

AFM-IR: Analyzing Organic Photovoltaic Materials

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Abstract

This note describes the application of the nanoIR™ system to obtain a set of high spatially (~ 100 nm) resolved chemical analysis of photovoltaic materials, namely, P3HT (poly(3-hexylthiophene)) and PCBM ((6,6)-phenyl-C₆₁-butyric acid methyl ester). Phase separation of the material is readily detected by comparing the spectrum of interest with the pure component spectrum. By combining the powerful AFM microscopy to IR spectroscopy in one instrument, the topology of the samples and defects are linked directly. Spectral changes are observed within 100 nm when a series of spectra is acquired across a flat area. The relative mechanical stiffness within a defect is evaluated in a contact stiffness image.

Background

Organic photovoltaic (PV) materials are heavily pursued in harnessing solar power as an alternate energy source. In both private and academic sectors, major efforts are put forth to prepare solar panels with the highest power conversion efficiency (η) at the lowest possible cost. Polymer blends of poly(3-hexylthiophene), P3HT, and (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM) are a popular donor-acceptor (DA) bulk heterojunction (BHJ) that has been used for this purpose. Such material can be solution-processed before grafting onto surfaces and can yield a high η ($> 5\%$). In a typical organic solar cell, P3HT and PCBM are not miscible and are eventually phase separated into microdomains.[1] This phase-separation is critical in the long-term stability and performance of the PV. Covalently linking PCBM to polymeric P3HT would yield small feature sizes, but the performance suffers as the P3HT backbone is believed to conduct charges poorly.[2] AFM and TEM have been used to characterize the morphology of the PV films at high-spatial resolution; but chemical information is not readily available at the nanoscale. In this application note, we will correlate topological features to local chemical spectroscopy on P3HT and PCBM-doped P3HT films using the novel nanoIR™ technology.



Fig 1. The nanoIR Platform

Introduction to the nanoIR

Infrared (IR) spectroscopy is one of the most practiced analytical measurement techniques in industrial and academic R&D laboratories. Unfortunately, diffraction physics limits its spatial resolution to a few microns to 10's of microns depending on the optics involved and the wavelength of the light. This major limitation has now been eliminated by Anasys Instruments with the development of the nanoIR platform.. The spatial resolution breakthrough is obtained via a novel technique that uses a nanoscale probe from an atomic force microscope or AFM, acting as the IR absorbance detector. The nature of the IR absorbance detection results in simultaneous measurements of nanoscale mechanical properties and nanoscale morphology, along with the chemical composition. The nanoIR also has integrated nanoscale thermal property mapping resulting in a multifunctional tool that provides nanoscale structure, chemical, mechanical and thermal properties.

At the heart of the nanoIR platform (shown in Fig 1) is patented technology based on a combination of AFM and IR Spectroscopy (AFM-IR), a technique pioneered by award-winning researcher Dr. Alexandre Dazzi from the Laboratoire de Chimie Physique, CLIO, Université Paris-Sud, Orsay, France.

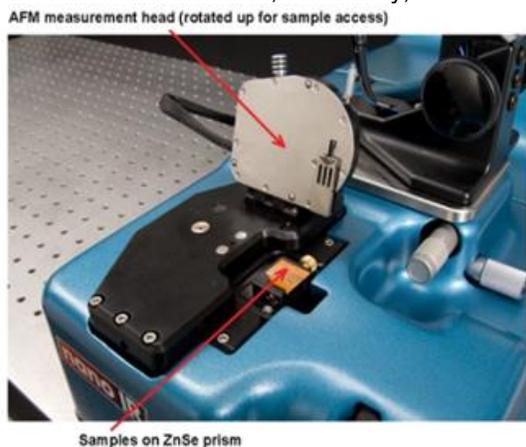


Fig 2. Close up view of the prism and AFM measurement head

The nanoIR system uses a pulsed, tunable IR source to excite molecular vibrations in a sample that has been mounted on an IR transparent (ZnSe) prism. This creates an illumination configuration similar to conventional attenuated-total-reflectance (ATR) spectroscopy. The

system's IR source is designed using a proprietary technology which is continuously tunable from 1200 to 3600 cm^{-1} covering a broad range of the mid-IR spectrum. As the sample absorbs radiation, it heats up, leading to rapid thermal expansion that excites resonant oscillations of the cantilever. The induced oscillations decay in a characteristic ringdown as shown in Fig 3.

The ringdown is Fourier transformed to extract the amplitudes and frequencies of the oscillations. Measuring the amplitudes of the cantilever oscillation as a function of the source wavelength creates local absorption spectra; the oscillation frequencies of the ringdown are related to the mechanical stiffness of the sample.

Users of the nanoIR can quickly survey regions of a sample via AFM imaging and then rapidly acquire high resolution chemical spectra at selected regions on the sample. As shown in Fig 4., polymer spectra acquired with the nanoIR system have demonstrated good correlation with bulk Fourier transform infrared (FT-IR) spectra.

