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High-Resolution Chemical Imaging with Tapping AFM-IR

Where the spatial resolution of conventional bulk IR spectroscopy is limited by diffraction to ~3-10 μm, atomic force microscopy (AFM) provides a nanoscale topographic map of a sample surface. However, AFM has been unable traditionally to chemically characterize materials. This article discusses Tapping AFM-IR, which is a photothermal technique that combines AFM and IR spectroscopy to unambiguously identify the chemical composition of a sample with tens-of-nanometers spatial resolution.

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Application Note #201
High-Resolution Chemical Imaging with Tapping AFM-IR

Infrared (IR) spectroscopy is one of the most recognized analytical measurement techniques for the characterization of materials in academic, government, and industrial R&D laboratories. The spatial resolution of conventional bulk IR spectroscopy is limited by diffraction to around 3-10 μm, depending on the method used. Atomic force microscopy (AFM) is a widely used nanoscale imaging technique that provides the user with a high spatial resolution topographic map of a sample surface. Until now, the major drawback of AFM has been its inability to chemically characterize the material underneath the tip. AFM-IR is a photothermal technique that combines AFM and IR spectroscopy to unambiguously identify the chemical composition of a sample with tens-of-nanometers spatial resolution. So far, it has been successfully used in contact mode in a variety of applications. However, contact mode has proven unsuitable for soft or loosely adhesive samples, such as the less than 200 nm polystyrene nanoparticles (PS-NPs) that are of wide interest for biomedical applications. This application note discusses how Tapping AFM-IR overcomes such limitations, bringing the power of both IR spectroscopy and AFM topography mapping to a much wider range of applications.

When the sample absorbs photons from a pulsed tunable monochromatic IR laser light source, it heats up and rapidly expands, inducing an impulse to the AFM probe in contact with the sample. This causes an oscillation of the AFM cantilever at its contact resonant frequencies. The amplitude of each of the contact resonant frequencies has been proven to be proportional to the IR absorbance. As a consequence, by tuning the laser through a range of wavenumbers, an IR spectrum can be collected that correlates with conventional Fourier transform infrared (FTIR) spectra. The spatial resolution of the measurement is no longer limited by the diffraction-limited spot size of the IR beam, but instead, is determined by a number of factors including the diameter of the AFM tip, which is on the order of 50-200 nm. The use of fast, tunable pulsed IR laser sources with variable repetition rates, such as quantum cascade lasers (QCLs), has significantly improved the speed and sensitivity of photothermal AFM-IR, and has also enabled the measurement of IR spectra in AFM tapping mode.^{1,2}

Principles of Tapping AFM-IR

AFM-IR spectra are typically collected with the AFM probe in direct contact with the surface of the sample. This is not a problem when collecting point spectra where the AFM tip is held at a fixed location on the sample, unless the sample is particularly soft or mobile. However, during IR image acquisition, where the IR source wavelength is fixed and the AFM tip is scanned across the sample surface, the contact mode can be more problematic for soft or loosely adhered samples.

Enabling the AFM-IR technique to include softer samples was enabled by the development of tapping mode-based IR measurements, where the tip is not continuously in contact with the sample but instead taps, making intermittent contact with the surface. This allows highly reproducible imaging of a broader range of samples, even if they are very soft or loosely adhered. Tapping mode is typically performed by driving the AFM cantilever at its fundamental free resonance and bringing the AFM tip down to the sample such that the amplitude is limited by contact with the sample surface. The tip is then scanned across the sample surface and the topography of the sample is recorded by maintaining a constant collision amplitude.

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