

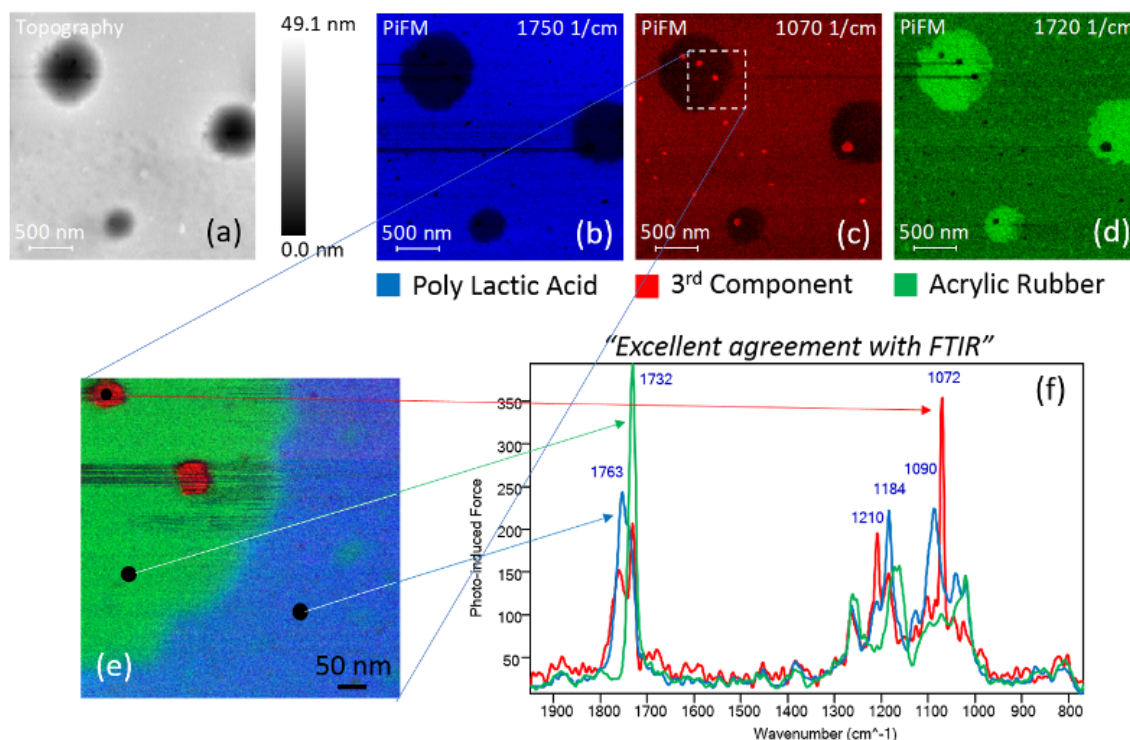
## Application Note

## Chemical Mapping

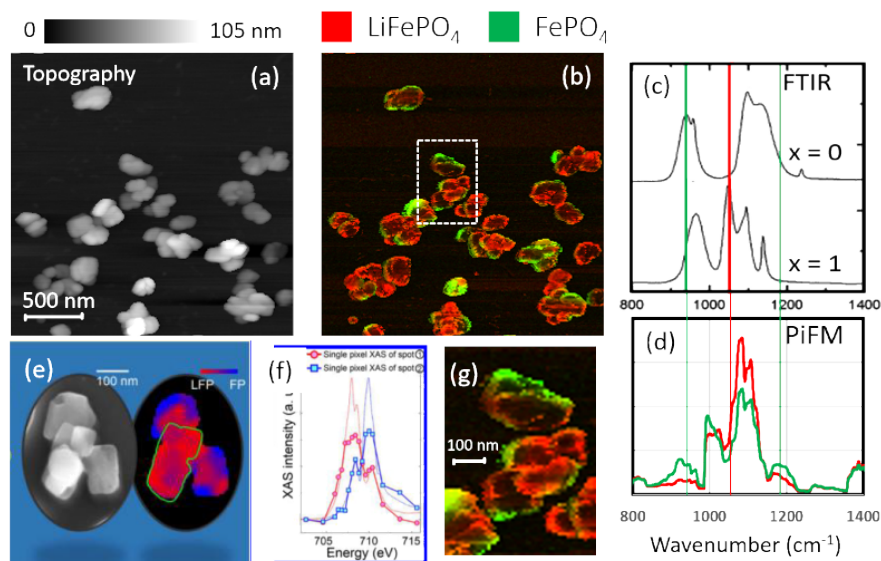
Advances in nanotechnology have intensified the need for analytical tools that can chemically characterize newly synthesized nanomaterials. While electron microscopy (EM) techniques can identify atomic species through energy dispersive X-ray analysis, they offer little help for identification of molecular materials. For identification of molecular species, well established optical spectroscopy (OS) techniques such as Raman and Fourier Transform Infrared (FTIR) are used; their spatial resolutions are governed by the diffraction limit, on the order of a micron,

