Supporting Information

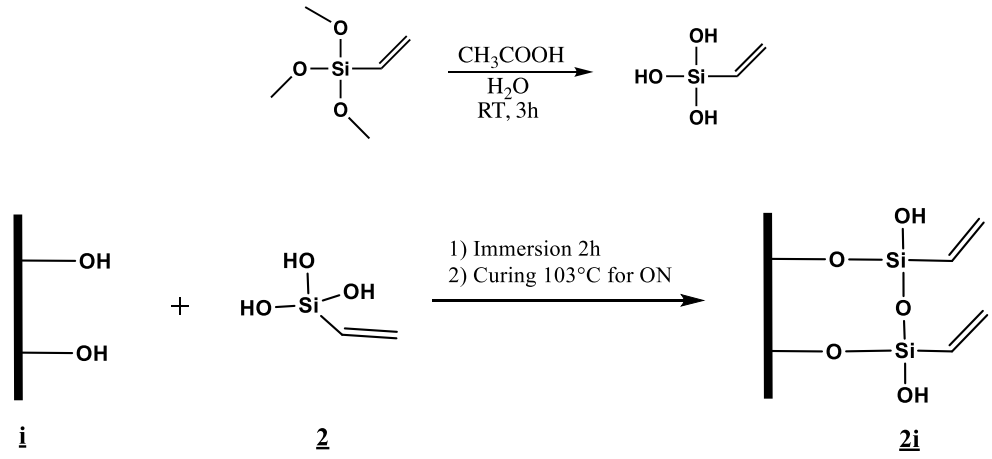
A straightforward thiol-ene click reaction to modify lignocellulosic scaffolds in water

S. Kostić,[a,b] J. K. Berg,[a,b] K. Casdorff,[a,b] V. Merk,[a,b] I. Burgert[a,b] and E. Cabane*[a,b]

[a.] Wood Materials Science, ETH Zürich, Stefano-Franscini-Platz 3, CH-8093 Zürich, Switzerland. E-Mail: cabanee@ethz.ch
[b.] Applied Wood Materials, EMPA – Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.

Chemical Procedure

1. VMTS hydrolysis and condensation



1.1. Chemicals set for 5 specimen (20x20mm rotary-cut beech veneers)

	CAS-NR.	M [g/mol]	m [g]	n [mmol]	ρ [g/ml]	V [ml]
VTMS	78-10-4	208.33	2.79	13.43	0.933	3
Acetic Acid	64-19-7	60.05	1.049	17.48	1.049	1
H_2O		18.01	25			25

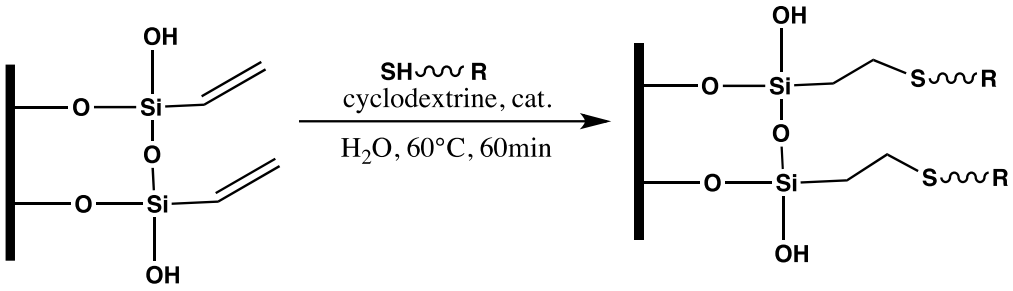
1.2. Procedure

VTMS was hydrolysed prior to impregnation for 3h at room temperature followed by immersion of the wood specimen for 120 min. The specimen were left to dry at room temperature followed by curing at 103°C for overnight

Weight Percent Gain (WPG): $\frac{(m_{mod}-m_{o.d})}{m_{o.d}} \times \mathbf{100}(\%) = 8\%$

Where m_{mod} is the mass of the modified sample, and $m_{o.d.}$ is the dry mass of the initial untreated sample.

