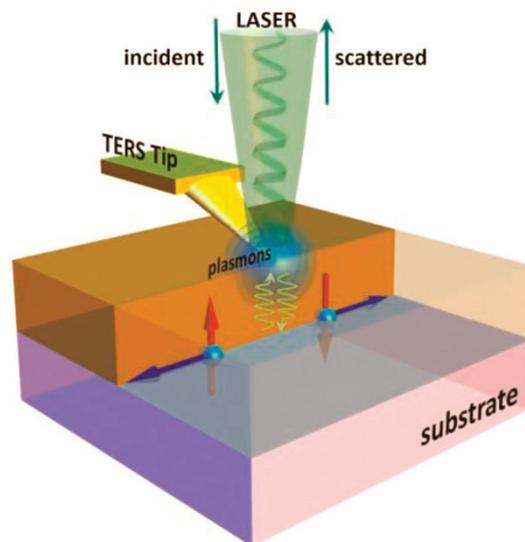


## Tip-Enhanced Raman Scattering



Tip-Enhanced Raman Scattering (TERS, nano-Raman) is the technique for enhancement of weak Raman signals and for super-resolution Raman imaging with spatial resolution  $\sim 10$  nm. Nano-Raman imaging provides unique insights into sample structure and chemical composition on the nanometer scale.

In TERS, a sharp metal probe (nano-antenna) is used to localize and enhance optical field at the tip apex. The light enhancement is typically appeared when excitation laser light is in resonance with localized surface plasmon at the end of the TERS probe. Enhancement of electromagnetic field (light) intensity on the TERS probe apex can reach many orders of magnitudes. In TERS mapping the sample is scanned with respect to the nano-antenna. Therefore the enhanced Raman signal localized near the probe apex approached to the sample resulting in Raman map of the sample surface with nanometer scale resolution.



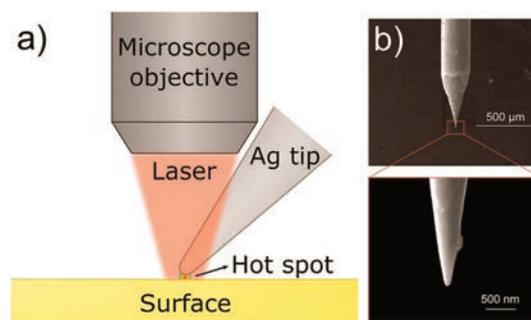
## Development of a Candidate Reference Sample for the Characterization of Tip-Enhanced Raman Spectroscopy Spatial Resolution

Alessio Sacco, Dario Imbraguglio, Andrea M. Giovannozzi, Chiara Portesi and Andrea M. Rossi

RSC Advances 2018, 8, 27863-27869

<http://xlink.rsc.org/?DOI=c8ra03762k>

Tip-Enhanced Raman Spectroscopy (TERS) is a topographic and chemical analysis technique with nanoscale resolution, consisting of the combination of Scanning Probe Microscopy (SPM) and Localized Surface Plasmon Resonance (LSPR) for the enhancement of Raman scattering in the vicinity of the probe. The quantification of spatial resolution represents an important issue, and, as of now, standards for calibration are not available. In the present work a candidate reference sample for TERS measurements was fabricated. It consists of a flat, conductive gold surface with a nanometric grating of a self-assembled monolayer of Raman-active organic molecules fabricated by an optimized Electron Beam Lithography (EBL) method to replicate established SPM calibration standards. Its feasibility as a TERS standard was tested by STM-TERS imaging.



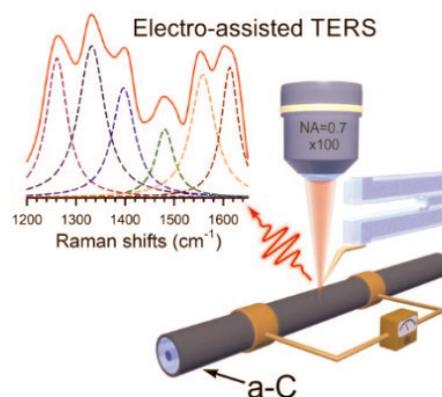
## Spectrally Resolving Coherent TERS Spectroscopy of Electrically Biased Carbon-Coated Fibers

