HORIBA Scientific

NanoRaman™ Platform

AFM-Raman, TERS, SNOM
Chemical and physical
imaging at the nanoscale

AIST-NT Technology

Since its introduction in the early 80's, **Scanning Probe Microscopy** (SPM) has made nanoscale imaging an affordable reality. The technique provides a continuously growing variety of surface analysis methods for the physical characterization of materials, yet label-free chemical sensitivity is still challenging....

Raman spectroscopy has long provided a versatile way to determine the structure and chemical composition of molecules and, despite its diffraction-limited spatial resolution, has become a standard method in high-speed ranging from materials science to life sciences.

In combination, **the two techniques** yield an attractive and unique tool for entering the nano-world.
With over a decade of experience in this exciting new field, we have refined the technique to its utmost with uncompromised performance to bring you a tool that is not only extremely powerful and versatile, but is also so easy to use, fast and reliable that generating outstanding data is virtually effortless.

Nano Raman™

Key Features

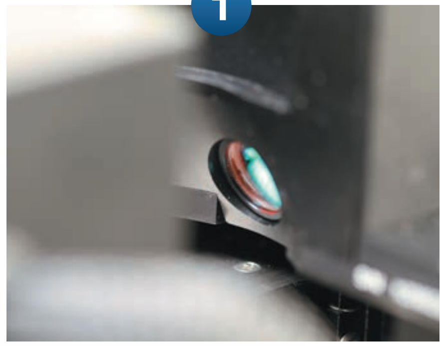
- **MULTI-SAMPLE ANALYSIS PLATFORM**
  Macro, micro and nano scale measurements can be performed on the same platform.
- **EASE OF USE**
  Fully automated operation, start measuring within minutes, not hours!
- **TRUE CONFOCALITY**
  High spatial resolution, automated mapping stages, full microscope visualization options.
- **HIGH COLLECTION EFFICIENCY**
  Top-down, oblique and bottom Raman detection for optimum resolution and throughput in both co-localized and Tip-Enhanced measurement.
- **HIGH SPECTRAL RESOLUTION**
  Ultimate spectral resolution performance, multiple gratings with automated switching, wide spectral range analysis for Raman and Photoluminescence.
- **HIGH SPATIAL RESOLUTION**
  Nanoscale spectroscopic resolution (down to 10 nm) through Tip-Enhanced Optical Spectroscopies (Raman and Photoluminescence).
- **MULTI-TECHNIQUE / MULTI-ENVIRONMENT**
  Numerous SPM modes including AFM, conductive and electrical modes (cAFM, KPFM), STM, liquid cell and electrochemical environment, together with chemical mapping through TERS/TEPL.
  Full control of the two instruments through one workstation and a powerful software control, SPM and spectrometer can be operated simultaneously or independently.
- **ROBUSTNESS / STABILITY**
  High resonance frequency AFM scanners, operation far away from noises! High performance is obtained without active vibration isolation.

The ultimate versatile platform for physical and chemical characterization

Powerful

- Simultaneous SPM and spectroscopic measurements.
- High numerical aperture objectives from both top and side for best co-localized spatial resolution and best TERS collection efficiency.
- High-throughput and high speed measurements with SWIFT XS and EMCCD detector.
- Broad range of detection wavelengths, from deep UV to Infrared.
- High spectral resolution with the LabRAM HR Evolution spectrometer.

1



Enabling feature: IR laser diode for AFM feedback *Avoiding Optical Interferences for TERS application*

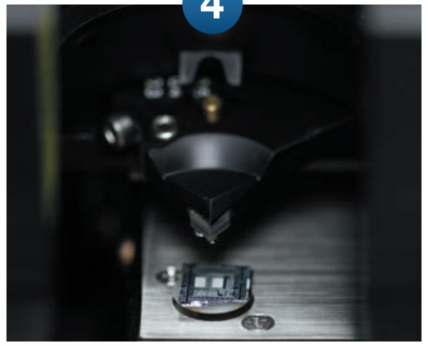
2

High collection: Wide optical access *High numerical aperture objectives for both top and side illumination*

3

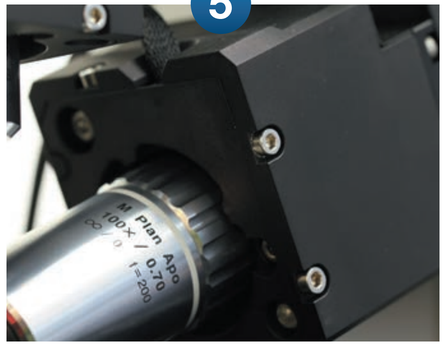
Ease of use: tip replacement *Tip replacement without removing the sample or disturbing the optics*

4



Ease of use: Auto tip-alignment and tuning *Operator independent, great reproducibility in tip exchange*