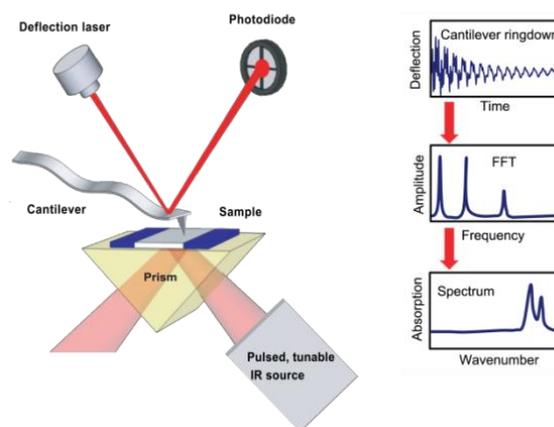


Fig 3. Schematic showing the technique behind the nanoIR

This allows the researcher to import an individual nanoIR spectrum into commercial IR databases where they can be digitally searched in order to chemically identify the materials at the specific sample locations measured. Alternatively, the IR source can be tuned to a single wavelength to map compositional variations across the sample surface.

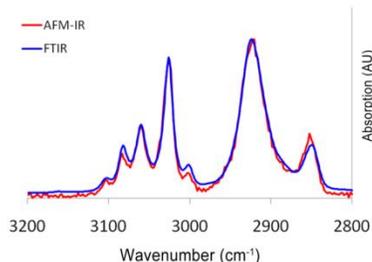


Fig 4. A comparison of the spectrum generated by the nanoIR (red) and conventional FT-IR (blue) of a polystyrene sample.

In addition to its ability to provide high-resolution infrared spectra, the nanoIR system provides information on the mechanical properties of the sample. This is accomplished, as mentioned above, by monitoring the frequency of the fundamental or higher resonant modes of the cantilever. This is analogous to the contact resonance method used for a number of years in the AFM community. The contact resonant frequency of the cantilever correlates to the stiffness of the sample and can be used to map the modulus of the sample qualitatively.

The nanoIR platform can also perform nanoscale thermal analysis utilizing novel AFM cantilevers that incorporate a resistive heating element into the end of the cantilever. Using these cantilevers in combination with the system allows the local measurement of the transition temperature of materials a single point or an array of points across a sample. This allows identification or mapping of the amorphous/crystalline content, stress, extent of cure, or other material properties which can be characterized by the transition temperature of the material.

This combination of measurement capabilities creates a multifunctional tool that provides nanoscale structure, chemical, mechanical and thermal properties.

Measurements of drop-casted P3HT and PCBM-doped P3HT films

The nanoIR technique is ideal for measuring polymeric samples in which there are local material variations. The sampling system requires the material of interest be deposited as a thin film on a ZnSe prism. This prerequisite is satisfied by drop-casting the materials from solution directly onto the prism.

nanoIRTM spectra of features on a P3HT film

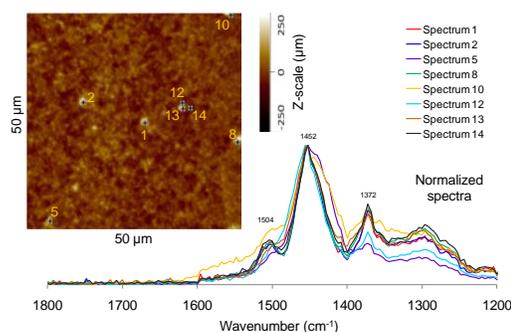


Fig 5. Point-and-click spectral acquisition over a large area of a thin P3HT film on a ZnSe prism

Not all surface features on the same AFM image share the same infrared absorption characteristics. An area of interest is illustrated in Fig 5, where small protrusions on the order of a few microns can be seen. Normalized point-and-click IR spectral acquisition reveals that only some locations have slightly broadened absorption characteristics, i.e., a long absorption tail (Spectrum 10) and the shoulder near 1500 cm^{-1} is less defined. The other locations yield spectra similar to the bulk P3HT material. Near points correlating to spectrum 12 – 14, the broadened absorption appears to be away from the height feature.

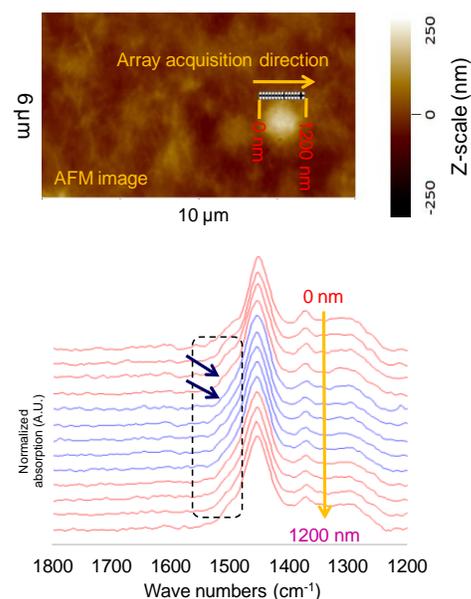


Fig 6. A spectral array acquisition showing the AFM image (top) and the corresponding spectra (bottom) near the spots 12-14 in Fig 5; spacing between each marker is ~100 nm.

