hyper-Raman spectroscopy (TEHRS) [2]. In this two-photon-one-phonon process, detected around the second harmonic of the excitation wavelength, the selection rules differ from conventional Raman spectroscopy and allow for additional information to be retrieved from the sample with respect to TERS.

In this study, we simulate the nonlinear propagation of Surface Plasmon Polariton (SPP) on a silver tip excited on its apex by an Nd: YAG (1064 nm) laser with a pulse duration  $\Delta\delta = 25$  fs. We study a coupled silver nanoprobe-lead titanate ( $\text{PbTiO}_3$ ) thin film on a platinum (Pt) substrate system and report on the theoretical study of the net enhancement factor to be dependent on tip-to- $\text{PbTiO}_3$  separation distance for a femtosecond time delays. Additionally, we showed the optimized laser pulse duration allowing for a reduced dissipation of the energy. The model we develop applies to a wider range of material systems due to its generic character and can readily be adapted to different tips or other non-centrosymmetric sample configurations.

### References:

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- [2] N.L. Gruenke; M.F. Cardinal; M.O. McAnally; R.R. Frontiera, G.C. Schatz and R.P. Van Duyne, "Ultrafast and nonlinear surface enhanced Raman spectroscopy", *Royal Society of Chemistry*, **45**(8), 2263-90 (2016).

## **Photothermal Induced Resonance, a Novel AFM Method to Measure (IR) Chemical Composition, Band Gap and Thermal Conductivity at the Nanoscale**

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### **Abstract**

Photothermal induced resonance (PTIR)<sup>[1]</sup> is an emergent technique that combines the spatial resolution of AFM with the specificity of absorption spectroscopy. In PTIR, the absorption of a laser pulse induces a rapid thermal expansion of the sample. Conventional cantilevers are too slow to track the sample thermal expansion dynamics; however, the fast sample expansion kicks the cantilever in oscillation (like a struck tuning fork), with amplitude proportional to the absorbed energy, thus enabling material identification, mapping of composition and bandgap at the nanoscale.

In the first part, I will discuss the PTIR working principles, and a couple of characterization examples on plasmonics<sup>[2]</sup> and on photovoltaics materials.<sup>[3]</sup>

In the second part, I will introduce novel nanosized/picogram scale AFM probes that leverage integrated cavity-optomechanics for that sensing motion with unprecedented precision and bandwidth; thereby breaking the trade-off between AFM measurement precision and ability to capture transient events. Applied in PTIR, the probe near-field ultralow detection noise and wide bandwidth improves the time resolution, signal-to-noise ratio and throughput by a few orders of magnitude each. Remarkably, this synergy enables a new PTIR measurement modality: capturing the previously inaccessible fast thermal-expansion response of the sample, thus allowing concurrent measurement of the chemical composition and thermal conductivity, at the nanoscale, for the first time. Additionally, the improved sensitivity enable measurement of nanoscale IR spectra of monolayer this sample with high signal to noise ratio ( $\approx 170$ ).

Finally, if time allows I will provide my perspective on the complementarity of the PTIR and TERS techniques.

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## Tip-enhanced Raman spectroscopy of isotopically engineered $^{12}\text{C}/^{13}\text{C}$ graphene superlattices and channels.

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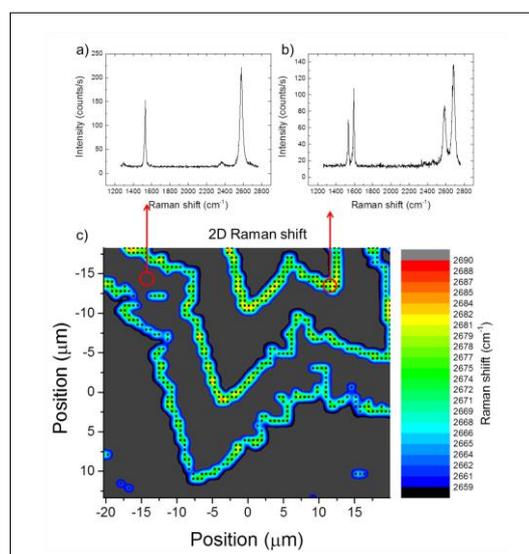
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### Abstract

The intentional increase of the  $^{13}\text{C}$  isotope during the chemical vapor deposition growth of graphene gives the possibility to engineer graphene. By pulsing or modulating the concentration of  $^{13}\text{C}$  and  $^{12}\text{C}$  during the growth, it is possible to create isolated one-dimensional channels of  $^{12}\text{C}$  or periodic structures made of  $^{12}\text{C}$  and  $^{13}\text{C}$  or a mixture of both [1]. Because of the nanometric dimension of these structures, tip-enhanced Raman spectroscopy (TERS) is a suitable method for characterization on the nanoscale [2]. We present a preliminary study of a single isotopic channel and an isotopic superlattice in order to understand the atomic arrangement as a function of the growth conditions. In the single isotopic channel we detect the coexistence of  $^{13}\text{C}$  and  $^{12}\text{C}$  Raman features. From the intensities of the two Raman modes we conclude that this particular growth condition creates a dendritic area of  $^{13}\text{C}$  and  $^{12}\text{C}$  clusters with domains smaller than the spatial resolution of our equipment. In the isotopic superlattice instead, we detect with approximately 5 nm of spatial resolution a single Raman peak which shifts in energy. We interpret the phonon energy shift as a spatially periodic variation of  $^{13}\text{C}$  concentration which matches the expected periodicity.



