Optonanomechanical Spectroscopic Imaging

Frequency Mixing via Photoacoustic and Mechanical Excitation

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An outstanding problem in biomass based biofuel production is the efficient extraction of cellulosic material trapped in the lignin network in plant cell walls. Lignin can be removed by chemical processing. However, the resulting chemical and morphological traits need to be studied at the nanoscale. To achieve this, we introduce the hybrid photonic nanomechanical force microscopy as a new nanometrological technique with promising capabilities to aid in the chemical imaging of biomass and beyond.

While optical microscopy has contributed tremendously to the understanding of matter and further development of powerful "super-resolution" techniques [1], during the last few decades, atomic resolution mechanical microscopy has opened up new opportunities in the field of nanometrology by providing a largely noninvasive method to map topography and surface properties of materials [2]. The plant cells, in all its biomolecular and morphological complexity [3], provides a challenging test bed for the optical and mechanical modalities so that no single modality is indeed capable of providing a full description of its substructures and organization. Removing lignin from the plant cell walls requires studying its chemical and morphological characteristics at the nanoscale [4]. The hybrid photonic nanomechanical force microscopy is an emerging opto-mechanical multi-frequency mixed modality with promising capabilities to aid in the chemical imaging of materials. Specifically, here we study samples of biomass by comparing images of extractive free poplar cross-section of 20 µm thickness acquired from three scanning probe microscopy modalities.

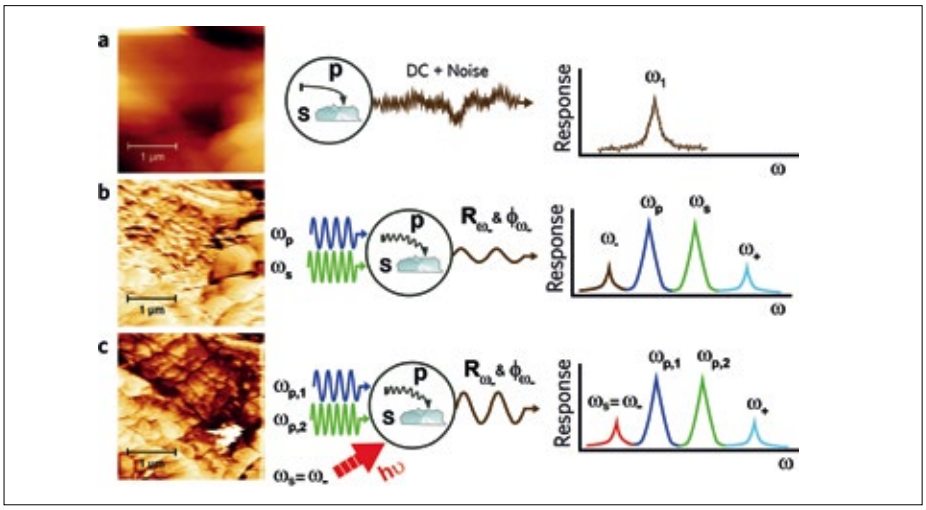

Fig. 1: Characterization of extractive-free, 20 µm-thick Poplar cross sections using three scanning probe modalities. a, Atomic force microscopy (AFM). b, Mode synthesizing atomic force microscopy (MSAFM) where the interacting coupled probe-substrate ensemble with applied stimuli at ω_s and ω_p synthesizes new modes at $\omega_-=|\omega_s-\omega_p|$ and $\omega+=\omega_s+\omega_p$. c, Hybrid photonic force microscopy (HPFM) applies modulated IR light $h\upsilon$ to the sample at the first mode produced by the probe excitations ($\omega_s=\omega_-$), thus revealing cellulose-rich and lignin-rich regions.

More information on nanospectroscopy: http://bit.ly/nano-spectroscopy

Read more about cantilever used in AFM: http://bit.ly/AFM-cantilever

[1] References: http://bit.ly/IM-Passian-1

Non-Invasive Surface and Subsurface Analysis

To understand the organization and distribution of both synthetic and biological materials, it is important to be able to examine surface and subsurface domains for the presence of spatial and spectroscopic inhomogenities in a non-invasive manner. The most straightforward approach is atomic force microscopy (AFM) [5], where a force-sensing cantilever with a sharp tip is used to measure the topography and other properties of surfaces, shown in figure 1a. As the tip is scanned over the surface it experiences attractive and repulsive forces that depend on the chemical and mechanical properties of the sample as well as environmental parameters, such as humidity and temperature [2]. Various scanning probe microscopies have been developed, such as kelvin probe force microscopy (KPFM), magnetic force microscopy (MFM), photon scanning tunneling microscopy (PSTM), near-field scanning optical microscopy (NSOM), and scanning capacitance microscopy (SCM), where electromagnetic and intermolecular processes generate a signal. While probe-based scanning systems are largely limited to surface characterization, if the material has certain electro-magnetic properties then some subsurface information may be obtained using these specialized modalities.

