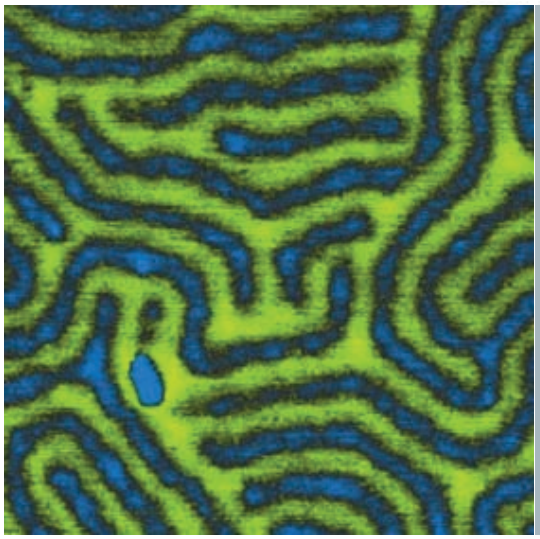
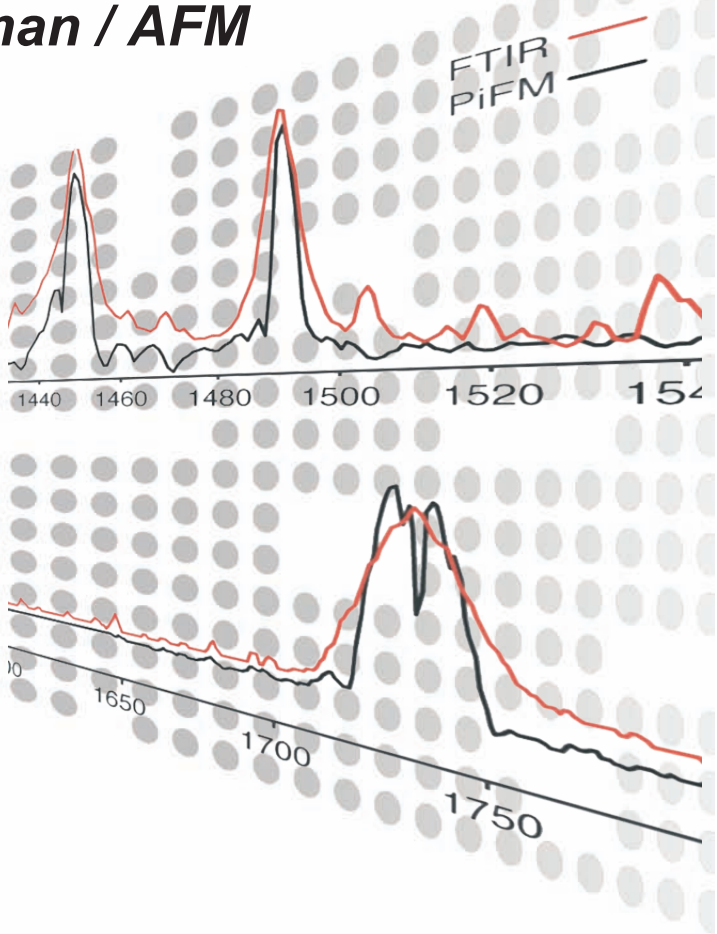
molecular VISTA

