NanoRaman™ Platform

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

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 / MULTIENVIRONMENT**
  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.

**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.
In TERS, the Raman excitation laser is focused at the tip of an SPM probe coated with either gold or silver. Matching the wavelength of the Raman laser to the natural surface plasmonic frequency of the noble metal generates an intense localized evanescent electromagnetic field or a “hot spot” at the probe tip. 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 $10^6$.

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 μm² area), on the other hand confocal Raman spectroscopy and imaging provides specific chemical information about the material, with a diffraction limited spatial resolution.

**How TERS works?**

**What is co-localized AFM-Raman?**

**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

**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

True confocality - 3D maps

High spectral resolution - High selectivity

Co-localized AFM-Raman

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 – MoS2 flake on Si substrate (Sample courtesy of Dr. Rippo Fabbri (IMEM))
TERS/TEPL image – CVD grown WS2 on Si substrate (Sample courtesy of Dr. Adam Schwartzberg (Berkeley Lab))
TERS image – Single wall carbon nanotube on gold – spatial resolution 8 nm
TERS image – Engineered DNA – (left) A/T and (right) G/C homopolymeric blocks

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 – SAMs of Palmityl Palmitate – the pitch between the adjacent alkane chains is about 4 Å

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
STM (constant current mode) - HOPG

STM (atomic force microscopy) - HOPG

Tip-Enhanced Raman Spectroscopy

CH stretching (Polymer)
G band (Graphene)
2D band (Graphene)
D band (defects)
2D band (Graphitic structure)

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
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).

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 has 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. The 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

**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 usability of this fully motorized/automated system that can deliver correlated surface characterization data from microscale down to nanoscale resolution. With the 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 TMDs with unprecedented spatial resolution down to 2 nm.

**Prof. Dietrich R.T. Zahn**
Head of the Semiconductor Physics Research Group
Technische Universität Chemnitz, Germany
Worldwide Training and Technical Support

Jobin Yvon, established in 1819, and now part of the HORIBA Scientific is one of the world’s largest manufacturers of analytical and spectroscopic systems and components.

The HORIBA Scientific teams are committed to serving our customers with high performance products and superior technical support.

Our staff of experienced application and service engineers, located around the world, provides full support for your instrument and its future upgrades.

Well equipped application laboratories allow for sample analysis and hands-on training for new and experienced users.

Free learning tools for new and experienced Raman users. Available to anyone who is interested in learning more about Raman.