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Nanometrology of Populus plant cell walls

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Abstract

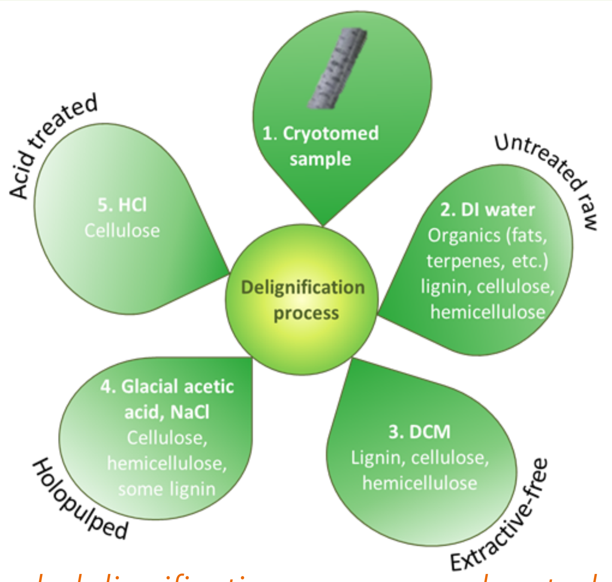
Populus is an abundant plant species suitable as lignocellulosic feedstock for biofuel production. Delignification of the biomass is a necessary step toward large-scale production of biofuel. How the various chemical treatments that have been explored for biomass deconstruction affect the morphology and chemical composition of the plant cell walls is not well-understood. In this purpose, nanometrology of biomass can greatly help developing better understanding of the cell wall properties and can thus lead to better biomass treatment and ultimately to a more efficient biofuel production.

