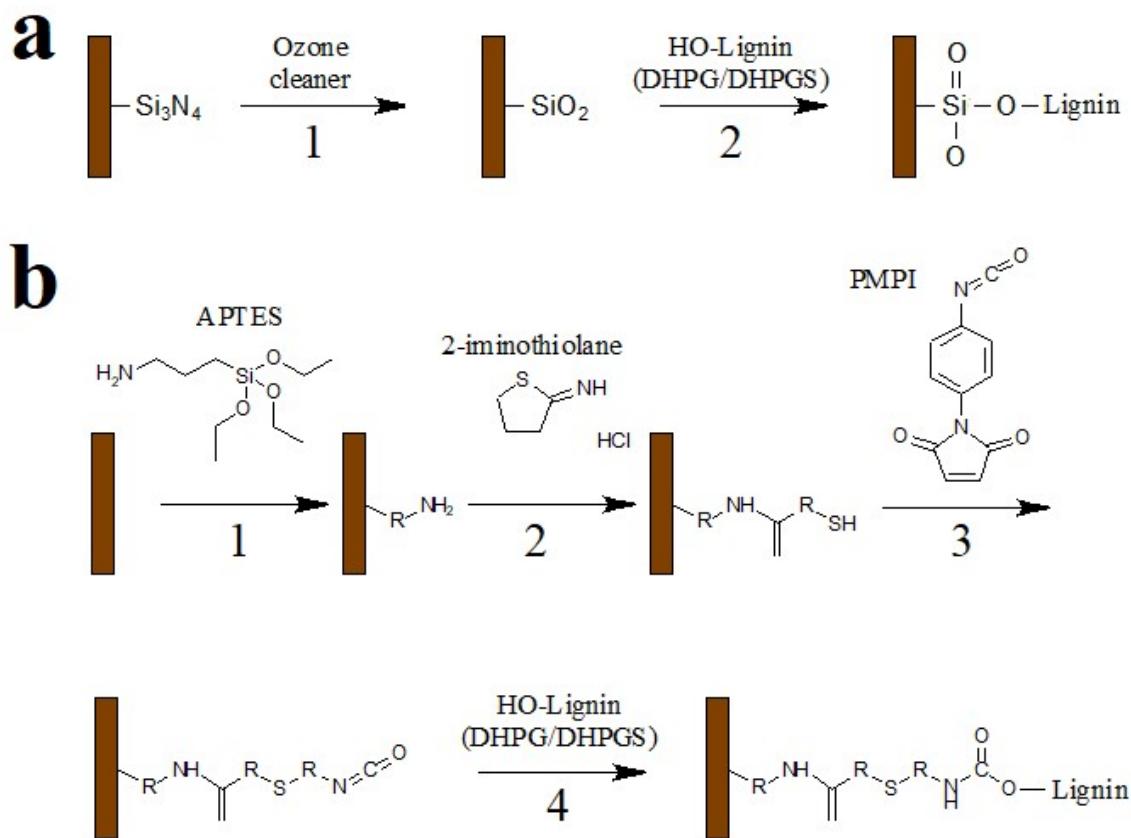


## SUPPLEMENTARY INFORMATION

### Materials and Methods

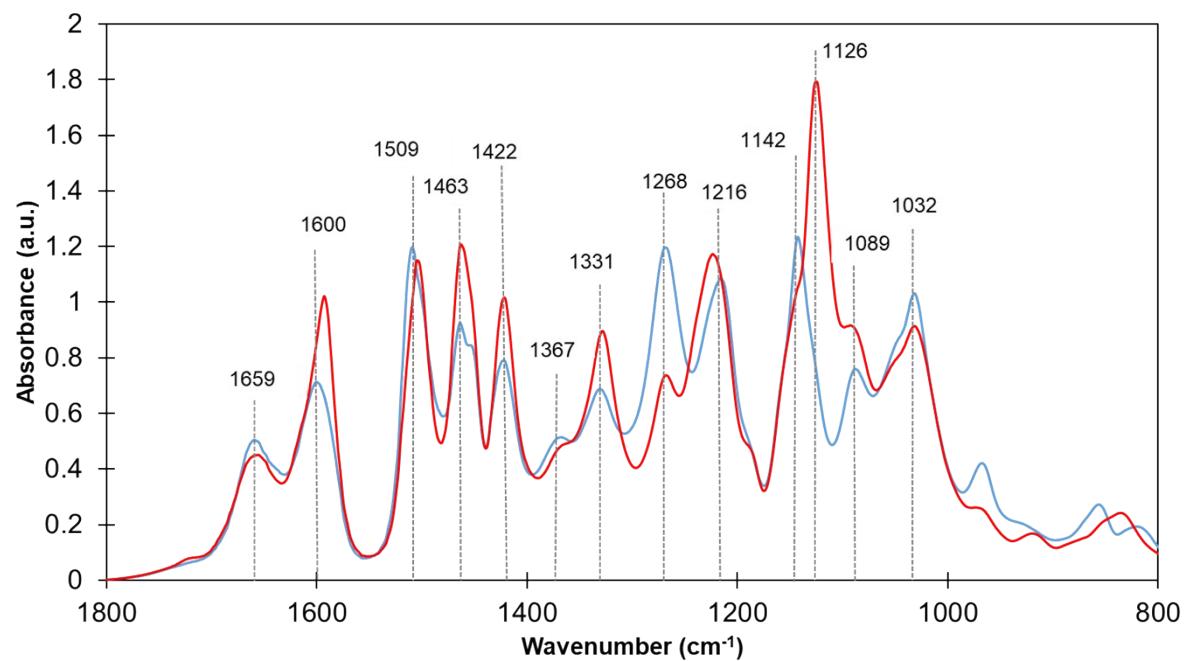
#### Chemical grafting procedure and Langmuir-Blodgett (LB) procedure



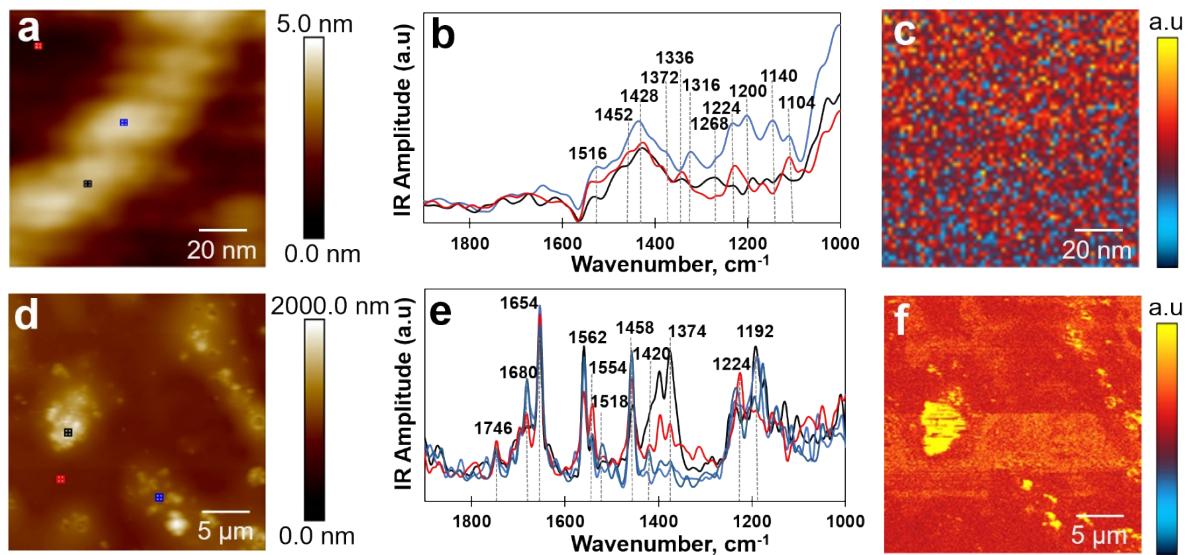
**Figure S1.** (a) Representation silicon surface modification following LB strategy. 1) Ozone exposition oxidizes silicon nitride moieties from the flat surface exposing silicon dioxide groups. 2) After LB procedure, DHP-G/DHP-GS are covalently tethered to the silicon surface by Si-O linkage. (b) Scheme of the subsequent chemical steps to covalent lignin attachment on silicon flat surfaces. 1) Exposition of amine groups after aminofunctionalization procedure in presence of APTES in vapour phase. 2) Reaction of previous formed amine groups with Traut's reagent facing up active sulphydryl moieties. 3) Thioether linkage between previously formed  $-\text{SH}$  group and maleimide from heterobifunctional PMPI linker. 4) Formation of stable covalent urethane bonds between isocyanate group from prefunctionalized surface and DHP-G/DHP-GS hydroxyl groups.