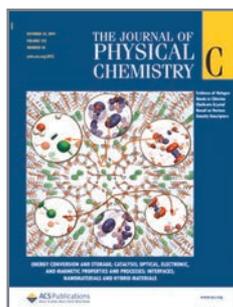
Sergey S. Kharintsev, Svetlana V. Saporina, Alexandr I. Fishman, Andrei A. Stolov, and Jie Li

J. Phys. Chem. C 2020, 124, 27, 14752–14758

<https://doi.org/10.1021/acs.jpcc.0c05228>

Tip-Enhanced Raman Scattering (TERS) represents an advanced spectroscopic tool that enables probing a specimen on scales far beyond the diffraction limit. An investigation of two-dimensional systems reveals a striking feature of TERS, when the near-field intensity is governed by the 8<sup>th</sup> and 10<sup>th</sup> power of the tip-sample distance for the coherent and incoherent scattering cases, respectively. We demonstrate spectrally resolving capabilities of coherent TERS spectroscopy when studying electrically biased amorphous carbon films. Local electro-annealing at hot spots was found to activate temperature-dependent molecular transformations such as an expansion of the defect-free sp<sup>2</sup> domains network at temperatures above 400 °C. Electro-assisted TERS allows one to directly visualize the presence of water-decorated carboxyl/hydroxyl groups at the edge carbon atoms.

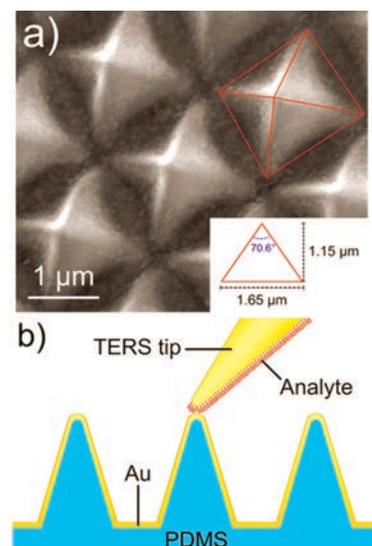




## Novel Approaches in Tip-Enhanced Raman Spectroscopy: Accurate Measurement of Enhancement Factors and Pesticide Detection in Tip Dimer Configuration

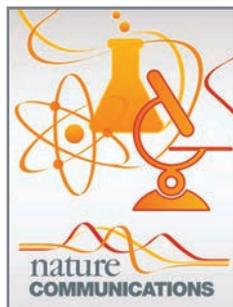
Sacco, A., Mangino, S., Portesi, C., Vittone, E., & Rossi, A. M.  
*Journal of Physical Chemistry C*, 2019, 123(40), 24723–24730  
<https://doi.org/10.1021/acs.jpcc.9b07016>

Tip-Enhanced Raman Spectroscopy (TERS) allows the precise manipulation of a nanometric probe for surface chemical analysis by plasmon-based amplification of Raman signals; however, acknowledged procedures and materials for assessing the enhancement factor in different configurations are still lacking. In this work, we propose a technique for the standardization of TERS intensity measurements, by chemisorption of different organic Raman-active molecules on plasmonic probes, and compare it to the conventional procedures addressed to the same goals. In addition, by ideally considering TERS as a special case of surface-enhanced Raman (SERS) involving a single nanoparticle, it was experimentally realized the three most common configurations in SERS: isolated particle, single scattering probe on a surface, and nanoparticle dimers.

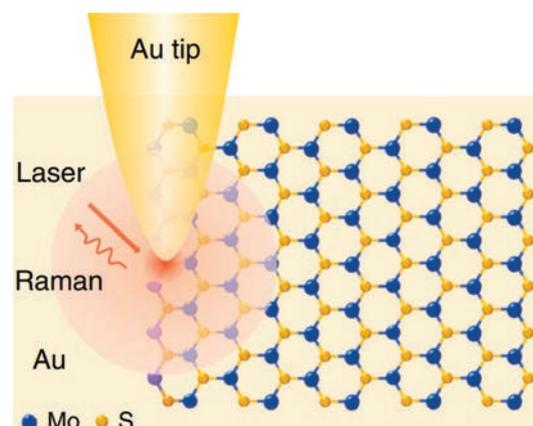


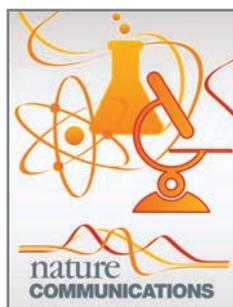
## Probing the Edge-related Properties of Atomically thin MoS<sub>2</sub> at Nanoscale