PiFM / AFM-IR / s-SNOM / Raman / AFM



PS-b-PMMA Block Copolymer



VISTA-IR

Photo-induced Force Microscopy

Sub-10nm Chemical Mapping

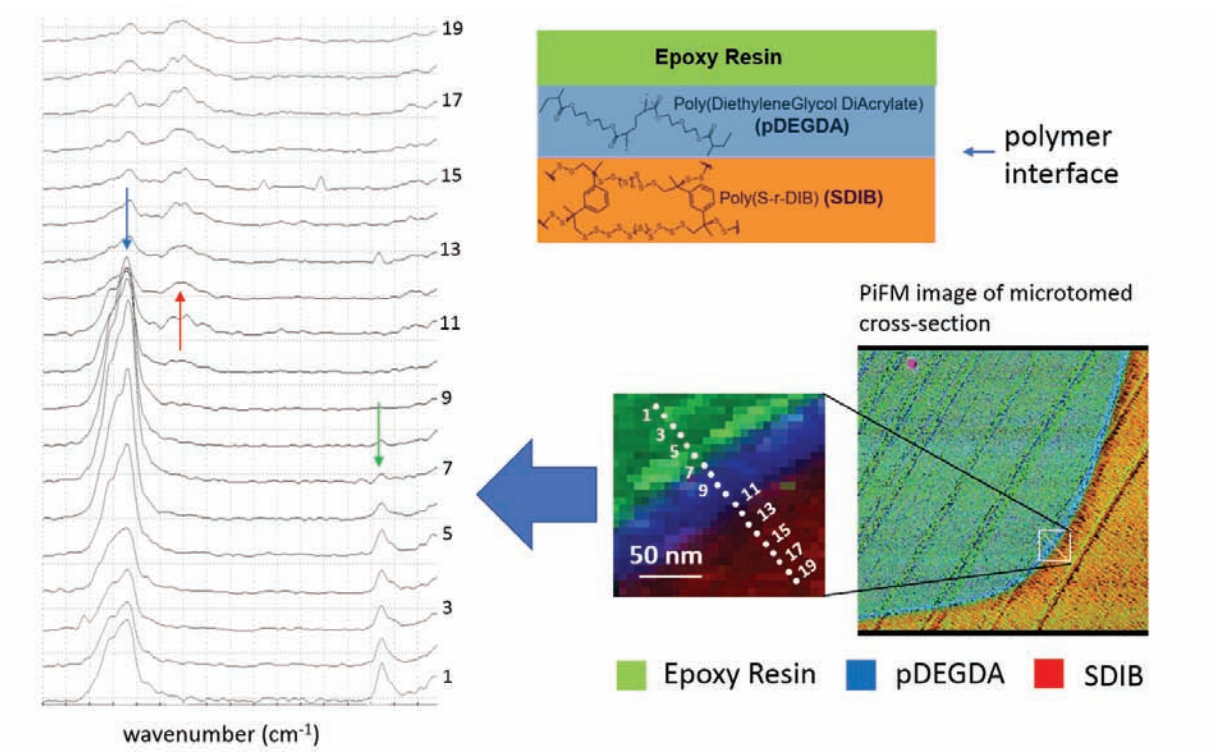
Nano IR Spectroscopy

Nanoscale Chemical & E-Field Imaging

Chemical Analysis with Sub-10nm Spatial Resolution

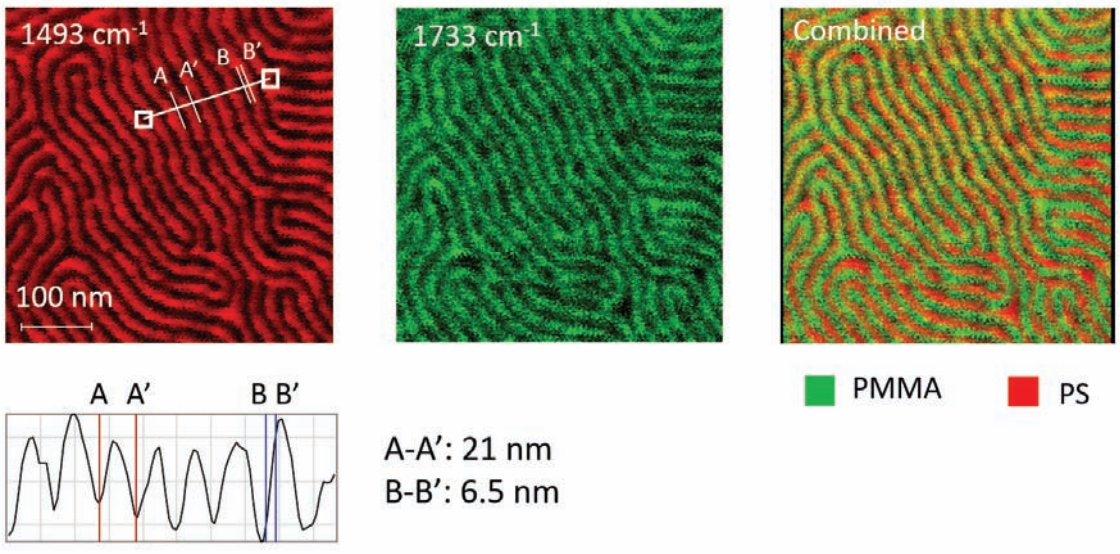
Chemical analysis across polymer interfaces

IR PiFM provides chemical analysis with ~ 10 nm spatial resolution as demonstrated by these 19 spectra taken across a curved polymer interface. The peak associated with SDIB (red arrow) starts to appear at the 10th spectrum and gets stronger as the AFM tip moves further into the SDIB layer. Each spectrum is separated by 12 nm from each other.



High resolution images of phase separation on a 10 nm scale

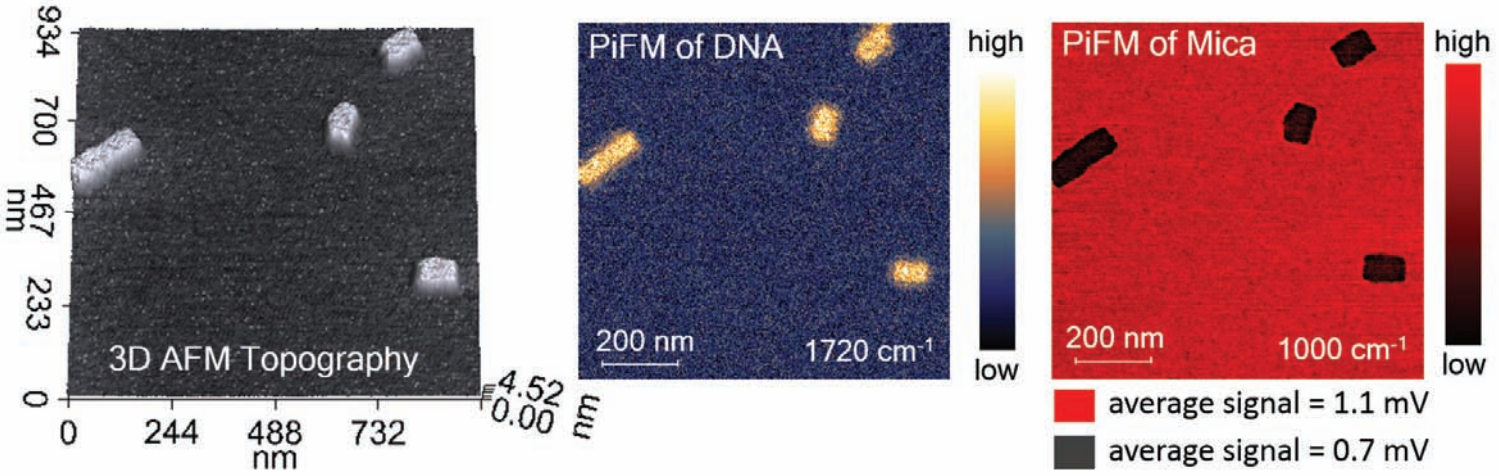
The family of phase-separated block copolymers provides ample demonstration of PiFM's capability to resolve different molecular species with sub-10 nm resolution. In the example pictured below, polystyrene (PS) and polymethylmethacrylate (PMMA) are distinguished by their PiFM images at 1493 cm^{-1} and 1733 cm^{-1}, respectively. The combined PiFM images and the cross-section profile clearly show the 21 nm pitch of the block copolymer's lamellar phase separation.