**Fig. 1:** Representative spectra and spatial distribution of monodimensional channels of  $^{12}\text{C}$  in a  $^{13}\text{C}$  graphene flake.

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## Revealing defect-related Raman mode of monolayer WS<sub>2</sub> via resonant tip-enhanced Raman scattering

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### Abstract

Monolayer tungsten disulfide (WS<sub>2</sub>) has emerged as a material for optoelectronic applications because of its remarkable quantum yield of photoluminescence<sup>1</sup>. To achieve the high performance of optoelectronic devices, the defect-free WS<sub>2</sub> is highly required. Accordingly, it is necessary to establish a quality evaluation method by investigating the defects of monolayer WS<sub>2</sub>. In the case of graphene, a D mode in the Raman scattering is widely used to evaluate the sample quality<sup>2</sup>, since Raman spectroscopy is a simple and nondestructive technique compared to other complicated methods such as electron microscopy. However, an exact indicator to easily judge the quality of monolayer WS<sub>2</sub> has not been determined yet.

We perform resonant TERS experiments. The high-resolution images of the TERS and scanning tunneling microscopy (STM) show alterations in TERS spectra depending on surface positions. We also demonstrate that the red-shifted A<sub>1g</sub> mode accompanied with the D and D' modes can be attributed to the defects in monolayer WS<sub>2</sub>. Furthermore, we identify that the emergence of the shifted and new modes can be introduced by S vacancies through our density functional theory calculations.

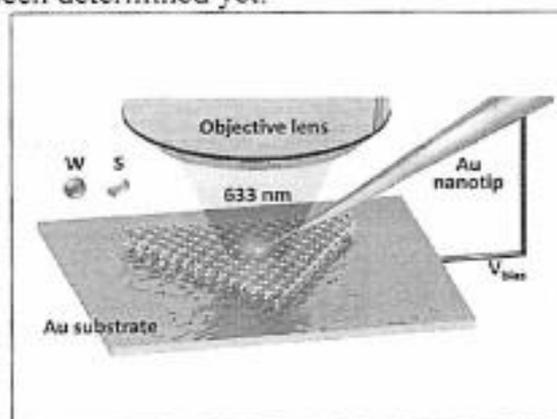


Fig. 1: Schematic of STM-TERS experiment of monolayer WS<sub>2</sub>.

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## Understanding photodamage in plasmonic hot spots

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### Abstract

Decomposition of the sample upon enhanced laser illumination is a key obstacle for ambient TERS imaging of sensitive materials, like organic films or biological membranes. The intense electric field under the TERS tip can lead to sample degradation and loss of enhancement by the tip. Here we investigate the mechanism of tip and sample damage in TERS upon laser illumination and propose strategies to overcome it.

Sample decomposition is accompanied by the appearance of intense sharp bands in the region 1300-1700 cm<sup>-1</sup>, which correspond to products of photodegradation (like polycyclic aromatic hydrocarbons or amorphous carbon). These bands fluctuate in position and intensity, but usually they dominate the spectrum of the sample and may lead to its misinterpretation.

The degradation can be of thermal origin or be induced by hot electrons in the hot spot. In order to explain the interplay between the two mechanisms, we investigate the degradation of self-assembled monolayers with different tail groups and measure the tip temperature at which carbonaceous features appear in the TER spectrum. We also compare this temperature with the onset of sample desorption.

The temperature in the hot spot is estimated based on the Boltzmann decay of the anti-Stokes background. This method gives correct values of the temperature, as verified against a sample heater. In contrast, the popular method to evaluate the temperature from Stokes/anti-Stokes ratios of TERS bands was found to give wrong results. For example, it does not even reflect trends like a temperature increase or decrease, and should not be used in TERS.

Our findings explain laser damage in both ambient TERS and single molecule SERS. Several strategies to mitigate the photodamage will be outlined in the presentation.