Huang, T. X., Cong, X., Wu, S. S., Lin, K. Q., Yao, X., He, Y. H., Wu, J. Bin, Bao, Y. F., Huang, S. C., Wang, X., Tan, P. H., & Ren, B.  
*Nature Communications*, 2019, 10(1), 4–11  
<https://doi.org/10.1038/s41467-019-13486-7>



Defects can induce drastic changes of the electronic properties of two-dimensional transition metal dichalcogenides and influence their applications. It is still a great challenge to characterize small defects and correlate their structures with properties. Here, we show that Tip-Enhanced Raman Spectroscopy (TERS) can obtain distinctly different Raman features of edge defects in atomically thin MoS<sub>2</sub>, which allows us to probe their unique electronic properties and identify defect types (e.g., armchair and zigzag edges) in ambient. We observed an edge-induced Raman peak (396 cm<sup>-1</sup>) activated by the double resonance Raman scattering process and revealed electron–phonon interaction in edges. The power of TERS demonstrated in MoS<sub>2</sub> can also be extended to other 2D materials, which may guide the defect engineering for desired properties.

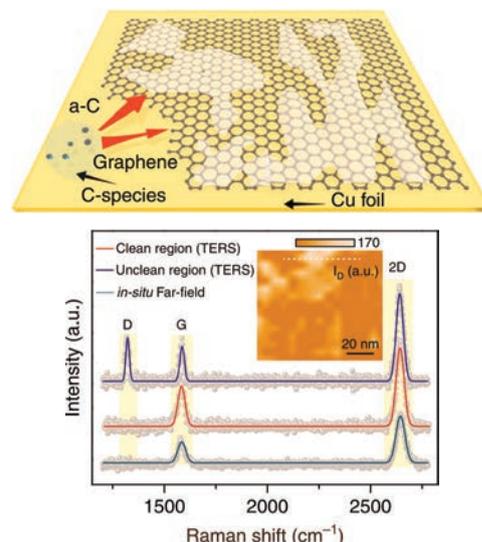




## Towards Super-Clean Graphene

Lin, L., Zhang, J., Su, H., Li, J., Sun, L., Wang, Z., Xu, F., Liu, C., Lopatin, S., Zhu, Y., Jia, K., Chen, S., Rui, D., Sun, J., Xue, R., Gao, P., Kang, N., Han, Y., Xu, H. Q., Liu, Z. *Nature Communications*, 2019, 10(1), 1–7  
<https://doi.org/10.1038/s41467-019-09565-4>

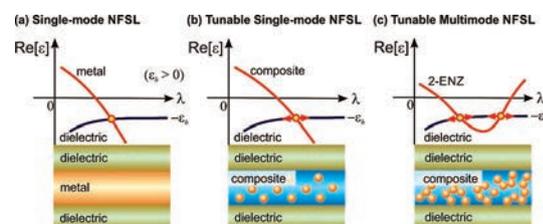
Among the various methods for graphene synthesis, chemical vapour deposition (CVD) approach holds great potentials in the scalable and cost-efficient production in a controllable fashion. Typically CVD graphene consist of unavoidable contamination on the surface during the growth process. Confocal micro Raman does not allow identify defect regions as amount of defects is not so large. Thanks to local enhancement and few nm lateral resolution by TERS technique one can clearly identify regions with defects (bright color on the map) and without (dark color on the map). It is possible due to strong D-band in the TERS spectra (upper spectrum) produced by defects. On the image there are TERS spectra of the unclean (blue line) and clean (red line) graphene regions in unclean graphene sample with Lorentzian line fit analysis, and in-situ far-field Raman spectrum of graphene in the same region (dark cyan line).