Excellent Surface Sensitivity

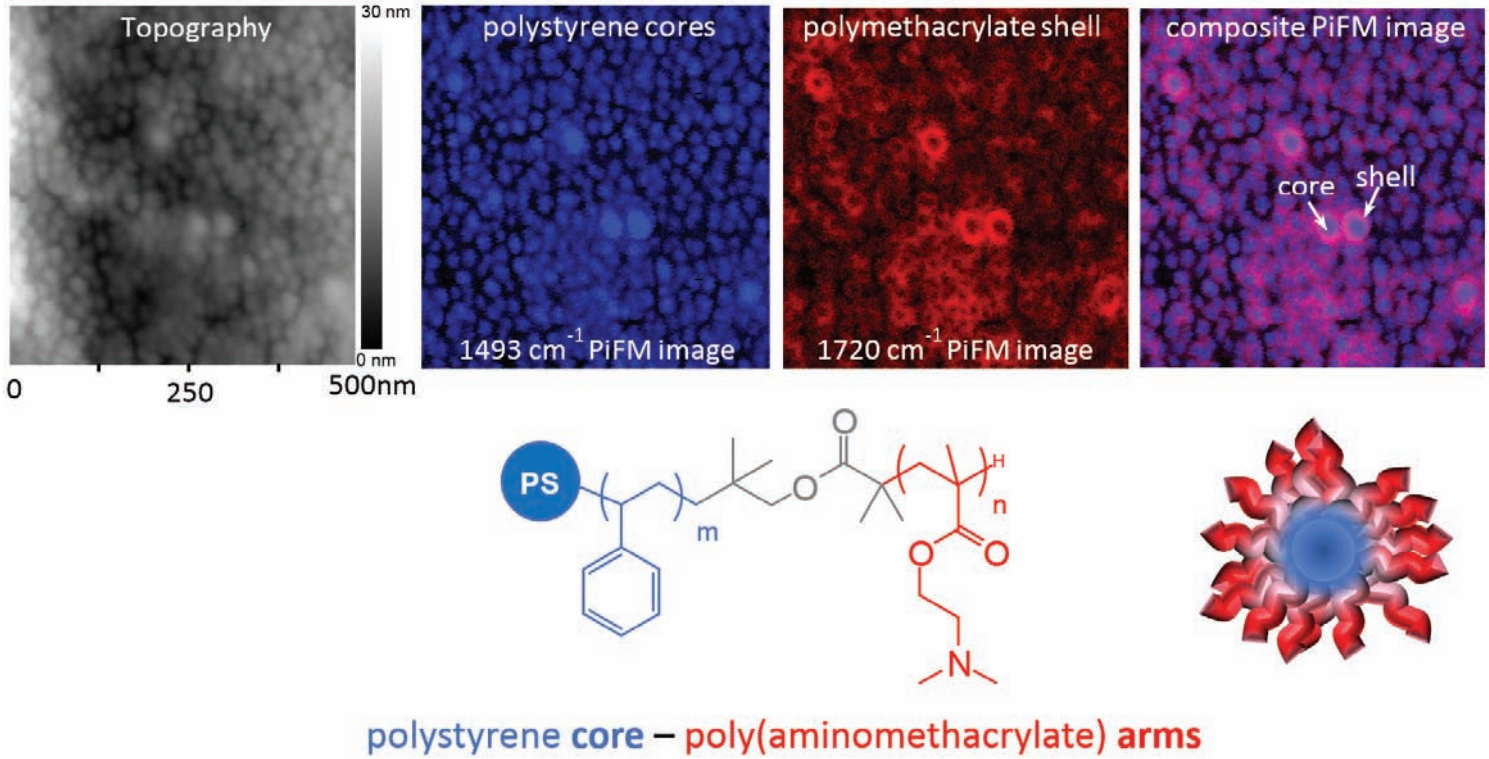
Biologicals: DNA on inorganic substrate

DNA origami is identified by the specificity of DNA's 1720 cm^{-1} signal against the background of a mica substrate. The 1000 cm^{-1} signal from mica – a layered aluminosilicate – is starkly reduced when covered by the DNA nanostructure of only 2.5 nm thickness.



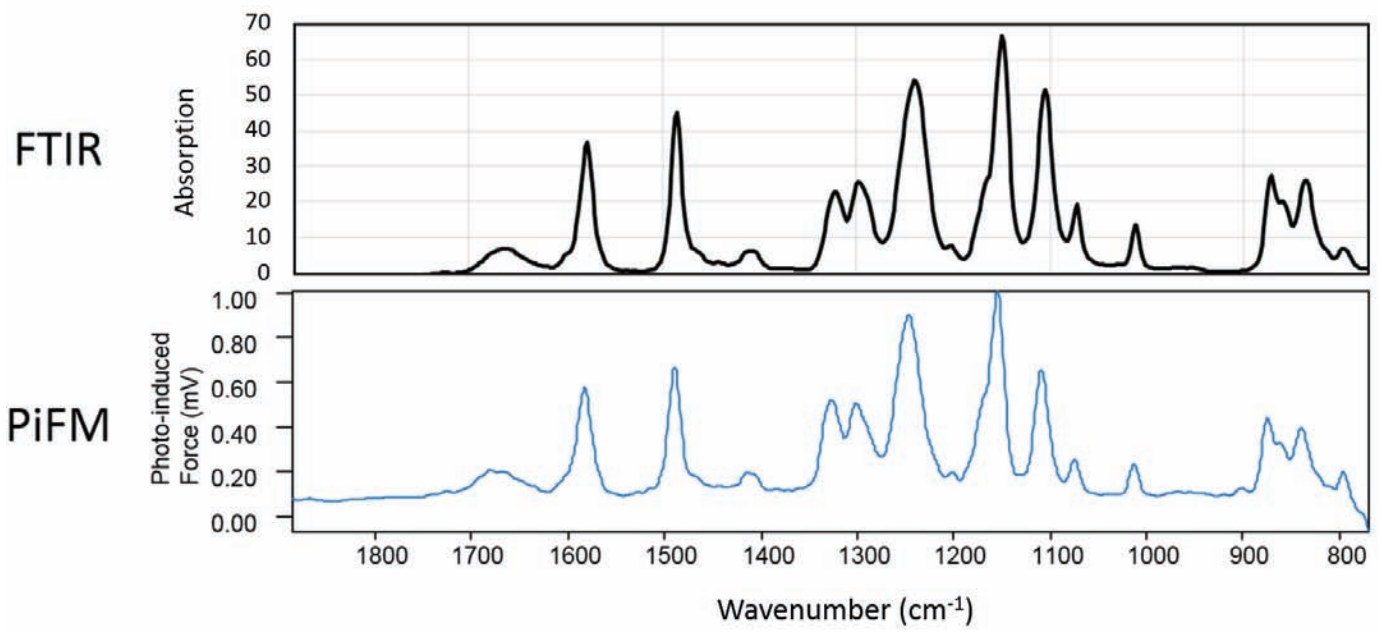
Resolving substructure in core-shell nanoparticles