## Organic Nanopatterned Samples by Electron Beam for Gap-Mode STM TERS and Chemical Imaging

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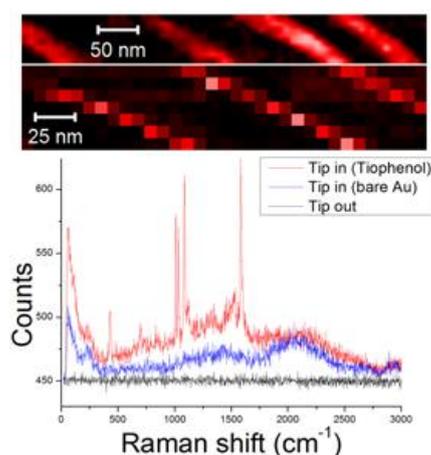
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### Abstract

In the present work, Tip Enhanced Raman Scattering (TERS) samples with nanometers line patterns of thiols have been fabricated using electron beam lithography. Nanopattern samples of TERS active molecules are interesting to build a reference material for metrology characterization of TERS apparatus imaging. A highly conductive, chemically stable and with low roughness thin film of gold with a titanium adhesion layer was evaporated by electron gun deposition method, on Si/SiO<sub>2</sub> substrate. Then, a nanopatterned self-assembled monolayer of thiol molecules was obtained on the gold substrate by electron beam lithography and subsequent soaking in a thiol solution. The resulting surface was tested not to be Raman enhancing so to exclude any signal contribution from the substrate. The obtained sample was suitable for measurements by both Scanning Tunneling Microscope (STM) and Atomic Force Microscope (AFM) TERS setups.

This fabrication method has been applied to manufacture organic molecule patterns of stripes with dimensions below 100nm in width. By STM TERS measurements the enhancement factors and the spatial resolutions of the Raman signals have been calculated. The STM TERS signals were obtained using a 633nm laser excitation wavelength in a top visual configuration with a 100× microscope objective (0.7 NA) and with a 3 cm<sup>-1</sup> resolution. The STM silver tips were electrochemically etched using an electronic control circuit. Chemical TERS images of periodic lines narrower than 25 nm were acquired (Fig.1). A remarkable spatial contrast was achieved, since no molecule signal could be observed in the areas previously covered by the mask. This configuration leads to no observable contamination of either the tip or the pristine gold areas, thus validating the aforementioned procedure for the production of a viable, custom nanopatterned sample of organic molecules for STM TERS imaging.



**Fig. 1:** Top: STM TERS mapping of thiophenol nanostructures. Bottom: comparison of TERS spectra.

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## **Intra-bubble strain texture controls nanoscale localization of defect-bound excitons in monolayer WSe<sub>2</sub> at room temperature**

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Monolayer WSe<sub>2</sub>, an atomically thin semiconductor, hosts defect-bound exciton states that behave as nanoscale single-photon sources at cryogenic temperatures. Recent work has shown that these defect-bound exciton states can be preferentially localized to nanoscale strained regions referred to as “nano-bubbles,” suggesting a compelling route towards systematically patterning arrays of single photon emitters in monolayer semiconductors. However, while the correlation between the single-photon emitters and nano-bubbles is firmly established, many pressing questions remain such as to precisely where the defect states localize within the nano-bubble and whether these spatially localized emitters be effectively isolated at room-temperature.

Using nano-optical imaging and spectroscopy[1,2], localization of defect-bound excitons within single nano-bubbles is directly imaged at sub-50 nm length scales in monolayer WSe<sub>2</sub> at room temperature. Multiple nano-bubbles are investigated and defect-bound exciton emission is observed in nano-bubbles that have lateral dimensions as small as 40 nm. In the larger nano-bubbles with lateral dimensions of ~150 nm, different spatial regions within the nano-bubbles are found to exhibit defect-bound exciton emission with distinct energies. Combined analysis of nanoscale, intra-bubble variations of the energy of the unbound exciton state as well as the topography reveal that strain is inhomogeneous across the bubble itself. Intra-bubble regions of larger strain are found to localize defect-bound excitons of lower energies and a nonlinear relationship between the energy of the defect-bound exciton and the local strain is uncovered, providing key insight into the underlying origins of the localization process and how strain can both localize the single-photon emitters as well as control their energy. And finally, the enhancement of nanoscale light-matter interactions by a plasmonic metal tip is found to preferentially enhance the defect state, enabling these localized emitters to be detected and imaged at room temperature with significantly higher fidelity than diffraction-limited optical techniques. All together, these results pinpoint important design rules for tailoring the position and energy of single-photon emitters in monolayer WSe<sub>2</sub> and as well as the potential critical importance of using plasmonic nano-antennas to utilize these states in photonic and optoelectronic devices at room temperature.

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# Plasmon-Enhanced Stimulated Raman Scattering With Refractory Titanium Nitride Nano-Stripes

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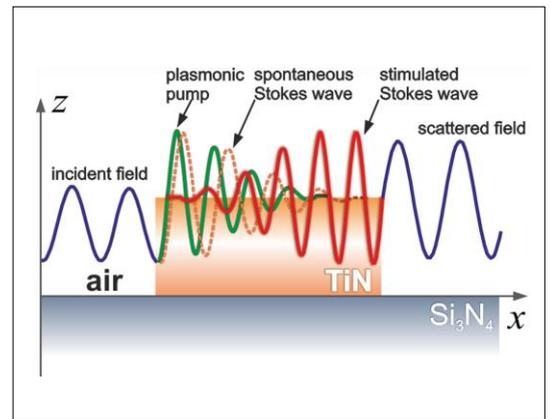
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## Abstract

Enhancement and localization of nonlinear optical effects due to surface plasmon-polariton excitation in confined metallic nanostructures routes towards the development of ultra-compact laser sources and bio-sensors.