## Superresolution Stimulated Raman Scattering Microscopy Using 2-ENZ Nano-Composites

Kharintsev, S. S., Kharitonov, A. V., Alekseev, A. M., & Kazarian, S. G. *Nanoscale*, 2019, 11(16), 7710–7719  
<https://doi.org/10.1039/c8nr09890e>

Superlensing plays a crucial role in near- and far-field optical imaging with sub-wavelength resolution. One of the ways to expand optical bandwidth is surface plasmon resonances in layered metal-dielectric nanostructures. These resonances are commonly excited at a tunable single frequency. In this study, we propose the concept of a multimode far-field superlens made of a titanium oxynitride (TiON) thin film, that is a disordered metal-dielectric refractory nano-composite. These films exhibit a double epsilon-near-zero (2-ENZ) behavior near the percolation threshold and, therefore, favor super-coupling the incident laser light to surface plasmon resonances, not using such couplers as a prism, a grating, etc. We experimentally observe stimulated Raman gain emission from nano-structured TiON thin films exposed to low-power continuous-wave laser light. It is shown that superresolution of  $<\lambda/80$  (near-field) and  $<\lambda/8$  (far-field) is



achieved due to both the enhanced third-order optical nonlinearity and the multiplicative nature of four-wave mixing. The multimode tunable far-field superlens will impact emerging diffraction-free far-field optical microscopy, random Raman lasing on meta-atoms and broadband thermophotovoltaics.



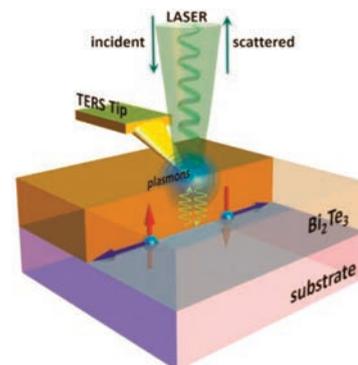
## The Effect of Substrate and Surface Plasmons on Symmetry Breaking at the Substrate Interface of the Topological Insulator $\text{Bi}_2\text{Te}_3$

Wiesner, M., Roberts, R. H., Lin, J. F., Akinwande, D., Hesjedal, T., Duffy, L. B., Wang, S., Song, Y., Jenczyk, J., Jurga, S., & Mroz, B.

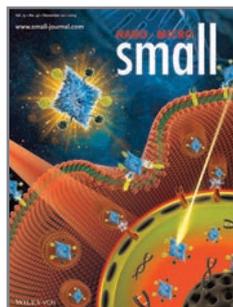
*Scientific Reports*, 2019, 9, 6147

<https://doi.org/10.1038/s41598-019-42598-9>

A pressing challenge in engineering devices with topological insulators (TIs) is that electron transport is dominated by the bulk conductance, and so dissipationless surface states account for only a small fraction of the conductance. Enhancing the surface-to-volume ratio is a common method to enhance the relative contribution of such states. In thin films with reduced thickness, the confinement results in symmetry-breaking and is critical for the experimental observation of topologically protected surface states. We employ micro-Raman and Tip-Enhanced Raman Spectroscopy to examine three different mechanisms of symmetry breaking in  $\text{Bi}_2\text{Te}_3$  TI thin films: surface plasmon generation, charge transfer, and application of a periodic strain potential. We confirm the symmetry breaking in  $\text{Bi}_2\text{Te}_3$  via the emergence of the Raman-forbidden  $A_{2u}^2$  mode. Our results suggest that topological surface states can exist at the  $\text{Bi}_2\text{Te}_3$ /substrate interface, which is in



a good agreement with previous theoretical results predicting the tunability of the vertical location of helical surface states in TI/substrate heterostructures.



