New Hybrid Peak-Force Tapping/Near-Field Microscope for Nano-Chemical and Nano-Mechanical Imaging of Graphene Plasmons, Polymers and Proteins

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Heterogeneous material systems in biomedical and chemical sciences as well as ever decreasing feature sizes in nanotechnology require new nanoscale material characterization techniques. Infrared spectroscopy can give valuable information on chemical composition, but conventional, far-field techniques such as Fourier-Transform Infrared (FTIR) spectroscopy are limited in spatial resolution to approximately the employed wavelength, i.e. several micrometer. Scattering-type scanning near-field optical microscopy (s-SNOM) is a near-field technique that is based on an atomic force microscope (AFM) and detects tip-scattered light in the infrared spectral region [1]. Spatial resolution in s-SNOM is only determined by the AFM tip radius and can reach down to 10nm, making s-SNOM a widely accepted tool for nanoscale chemical characterization.

Another valuable AFM technique for material characterization is Bruker's peak-force tapping that allows precise force control between tip and sample down to 10s of pN which is essential for imaging fragile material systems [2]. Nano-mechanical properties such as modulus, deformation or adhesion can be quantitatively extracted from the measured force-distance curves down to atomic defect resolution. This technique can be complemented by Kelvin-probe force microscopy (KPFM) to extract electrical information such as the work function.

Here, we present the first combination of optical, mechanical and electrical characterization techniques with sub-20nm resolution. We employ a hybrid system based on s-SNOM and peak-force tapping which is implemented in the Inspire instrument, built on the MultiMode AFM platform. The MultiMode AFM with peak-force tapping enables ultrahigh resolution imaging as demonstrated for atomic defects or the DNA double helix [3]. The s-SNOM imaging tool allows direct measurement of nanoscale absorption and reflection properties with up to 10 Hz imaging speed.

In our presentation we will discuss how the different measurement modes are combined and we will give examples of the benefits of such a hybrid system. We address several questions ranging from graphene plasmonics to material distributions in polymers. For instance, Fig. 1 shows representative, quantitative data obtained on a PS-LDPE polymer blend, revealing softer and less reflective LDPE domains in the PS matrix. Amongst other examples, we highlight a biological application where amelogenin protein samples were investigated. Amelogenin is a protein that is critical to dental enamel formation [4,5]. In the presence of calcium and phosphate ions it self-assembles into ordered, self-aligned nanoribbon bundles, which suggests that it could form a template for phosphate-based apatite crystals that comprise dental enamel with similar ordering. To help clarify that open question, mapping the distributions of phosphate and hydroxyapatite nanocrystals within the bundles is necessary. With a nanoribbon width of <30nm, s-SNOM is the ideal tool to simultaneously map topography and chemical content. Figure 2 shows that the amelogenin bundles absorb at 1097cm^{-1} close to the phosphate resonance, whereas no absorption is observed at 1020cm^{-1} away from the phosphate absorption line. While the presence of phosphate could be identified using s-SNOM, no apatite nanocrystals with higher

modulus than the ribbons could be distinguished in peak-force tapping in our preliminary data, indicating that for these *in vitro* preparation conditions apatite crystals have not formed yet (Fig. 3). We will also discuss a phosphorylated peptide derived from amelogenin amino acid sequence that assembles into ribbons without phosphate ions in solution. Here, s-SNOM is used to locate phosphate within the nanoribbon assembly, providing insight on the precise organization of the peptide molecules.

In conclusion, we present a novel tool for combined near-field optical, nano-mechanical and nano-electrical studies of heterogeneous material systems along with examples covering graphene plasmons, polymers and proteins involved in dental enamel formation.

References:

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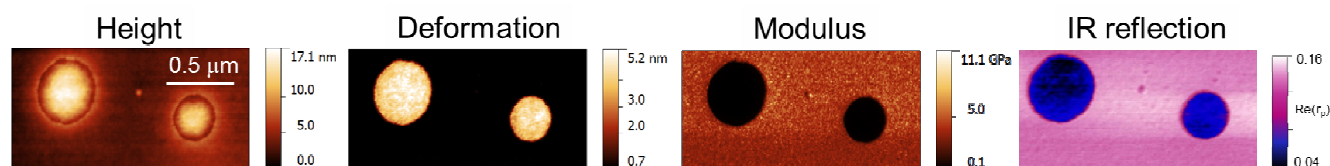
Figure 1. Quantitative nano-mechanical and nano-optical imaging of a PS-LDPE polymer blend. LDPE domains show higher deformation, lower modulus and lower reflection.
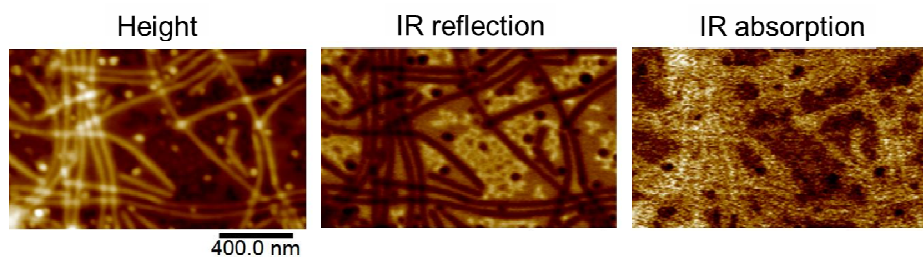
Figure 2. Amelogenin nanoribbons in topography, infrared reflection and absorption at 1097cm^{-1} close to the phosphate resonance. Phosphate is concentrated in the nanoribbons and partially on the Si substrate from preparation.
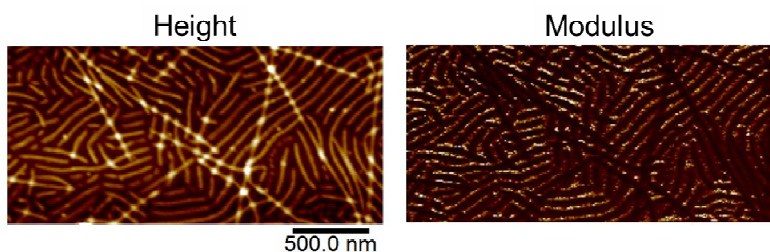
Figure 3. Topography and modulus map of Amelogenin nanoribbons. Hard apatite crystals are not present in the modulus image that reveals softer ribbons (dark areas) and hard Si substrate (bright areas).