In this study, we consider a nonlinear mechanism of localized light inelastic scattering within nano-patterned plasmonic and Raman-active titanium nitride (TiN) thin films<sup>1,2</sup> exposed to continuous-wave (cw) modest-power laser light. Due to the strong third-order nonlinear interaction between optically excited broadband surface plasmons and localized Stokes and anti-Stokes waves, both stimulated Raman (gain) emission,<sup>3</sup> as shown in Fig. 1, and (loss) absorption (referred to as inverse Raman effect) effects can be observed. We provide experimental evidences for coherent amplification of the localized Raman signals using a planar square shaped refractory TiN strip.



**Fig. 1:** Schematic illustration of the SRS effect within the TiN strip.

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## **Grain Boundaries and Nanoscale Heterogeneities in Monolayer MoSe<sub>2</sub> Revealed by Correlated SPM and TERS**

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### **Abstract**

Transition metal dichalcogenides (TMDs), a new class of two-dimensional (2D) semiconductors, have attracted significant attention for a number of unique optoelectronic properties and a broad variety of prospective applications. Use of TMDs for future transistors, quantum computing elements, or miniature sensing devices requires understanding of the morphological, electronic, and optical properties of these materials in the range of 1-100 nm.

We demonstrate that a combination of advanced scanning probe microscopy (SPM) and tip-enhanced Raman spectroscopy (TERS) can provide valuable information on the structural and optical properties of TMD monolayers. Specifically, using monolayers of MoSe<sub>2</sub> grown by chemical vapor deposition and transferred to gold substrates, we demonstrate that cross-correlating the results provided by scanning Kelvin probe microscopy and TERS can yield important information on rather unexpected spatial distribution of the grain boundaries in polycrystalline flakes. Based on increased capacitance and decreased TERS signal of the grain boundaries, we argue that the concentration of the charge carriers in these boundaries is increased compared to the bulk of the monolayer crystals. Thanks to high spatial resolution of TERS imaging, we also uncover that, even in monocrystalline flakes, there exist small (20-100 nm) domains with Raman signatures different from the rest of the flake. This behavior proved to be consistent over many flakes on different samples and does not seem to be related to one specific synthesis.

Despite good electrical contact between the MoSe<sub>2</sub> flakes and the gold substrate (confirmed by significant photocurrent measured in the process of TERS mapping), we further observed significantly enhanced photoluminescence in these flakes. Strong TERS and tip-enhanced photoluminescence (TEPL) mostly co-existed across of the flake area, though we found several locations about 100nm across, where TERS signal was suppressed despite strong TEPL and photocurrent recorded in these domains. Based on all the information collected, we conclude that correlated SPM and TERS/TEPL imaging of 2D semiconductors is a powerful technique of characterization of structural and spectroscopic properties of TMD at nanoscale.

## Electrochemical TERS: *In Situ* Mechanistic Studies.

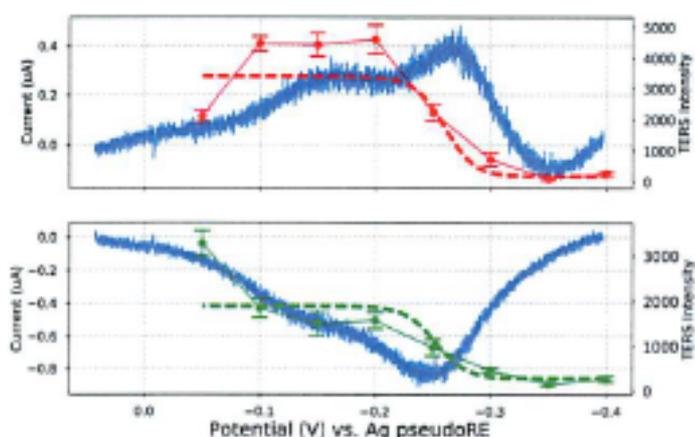
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### Abstract

We used electrochemical tip-enhanced Raman spectroscopy (EC-TERS), implemented on a scanning tunneling microscope (STM) platform, to probe the 2-electron transfer reaction of Nile Blue (NB) covalently attached to a Au(111) electrode. Unlike its physisorbed counterpart, it has been suggested that covalently attached NB undergoes two individual one-electron, one-proton transfer processes which can be resolved by standard electrochemical techniques.<sup>1</sup> Since NB loses its resonance enhancement upon reduction, by measuring and fitting the TERS intensity of NB at different electrochemical potentials to the Nernst equation, we extracted the formal potential for NB present under the tip (Figure 1). By comparing the formal potentials extracted from cyclic voltammetry and TERS, we established that the protonation of the central oxazine ring happens during the electrochemical wave at -0.25V. In contrast, no change in TERS intensity takes place during the wave at -0.14V. This shows that EC-TERS can reveal surface electrochemical information that conventional electrochemical methods cannot provide. In addition, we were able to decide if the molecules in the hot-spot were adsorbed on the tip or still attached to the substrate by independently varying the electrochemical potentials of the Au tip and the Au(111) substrate. This shows that STM-based EC-TERS can address reactions happening on the tip and sample separately.



