Spectroscopic Nanoscopy of Biological to Extraterrestric Materials

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***Abstract*—Near-field optical microscopy (by scattering from an AFM tip, s-SNOM) returns local absorbance from a tiny volume of only (20 nm)^3 under the tip apex, thus enabling VIS-to-IR-to-THz mapping at exciting 20 nm resolution. The mid-infrared is ideal for nanoscale chemical recognition by vibrational and phonon contrasts. Highlights will be presented of finding and characterizing natural nanoscale inhomogeneities, chemical as well as structural, in organic solar-conversion films, in bone/shell biomineral matter, and in slices through a cometary dust particle.—Nano-FTIR is no less than the continued success story of FTIR-based chemical analysis into resolutions hundreds, if not thousands of times better than previously attainable. It is a highly welcome solution to nanoanalysis requirements in all nanotechnologies and nanosciences.**

I. BASICS

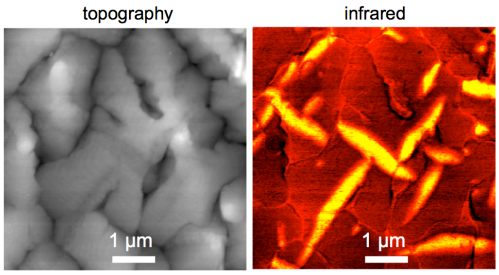
INFRARED spectroscopy and hyperspectral imaging are widespread not only in chemical analytics but also in physics, materials sciences, earth and biologal sciences etc. The value of these techniques rests on the fact that most materials exhibit resonances that identify their chemical nature, especially in the mid-infrared „fingerprint“ region. The long wavelengths (3–20 µm) of FTIR (Fourier-transform infrared) spectroscopy, however, have formerly prevented its use for nanoscale analytics. This limit is overcome owing to near-field techniques, since the advent of the infrared s-SNOM which is based on AFM (atomic force microscopy) but extended by an infrared scattering channel that indeed records local infrared spectra. The infrared resolution is as good as that offered by the AFM, limited only by the probing tip.[1]

II. SOLVING THE IR SOURCE PROBLEM

Since in s-SNOM the scattering efficiency is very weak, 10 mW coherent beams from step-tunable gas lasers and continuously tunable quantum cascade lasers have been the illumination sources of choice, but such spectroscopic mapping is time-consuming and prone to artifacts from sample drift and tip deterioration.[2] Thermal emitters were shown to work, but low S/N required long averaging.[3] A breakthrough came with the introduction of a coherent broadband-infrared illumination source that enables nano-FTIR, the swift acquisition of full 700 cm^{-1} wide spectra for each pixel while scanning,[4] at a beam power of 1 mW.[5] Even wider frequency coverage has recently been demonstrated at the Berkeley and Berlin synchrotron facilities.

III. NANOSCALE DOMAINS IN ORGANIC THIN FILM

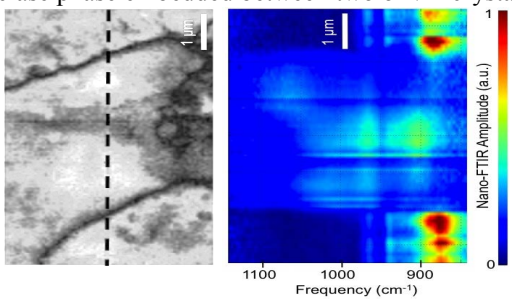
Coexistence of structural phases in thin-film pentacene had been suspected from X-ray diffraction, yet the scale of domains remained unknown. Infrared spectroscopy can distinguish structural phases by resonance shifts, and this is why infrared s-SNOM could readily discover ≈200 nm wide elliptical patches of changed molecular inclination, as in the following image taken at 907.3 cm^{-1}, that are seen to interpenetrate right through adjoining grain boundaries.[6] Such



domain interfaces and their observed motion (over months) point at hidden problems with solar-conversion materials development, possibly also with other molecular materials.

IV. A COMET'S GRAIN

The "stardust" mission of NASA returned µm-sized particles from a cometary tail that were embedded, microtomed and mapped by many methods to explore their formation mechanisms, invaluable for theories on primordial matter formation. Nano-FTIR indeed added substantial insights. As one point, it is the only method that can identify nanometer scale gradients of crystallinity in addition to chemical gradients, demonstrated, e.g., in the following spectroscopic line scan along a plagioclase phase embedded between two olivin crystals.[7]



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