Nanoscale Chemical Mapping by Local Infrared Spectroscopy (nano-FTIR)

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Introduction

Research and development of nanomaterials, especially those made of organic molecules, has rapidly increased in the last couple of years. Novel nanomaterials exhibit extraordinary material properties and will have a huge impact on chemical, pharmaceutical, and microelectronic products of the near future.

To further develop and analyze these nanomaterials, an ultimate goal in modern analytical chemistry is the non-invasive chemical mapping of materials with nanometer-scale resolution. A variety of nanoscale-resolution elemental analysis techniques exist, for example, electron microscopy (EDS/EDX), however, their sensitivity to molecular species is often not sufficient. Moreover, electron microscopy usually requires much effort regarding sample preparation (microtome sectioning), and electrons can damage highly sensitive organic materials during the examination process.

Infrared spectroscopy, on the other hand, is non-invasive and highly sensitive to molecular bonds, but its spatial resolution is limited by diffraction to about half the incident infrared wavelength, which is on the order of several micrometers, preventing nanoscale-resolved chemical mapping.

Nanoscale chemical identification and mapping of materials now becomes possible with nano-FTIR from Neaspec. This novel technique combines the nanoscale spatial resolution of near-field microscopy with the analytical power of Fourier transform infrared (FTIR) spectroscopy. Nano-FTIR allows fast and reliable chemical identification of organic and inorganic material at the nanometer scale with about 1000 times better spatial resolution when compared to the standard FTIR method [1]. Because nano-FTIR is based on atomic force microscopy (AFM) technology, it only requires standard AFM sample preparation.

For example, nano-FTIR can be applied to the chemical identification of nanoscale sample contaminations. Figure 1 shows AFM images of a polymethyl methacrylate (PMMA) film on a Si surface. Although the AFM phase image indicates the presence of 100 nm size contamination, the determination of its chemical identity remains elusive from such images. Recording a local infrared spectrum from the center of the particle reveals its chemical identity. By comparing the nano-FTIR absorption bands with standard FTIR database spectra, the contamination can be identified as polydimethylsiloxane (PDMS).

Nano-FTIR Beats the Diffraction Limit in Infrared Spectroscopy

The nano-FTIR method breaks the diffraction limit in FTIR by combining apertureless near-field microscopy, also known as scattering-type scanning near-field microscopy (s-SNOM), with Fourier transform infrared spectroscopy. The instrument works according to the following, patented principle [2]. As shown in Figure 2, a focused broadband infrared beam L illuminates a standard metal-coated AFM probing tip T. The metallic tip T acts as an antenna, concentrating the incident light at the apex of the tip [3]. In this way an infrared nanofocus N is created at the tip apex, the size of which is only determined by the size of the tip apex. For near-field optical microscopy and nano-FTIR, this means that sharper probes will produce both better field confinement and higher infrared field strength. The nanofocus N is about 1000 times smaller than the diffraction-limited infrared focus. The light S backscattered from the oscillating metallic tip, and particularly that emanating from the nanofocus, is analyzed with an asymmetric Fourier transform spectrometer, which is based on a Michelson interferometer (Figure 3). This detection scheme records both amplitude $s(\omega)$ and phase $\varphi(\omega)$ spectra of the backscattered light. The complex-valued scattering coefficient $\sigma(\omega) = s(\omega)e^{i\varphi(\omega)}$ relates the scattered field $E(\omega)$ to the incident field $E_{inc}(\omega)$ according to $E(\omega) = \sigma(\omega)E_{inc}(\omega)$. To separate the weak near-field signals (that is, the field scattered from the

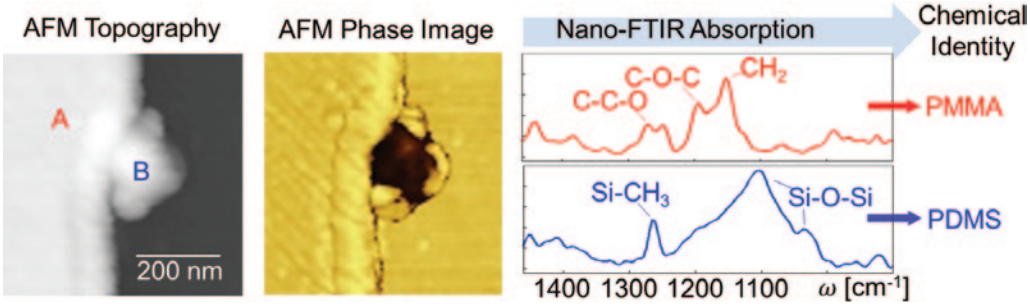

Figure 1: Chemical identification of nanoscale sample contaminations with nano-FTIR. In the AFM topographc image (left), a small sample contaminant (B) can be found next to a thin film of PMMA (A) on a Si substrate (dark region). In the AFM phase image (middle), the contrast indicates that the particle consists of a different material from the film and the substrate. Comparing the nano-FTIR absorption spectra at the positions A and B (right panel) with standard IR databases reveals the chemical identity of the film and the particle. Each spectrum was taken with a spectral resolution of 13 cm^{-1}. Reprinted with permission from F Huth et al., "Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution," *Nano Letters* 12(8) (2012) 3973–78. Copyright 2012 American Chemical Society.