**Fig. 1:** Superimposed cyclic voltammetry (blue line) and TERS (red and green lines) showing that the TERS amplitude is lost only during the electrochemical wave at -0.25V. Dashed lines show the fit to the Nernst equation. Top: Cathodic (reducing) potential ramp, bottom: anodic (oxidizing) potential ramp.

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## Capturing of electrochemical transformations by *in situ* Tip Enhanced Raman Spectroscopy (TERS)

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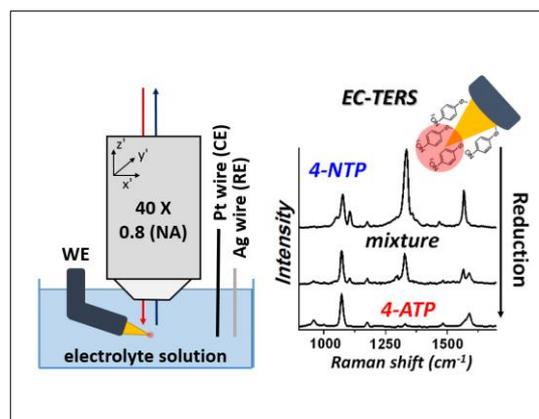
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### Abstract

Because of its powerful analytical capabilities, the analysis of electrochemical interfaces by *in situ* TERS will provide new insights in the understanding of the electron transfer with an unprecedented temporal and spatial resolution. Recent works have already demonstrated the possibility to carry out TERS experiments in liquids [1] and under electrochemical conditions (EC-TERS) [2].

After the first STM-TERS imaging of an opaque sample in an organic liquid has been reported by our group in 2016 [3], we recently demonstrated the ability for TERS to capture the electrochemical transformation of a molecular layer self-assembled on a tapered gold microelectrode. The proposed set-up (see Fig. 1) and protocol open new perspectives in the Raman characterization of redox architectures for molecular devices [4].

This communication will describe in details this new approach together with our last developments.



**Fig. 1:** Setup and progressive reduction of an organic monolayer at a functionalized microelectrode monitored by EC-TERS

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## Nano-Light-Source for Background-Free TERS

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Visible light can interact directly with the electronic or vibronic system of a sample and can extract rich information related to the intrinsic properties of the sample. This is the reasons why optical techniques, such as Raman spectroscopy, have always been convenient tools for analyzing and imaging various materials. However, Raman microscopy in its conventional form is not suitable for analyzing and imaging nanomaterials due to two major reasons. First, the poor spatial resolution restricted by the diffraction limits of the probing light, which makes it impossible to analyze materials smaller than about half of the wavelength (about 200-300 nm for visible light). And second, due to the extremely small volume of nanomaterials, Raman scattering intensity is extremely weak for such samples. However, when conventional Raman microscopy is combined with the near-field techniques, it achieves new and exciting features as it goes beyond the conventional limits of optical microscopy, in terms of both the spatial resolution and scattering intensity. This can be done by utilizing the technique of tip-enhanced Raman spectroscopy (TERS), which is based on plasmonic enhancement and confinement of light field near the apex of a sharp metallic nanotip for characterizing and imaging samples at nanoscale. This plasmonics-based technique allows us to have a spatial resolution down to about 10 nm in optical nanoimaging [1-4]. The spatial resolution, however, can be further improved if we combine TERS with some other mechanism. One of such examples is the inclusion of tip-applied pressure in TERS, which distorts the sample locally, where we have shown that a spatial resolution better than 4 nm can be achieved [5].

Here, I will show how such a high spatial resolution in TERS is obtained and how it can be useful in various applications. Further, I will discuss some new approaches to TERS, where one can obtain background-free nanoimaging for better contrast [6], or utilize the Raman scattered light generated from the base material of the tip, which is silicon, as the nano-light-source to image optical properties of a sample at nanoscale [7].

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## Nanoscale Strain Mapping via Photo-induced Force Microscopy (PiFM)

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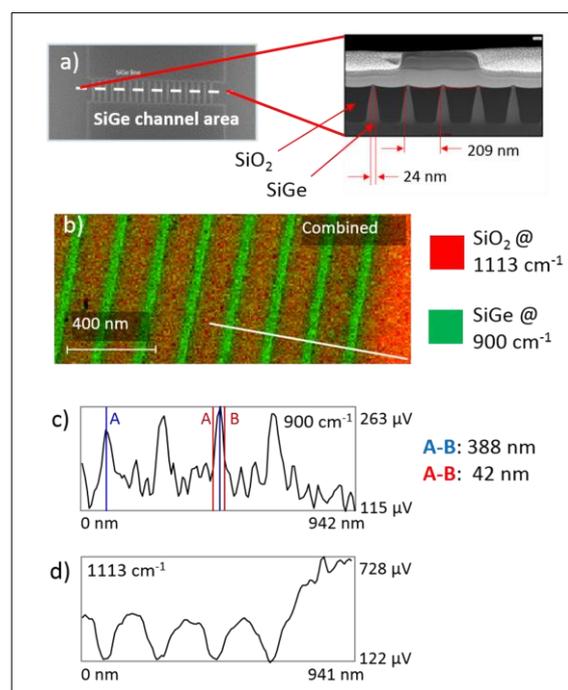
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### Abstract

