AFM-Raman Coupling and Tip-Enhanced Raman (TERS)

Raman microscopy has become an essential tool for the analysis of materials on the micron and even sub-micron scale. HORIBA Scientific's expertise in optical and mechanical design insures that HORIBA Raman instruments reach the optimal spatial resolution.

The advent of Scanning Probe Microscopy techniques (SPM) such as Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM), which allow measurement of topography, adhesion, electro-magnetic or electro-chemical properties and many other types of analysis at the nanometric scale, have benefitted innumerable fields of scientific research, especially material scientists and molecular biologists.

Coupling the two techniques (SPM and spectroscopy) soon became attractive in order to identify chemical composition of nano-objects of interest, or simply to establish the object's location through spectroscopic means before proceeding to characterization with near-field methods. Those co-localized measurements are particularly powerful with nano-objects showing strong Raman scattering such as carbon nanotubes, nanowires, and graphene or those showing strong luminescence like quantum dots.

The need for chemical characterization techniques to reach higher spatial resolution also became clear, however if near-field scanning optical microscopy (NSOM) brought relative success in detecting strong signals like in absorption spectroscopy or photoluminescence, obtaining specific chemical information at the nano-scale with Raman spectroscopy only became realistic with the development of tip-enhanced Raman scattering (TERS).

TERS takes advantage of surface plasmon resonance, dipole and chemical resonance effects, using special metal coatings on the SPM probe tip greatly enhancing the Raman scattering from the near-field directly under the probe. This enhanced near-field signal is then collected along with the far-field signal that can be discriminated against using different techniques, so as to extract the near-field Raman signal and generate nano-scale Raman profile or images.

The optical coupling to the SPM/AFM system essentially depends on the configuration of the SPM and its purpose. SPM systems designed for the biological field usually fit on a standard inverted optical microscope, while coupling to SPM systems designed for opaque samples depends on the SPM optical access. Top illumination is often possible and is preferred for co-localized measurements, but the shadowing effect from the cantilever limits TERS to the use of transparent probes or extended tips, so that oblique (side) illumination is required for use of standard metal-coated tips.

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HORIBA the leader in Spectroscopy teams up with the leaders in SPM

HORIBA Scientific partners with the leading SPM companies in the world to provide the best combined instrument for the application. Different partners offer different capabilities and lend their mastery in various fields of applications. HORIBA marries its expertise in Spectroscopy together with that of the major suppliers in the field of Scanning Probe Microscopy producing the highest performing instruments on the market.

HORIBA Scientific offers AFM coupling options for top, bottom and oblique illumination schemes (figure 1) to use with its high-spectral-resolution Raman microscope Labram HR as well as the more compact XploRA, in both their upright and inverted microscope versions, allowing coupling to a wide range of SPM systems (see compatibility chart below).
Co-located SPM and Optical measurements

The integration of hardware and software of both systems onto the same platform enables fast and user-friendly operation of both pieces of equipment at the same time. Furthermore, the AFM/Raman coupling does not compromise the individual capabilities of either system so that all imaging modes of the SPM remain available (EFM, MFM, Tapping Mode, etc.) and the Raman microscope is fully functional and can be used separately for micro or macro measurements without disturbing the AFM setup.

When performing co-located measurements on the combined system, the operator has direct access to the nanometric information about the sample given by the SPM system, and the chemical information from the micro-Raman measurement, from the same location.

Carbon Nanotubes

A typical field of application is that of carbon materials. Below is an example of co-located imaging of topography and Raman of the different bands characteristic of single wall carbon nanotubes.

In this sample (courtesy of Prof. Jun Jiao of Portland State University) solely composed of single wall carbon nanotubes (SWCNTs) spread between two electrodes, the radial breathing mode Raman band (RBM) does not show in all tubes. The AFM image performed at the same location shows that the tubes with no RBM band are in fact of very large diameter, corresponding to lower RBM frequency position than what the filter used could let through.

Graphene

AFM-Raman is also ideally suited for studies of another carbon material of high interest with strong Raman scattering: multi-layer and single-layer graphene.

In this sample of graphene (courtesy of Prof. Lukas Eng’s group, IAAP, Dresden, measured by Andrey Krayev, AIST-NT), Raman spectroscopy allows identification of the number of layers of graphene by fitting the 2D band (from double resonance effect) present in single and multi-layer graphene.