Remarkable distinction between the core and the shell of a nanoparticle has been shown in the example of a hydrophobic core surrounded by hydrophilic ligands. In this example of 25 nm diameter polymer nanoparticles, molecular information is readily apparent about particle-particle packing such as ligand distribution around the core and interdigitation between adjacent shells, exacting information that is not readily available by other analytical techniques.



Agreement between PiFM and conventional IR spectra

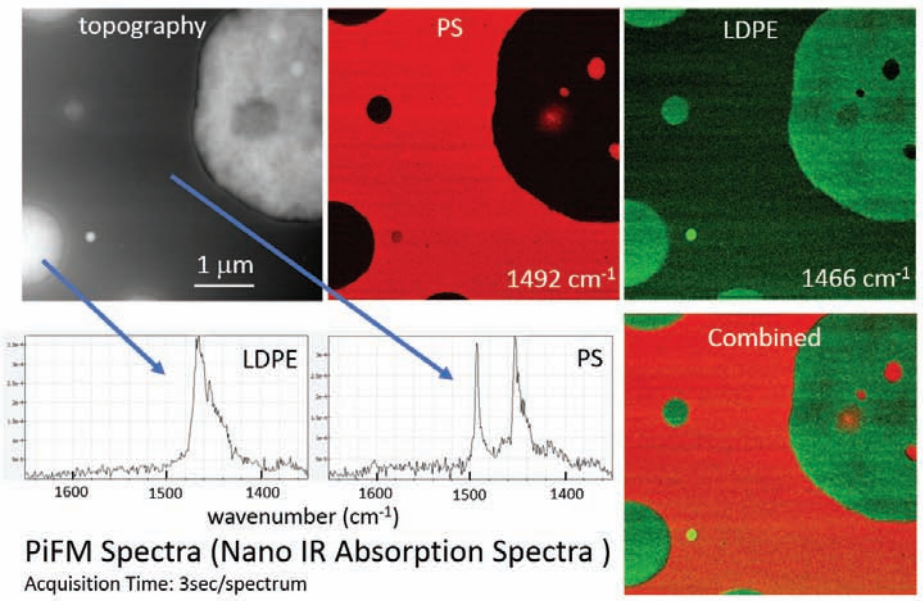
PiFM spectra generally replicate conventional IR spectra recorded from bulk samples, shown in this example of polyethersulfone (PES). Occasionally slight shifts in peak wavenumber and amplitude are observed in PiFM spectra, arising from the extreme sensitivity of PiFM to localized populations of molecules. One strength of the PiFM method is capturing the behavior of materials in very small amounts and in confined spaces – environments that can differ greatly from samples on larger scales.

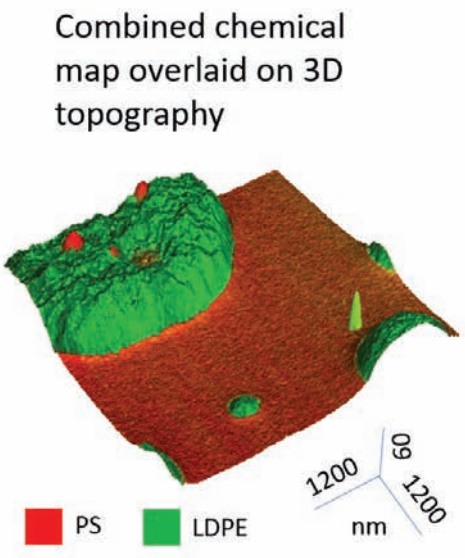


Discerning blends and identifying defects

Images of multiphase blends are often captured in AFM, but identification of each component is typically by inference. With PiFM, unambiguous identification of the components is achieved from their unique chemical functionalities. This example of circular domains in a continuous matrix unambiguously assigns the matrix as polystyrene (PS) and the circular domains as polyethylene (LDPE, low density polyethylene). Additional information is gleaned about defects in each of those two domains:

- small inclusions in the LDPE islands are clearly identified as polystyrene
- small features of varying heights scattered on the matrix are clearly identified as polyethylene