Carrier mobility enhancement through local stress in silicon is a critical means of improving transistor performance. In order to effectively validate device design and process conditions, a direct measurement of the strain in the nanoscale is desired. Among AFM-based (atomic force microscopy) techniques, Tip-enhanced Raman Spectroscopy [TERS] have shown some promising results in measuring strain [1, 2]. However, TERS is known to depend critically on the quality of the plasmonic tip, which is difficult to control [3]. In this study, a test structure was used to demonstrate the capability of photo-induced force microscopy with infrared excitation (IR PiFM) in direct measurement of strain with  $\sim 10$  nm spatial resolution [4].

PiFM measurements were performed on test patterns with SiGe line pattern with line width from sub 40 nm up to 7500 nm, which were generated via SiGe FinFET process flow (25% Ge). Figure 1 shows the SiGe channel area that is measured via PiFM with two fixed wavenumbers ( $1113\text{ cm}^{-1}$  for  $\text{SiO}_2$  and  $900\text{ cm}^{-1}$  for SiGe). The two PiFM images are combined to produce a chemical map of the channel area. The SiGe line pattern is clearly resolved at  $900\text{ cm}^{-1}$ , measuring slightly larger linewidth than the value measured from the SEM of the cross-section (Fig. 1c versus 1a). The PiFM signal for  $\text{SiO}_2$  in between the SiGe lines shows that stress from the adjoining SiGe lines causes the signal to be much smaller than the unstrained PiFM value for  $\text{SiO}_2$  (see Fig. 1d where the PiFM signal for  $\text{SiO}_2$  after the last SiGe line continues to rise toward the unstrained value). Detailed nanoscale PiFM spectra will be used to explain the observed chemical map.

The results show extremely promising potential to map strain with spatial resolution that meets the demands of the latest semiconductor processing requirements.



**Fig. 1:** Figure showing (a) the test structure with repeating SiGe test pattern, (b) PiFM images acquired at  $1113\text{ cm}^{-1}$  for  $\text{SiO}_2$  and  $900\text{ cm}^{-1}$  for SiGe, combined to produce a chemical map of the test region, (c) PiFM signal for SiGe along the white line in (b), and (d) PiFM signal for  $\text{SiO}_2$  along the white line in (b).

***TERS-6, The 6<sup>th</sup> International Conference on Tip-Enhanced Raman Spectroscopy***  
***Aug. 16-18, 2017, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.***

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## TERS of 2D Materials in the Quantum Limit

Dmitri Voronine

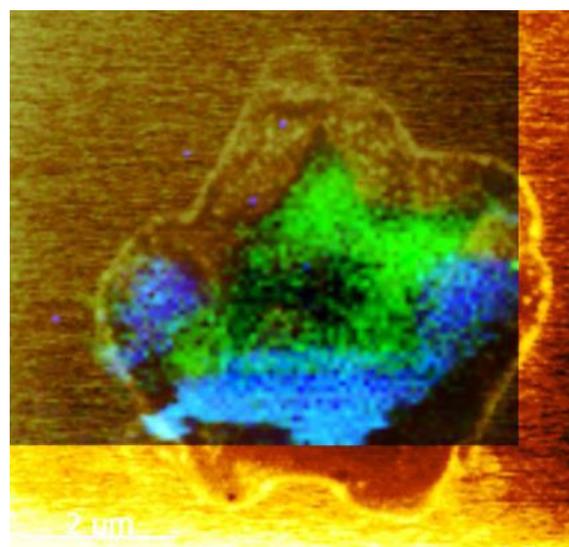
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### Abstract

Transition metal dichalcogenides such as MoS<sub>2</sub> and WS<sub>2</sub> are promising 2D materials with interesting optoelectronic, catalytic and sensing applications. Their nanoscale optical characterization using tip-enhanced Raman scattering (TERS) and tip-enhanced photoluminescence (TEPL) spectroscopy provides detailed structure-function information which is typically not available using far-field diffraction-limited techniques [1,2]. Nanoscale optical imaging provides an improved understanding of optoelectronic properties of edge states, defects and grain boundaries in 2D materials. We investigate monolayer and few-layer 2D materials using TERS and TEPL in combination with AFM and Kelvin probe force microscopy (KPFM). These combined measurements reveal a rich picture of co-localized topography, surface potential, vibrational and electronic properties with a few nanometer resolution (Fig. 1). The high

spatial resolution is due to strong signal enhancement via resonant Raman scattering and gap-mode surface plasmon confinement of the metallic tip. We investigate the limits of signal enhancement on various substrates by varying the tip-sample gap with picoscale precision and reveal quantum plasmonic quenching for sub-nanometer gaps. In addition to nano-imaging, using the plasmonic tip in the quantum limit provides a new control mechanism for the generation of excitons and trions in 2D materials. These results may be used for improving the understanding of nanoscale properties of 2D materials and for designing novel quantum optoelectronic devices.