5



Ease of use: XYZ Objective Scanner *Easy Raman laser to tip alignment for long-term stability*

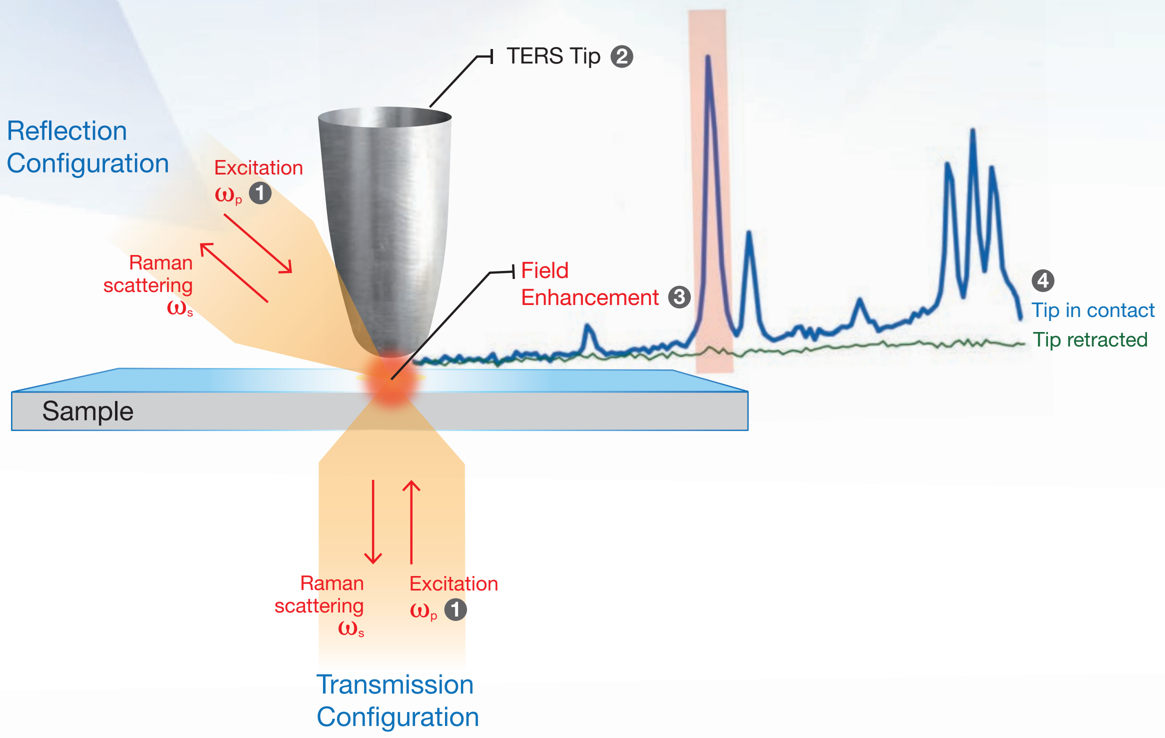
6

Stability: high resonance frequency AFM scanners *High performance without active vibration isolation*

Simple and Fast

- One-click cantilever alignment, frequency tuning and optimization, requiring no manual adjustments.
- Easy cantilever exchange without affecting the sample and breaking the alignment.
- Fast and intuitive Raman laser to AFM tip alignment with Objective Scanners.
- Full control through one workstation.

AFM-Raman and TERS made easy



How TERS works?

In TERS, the Raman excitation laser ❶ is focused at the tip of an SPM probe coated with either gold or silver ❷. Matching the wavelength of the Raman laser to the natural surface plasmonic frequency of the noble metal generates an intense localized evanescent electromagnetic fied or «hot spot» at the probe tip ❸. The field extends only for a few nanometers from the tip surface. Since the intensity of the Raman spectra from the sample is proportional to the local electric field, bringing the hot spot close to the sample significantly enhances the Raman signal, often by a power of 10^5 or 10^6 ❹.

What is co-localized AFM-Raman?