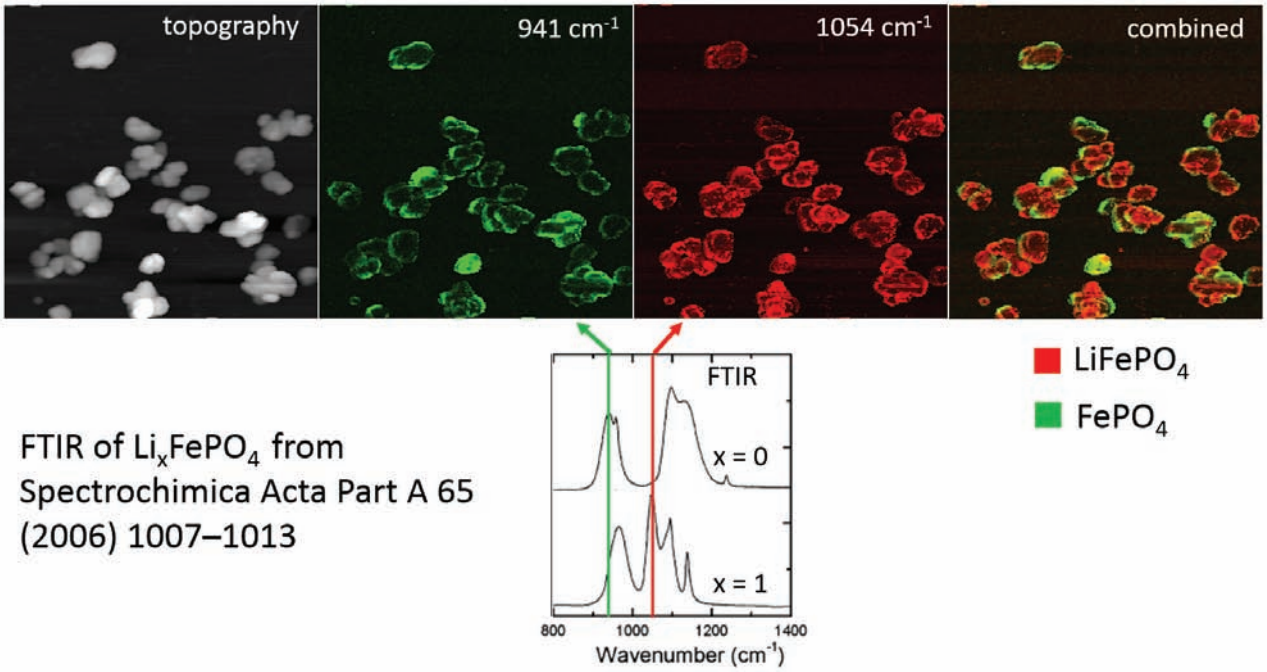




PiFM on Inorganic Materials

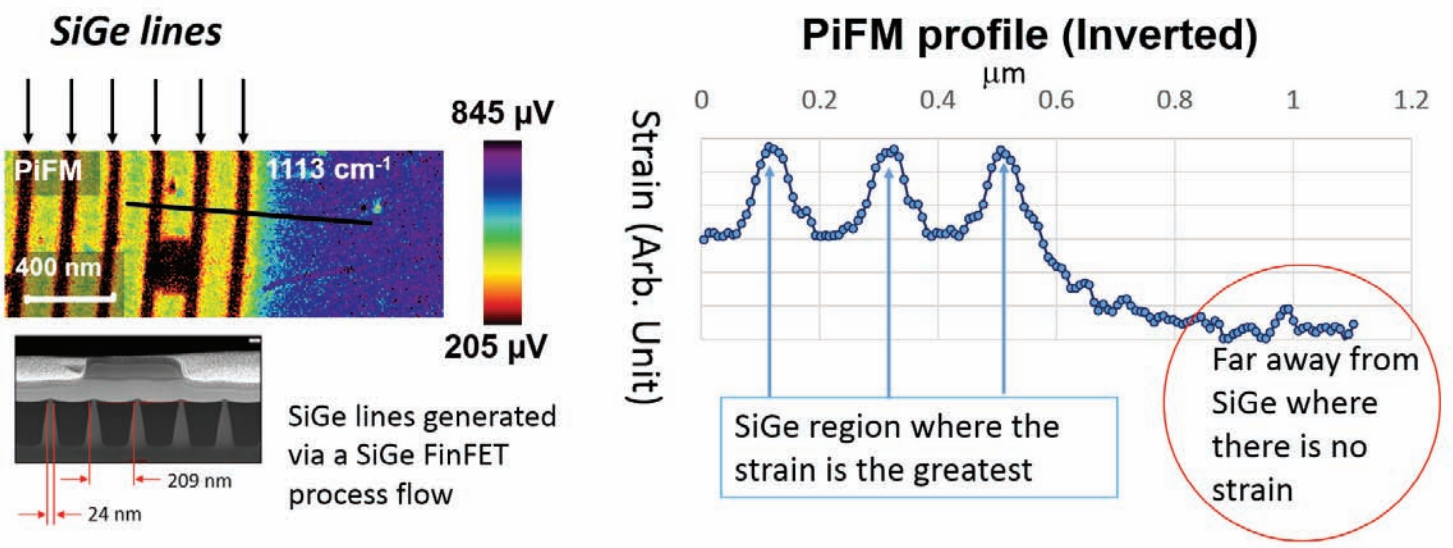
Distinguishing between iron phosphate phases

The charge/discharge cycle of a lithium ion battery cycles the cathode between two phases: $LiFePO_4$ and $FePO_4$. PiFM analysis distinguishes between these two phases with distinct signals at 941cm^{-1} for the de-lithiated FePO4 species and 1054cm^{-1} for $LiFePO_4$. In these images, the delithiated species is found to be more prominent at the periphery of the grains. Resolution at this scale contributes to mechanistic discussion of whether phase transformation is controlled by diffusion or by phase boundary reactions.