**Fig. 1:** TERS (green) and TEPL (blue) maps overlapped with AFM image of WS<sub>2</sub>

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- [1] Zhang, Y.; Voronine, D. V.; Qiu, S.; Sinyukov, A. M.; Hamilton, M.; Liege, Z.; Sokolov, A. V.; Zhang, Z.; Scully, M. O. "Improving resolution in quantum subnanometer-gap tip-enhanced Raman nanoimaging" *Sci. Rep.* **6**, 25788 (2016).
- [2] Voronine, D. V.; Lu, G.; Zhu, D.; Krayev, A. "Tip-enhanced Raman scattering of MoS<sub>2</sub>" *IEEE J. Sel. Top. Quantum Electron.* **23**, 4600506 (2016).

***TERS-6, The 6<sup>th</sup> International Conference on Tip-Enhanced Raman Spectroscopy***  
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## **A Systematic Evaluation of Lithographically Printed Strained Si Test Structures**

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### **Abstract**

In this talk, we present updated efforts to further characterize a lithographic test structure, composed of SiGe, an industrially important material through tip-enhanced Raman spectroscopy (TERS). We detail our analytical techniques, as well as present a systematic evaluation of the effect of the line-width and pitch, especially with respect to confocal excitation spot-size. This test structure is a valuable tool in answering critical questions surrounding techniques, such as TERS, especially questions involving reproducibility, comparability, and robustness of the technique. However, it is also a valuable tool in helping us to understand the convolution of the farfield and nearfield with pitches exceeding the confocal excitation spot size to limit farfield contributions.

### Reference:

Hung, P.Y. *et al Proc. SPIE 9424, Metrology, Inspection, and Process Control for Microlithography XXIX, 94241S* (March 19, 2015); doi:10.1117/12.2175623

## Investigations on the Use of Thin Adhesion Layers in Top-Illumination AFM Tip-Enhanced Raman Spectroscopy

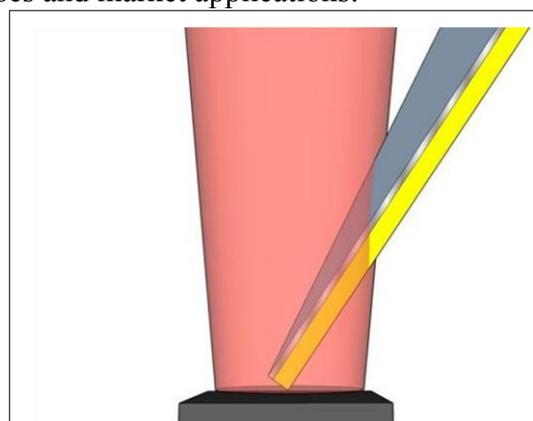
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### Abstract

Tip-enhanced Raman spectroscopy (TERS) is known to work in different configurations, modes and combinations of tip materials and excitation laser wavelengths. Although very promising, atomic force microscopy (AFM)-based TERS is not yet at the level of other competitive techniques like scanning tunneling microscopy or shear force based TERS, for instance, in terms of imaging resolution or tips control and usability. However, AFM TERS has several structural advantages over others, such as the versatility in the characterization of both electrical conducting and non-conducting samples or the abundance of collateral information provided, which make it ideal for future routine analyses and market applications.

One of the main issues in AFM TERS concerns the fabrication processes of tips, which generally make use of commercial silicon cantilevers as starting supports for the plasmonic materials, like silver or gold, required in TERS. These can be chemically deposited or vacuum evaporated directly on the pristine silicon tips, but they can easily peel off due to dynamics of measurements and mechanical interaction with the sample surface. In particular, gold has a bad adhesion with silicon oxide surfaces, and commercial tips have a native oxide layer which is difficult to remove, without dulling the tip apex, with other than wet chemical etching methods.

In the present contribution, we explore with TERS, in the top-illumination geometry, the possibility to use thin adhesion layers to avoid metal detachment without severely affecting, like in other plasmonic applications, the sensing performances.



**Fig. 1:** Cross-sectional sketch of a top-illumination TERS configuration.

### Reference:

- [1] B. Pettinger, (Ed: K. Kneipp, M. Moskovits, H. Kneipp), Surface-Enhanced Raman Scattering, Tip-Enhanced Raman Spectroscopy (TERS). (Springer, Berlin Heidelberg, 2006).
- [2] L. Ngoc et al., "Suppression of Surface-Enhanced Raman Scattering on Gold Nanostructures by Metal Adhesion Layers," *The Journal of Physical Chemistry C*, **120 (33)**, 18756-18762 (2016).