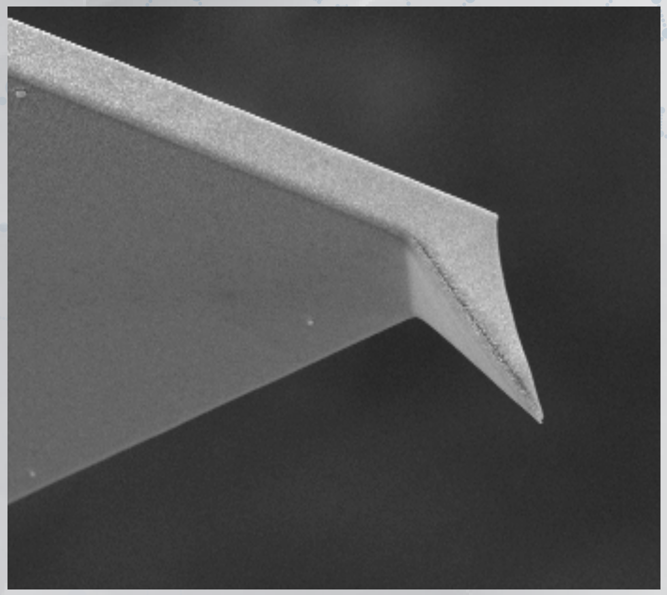
Raman and SPM (Scanning Probe Microscope) analysis can be combined on a single microscope system. Co-localized AFM-Raman measurement is the sequential or simultaneous acquisition of correlated SPM and Raman maps.
AFM and other SPM techniques like STM or tuning-fork Shear-Force or Normal-Force microscopy, provide topographic, mechanical, thermal, electrical, and magnetic properties down to molecular resolution (on the order of nm, over μm^2 area), on the other hand confocal Raman spectroscopy and imaging provides specific chemical information about the material, with a diffraction limited spatial resolution.

Reliable AFM-TERS tips

Omni™ Tip-Enhanced Raman Spectroscopy TERS probes* are designed to acquire topography and Raman spectral information of a sample simultaneously.

The combination of HORIBA's NanoRaman system with Omni™ TERS probes provides the ideal high-enhancement TERS solution.

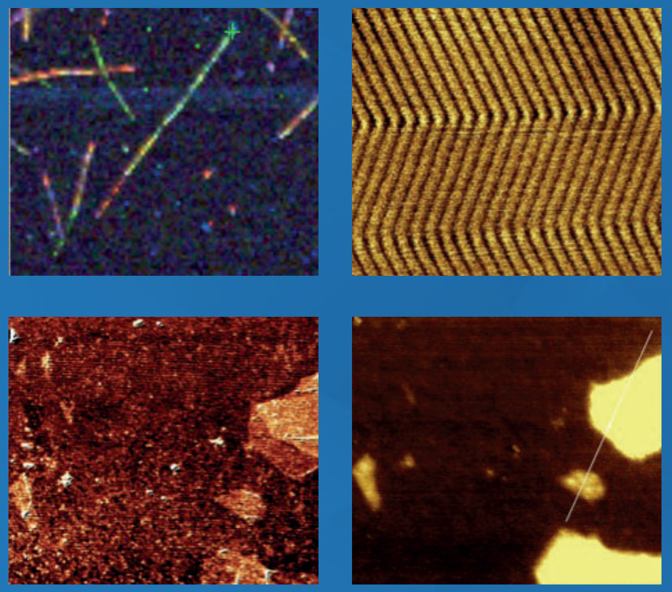
- **Allow all modes of TERS operation: top, side and bottom optical access**
- Multilayer structure: tip optimized to minimize interference from silicon substrate in the spectra
- **Innovative package to enhance tip shelf life**
- TERS active layer: silver with protective layers



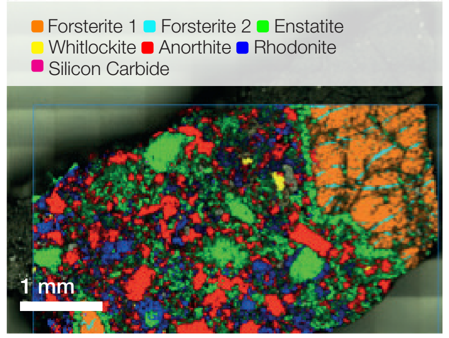
*Manufactured for HORIBA by APP NANO

TERS proven samples

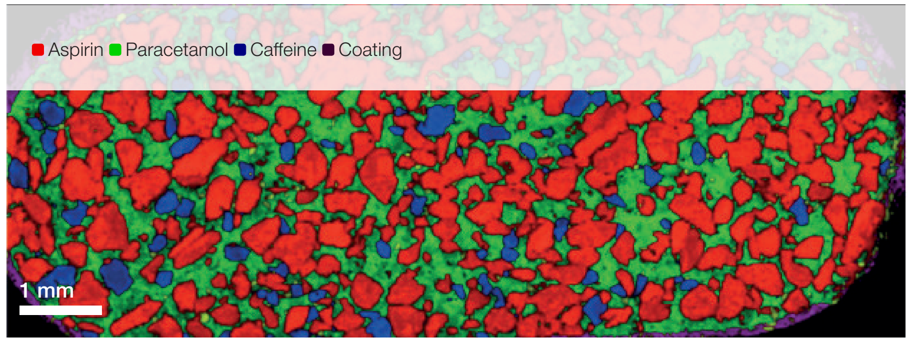
HORIBA offers a set of test samples including single-wall carbon nanotubes (CNTs) together with graphene oxide flakes (GO), suitably dispersed to allow easy imaging.
The samples are used to demonstrate the AFM molecular resolution and a routine 20 nm resolution in TERS imaging.