Context

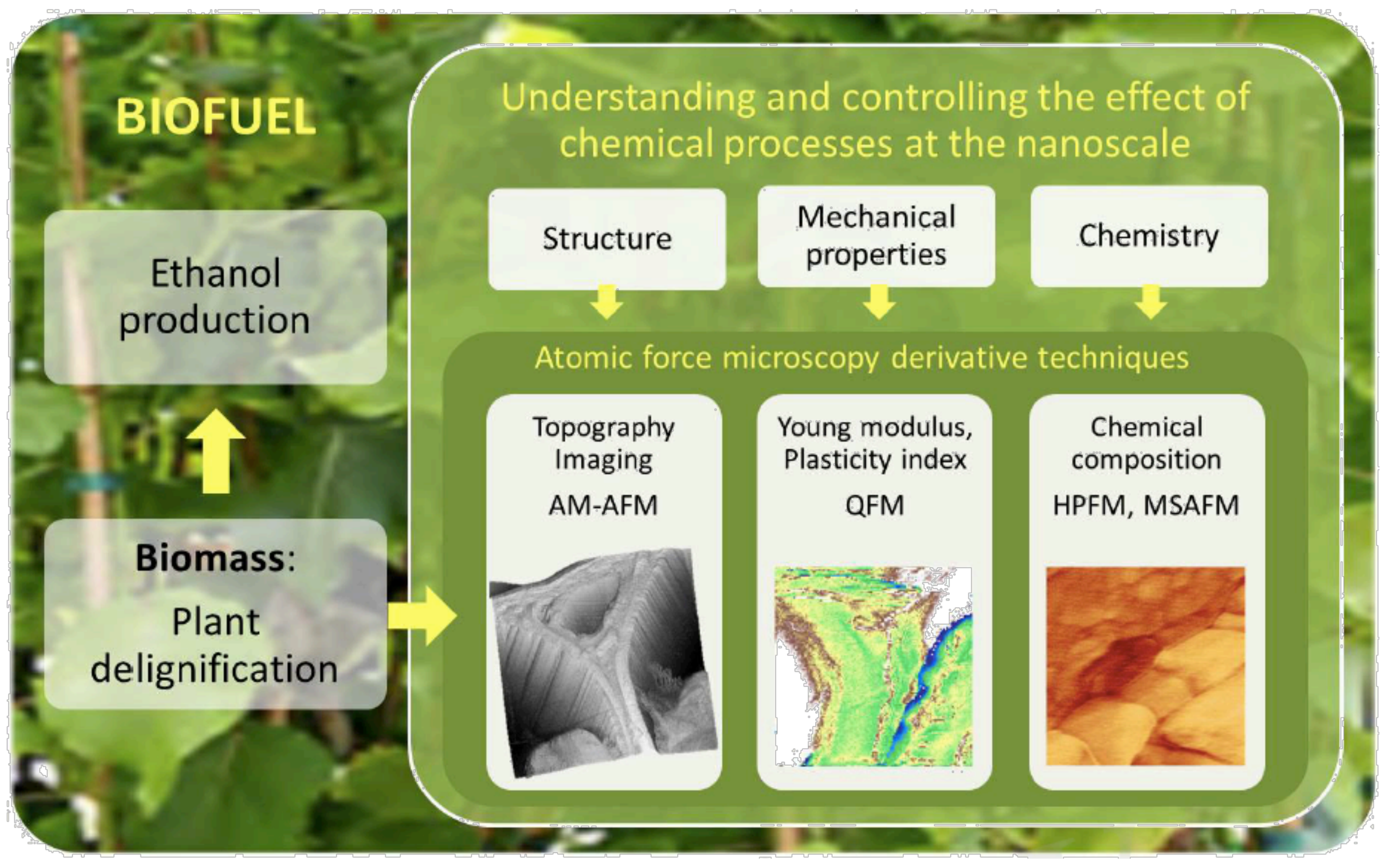
Biofuel production

We aim in exploring delignification process using chemical treatments over Populus cross-section samples at the nanoscale through the chemical compositon, the structural changes and the mechanical properties.

We therefore involved Atomic Force Microscopy and derivative modes (AFM, QFM, and HPFM).



Chemical delignification process under study starting from cryotomed cross-section samples

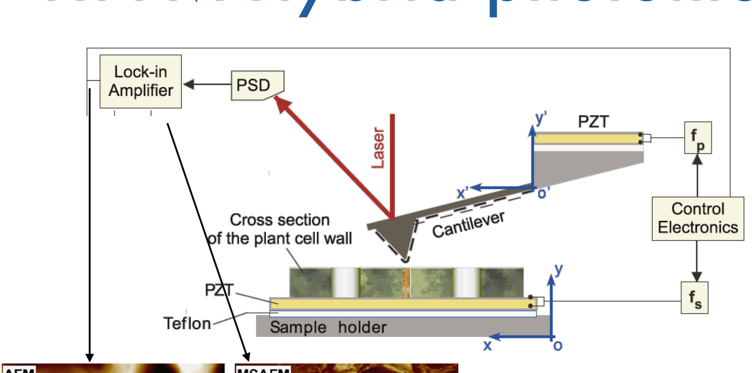


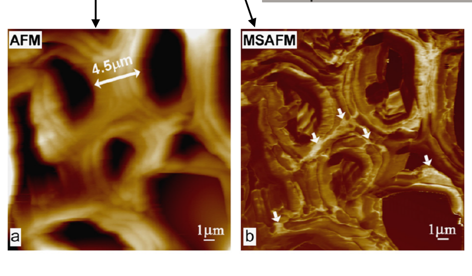
General scheme illustrating the inputs of AFM measurements in understanding and controlling the effect of chemical processes for biomass extraction towards biofuel production. Structural, mechanical and chemical properties are extracted and correlated using various AFM modes