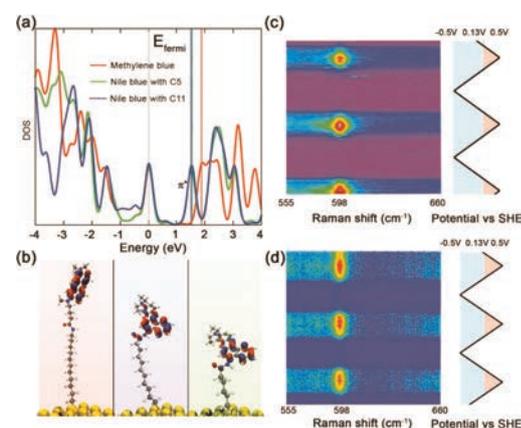
## Nanoscale Surface Redox Chemistry Triggered by Plasmon-Generated Hot Carriers

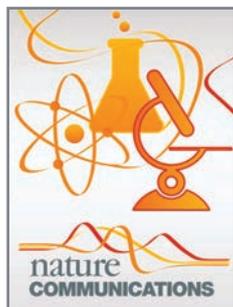
Yin, H., Lan, J. G., Goubert, G., Wang, Y. H., Li, J. F., & Zenobi, R.

*Small*, 2019, 15(47), 1903674

<https://doi.org/10.1002/smll.201903674>

Direct photoexcitation of charges at a plasmonic metal hotspot produces energetic carriers that are capable of performing photocatalysis in the visible spectrum. However, the mechanisms of generation and transport of hot carriers are still not fully understood and under intense investigation. Here, spectroscopic evidence proves that the reduction of dye molecules tethered to a Au(111) surface can be triggered by plasmonic carriers via a tunneling mechanism, which results in anomalous Raman intensity fluctuations. Tip-Enhanced Raman Spectroscopy (TERS) helps to correlate Raman intensity fluctuations with temperature and with properties of the molecular spacer. In combination with electrochemical surface-enhanced Raman spectroscopy, TERS results show that plasmon-induced energetic carriers can directly tunnel to the dye through the spacer, which offers new possibilities for optimizing plasmon-induced photo-catalytic systems.





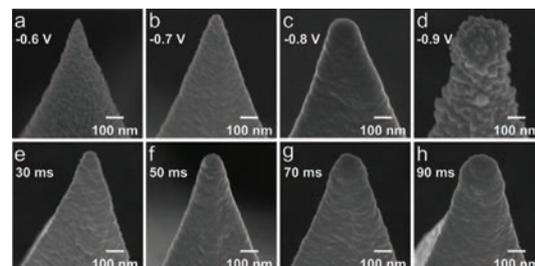
## Rational Fabrication of Silver-Coated AFM TERS Tips with a High Enhancement and Long Lifetime

T. Huang, C. Li, L. Yang, J. Zhu, X. Yao, C. Liu, K. Lin, Z. Zeng, S. Wu, X. Wang, F. Yang and B. Ren

*Nanoscale*, 2018, 10, 4398-4405

<https://doi.org/10.1039/C7NR08186C>

Tip-Enhanced Raman Spectroscopy (TERS), known as nanospectroscopy, has received increasing interest as it can provide nanometer spatial resolution and chemical fingerprint information of samples simultaneously. Since Ag tips are well accepted to show a higher TERS enhancement than that of gold tips, there is an urgent quest for Ag TERS tips with a high enhancement, long lifetime, and high reproducibility, especially for atomic force microscopy (AFM)-based TERS. Herein, we developed an electrodeposition method to fabricate Ag-coated AFM TERS tips in a highly controllable and reproducible way. We investigated the influence of the electrodeposition potential and time on the morphology and radius of the tip. The radii of Ag-coated AFM tips can be rationally controlled at a few to hundreds nanometers, which allows us to systematically study the dependence of the TERS enhancement on the tip radius. The Ag-coated AFM tips show the highest TERS



enhancement under 632.8 nm laser excitation and a broad localized surface plasmon resonance (LSPR) response when coupled to a Au substrate. The tips exhibit a lifetime of 13 days, which is particularly important for applications that need a long measuring time.