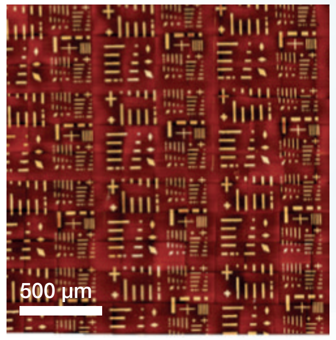
Large area - difficult samples



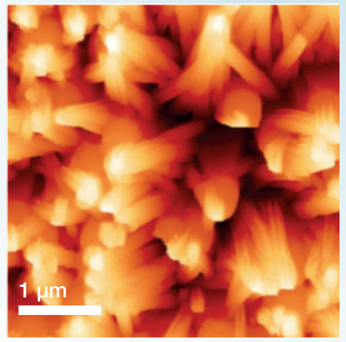
Raman image - Mineral - Macro map across a sectioned meteorite



Raman image - Sectioned pharmaceutical tablet

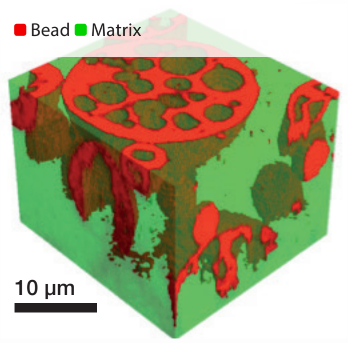


Automatic panoramic AFM (contact mode) – 120 scans – CoCr features on Si surface
Sample courtesy of Dr A.N. Shokin, NIIFP; Image courtesy of Dr A. Temiryazev, IRE RAS.

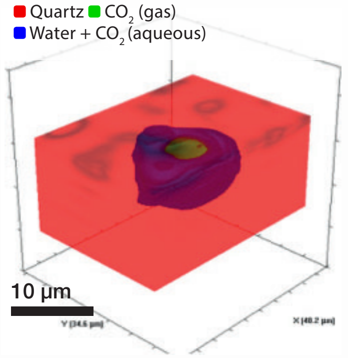


AFM (topography) – Zinc oxide nanorods - Z range is 3.6 µm

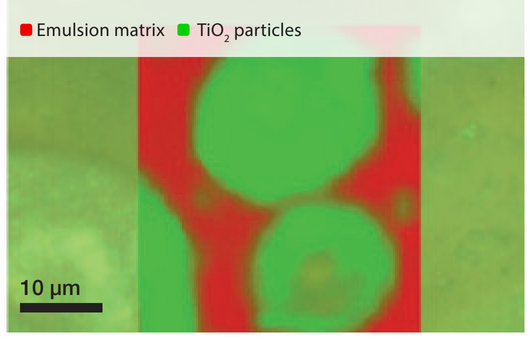
True confocality - 3D maps



Raman image - XYZ volume map of expanded polymer bead in matrix

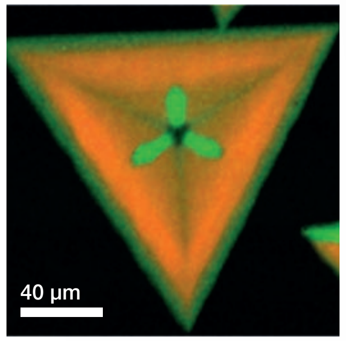


Raman image - Fluid inclusion- XYZ volume map through fluid inclusion in a quartz matrix

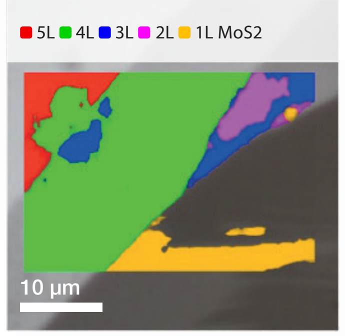


Raman image - Emulsion - Titanium dioxide particles in emulsion

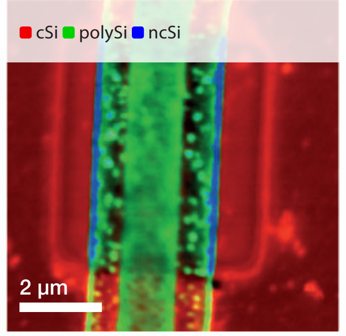
High spectral resolution - High selectivity



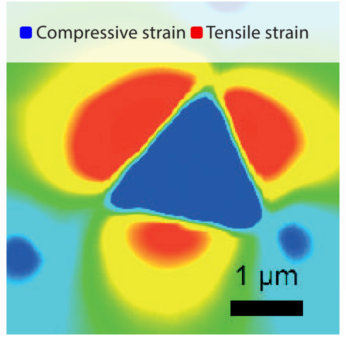
Combined Photoluminescence and Raman image - 2D crystal of WS_2