To enhance the spectral analysis, the area near the spectrum labeled 12 – 14 was rescanned with a high spatial resolution and the corresponding image is shown in Fig 6 (top), where a spectral array acquisition (bottom) about the region was collected immediately afterward. Here, each spectrum is taken ~ 100 nm apart and spectral changes are seen within the same length scale (from second to third and from fifth to sixth spectra). As the shoulder around 1500 cm^{-1} disappears and reappears (at the arrows), the signal near 1380 cm^{-1} appears to broaden. With the nanoIRTM, these IR spectral changes can be seen at an unprecedentedly high spatial resolution.

PCBM-doped P3HT blend

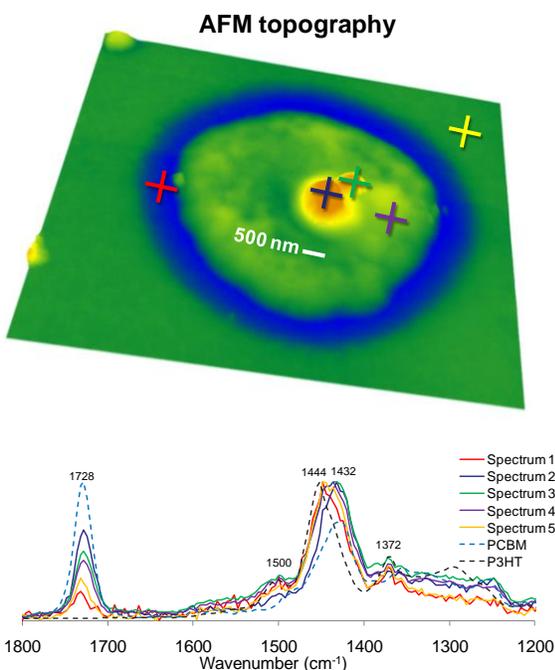


Fig 7. An AFM image and the spectra of the heat-treated PCBM-doped P3HT sample

Phase separation of PCBM and P3HT is commonly observed in such PV blends. In this example, a defect can be seen on the surface in Fig 7, which shows an AFM image of a heat treated P3HT-PCBM sample. The localized IR spectra pertinent to surface features are shown directly below the image. When the nanoIR spectra are compared to the nanoIRTM spectra for the pure components, local variations are distinguished. The methylene bending modes at 1444 cm^{-1} and 1432 cm^{-1} corresponds to the P3HT and PCBM, respectively. The 1444 cm^{-1} band also contains a contribution from an

overlapping ring semicircle stretching mode. The corresponding spectrum for the yellow hash mark appears to have both components. At the outer ring (red mark/spectrum 1), the peak at 1732 cm^{-1} (PCBM) is small and the component at 1444 cm^{-1} (P3HT) dominates. At both green and purple hash marks (spectra 3 and 4), the band near 1432 cm^{-1} is mainly contributed by PCBM. Finally, the sharpness of the band at 1432 cm^{-1} and a stronger 1732 cm^{-1} signal suggest the lobe at the center is mostly PCBM. By combining the AFM and IR into a single instrument, the topological information is readily correlated with the local chemical analysis. The above data suggests there is local phase-separation of PCBM and P3HT within this surface defect.

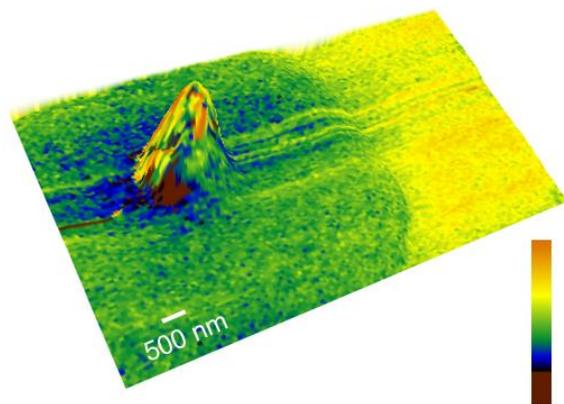


Fig 8. Contact frequency image of a chemical defect mapped over the corresponding height image; the range of the frequency is approximately 30 kHz (color bar; orange – stiffer; deep brown – softer)

The stiffness of the surface defect relative to P3HT-PCBM blend can be imaged using the nanoIRTM. Under the exposure of a continuously-pulsing IR laser radiation at 1450 cm^{-1} (other overlapping wavenumbers for both materials can also be used), the contact frequency of the cantilever is traced continuously as the AFM tip rasters across the sample. Here the bulk material (yellow/orange) appears stiffer than most of the interior areas of the defect (green).

Summary

The data presented in this text above has demonstrated the strong capability of the nanoIR™ in analyzing a set of photovoltaic materials in high spatial resolution (~100 nm). The topological features can be conveniently linked to its corresponding chemical infrared signatures. 100 nm spatial resolution can be readily achieved in applications where domain boundaries are unknown. Local phase separation of materials is identified by comparing local nanoIR™ spectra at the defect sites with the bulk spectra of the pure components. In addition, the relative contact frequencies surrounding the defect are mapped simultaneously with the corresponding topology.

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References

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