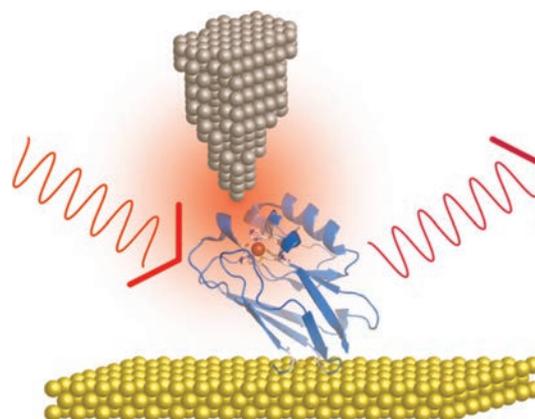
## Vibrational Changes Induced by Electron Transfer in Surface Bound Azurin Metalloprotein Studied by Tip-Enhanced Raman Spectroscopy and Scanning Tunneling Microscopy

Stefan Kradolfer, Ewelina Lipiec, Chiara Baldacchini, Anna Rita Bizzarri, Salvatore Cannistraro and Renato Zenobi

*ACS Nano* 2017, 11, 12, 12824–12831

<https://doi.org/10.1021/acsnano.7b07768>

The copper protein azurin, due to the peculiar coupling of its optical and vibronic properties with electron transfer (ET) and its biorecognition capabilities, is a very promising candidate for bioelectronic, bio-optoelectronic and biosensor applications. However, a complete understanding of the fundamental processes relating azurin ET and its optical and vibronic characteristics with the charge transport mechanisms occurring in proteins bound to a conductive surface, the typical scenario for a biosensor or bioelectronic component, is still lacking. We studied azurin proteins bound to a gold electrode surface by scanning tunneling microscopy combined with TERS. Robust TER spectra were obtained, and the protein's vibronic response under optical excitation in resonance with its ligand-to-metal charge transfer band was found to be affected by the tunneling parameters, indicating a direct involvement of the active site vibrations in the electron transport process.





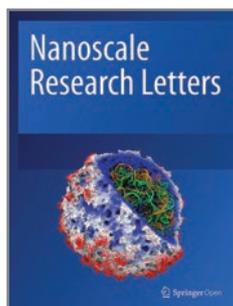
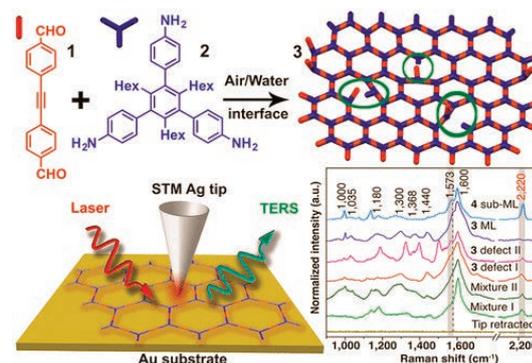
## Chemical Mapping of Nanodefects within 2D Covalent Monolayers by Tip-Enhanced Raman Spectroscopy

Feng Shao, Wenyang Dai, Yao Zhang, Wei Zhang, A. Dieter Schlüter and Renato Zenobi

ACS Nano 2018, 12, 5, 5021–5029

<https://doi.org/10.1021/acsnano.8b02513>

Nanoscale defects in monolayers (MLs) of two-dimensional (2D) materials, such as graphene, transition-metal dichalcogenides, and 2D polymers, can alter their physical, mechanical, optoelectronic, and chemical properties. However, detailed information about nanodefects within 2D covalent monolayers is difficult to obtain because it requires highly selective and sensitive techniques that can provide chemical information at the nanoscale. Here a 2D imine-linked ML prepared from two custom-designed building blocks by dynamic imine chemistry at the air/water interface, in which an acetylenic moiety in one of the blocks was used as a spectroscopic reporter for nanodefects. Combined with density functional theory calculations that take into account surface selection rules, Tip-Enhanced Raman Spectroscopy (TERS) imaging provides information on the chemical bonds, molecular orientation, as well as nanodefects in the resulting ML.



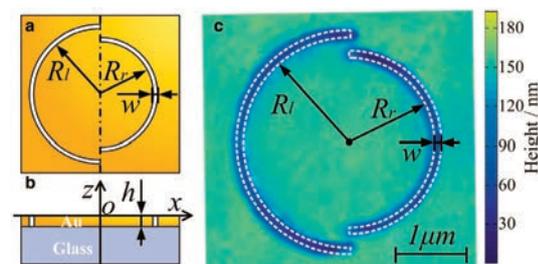
## Plasmonic Lens Focused Longitudinal Field Excitation for Tip-Enhanced Raman Spectroscopy

Mingqian Zhang, Jia Wang.