2. Grafting to of the thiols with aliphatic functionalities



2.1. Chemicals set for 5 specimen (20x20mm veneers)

	CAS-NR.	M [g/mol]	m [g]	n [mmol]	ρ [g/ml]	V [ml]
1-Butanethiol	109-79-5	90.19	0.45	5	0.842	0.530
Beta Cyclodextrine	7585-39-9	1134.98	1.138	1	-	-
Acetone	67-64-1	58.08	0.791	13.6	0.791	1

2.2. Procedure

Beta Cyclodextrine was suspended in 15ml H_2O, warmed up to 60°C, and kept at this temperature until it was dissolved. The thiol was prepared with 1ml of acetone and added dropwise to the warm sugar solution. After 5min at 60°C, the reaction was allowed to cool down to room temperature followed by the addition of the wood specimen. It was kept in solution for 60min then rinsed with water/methanol and washed for 3 days in water/methanol to get rid of the non-reacted thiols. The specimen was air dried then kept at 65°C till constant mass was reached.

Weight Percent Gain (WPG) (overall): 10%

Characterization

Fourier transform infrared (FTIR) spectroscopy
Wood veneers were used directly for the measurements. Spectra were acquired on a Bruker Tensor 27 equipped with an ATR module. Spectra were baseline-corrected, smoothed in the OPUS software and plotted in OriginPro 9.1.

Scanning electron microscopy (SEM)
The treated veneer specimens were gold-sputtered prior to measurement. A FEI Quanta 600 probe in the low-vacuum mode (0.53 Torr) and driven at an accelerating voltage of 20 kV equipped with a backscattered electron and secondary electron detector was used.

Energy-dispersive X-ray spectroscopy (EDX)
Elemental analysis was performed on the very same specimen by in situ analysis, using the same experimental conditions for data acquisition. The accelerating voltage was 20kV with a recording time of 20 minutes.

Contact Angle (CA) measurement
CA was measured on veneers by a SCA 20 Dataphysics device in longitudinal x radial face. Distilled water droplets of 10.5 µl were placed onto the wood surface and images were taken at a frequency of 5 minutes for an overall time of 60 minutes. The CA evolution was analysed by the device software.
Sliding angles were measured by tilting the sample. The minimum angle at which the water drop rolls off the surface was taken as the SA.
The contact angle hysteresis was measured with the sessile drop method (advancing sate generated by increasing the droplet volume, and receding state by a decrease in the drop volume).

Atomic Force Microscopy (AFM)
The treated specimens were directly measured at a JPK NanoWizard4 in Quantitative Imaging mode (QI^{TM}) andcontrolled climatic conditions (temperature 20 °C, humidity 65 %) with a force modulation cantilever (Multi75, Budget Sensors, tip radius 10 nm). The set point was 6 nN, z-length 200 nm, pixel time 10 ms, 256 x256 pixels, extended speed 50 m/s, extended sample rate 75 kHz, size: 2x2 µm, overview 5x5 µm, close-up 0.5x0.5 µm. The received FD curves were batch-analyzed in the JPK image processing software (JPK Instruments AG), with the cantilever being calibrated based on the thermal noise method.

Abrasion tests

Scratch Test
A 200g weight was placed on the modified veneer (5 kPa), and the wood surface was rubbed against the sandpaper (1500 mesh) and moved for 25 cm along a ruler. One movement is defined as one cycle, and totally ten cycles were conducted. The contact angle was measured after 1, 5, and 10 cycles.

Water Jet Test
The coated veneer samples were exposed to a water jet at a distance of 30 cm. The water pressure was 35 kPa acting on the surface. The veneer was placed under the water jet for 10 seconds, which is defined as one cycle. The test consists of ten cycles. The contact angle was measured after 1, 5, and 10 cycles.

Scotch Tape Test
A scotch tape band was applied on the modified veneer surface, and a 500g weight was placed on top. After 5 minutes, the scotch tape was removed. This is defined as one cycle, and a total of ten cycles were conducted. The contact angle was measured after 1, 5, and 10 cycles.

AFM Results

The wood surface is very uneven: the amplitude of peaks and valleys is extreme, and the cantilever cannot reach all depth or heights on a rough wood surface. The cell wall regions on a veneer cut are damaged by the wood cutting process, and are therefore extremely rough, with large height differences. This is shown in the AFM image provided below. As opposed to the cell wall region, the lumen is a flat surface (at the microscale), that is well suited for an AFM cantilever, yielding clearer images. The characterization of nano- or micro-sized new structures is therefore easier in the lumen area. To obtain the best data and to be able to properly compare our results, we decided to measure in the lumen, rather than on the cut cell wall.

