

Tip-enhanced Raman spectroscopy with ultra high sensitivity

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Application Note

Introduction

In order to reveal chemical processes occurring at catalysts it is necessary to disclose chemical and structural information on the nanoscale. While structural information can be obtained by employing a scanning probe device, it is still difficult to excavate the chemical identity of species at or near individual catalysts. Tip-enhanced Raman spectroscopy (TERS) is a technique that is very promising in this respect. TERS is based on the excitation of localized surface plasmons, which are quanta of an electromagnetic wave associated with electron oscillations near the metallic tip apex. These electron oscillations, excited in a suitable tip by the incident light, produce localized electromagnetic fields that can be enhanced strongly in comparison with the incident field. Using a gold tip, sharpened by electrochemical etching, the overall enhancement factor can be million-fold or even higher, where the enhanced field is confined roughly to the size of the tip apex: Due to the huge enhancement and the strong spatial confinement of the electromagnetic field, TERS becomes a technique with hitherto unprecedented sensitivity and spatial resolution [1-4].

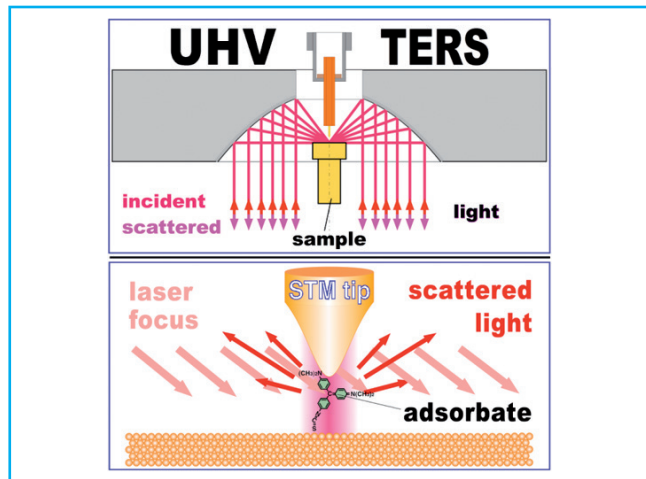


Figure 1:
Top panel: Scheme of UHV-TERS by using a parabolic mirror to focus the incident light and to record the inelastically scattered light.
Bottom panel: Scheme of TERS. The incident light creates an enhanced nearfield in the gap between tip and sample, causing an enhanced Raman scattering from the adsorbate.

Experimentals

An UHV-TERS system has been constructed. It combines a commercial STM (Danish Micro Engineering) with a self developed optical platform to which the incident laser light is delivered by single mode fiber and from which the emitted Raman light is guided via a multi-mode fiber toward the spectrograph [2].

A further improvement of the UHVTERS system includes among many other important steps the installation of a Shamrock spectrograph equipped with a Newton^{EM} CCD camera from ANDOR. Figure 1a shows a scheme of the UHVTERS setup with the main focus on the light pass and Figure 1b illustrates the scheme of tip-enhanced Raman scattering, depicting the nanometer scale of the high field zone between tip and sample. Thus, it also highlights the excellent spatial resolution ($\leq \lambda/30$) of this technique being much beyond the Abbe limit of optical resolution of $\sim \lambda/2$.

Results and Discussion

Our group at the department of Physical Chemistry of the Fritz Haber Institute of the Max Planck Society, has for the first time successfully employed TERS in an ultra high vacuum system, showing the power of this approach [2].

The use of a modern spectrograph and camera system provides a number of advantages: An improved sensitivity, a fast recording of a wide spectral range, virtually from zero to several thousand wavenumbers, a higher spectral resolution and, using the EM technology, an improved discrimination of noise with respect to the optical signal and ultra fast recording of spectral data particularly suitable of Raman imaging.

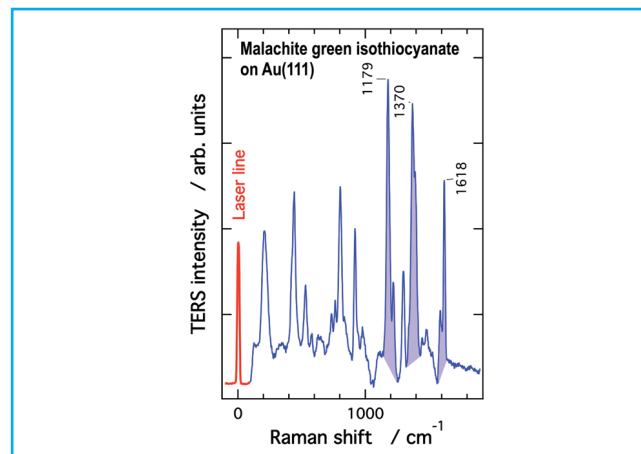


Figure 2:
TERS intensity of a monolayer of malachite green isothiocyanate (MGITC) adsorbed on a single crystalline gold surface with (111) orientation. Integral intensities of the three gray colored bands: ~90.000, 100.000 and 60.000 counts, respectively. The spectrum is background corrected.

Figure 2 shows the characteristic spectrum of malachite green isothiocyanate (MGITC) adsorbed at an Au(111) surface. The three major bands at 1179 cm^{-1} , 1370 cm^{-1} , and 1618 cm^{-1} exhibit strong, integral intensities of ~90.000, 100.000 and 60.000 counts,

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respectively. These huge signals arise from about 300 MGITC molecules located in the enhanced field zone with a radius of about 10 nm. Thus, each molecule contributes by about 200- 300 counts to each of the major Raman bands shown in Figure 2.

Conclusions

The advantage of TERS is that Raman scattering can be boosted to a signal level usually only known for highly fluorescent species. Thus, single molecule detection is at reach [2,4]. One key of success is the use of modern spectrographs such as the Andor Shamrock SR-303i-B with the Andor NewtonEM CCD-camera, which provides not only a high sensitivity but also means for fast recording of even weak signals in rather short time intervals, an absolutely essential property when it comes to parallel imaging of Raman and STM signals.

References

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