Nanoscale Research Letters (2015) 10:189

<https://doi.org/10.1186/s11671-015-0897-0>

A novel TERS setup with longitudinal field excitation generated by a plasmonic lens is investigated. A symmetry-breaking structure plasmonic lens that is expected to realize a strong longitudinal electric field focus has been designed to generate suitable excitation for enhancement in a tip antenna. The focusing performance of the plasmonic lens is theoretically simulated by the finite-difference time-domain method and experimentally verified by the detection of optical near-field distribution. A plasmonic lens assisted Tip-Enhanced Raman Spectroscopy setup has been constructed and used to investigate specimens of carbon nanotubes. Tip-Enhanced Raman spectra with distinct excitation wavelengths show similar Raman shifts but different intensities. Experimental results demonstrate that the Raman signal is considerably enhanced. It indicates that the novel TERS configuration is feasible and is a promising technique for TERS measurements and characterizations.



# Tip-Enhanced Raman Scattering

Scientific Digest

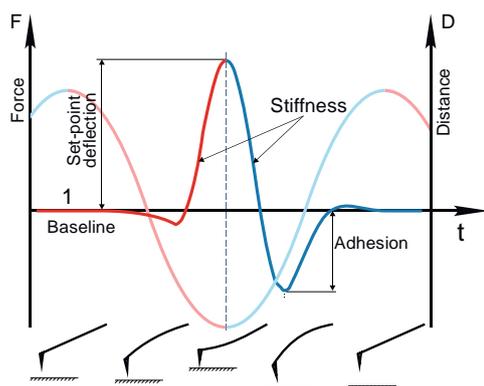
## Related Products & Features

### NTEFRA Spectra II

- High-performance versatile AFM
- Optical access from top, side and bottom optimized for Raman, TERS and SNOM
- Flexible optical design providing any combination of excitation/collection configurations
- Automated AFM laser, probe and photodiode alignment
- User-friendly change of wavelength of AFM registration system laser and photodiode
- Easy and user-friendly change of objectives
- Integration with IR s-SNOM (optional)



<https://www.ntmdt-si.com/products/afm-raman-nano-ir-systems/ntegra-spectra-ii>



### Hybrid Mode

In Hybrid mode (US Pat 9,110,092) the tip-sample distance is modulated according to the quasi-harmonic law. Thus tip enters a force interaction with the sample thousands of times per second. Force-distance curve analysis enables maps of topographical, nanomechanical, electrical, thermal and piezoelectric properties of the sample to be extracted with high spatial resolution and minimized lateral forces.

Combining Hybrid mode with cutting-edge optical microscopy and spectroscopy techniques opens-up novel opportunities of cantilever-based Tip-Enhanced Raman Scattering (TERS) and scattering scanning near-field optical microscopy (s-SNOM).

[www.ntmdt-si.com/products/features/hybrid-mode](http://www.ntmdt-si.com/products/features/hybrid-mode)

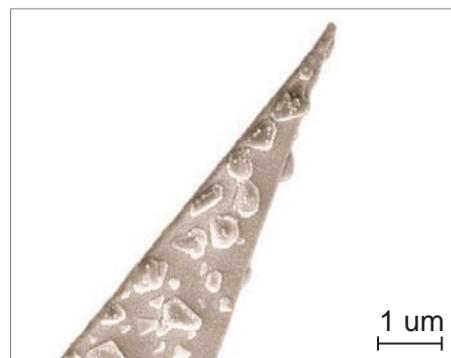
### TERS Probes

As a result of comprehensive research NT-MDT Spectrum Instruments is now able to offer mass produced reproducible cantilever-type TERS probes. The probes are prepared based on AFM Si cantilevers with optical access to the tip apex which make them compatible with top illumination configuration. Special proprietary probe preparation and TERS-active metal coating are applied.

AFM probes provided with different stiffness to be optimized for contact, Hybrid and non-contact modes.

The probes provide guaranteed TERS performance on a test sample:

<https://www.ntmdt-tips.com/products/group/ters-afm-probes-new>



- Enhancement factor >50x (Tip IN vs. Tip. OUT) for ~70% of probes.
- Typical enhancement factor : > 100x.
- Some probes reach >500x enhancement