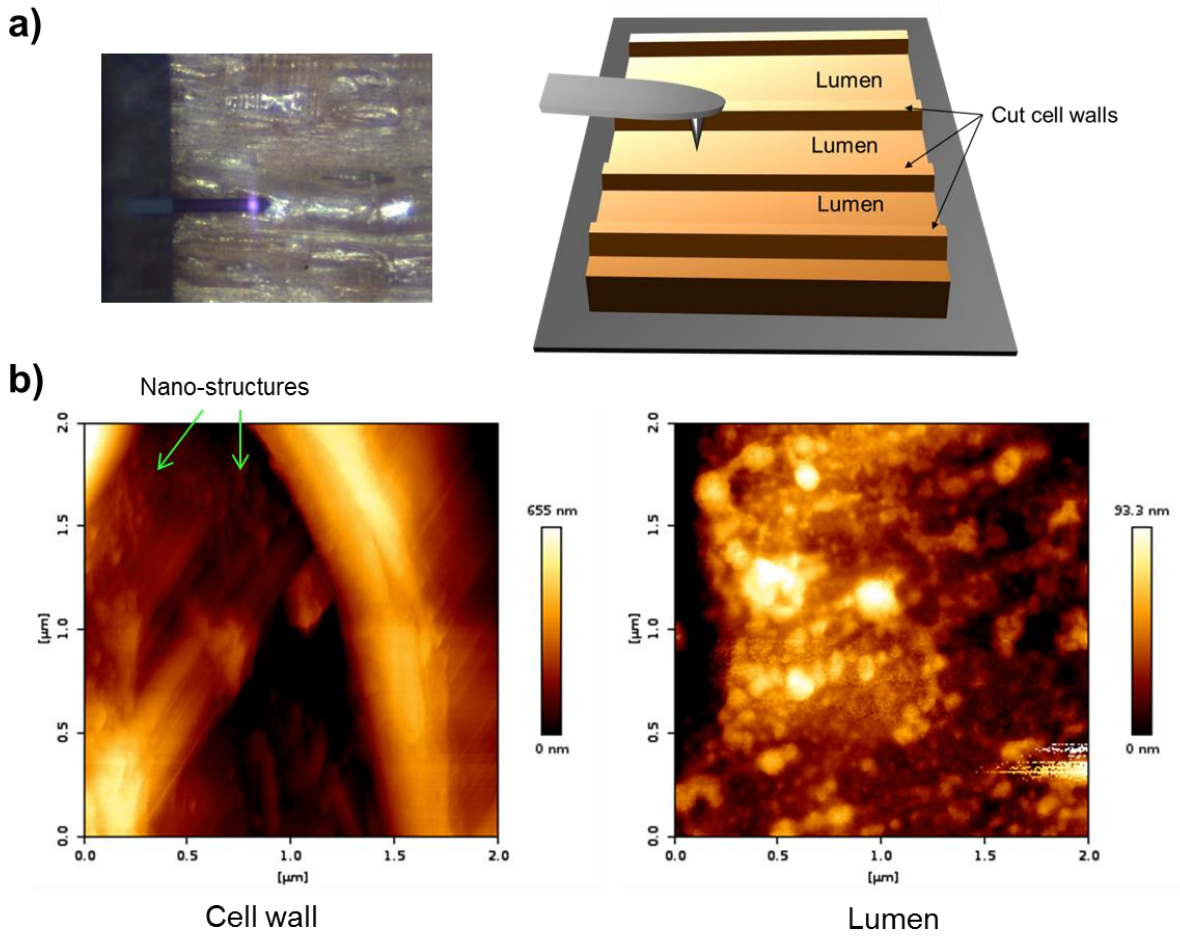


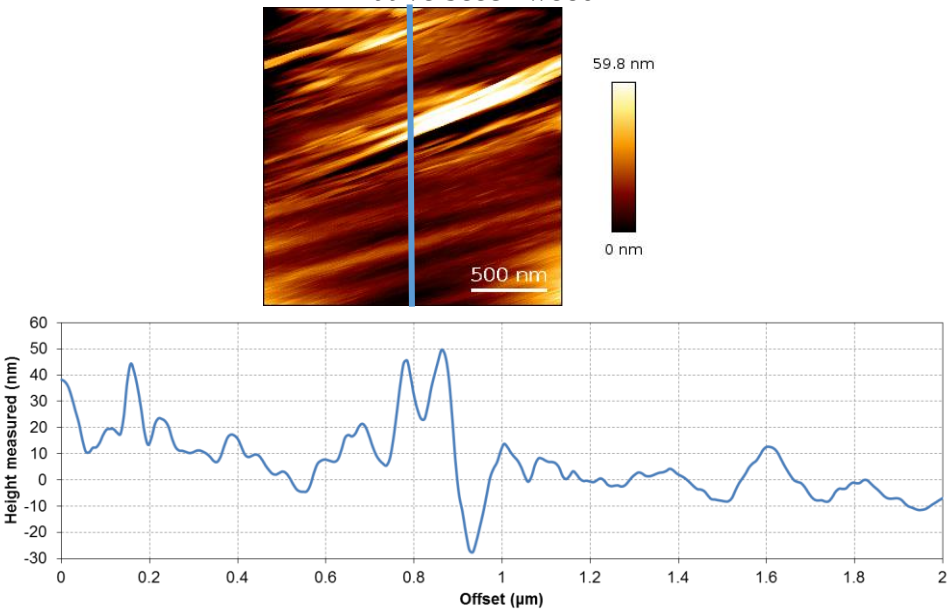
Figure S1: AFM measurements in the lumen and cut cell wall regions of the beech wood surface. a) optical microscopy image and scheme describing the position of the cantilever over the lumen of an open vessel, for optimum measurement conditions. b) AFM images from measurement on cell wall and lumen areas. Although nanostructures can be observed in

the cell wall image, they are better visualized on the lumen mapping. Please not in