Raman image - Layered MoS_2 structure - Map image was created from low frequency (<30cm⁻¹) interlayer peaks

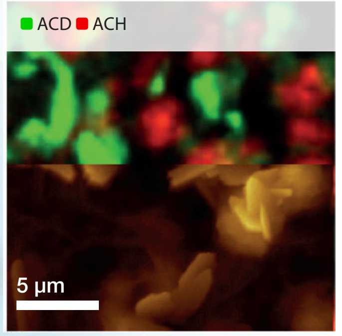


Raman image - Silicon chip - crystalline, poly and nano-crystalline silicon regions

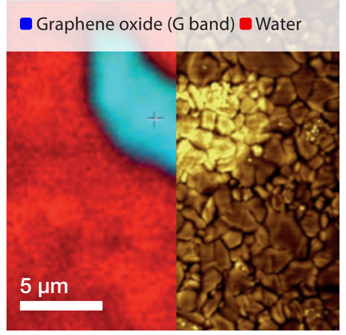


Raman image - Nano-indented silicon – mapping of mechanical stress

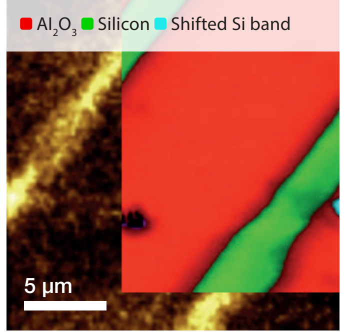
Co-localized AFM-Raman



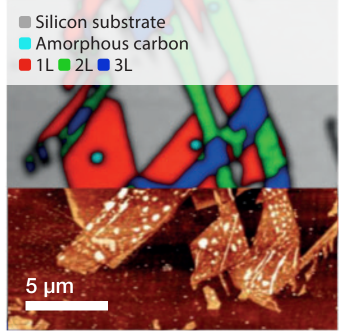
Co-localized AFM-Raman images - Lipid crystals



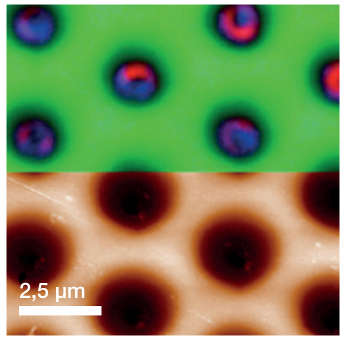
Co-localized AFM-Raman images in liquid - Graphene oxide flake



Co-localized AFM-Raman images - Silicon structures on Al_2O_3 substrate



Co-localized AFM-Raman image - Layered Graphene structure.

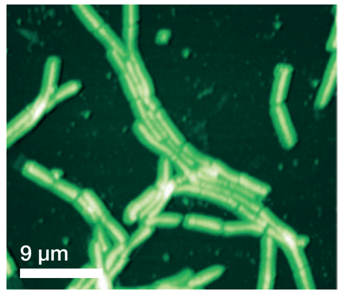


Co-localized AFM-Raman images - Array of holes in gold film functionalized with a reporter molecule

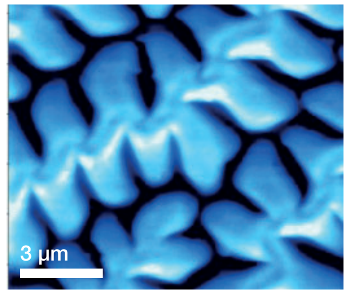
10^{-2}m | 10^{-3}m | 10^{-4}m | 10^{-5}m | 10^{-6}m

From Macro ... Micro...

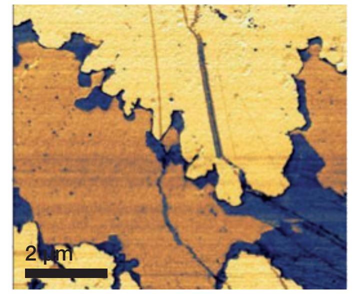
Multi SPM techniques



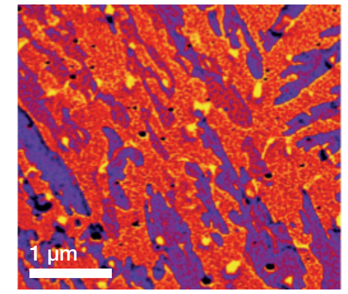
AFM – Bacillus Cereus vegetative cells



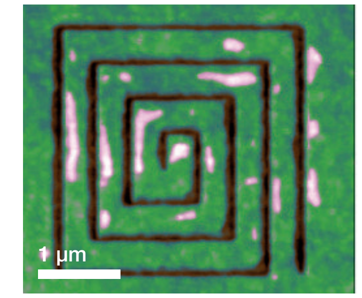
MFM - Yttrium Iron Garnet (YIG) film *Sample courtesy of Dr. A.V. Maryakhin*