## Results and discussion

### AFM-nanoIR measurements

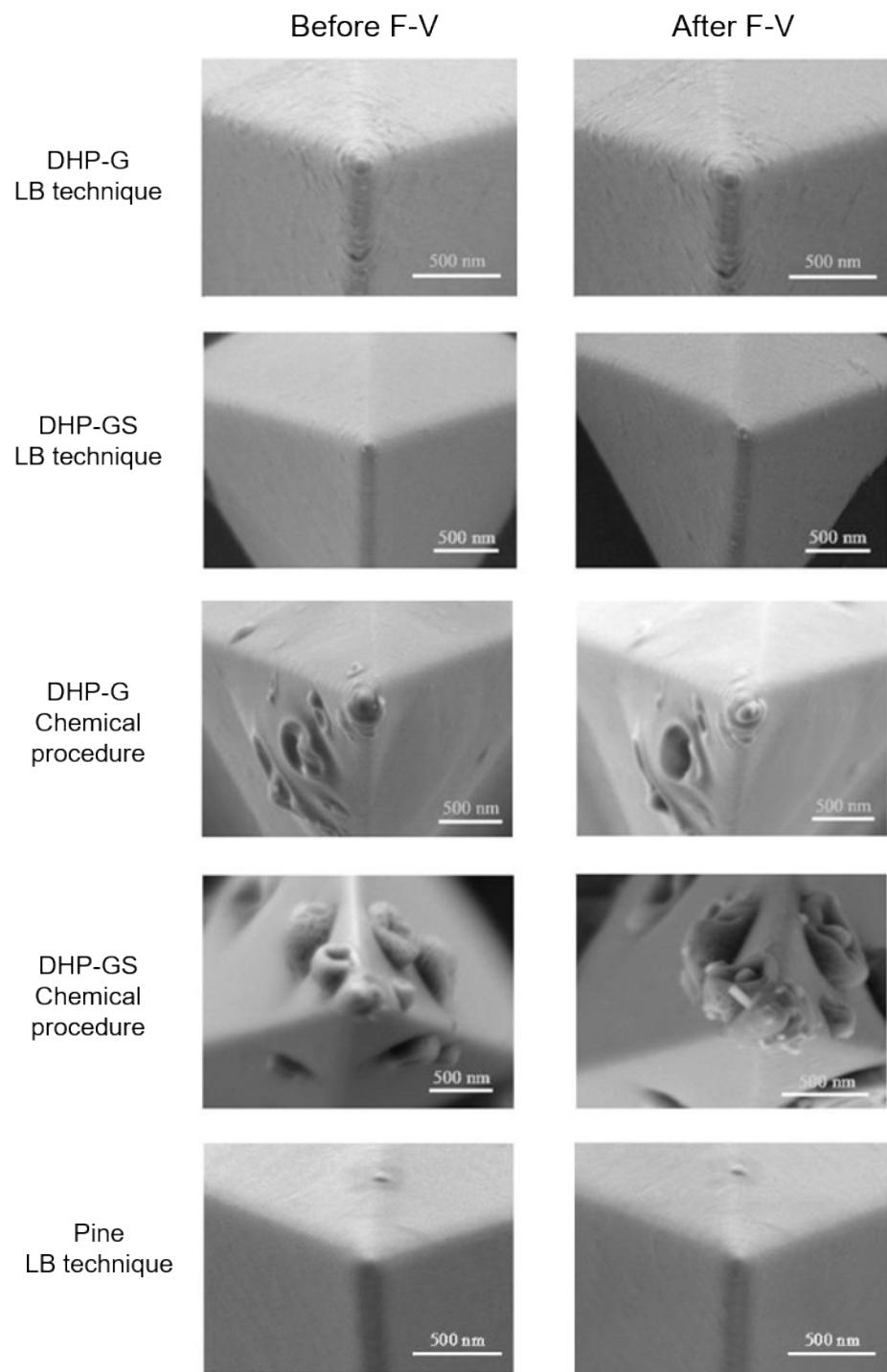


**Figure S2.** FTIR spectra of DHP-G (blue line) and DHP-GS (red line). Spectral region ranges from 800 cm<sup>-1</sup> – 2000 cm<sup>-1</sup>. Black arrows indicate IR peaks corresponding to DHP-G/DHP-GS.

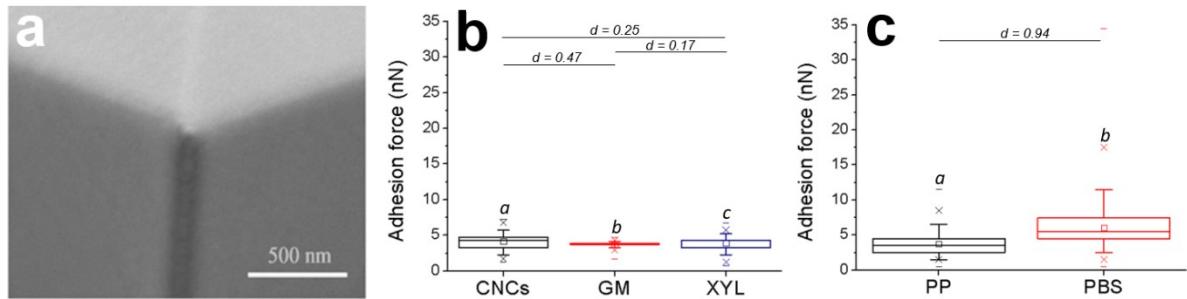


**Figure S3.** AFM-nanoIR measurements of functionalized thin silicon surfaces with DHP-GS by LB technique (**a-c**) and the chemical procedure (**d-f**). Topography image (**a, d**) with full IR spectra (**b, e**) - wavenumbers from  $1000\text{ cm}^{-1}$  to  $2000\text{ cm}^{-1}$ ). Local IR spectrum was recorded at color points selected from AFM topography image (resolution  $4\text{ cm}^{-1}$ ). AFM-nanoIR maps (**c, f**) at  $1520\text{ cm}^{-1}$  from the same scanned area (**a, d** respectively).

**Force spectroscopy experiments with AFM tips functionalized with DHP-G/DHP-GS.**



**Figure S4.** SEM images of functionalized AFM tips with DHPs by chemical procedure and LB technology before and after F-V experiments. Scale bar is 500 nm for all images.



**Figure S5.** SEM image of AFM tip negative control after spectroscopy force experiments (a). Scale bar is 500 nm. Boxplots of force distribution values in air between unmodified AFM tip and CNCs, GM and XYL films (b), PP and PBS surfaces (c). RH is fixed at  $45 \pm 0.3$ . Boxplot legend: dot = mean, line = median. Values with different letters (a, b, c) are significantly different at  $p < 0.05$  according to ANOVA. Cohen's d effect size is indicated between the means in pairs.