Polymers

Polymer studies are another field where co-located Raman and SPM measurements can bring complementary information. In the cross-section of a polystyrene/polypropylene polymer stack below, a 40umx40um area was scanned with PeakForce tapping mode (Bruker).

While the topographic image (Image A) gives high resolution information about the surface aspect of the sample, it is difficult to distinguish the two polymers.

The Young modulus image (Image B) provides information on the elasticity/stiffness of the polymers, and good contrast is achieved allowing the discrimination of the two polymer compounds.

The Raman image (Image C) confirms the localization of the different polymers and provides specific chemical composition allowing identification; the red area corresponds to the location of the polypropylene, and the green area to the polystyrene. This perfectly correlates to the elasticity information given by the Young modulus image since the polystyrene has higher elastic constant (darker) compared to the polypropylene (lighter).
Tip Enhanced Raman Scattering (TERS)

Surface Enhanced Raman Scattering (SERS) has long been used to enhance weak Raman signals by taking advantage of surface plasmon resonance, and chemical resonance, using nano-particle colloids or rough metallic substrates, allowing detection of chemical species at ppm levels.

The TERS effect is based on a similar principle, but uses a metal-coated AFM tip (or a single nanoparticle attached to the tip) as a dipole antenna that enhances the Raman signal coming from the sample area at the end of the tip (near-field). Although not yet fully understood, the TERS effect has attracted a lot of interest, as it holds the promise of producing chemical images with nanometric resolution.

The different coupling schemes available (figure 1) to perform TERS on the Labram HR series or XploRA series offer an ideal integrated platform for diverse applications. Software developed for communication with SPMs from different manufacturers allows seamless integration of the two techniques while keeping the full capabilities of the individual instruments. Specific methods were also developed to optimize laser-tip alignment and maximize throughput.

With these combined expertise, TERS can be approached with confidence.

Azobenzene

Azobenzene is a good candidate for TERS as it is easily adsorbed as a monolayer on a gold substrate and barely exhibits any Raman signal from the far-field, so that when signal is observed, it is proof that enhancement is occurring and that is proof of TERS.

The blue spectrum below shows the far-field Raman signal with a 30s integration time, while the red spectrum (1s integration time) is the TERS spectrum.

Carbon Nanotubes

Carbon nanotubes are ideal samples to illustrate spatial resolution of the TERS technique. In the example below, (courtesy of Mark Chaigneau, Ecole Polytechnique, Razvigor group) the STM image shows two aligned multi-wall carbon nanotubes side-by-side. The STM profile across those tubes shows that they are separated by about 70nm. The Raman profile of the G band at 1590cm⁻¹ is fitted to determine the apparent width of the tubes, and finds the smaller tube to be about 30nm diameter.

Silicon Germanium Trench

Silicon Germanium (SiGe) is a very popular semiconductor used for microchips, which now have critical dimensions below 50nm. This sample (courtesy of Ecole Polytechnique), contains a 150nm wide by 50nm deep trench of Ge in doped silicon. The Raman profile shows the trench is well resolved with TERS.
# AFM Compatibility chart

<table>
<thead>
<tr>
<th>SPM</th>
<th>Model</th>
<th>Bottom Illumination</th>
<th>Top Illumination</th>
<th>Side Illumination</th>
<th>Top &amp; Side Illumination</th>
<th>Bottom &amp; Top Illumination</th>
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<td>Aist-NT</td>
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<tr>
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<td>* TERS using top illumination exclusively with Nanonics transparent probes</td>
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<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td>* Tip-Enhanced (TERS) ready. Also allows co-located SPM and optical measurements</td>
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<tr>
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<td>* Top and Bottom under different microscopes</td>
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<td>* Park transmission NSOM only</td>
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</table>

- SPM systems designed for inverted microscopes are compatible with the Labram HR INV and XploRA INV without any additional optics.
- SPM systems that include their own sampling optics can be coupled to the Labram HR, Labram HR INV and XploRA using the microscope horizontal exit port (option).
- SPM systems that do not include sampling optics can be coupled to the Labram HR, Labram HR INV and XploRA using the side coupling optical module (option, which includes horizontal exit port option).