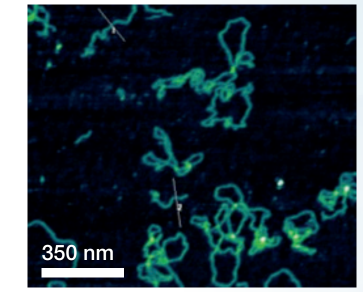
Lateral Force Modulation – Polymer-fullerene blend (P3HT:PCBM)



KPFM – DTP (pentacene derivative) on gold

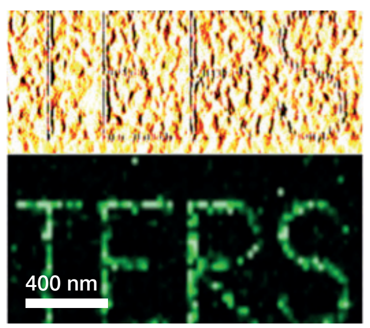


Nano Lithography – Vector force scratching on polycarbonate

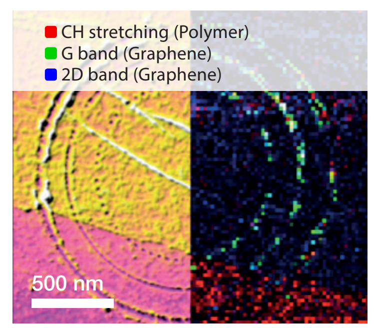


AFM in liquid – plasmid DNA on mica

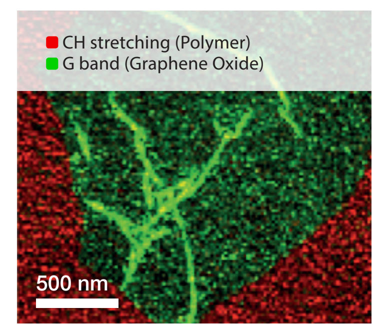
Tip-Enhanced Raman Spectroscopy



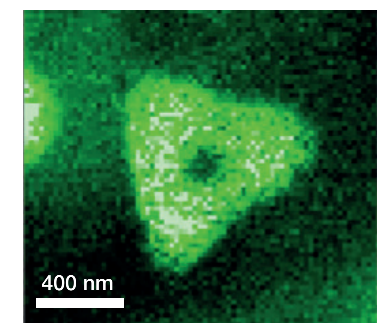
AFM and TERS images - Patterned graphene oxide flake by "pulsed-force lithography"



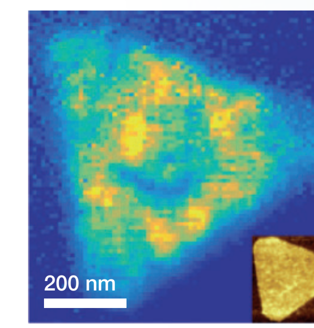
AFM and TERS images - Circular pattern imprinted in CVD grown graphene transferred to gold



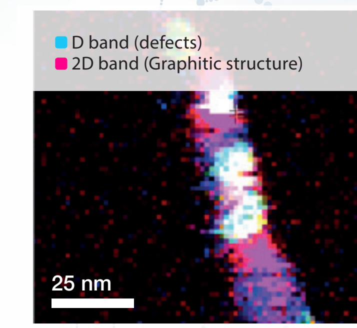
TERS image – Graphene oxide on gold



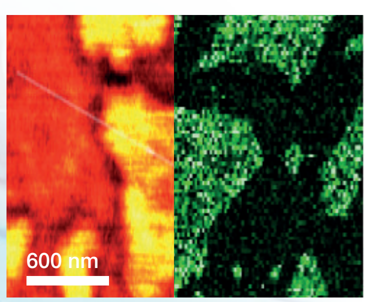
TERS/TEPL image – MoS_2 flake on Si substrate *Sample courtesy of Dr Filippo Fabbri (IMEM)*



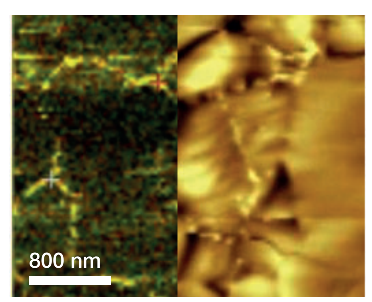
TERS/TEPL image – CVD grown WS_2 on Si substrate *Sample courtesy of Dr Adam Schwartzberg (Berkeley Lab)*



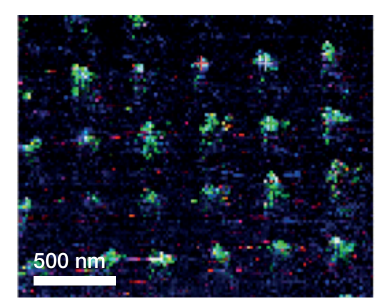
TERS image – Single wall carbon nanotube on gold – spatial resolution 8 nm