Chemical composition

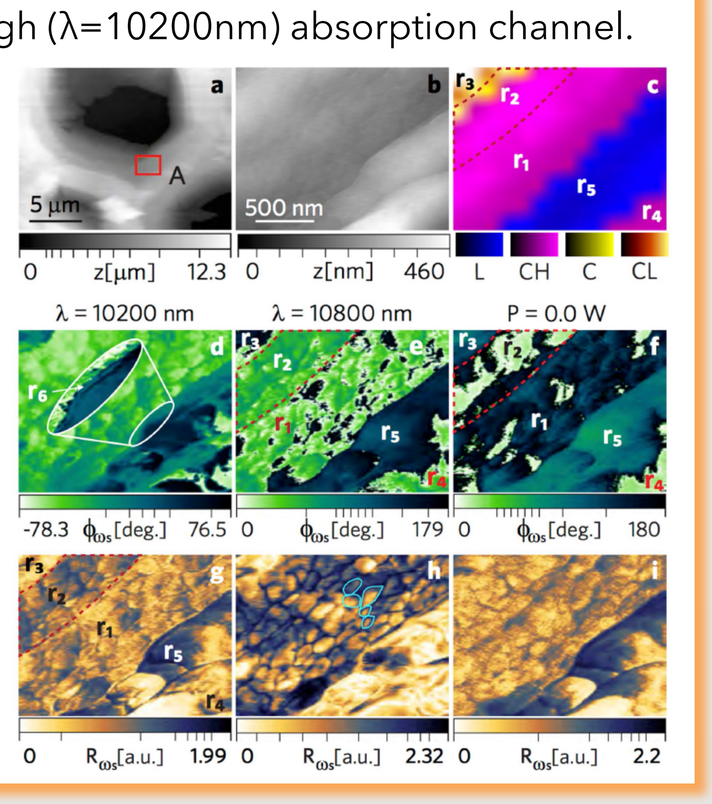
HPFM-Hybrid photonic FM

Resolving cell wall ultrastructure and chemistry. HPFM image acquisition via frequency mixing involving photoacoustic sample (EF) actuation and cantilever multifrequency oscillations. The photoacoustic sample actuation is achieved using an amplitude modulated QCL tuned to a low (λ=10800nm) and high (λ=10200nm) absorption channel.





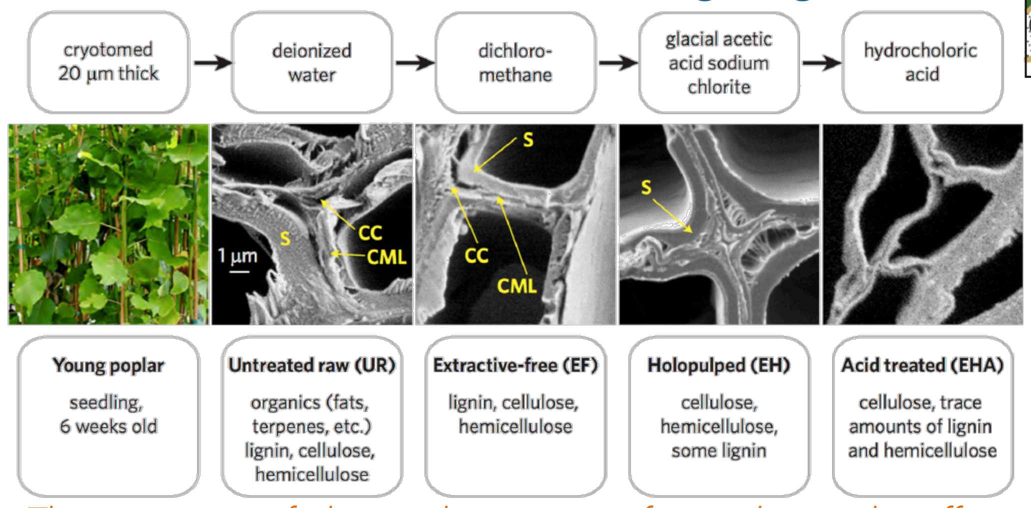
-Tip-surface with a driven frequency f=nfs+mfp
-Large number of mode-synthesized for in-depth imaging
-Resolution of few nm evidencing new features



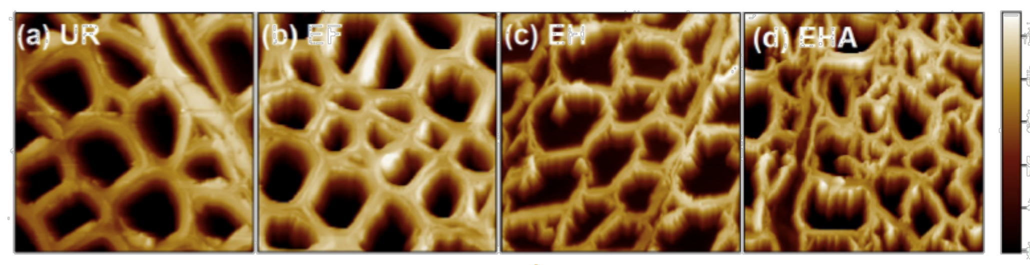
(a) Contextual AFM image (in contact mode) indicating the examination area, A imaged in (b). (c) Raman image over A with marked regions, r1 through r5, of the cell structure. (d,e,f) Phase images at laser wavelengths of λ = 10200 nm and λ = 10800 nm at P = 1.3 mW, and P = 0 mW (no photonic actuation). (g,h,i) Corresponding amplitude images to the above phase images, with 100 to 200 nm wide cellulose agglomerates outlined in (h).