Application of Mode-Synthesizing Atomic Force Microscopy

However, the generalized ability to explore the interior of materials for the presence of anisotropy or nonuniformity (e.g., structural or density variations, presence of contaminant, etc.) remains a challenge, especially for biological materials. Inspired by earlier work on ultrasonic microscopy, AFM can be configured to provide acoustic/mechanical stimulation to reveal the local physical properties of the material at high spatial resolution [6]. By making use of the nonlinear nanomechanical coupling between the probe and the sample, a range of surface and subsurface information can be obtained. This technique, which we termed mode-synthesizing atomic force microscopy (MSAFM), relies on multi-harmonic excitation of the sample and the probe [7]. Shown in figure 1b, a micro-cantilever, a mechanical oscillator with frequency ω_p, interacts with a surface of interest by means of a van der Waals potential prevailing in the nanometer interfacial region between the surface s and the cantilever probe tip p. The (sample) surface may be considered to constitute a second mechanical oscillator, with a frequency ω_s resulting from a force exerted on the sample by the ultrasonic vibrations of a piezoelectric material at the contact interface. The resulting MSAFM image, acquired from the amplitude R of the signal by locking onto the cantilever motion with reference to the difference between the sample and probe frequencies ($\omega_- = |\omega_s - \omega_p|$), reveals new detail of the substructure by detecting the localized changes in the sample elastic properties. The identification of material inhomogeneities using MSAFM can be remarkable. Single-walled carbon nanohorns (70-100 nm) inside mouse cells, undetected with AFM, have been imaged with ultrasonic microscopy due to the difference in elasticity and density between the nanoparticles and the cellular material [7].

Combining Scanning Probe System with Chemical Identification Capability

While MSAFM can make precise domain distinctions via the materials' mechanical response, the interpretation of chemical content can be ambiguous. Due to such limitations of individual techniques, hybrid approaches that integrate complementary capabilities offer powerful characterization tools [8]. Borrowing from infrared photoacoustic spectroscopy, chemical identification can be achieved by photothermally stimulating the sample via its available absorption bands. However, due to the diffraction limit, high spatial resolution infrared spectroscopy using conventional optical methods is prohibitive. Noting that optical absorption due to atomic and molecular composition of the material can lead to small mechanical actuations, we introduce an infrared beam of light $h\upsilon$ to an MSAFM system as another mechanical stimulant to the sample, combining the high resolution afforded by the scanning probe system and chemical identification capability from absorption spectroscopy. By modulating the infrared beam $h\upsilon$ at frequency ω_s in the 9-10 µm "fingerprint" spectral region at the difference mode ω_- of a dual-excited probe, that is, at $\omega_- = |\omega_{p2} - \omega_{p1}|$, we create a new signal modality, the hybrid photonic force microscopy (HPFM) [9], shown in figure 1c. The HPFM image of the Poplar cross-section provides further clarity to the sample's substructure compared to MSAFM. Additionally the HPFM image reveals cellulose-rich (darker) and lignin-rich (lighter) domains due to the overall difference in photothermal response of the material composition. Thus, both optical spectroscopy and high-resolution microscopy can be simultaneously achieved with HPFM. Furthermore, MSAFM and HPFM signal transduction and image formation can occur in an expanded frequency space via the various levels of coupling facilitated by the nonlinear probe–surface interaction [10]. The subsurface capability of the MSAFM and HPFM, which has not been fully investigated, may be conceptually illustrated, for example by computational means. It is possible to demonstrate subsurface detection of embedded inhomogenities computationally [10] by obtaining sample surface traction forces and velocity due to mechanical excitation from the sample-substrate interface. Other modeling efforts continue to contribute to the understanding of the subsurface signal formation [11].

Conclusion

In conclusion, multifaceted material characterization is the key to consistent and holistic investigation of complex biomaterials. An example is finding solutions to achieve economical biofuel production, which is still an ongoing challenge in part due to lack of adequate nanometrology. Gaining better insight into the chemical and mechanical aspects of the plant structure at the nanoscale through HPFM imaging is one contribution that can aid in this goal. As an emerging technology, the possibilities of HPFM such as imaging by employing multiple frequencies still have yet to be explored.

References

All reference you can find online:
http://bit.ly/IM-Passian-1

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