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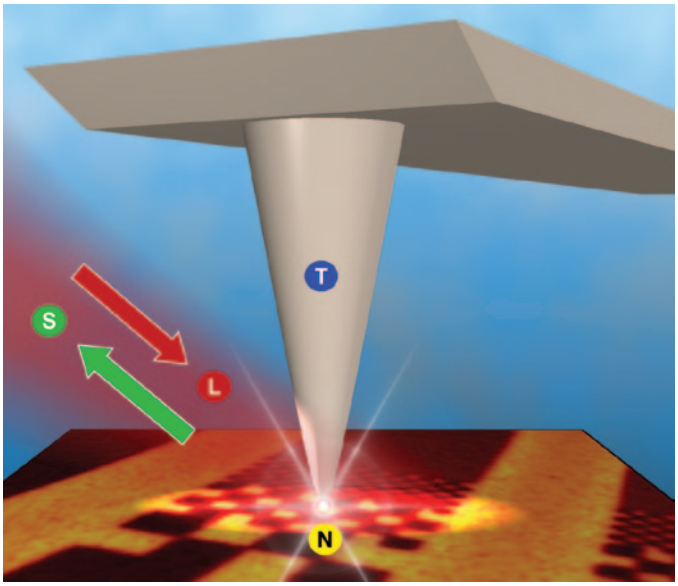

Figure 2: Working principle of s-SNOM technology. A focused broadband infrared beam L illuminates a standard metal-coated AFM probing tip T. The metallic tip T acts as an antenna that concentrates the incident light to the apex of the tip [3]. In this way an infrared nanofocus N is created at the tip apex. The nanofocus N is about 1000 times smaller than the diffraction-limited infrared focus. The light S backscattered from the oscillating metallic tip is analyzed with an asymmetric Fourier transform spectrometer based on a Michelson interferometer (Figure 3).

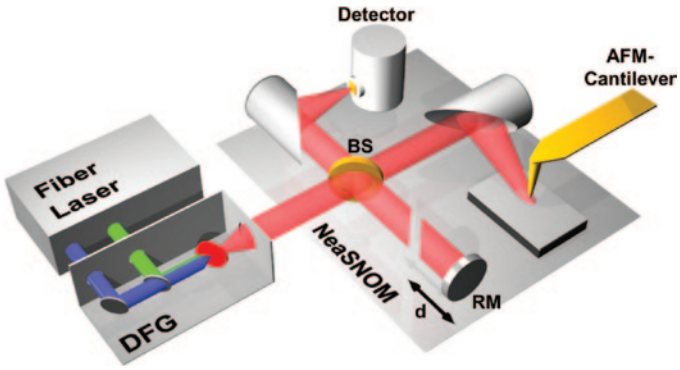

Figure 3: Schematic diagram showing instrument components. A broadband mid-infrared laser source, consisting of a fiberlaser and a difference frequency generator (DFG [1]), is coupled to the near-field microscope (NeaSNOM from Neaspec) where it illuminates the metallic AFM tip. The backscattered light is analyzed with an internal Fourier transform spectrometer consisting of a beam splitter (BS), a reference mirror (RM), and a detector. Adapted with permission from F Huth et al., "Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution," *Nano Letters* 12(8) (2012) 3973–78. Copyright 2012 American Chemical Society.

nanofocus) from the dominant background contributions, the detector signal is demodulated at a higher harmonic nΩ of the tip vibration frequency Ω. Translation of the reference mirror with a piezo stage yields an interferogram of the demodulated signal. By subsequent Fourier transformation of the interferogram, the complex-valued near-field spectrum is obtained, which carries information about the local dielectric function, the refractive index, and the local absorption of the sample.

Nano-FTIR Spectra Match Well with Standard FTIR Spectra

An important aspect of both fundamental and practical importance is that the nano-FTIR absorption spectrum (defined as the imaginary part of $\sigma_n(\omega)$, $\mathrm{Im}[\sigma_n(\omega)] = s_n(\omega)\sin[\varphi_n(\omega)]$) is connected with the local absorption of the sample and matches well with molecular fingerprints from conventional FTIR spectroscopy without the need of modeling.