Structural changes

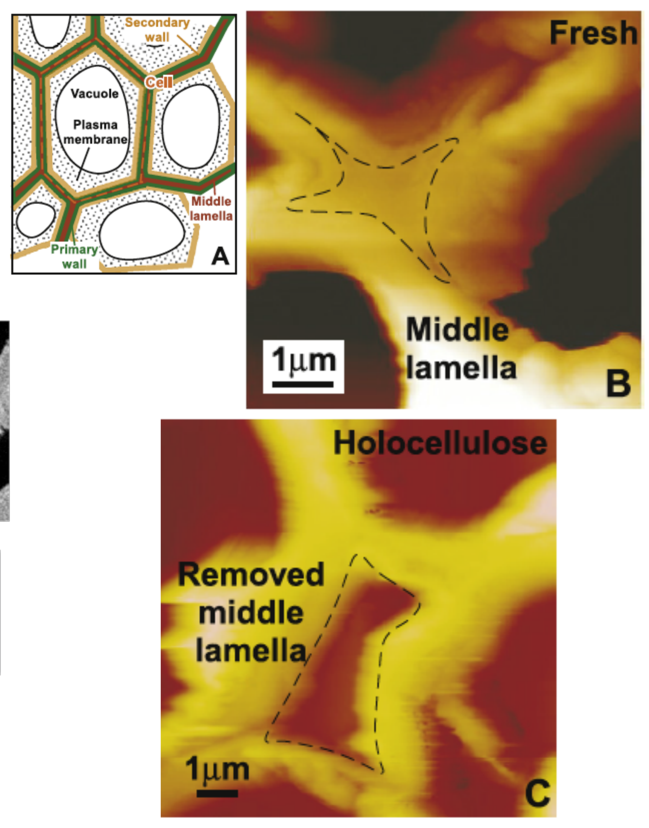
SEM and AFM imaging



The sequence of chemical treatments for exploring the effect of lignin loss. The scanning electron microscope images (5000xmagnification) of the samples at each stage of the chemical processing.



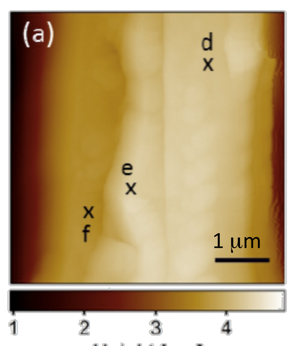
AM-AFM topographic images of untreated raw (UR), extractive-free (EF), holopulped (EH) and acid-treated (EHA) samples showing the structural changes along the delignification process (image size 50 × 50 µm²).



Effect of the chemical treatment on the cell walls (B) and (C). Topography images of the fresh Populus (B), and holocellulose Populus (C). The chemical treatment contributed to the removal of the middle lamella across the sample as shown in brown in (A), resulting in a change of mechanical properties of the cell walls.