Visualization of strain in semiconductor devices at individual fin level

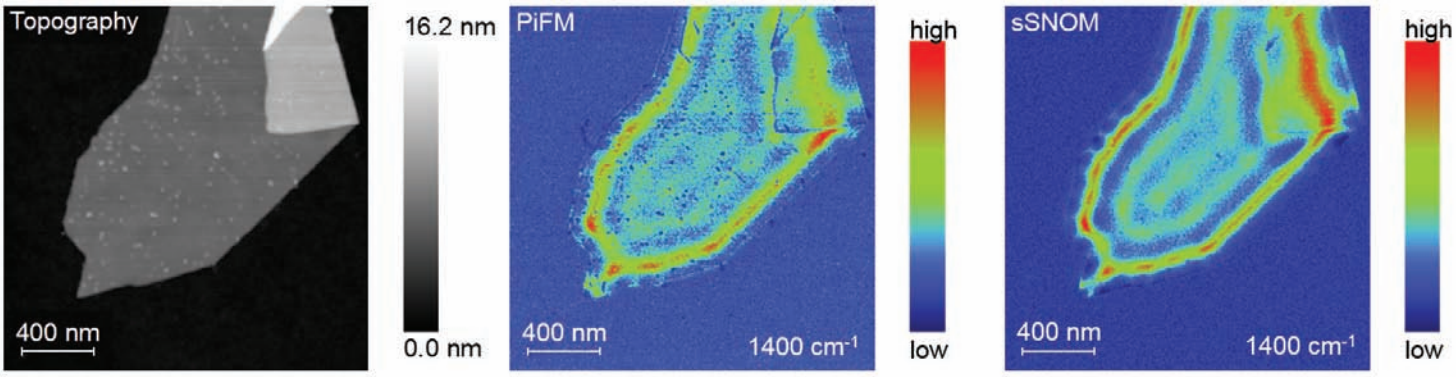
True nanoscale strain mapping is demonstrated via PiFM on SiO_2 regions sandwiched between SiGe lines. The inverted profile drawn across the PiFM image shows that strain is (1) highest on the SiGe lines, (2) frozen in at a constant level in the 200 nm space between the lines, and (3) relaxes away to near zero at a distance of ~400 nm from the SiGe lines.



PiFM on 2D Materials

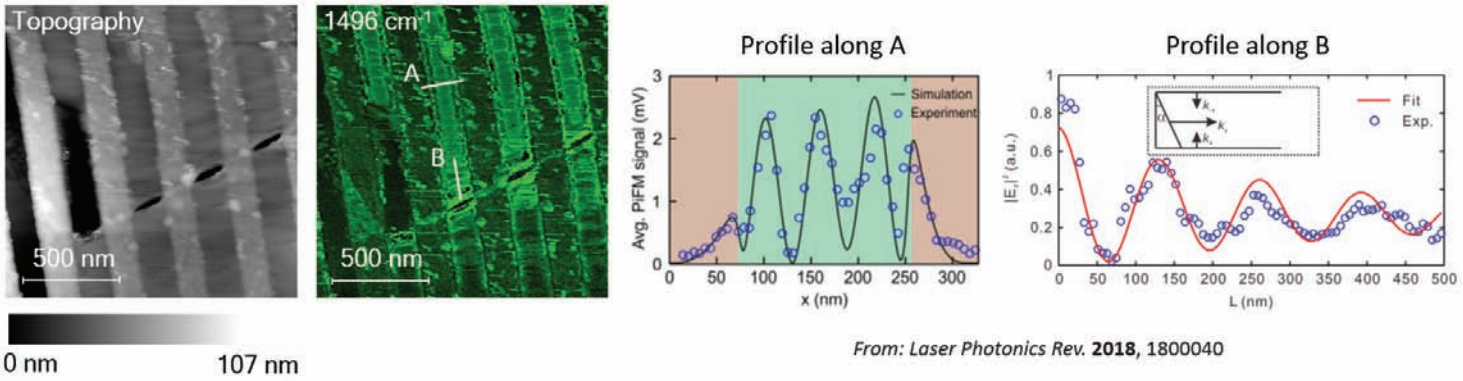
Surface phonon polaritons on hBN

Phonon polaritons in a hexagonal boron nitride flake are imaged by PiFM and scattering-type scanning near field microscope (s-SNOM, available as an option for Vista-IR) concurrently. Use of both PiFM and s-SNOM on van der Waals nanostructures is nicely covered in Science Advances, **4**:eaat7189, 2018.



Graphene plasmons

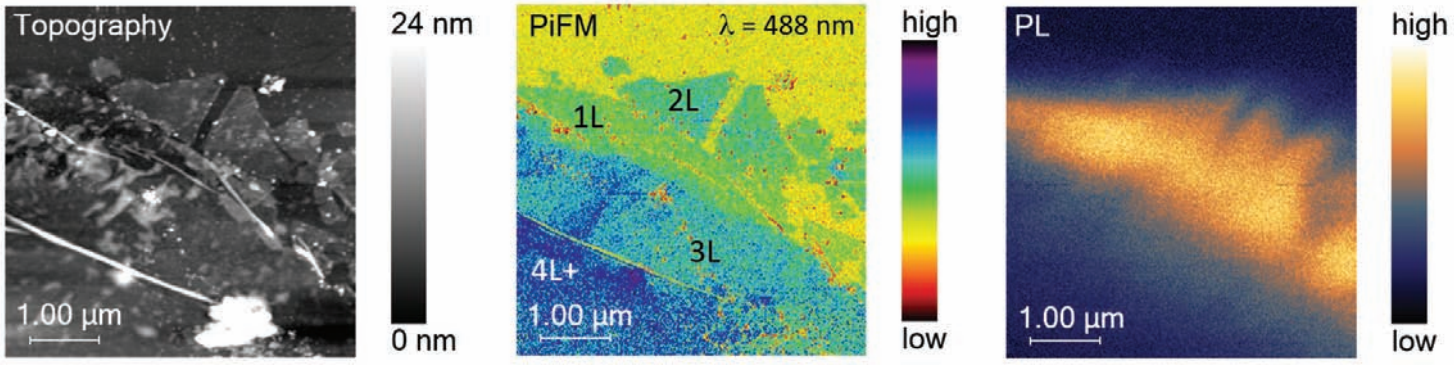
Graphene plasmons (GPs) excited by an infrared laser beam obliquely incident on graphene suspended over a metallic grating with a dielectric spacer are imaged by PiFM. The interference patterns of GPs on the grating trenches (in orthogonal directions) allows the wavelength and propagation distance of GPs to be obtained.