This fundamental aspect was experimentally proven by F. Huth. et al. [1] with a PMMA sample. In this study, nano-FTIR absorption spectra in the infrared spectral region from 2000 to 800 cm^{-1} at a spectral resolution of 6 cm^{-1} were recorded in about 40 minutes (Figure 4). For comparison, a conventional (far-field) FTIR spectrum of the same material is shown, taken in about 20 minutes with a spectral resolution of 4 cm^{-1}. The overall agreement of peak positions, peak shapes, and relative peak heights provides clear experimental evidence that nano-FTIR indeed directly measures the local absorption of the sample and thus allows for interpretation of nano-FTIR spectra by simple comparison with conventional FTIR spectra found in established databases. Thus, nano-FTIR allows fast and reliable chemical identification of materials on the nanometer scale.

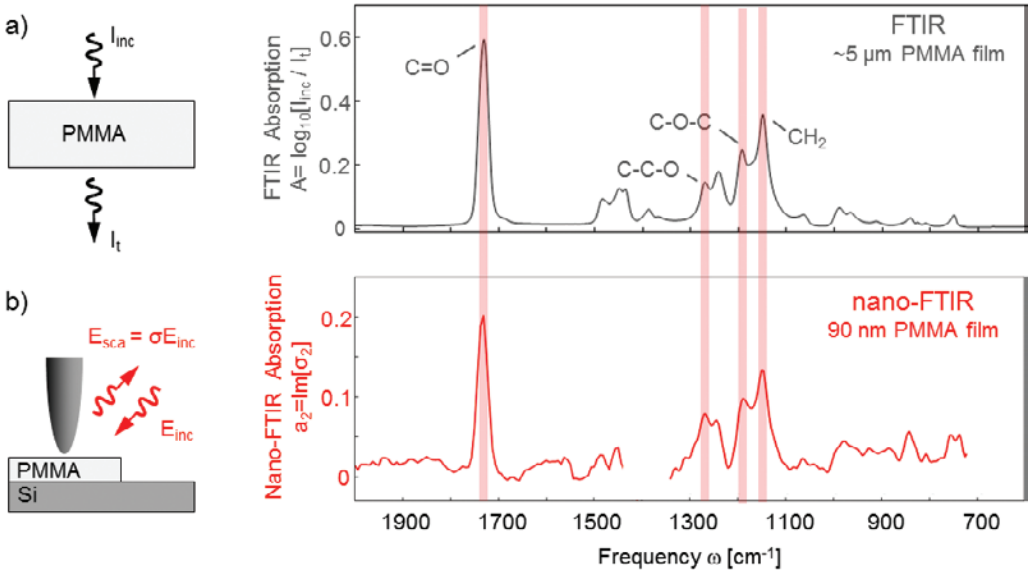

Figure 4: Comparison of conventional FTIR spectra (a) with nano-FTIR spectra (b) of a PMMA sample. Far-field and near-field spectra match very well without the need of modeling. Thus nano-FTIR spectra can readily be used for chemical identification by simple comparison with conventional FTIR spectra databases. Adapted with permission from F Huth et al., "Nano-FTIR Absorption Spectroscopy of Molecular Fingerprints at 20 nm Spatial Resolution," *Nano Letters* 12(8) (2012) 3973–78. Copyright 2012 American Chemical Society.

Nano-FTIR's Advantages Compared to Related Methods

In parallel to the s-SNOM-based nano-FTIR technology, another method for chemical nano identification, termed nanoIR, has been developed. In nanoIR a pulsed infrared laser beam illuminates a thin sample, which absorbs the infrared light and undergoes rapid thermomechanical expansion. An AFM tip in contact with the sample surface monitors the thermomechanical expansion, allowing measurement of the infrared absorption as a function of wavelength and tip position [4]. Comparing these methods, nano-FTIR offers the advantage of pure optical detection of the sample response by recording the scattered light from the tip. Because of this, a wide range of materials can be studied [5–9] with a spatial resolution better than 20 nm. Nano-FTIR requires only standard AFM sample preparation, and its interferometric detection scheme provides access to the complex-valued local dielectric function of the sample, similar to what is measured in ellipsometry. The s-SNOM technology of nano-FTIR additionally allows for mapping the near fields of nanophotonic and plasmonic structures [10–13].

Conclusion

Nano-FTIR combines the nanoscale resolution of apertureless near-field microscopy (s-SNOM) with the analytical power of Fourier Transform Infrared Spectroscopy (FTIR). The resulting instrument provides surface imaging plus nanoscale infrared spectroscopic analysis with 20 nm spatial resolution [1]. This technology can be applied in many disciplines where high-resolution chemical identification is required, such as chemistry, organic and inorganic semiconductor technology, photovoltaic technology, organic electronics, polymer science, and even life sciences (see www.neaspec.com/references).

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