falling far short of the needs of the nanotechnology and nanomaterial researchers. IR PiFM, which combines AFM with IR spectroscopy, overcomes the diffraction limit of the OS techniques.

Figure 1 shows how PiFM can be used to study a polymer blend, in this case, of poly(lactic acid) (PLA)/acrylic rubber (ACM), which combines a biodegradable thermoplastic and a natural elastomer to create a usable and more eco-friendly material. In practice, especially when the sample constituents are unknown, AFM topography



**FIGURE 1:** (a) Topography and PiFM images at (b) 1750 cm<sup>-1</sup>, (c) 1070 cm<sup>-1</sup>, and (d) 1720 cm<sup>-1</sup> for PLA, 3rd component, and ACM respectively. A zoomed in (e) composite image consisting of three PiFM images and (f) three spectra from locations shown in (e).



**FIGURE 2:** (a) Topography and (b) composite PiFM images at 1054 cm<sup>-1</sup> (for LFP) and at 941 cm<sup>-1</sup> (for FP); (c) FTIR spectra from reference 1; (d) PiFM spectra for green and red regions in (b); (e) and (f) XAS microscopy results from reference 2; and (g) digitally zoomed region defined by white dotted rectangle in (b) digitally zoomed region.

(figure 1a) may be acquired first. Then a few photo-induced force (PiF) spectra can be acquired at unique features in the topography as shown in figure 1f. These spectra have several strong peaks above 1700 cm<sup>-1</sup>. The PiFM laser can then be tuned to one wavenumber to map the absorption response across the sample surface. Image 1b maps PLA via the PiFM response at 1750 cm<sup>-1</sup>. The process can be repeated to acquire PiFM images that show unique features with accompanying spectra (figures 1c and 1d). Different PiFM images can be artificially colored and then combined to form a chemical map as shown in figure 1e where three PiFM images at 1750, 1720, and 1070 cm<sup>-1</sup> are colored blue, green, and red to represent poly(lactic acid), acrylic rubber, and a third component respectively, and combined into one chemical map image. Note that three distinct spectra are acquired from three locations shown in figure 1e and displayed in figure 1f; PiFM spectra can be reliably acquired from regions as small as ~10 nm in size.

PiFM works equally well with inorganics. In the next example, IR PiFM is used to study the chemical changes in lithium iron phosphate (LiFePO<sub>4</sub>) micro- and nanocrystals that occur upon delithiation. LiFePO<sub>4</sub> is commonly used as a cathode material for lithium-ion batteries. X-ray absorp-

tion spectroscopy/microscopy has been used to understand the phase transition from LiFePO<sub>4</sub> to FePO<sub>4</sub> since LiFePO<sub>4</sub> is known to be unstable under electron beams.

Partially delithiated LiFePO<sub>4</sub> (LFP) nanocrystals were analyzed by IR PiFM. Given the small feature sizes, a hyPIR (hyperspectral IR PiFM) image of 256 x 256 pixels (2.5 μm x 2.5 μm scan size) was acquired; such a hyPIR image consists of 65,536 IR PiFM spectra since each pixel contains a spectrum. Figure 2a is the AFM topography of the nanocrystals. Figure 2b is a composite image of two PiFM images, red at 1054 cm<sup>-1</sup> and green at 941 cm<sup>-1</sup>, both derived from the hyPIR image. Figure c shows published FTIR spectra for Li<sub>x</sub>FePO<sub>4</sub> at x=1 and 0. Figure 2d shows two spectra, which are the averages of all the spectra in the respective colored regions in 2b, i.e., the green (red) spectrum is the average of all the spectra that are associated with the green (red) region in figure 2b. Comparing 2d and 2c, we can see that the green and red spectra resemble the x=0 and x=1 spectra, respectively. Most notably, when lithium is absent (x=0), PiFM develops a peak between 930 to 950 cm<sup>-1</sup>, consistent with the FTIR. At x=1, there is a clear shoulder in the PiFM spectrum at ~1050 cm<sup>-1</sup> where a prominent peak shows in the FTIR spectrum. Therefore, figure 2b shows that delithiation process starts from the external edges of