From: Laser Photonics Rev. **2018**, 1800040

Visualization of MoS_2 layers with visible PiFM

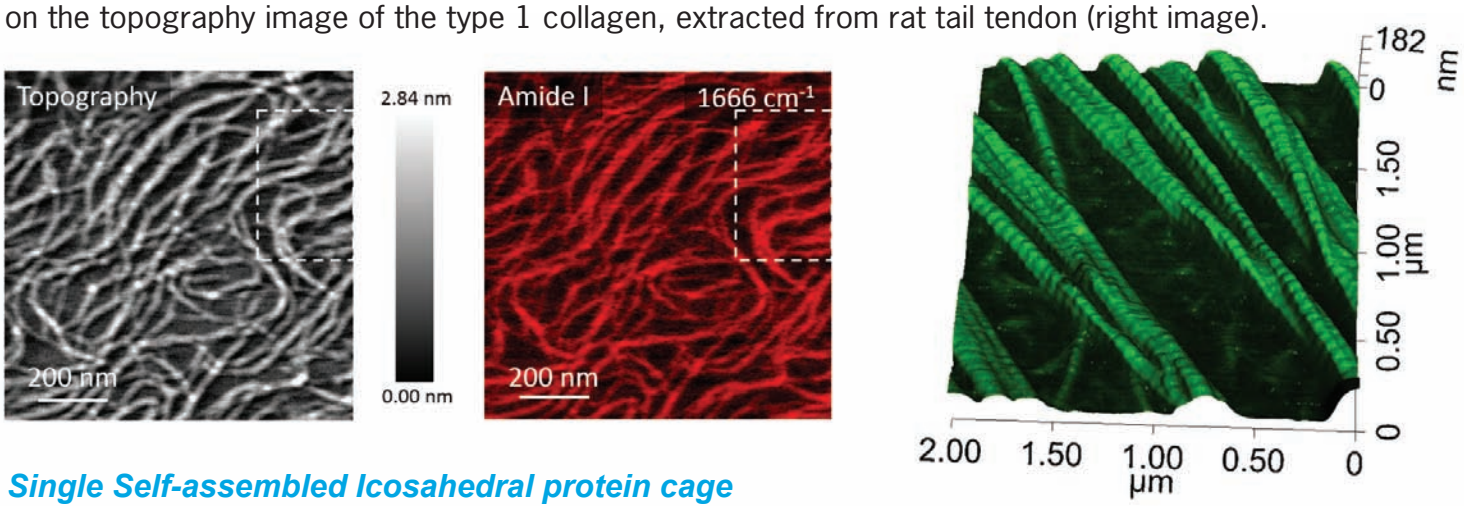
With the optional tunable supercontinuum visible laser (425 nm - 1400 nm), the absorption behavior of 2D materials can be probed with nanoscale spatial resolution. Images of topography, PiFM at 488 nm, and far-field photoluminescence at 680 nm are collected simultaneously, below:



PiFM for Biomedical Research

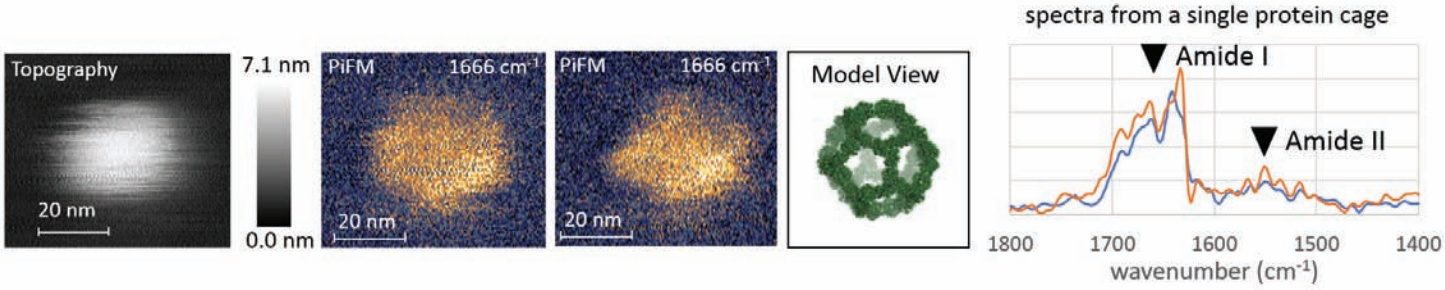
Collagen molecules

PiFM provides exceptional sensitivity to the Amide I band in proteins. Single molecules of triple helix collagen, ~1 nm in diameter, resolve with higher resolution (see details in the dashed box) in the PiFM image than in the topography image. On a separate sample, the Amide I PiFM 1666 cm^{-1} image is overlaid in green on the topography image of the type 1 collagen, extracted from rat tail tendon (right image).