Nanomechanical properties

QFM-Quantitative FM: nanoindentation

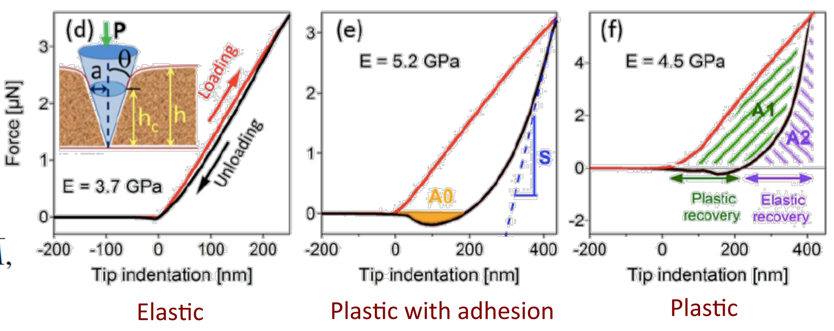


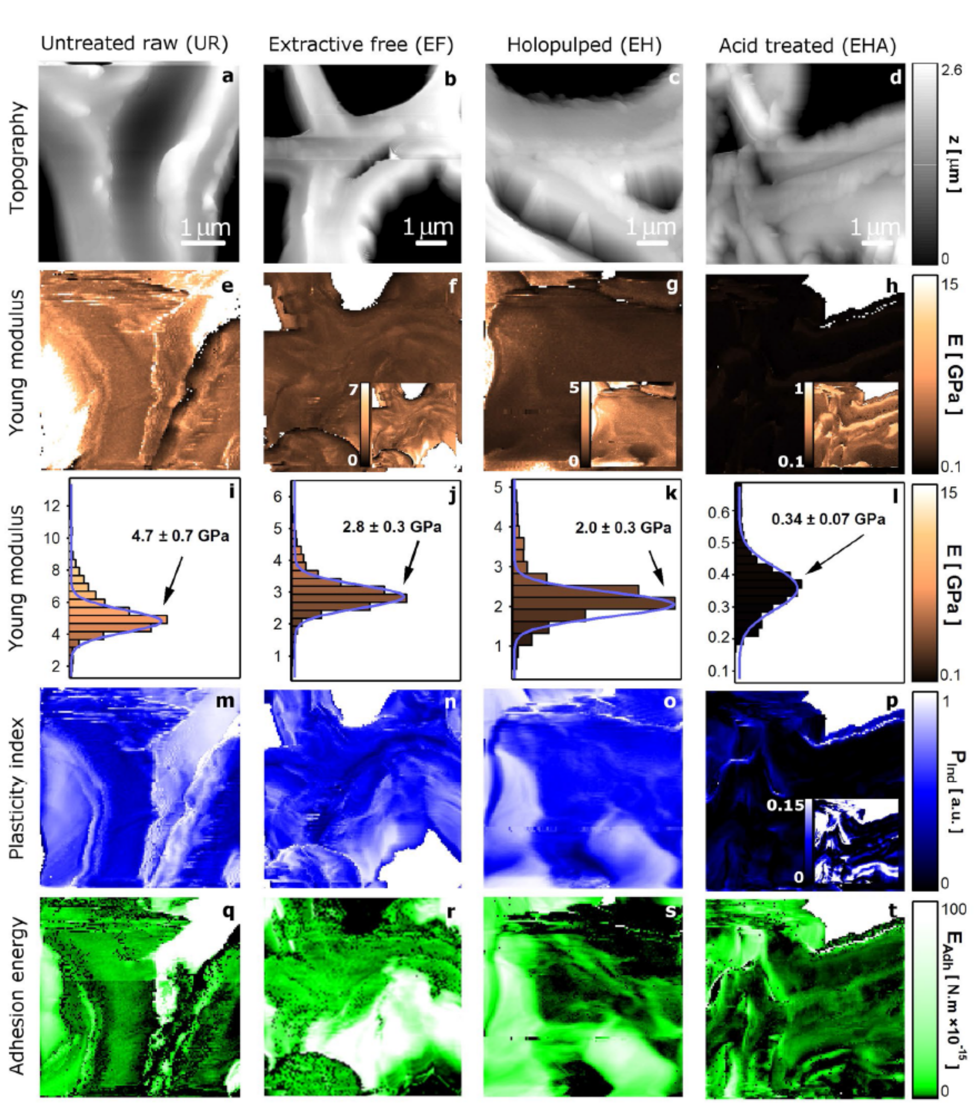
Force-indentation curves give the experimental determination of elastic, plastic and adhesion properties of the examined regions.

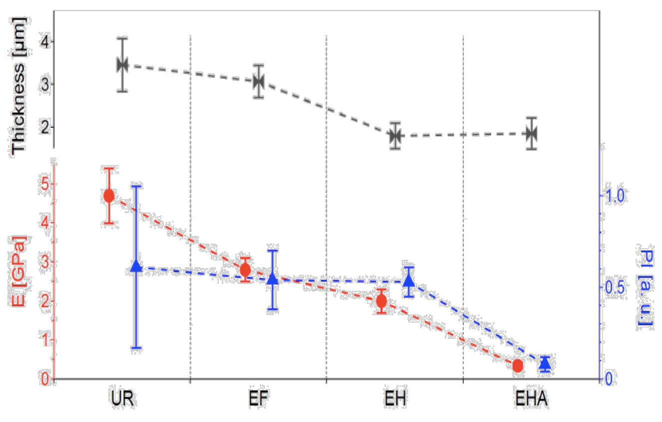
$$S = dP/dh = 2/\sqrt{\pi} \times E/(1-\nu^2) \times \sqrt{A},$$

$$0 \leq PI = A_1/(A_1+A_2) \leq 1$$

Perfectly elastic — *Fully viscoplastic*







Tracing the physical traits of the delignification sequence. (a-d) Topographic effects on the treated cell walls by AFM. (e-h) Mapping of the elasticity variations due to lignin removal. The contrast presents computed Young moduli E assuming Sneddon model. The reduced Young moduli is notable in the EHA case. (i-l) Distribution of the computed E indicating the loss of elasticity caused by the drop in lignin content. (m-p) Observation of plasticity index P where plastic-like behavior emerges due to lignin removal and (q-t) mapping the localized surface adhesion energy.

Conclusion

We observe that the nanomechanical properties of the cell wall, as lignin is removed through the delignification process, expose a quantifiable reduction in Young modulus, visco-plasticity and adhesion energy associated to the chemical and structural changes during delignification process. This shows the real impact of AFM and derivative modes for correlative nanometrology to understand delignification of the biomass and in a long run serve in controlling lignocellulosic feedstock.

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