the nanocrystals. Figure 2e shows the nanocrystalline morphology along with the composite XAS microscopy image; red and blue represents  $\text{LiFePO}_4$  and  $\text{FePO}_4$ , respectively. Figure 2f shows the X-ray absorption curves associated with the two crystalline phases. Figure 2g is a digitally zoomed image of the section outlined in white rectangle in figure 2b to compare with 2e at the same magnification. The results agree quite quite nicely.

Next, we analyze a core-shell nanoparticle structure, which is found in many applications. For structures with

case with many other types of microscope. When we analyze the sample at  $1493\text{ cm}^{-1}$ , we can image the PS cores nicely since the shell layer is quite thin ( $< 10\text{ nm}$ ). At  $1720\text{ cm}^{-1}$ , the polymethacrylate shell appears as a donut shape because the PiF signal integrates over more material at the edges; the region shaded by white lines in the inset of the topography shows why the edges appear thicker and will produce stronger PiF signals. When you combine the two PiFM images into a composite image (bottom left), we can clearly map the core and shell materials as if we cross-sectioned through the nanoparticles.

Sample Credits: PLA-ACM: Dr. Rudiger Berger, Max Planck Institute, Mainz;  $\text{LiFePO}_4$ : Prof. Jordi Cabana, Univ. of Illinois, Chicago; core-shell star polymer: Dr. Young-Hye La, IBM Almaden Research Center.

## References

- [1] Spectrochimica Acta Part A 65 (2006) 1007–1013
- [2] Nano Lett. 2015, 15, 4282–4288

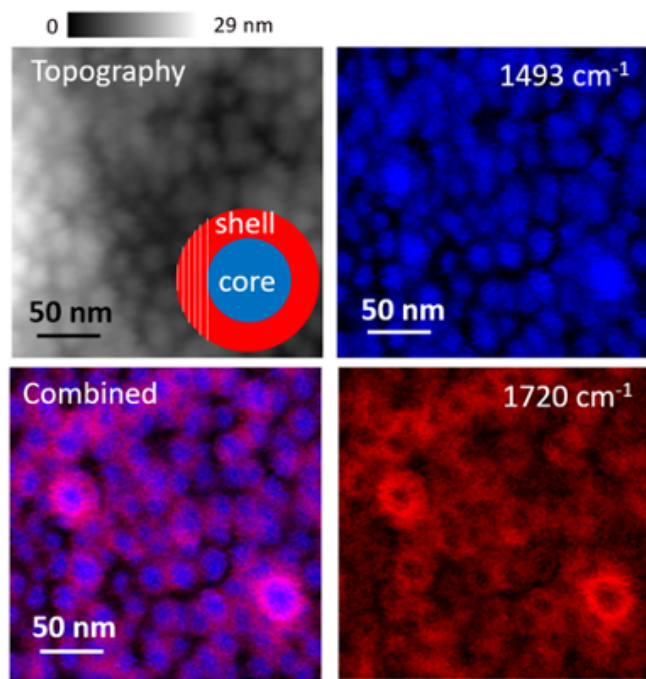


FIGURE 3: Topography and PiFM images of core-shell star block copolymer that consists of hydrophobic PS core and hydrophilic polymethacrylate shell.

ultrathin organic shell layer, there is no straightforward way to confirm the existence of the shell layer. With PiFM, the measured signal is integrated to a thickness of about 20 nm. Therefore, if the shell layer is not thicker than  $\sim 10\text{ nm}$ , we should be able to measure the core material through the shell layer. Figure 3 shows a core-shell star block copolymer that consists of hydrophobic PS core and hydrophilic polymethacrylate shell. AFM topography (top left image) shows spherical structures with no information about the presence of the shell layer as would be the