## Investigating Site-Specific Electrochemistry with TERS

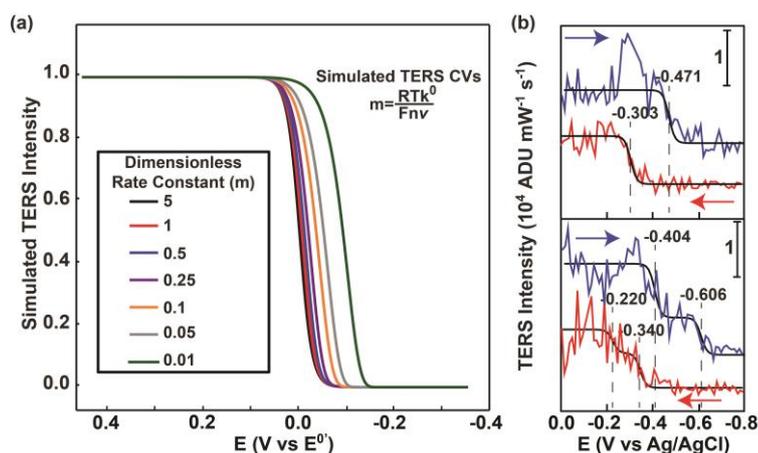
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**Abstract:** Recent progress in electrochemical tip-enhanced Raman spectroscopy on an atomic force microscopy platform (EC-AFM TERS) will be presented. Particular emphasis will be placed on the development and quantitative modeling of single-molecule TERS voltammetry. Analysis of single-molecule formal potentials provides new insights into how molecule-surface interactions impact local electrochemistry, and the relationship between single-molecule and ensemble electrochemical behavior.<sup>1</sup> Recent advances in EC-TERS imaging toward spatially resolving local electrochemical reactivity of surface-bound species will also be discussed.



**Fig. 1:** (s) Single-molecule TERS voltammograms simulated using Laviron's equation. (b) Experimental TERS voltammograms fit with Laviron's equation. The cathodic (blue) and anodic (red) waves are offset vertically for clarity. The dashed lines mark the single-molecule formal potentials extracted from the fit (solid black line).

### Reference:

- (1) Mattei, M.; Kang, G.; Goubert, G.; Chulhai, D. V.; Schatz, G. C.; Jensen, L.; Van Duyne, R. P. Tip-Enhanced Raman Voltammetry: Coverage Dependence and Quantitative Modeling. *Nano Letters* **2017**, *17*, 590-596.

## Probing the electronic properties of Pt-Au bimetallic catalyst by tip-enhanced Raman spectroscopy

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### Abstract

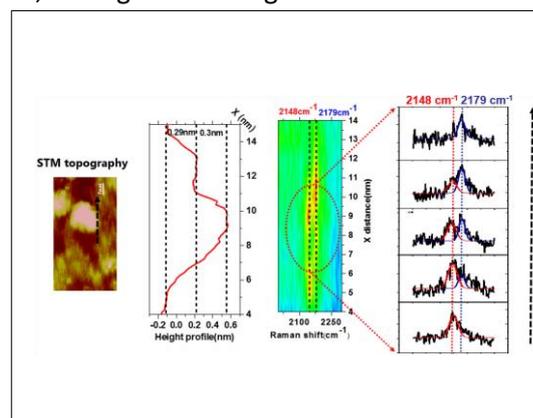
Heterogeneous catalysts have been demonstrated to be important to achieve high activity and (or) selectivity in catalysis. To understand the structure-function relationship, it is critical to probe the electronic and catalytic properties of the catalysts at a high spatial resolution. Tip-enhanced Raman spectroscopy (TERS), providing simultaneously the morphology and the fingerprint Raman spectrum, is a promising tool for studying such a surface [1].

Herein, we present a TERS study on bimetallic Pt island/Au(111) surface, aiming at revealing the structure-function relationship with a high spatial resolution. In order to deposit sub-monolayer of Pt on Au(111) surface, we used Cu monolayer as a template, followed by Pt atom replacement. The coverage of the Cu was controlled by the charge used for deposition. Because the N≡C triple bond is sensitive to the electronic structure of metals, the phenyl isocyanide molecule (Ph-N≡C, PI) was used as a probe molecule. In this work, we find that the TER spectral feature of PI adsorbed on the first layer and second layer of Pt are different, due to the difference in the electronic and geometrical properties of the Pt layers. On such a surface, we were able to achieve a spatial resolution better than 7nm, which is well beyond the diffraction limit.

All in all, we show that TERS is a promising technique for studying the heterogeneous catalysis, especially the understanding of the local structure correlated catalytic properties (activity and selectivity) on bi/tri-metallic surfaces.

### Reference:

- [1] J-H, Zhong; X, Jin; L, Meng; et al. "Probing the electronic and catalytic properties of a bimetallic surface with 3 nm resolution," *Nature Nanotechnology*, 12(2):132 (2006).



**Fig. 1:** TER spectra of PI adsorbed on Pt layer with different thickness.