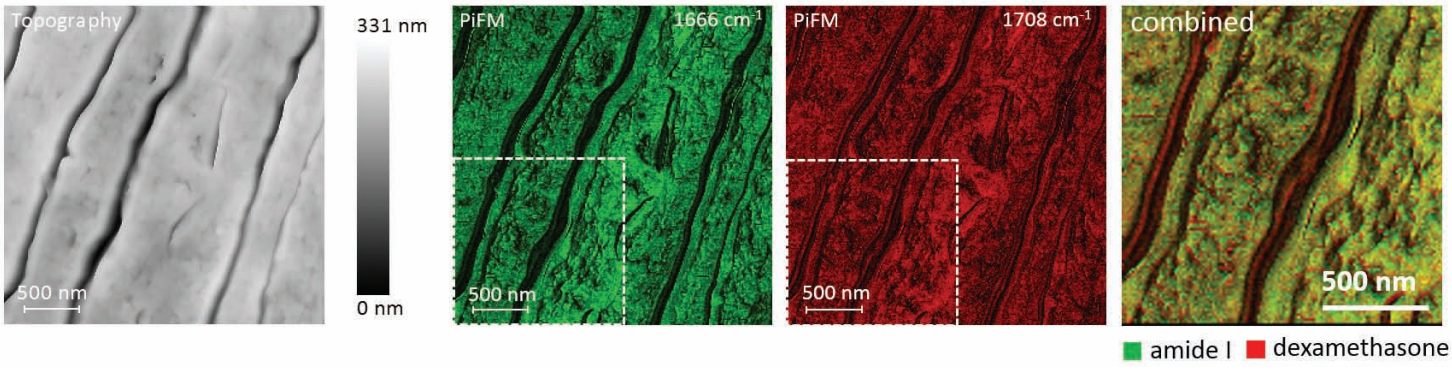
Single Self-assembled Icosahedral protein cage

A single protein cage (theoretical edge length of 7 nm and ~ 14 nm volume diagonal) is imaged via PiFM. While AFM topography image shows a nominally spherical shape, PiFM images hint at different facets whose edges and faces exhibit different amide I (1666 cm^{-1}) signal strength. Two subsequent PiFM spectra taken on the same cage are repeatable with minor variations in Amide I region.



Visualization of human skin samples

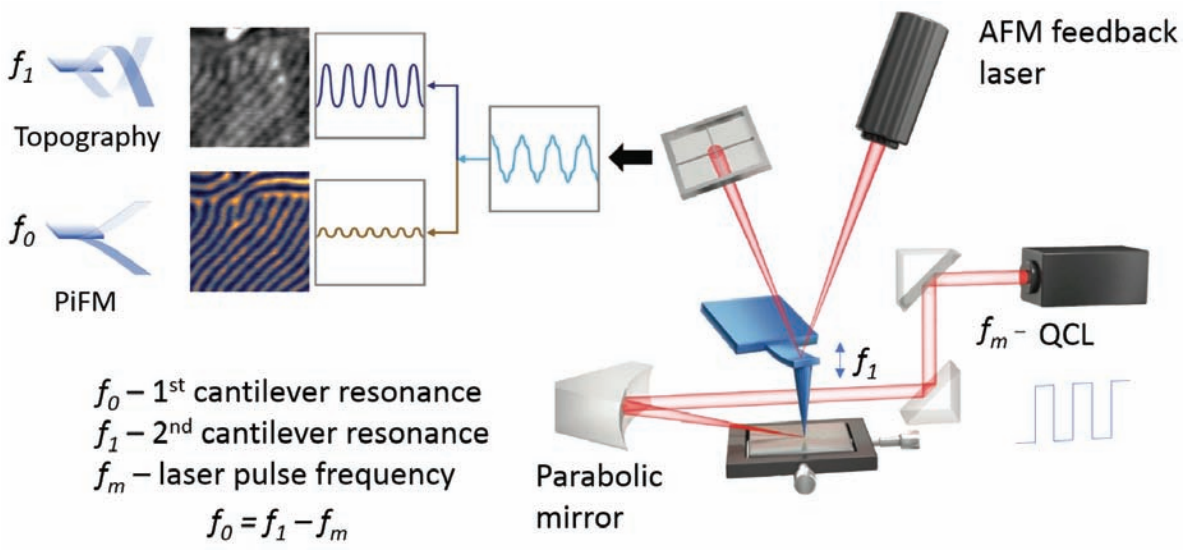
These images highlight the capability of selective label-free probing by PiFM on fixed human skin samples (sliced, 300 nm thick) that were penetrated by topically applied dexamethasone. The chemical contrast indicates that amides probed (green) are mostly located in the corneocytes. However, the topically applied drug penetrates into the lipid lamellae (red) between the corneocytes and fills them partially. The right-most image combines the regions from the dotted white boxes in the two PiFM images.



Infrared Photo-induced Force Microscopy (IR PiFM)

How it works

IR PiFM is an AFM-IR technique that records IR absorption from surfaces via force detection with the resolution of AFM. IR wavelengths specific to different chemical entities resolve the nanometer-scale distribution of each chemical species in diverse multi-phase and multi-component systems. Nanoscale IR spectra can be acquired easily and quickly from any number of sites on the sample surface.



Comparison to other surface analytical techniques

There is a critical void in nanoscale molecular and chemical analysis in contrast to the availability of several techniques for nanoscale elemental analysis. Requiring no special sample preparation, PiFM promises to be a versatile complementary technique to other well-known analytical techniques.

	IR PiFM	Raman	FTIR	TOF-SIMS	XPS	TXRF	SEM/EDS	TEM	Auger
Species Detected	M.I.	M.I.	M.I.	M.I.	M.I.	E.I.	E.I.	E.I.	E.I.
Imaging/ Mapping	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Lateral Resolution	< 10 nm	> 0.5 μm	> 10 μm	> 0.2 μm	10 μm – 2 mm	~ 10 mm	1 nm* 0.5μm EDS	0.2 nm	> 10 nm
Depth Probed	20 nm	> 500 nm	1 μm	1 nm	10 nm	10 nm	1 μm	~ 100 nm	10 nm

* Imaging M.I. Molecular information E.I. Elemental information