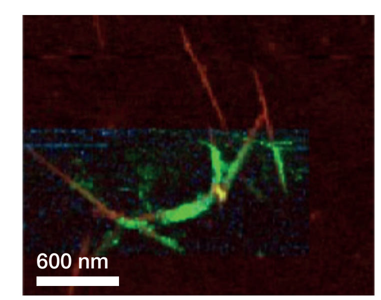
KPFM and TERS images – Graphene Oxide (COOH functionalized) flakes on gold



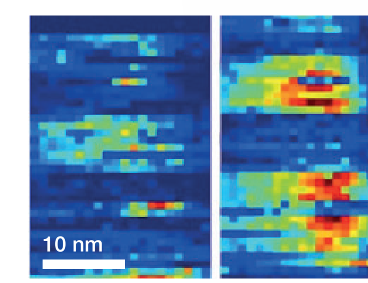
TERS and AFM images – SAMs of azobenzene thiols on gold



TERS images - Array of gold disks on Si functionalized with 1,4 Aminothiophenol. *Sample courtesy of Dr Evgeniya Sheremet, Technische Universität Chemnitz*

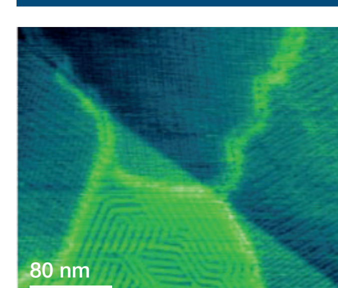


TERS and AFM images – Carbon nanotubes on glass

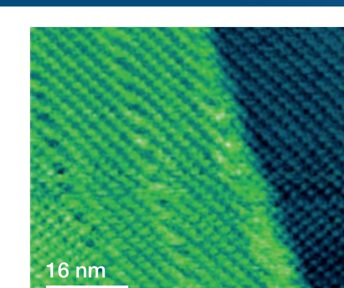


TERS images – Engineered DNA – (left) A/T and (right) G/C homopolymeric blocks *Data courtesy of Dr Noah Kolodjieski, RMD*

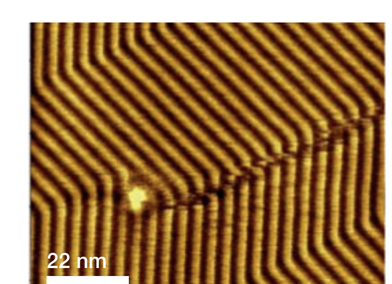
True molecular resolution



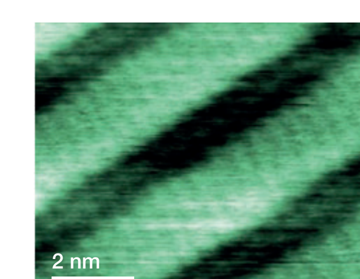
AFM (topography) - Molecular Resolution in Air - Melissic Acid



AFM (topography)- Cholesteryl Stearate on HOPG

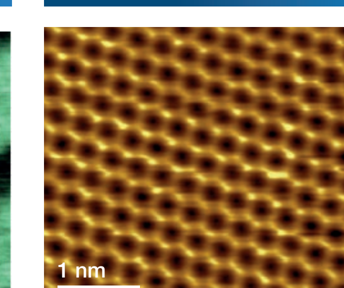


AFM (topography) - Palmityl Palmitate on HOPG



AFM (topography) - SAMs of Palmityl Palmitate - the pitch between the adjacent alkane chains is about 4 Å

Atomic resolution



STM (constant current mode) - HOPG

10^{-6}m | 10^{-7}m | 10^{-8}m | 10^{-9}m

...Micro... ... To Nanoscopy!

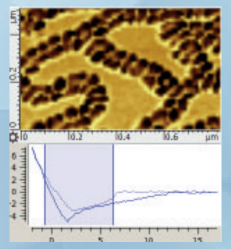
Integrated Software

NanoRaman data acquisition with ONE software

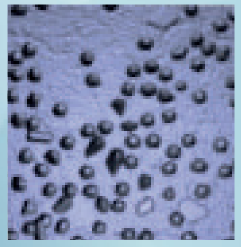
Key Features

- **ONE SOFTWARE** for the acquisition of all the NanoRaman platform techniques (AFM, Raman, Photoluminescence, co-localized measurements and TERS)
- **LabSpec 6 SPECTROSCOPY SUITE** for Integrated Multivariate and high level analysis at a touch of a button. PCA, MCR, HCA, DCA.
- **UNIQUE IMAGING MODES** and processing, including: **Spec-Top™ mode** - Original TERS imaging mode: TERS measurement is performed when the tip is in direct contact with the surface, transition between the pixels of the map is performed in semicontact mode, which preserves the sharpness and enhancing properties of the tip.
- **DUAL-SPEC MODE:** Acquisition of 2 different Raman maps. The far-field-map can be subtracted from the near-field-map, giving thus a pure TERS image.
- **MULTI-AREA ANALYSIS:** Because full rectangular scan-area can be too time-consuming, several trapezoidal areas can be selected on the AFM image for the Raman mapping.
- **CURVES MAP:** Spectroscopic and Force curves can be performed through images characterizing the local stiffness or the adhesion distribution. Force constant calibration (Sader method).

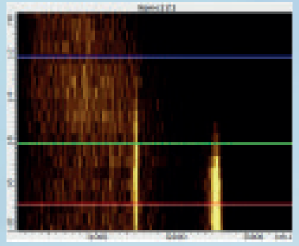
Multi-area Raman mapping (color); background image is the AFM topography



Force curves; Adhesion map distribution



3D topographic image



Spectroscopic curve; tip-to-sample distance VS Raman shift

CUSTOMER STORIES

A pioneer in TERS

"The NanoRaman team of LPICM lab, Ecole Polytechnique/CNRS, developed jointly with HORIBA Scientific the first HORIBA TERS system prototype a dozen or so years ago. Later commercialized, the prototype featured STM and AFM SPM modes combined with side illumination in Raman backscattering configuration. Owing to its excellent performance and relative ease of use, it was applied with success to the study of various materials and nanostructures such as self-assembled organic monolayers, carbon nanotubes, patterned semiconductors, etc. Among the outstanding scientific successes achieved with the system, the world premiere demonstration of stimulated (pump - probe) TERS is to be mentioned. Being quite user-open and versatile, the prototype measurement configuration could be successfully adapted to accommodate a polarization control of both excitation and scattered radiations, an external laser pump, as well as an additional detector for Tip-Enhanced Photoluminescence.
Since the pioneering years of the TERS prototype, HORIBA Scientific have developed a novel, module-based TERS system featuring a large number of SPM modes (STM, AFM, tuning-fork, etc.) implementable under various illumination – collection conditions (off-axis, top and bottom backscattering). Thanks to the customer-oriented culture of HORIBA, the NanoRaman team of LPICM is currently updating its "historical" prototype with the novel TERS system. It will allow us not only to pursue our actual research topics by adding new measurements, but also to initiate new research areas, impossible to address with the present system."

Prof. Razvigor Ossikovski
Nano-Raman team leader
LPICM, Ecole Polytechnique, France

A stable and versatile solution

"We are using the NanoRaman platform from HORIBA Scientific for research on carbon-based nanomaterials and especially the characterization of graphene oxide for energy applications. This AFM/Raman system is easy-to-use with help of the state-of-art hot spot search function and has number of unique build-in SPM techniques, including a unique imaging mode that makes TERS possible. HORIBA (and former AIST-NT) has developed one of the most stable and versatile scanning probe microscope for the combination with Raman spectroscopy. With the clever, fully motorized and automated instrument alignment, every advanced measurement at the nanoscale become an easy to configure experiment."

Prof. Masamichi Yoshimura
Head of the Surface Science Laboratory
Toyota Technological Institute, Japan

Great technical support

"We have been working for two years on a versatile configuration of the NanoRaman platform from HORIBA that allows both reflection and transmission measurements. As researchers in an electrochemistry Lab, we were searching for analytical tools which enable the characterization of materials at the nanoscale and under the condition of their operation. The stability of the SPM system (true atomic/molecular resolution) and the robustness of the optical coupling, which enables fast and effective TERS mappings, totally met our expectations. The versatility of the Horiba system already made possible new characterization pathways such as TERS in liquid and electrochemical TERS. We have also greatly enjoyed the technical assistance from Horiba which has definitively boosted our instrumental developments".

Dr. Ivan T. Lucas and Prof. Emmanuel Maisonhaute
Laboratory "Interfaces and Electrochemical Systems",
Sorbonne University, France

A fully automated system

With our NanoRaman instrument from HORIBA, we have the full power of Raman, AFM, TERS, TEPL, and many other related modes bundled into one system operating in reflection. Every member of my group from bachelor student level to postdoc researcher enjoys the easy usage of this fully motorized/automated system that can deliver correlated surface characterization data from microscale down to nanoscale resolution. We are using this AFM/Raman platform for research on optical and electrical properties of nanomaterials every day and we are appreciating the enormous potential of the TERS technique for studying nanomaterials such as CNTs and 2D TMDCs with unprecedented spatial resolution down to 2 nm.

Prof. Dietrich R.T. Zahn
Head of the Semiconductor Physics Research Group
Technische Universität Chemnitz, Germany

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