relation to the optical microscopy image, the AFM images are tilted clockwise by 90°.

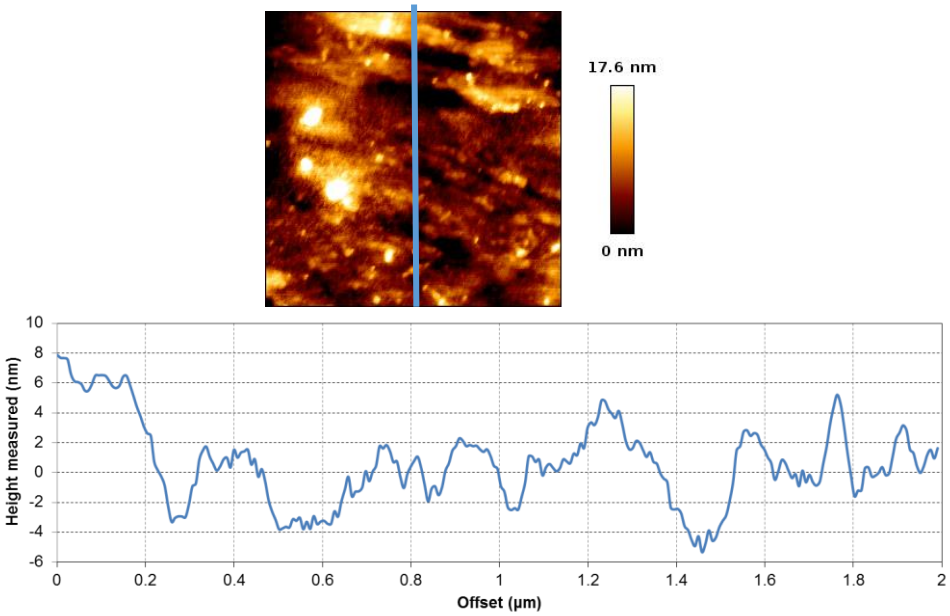
Table S1: roughness values from wood surfaces, averaged over the surfaces shown in Figure S1, lumen area. S_a, arithmetic mean height; S_q, root mean square height; S_t total height of the surface profile.

	Unmodified Wood Specimen	**VTMS Sol-Gel Treatment**	**W-SC8 After Click-Reaction**
S_a (nm)	6.2	2.8	18.3
S_q (nm)	8.3	4.0	23.3
S_t (nm)	89.6	51.4	176.5

Native beech wood



W-VTMS



W-SC8

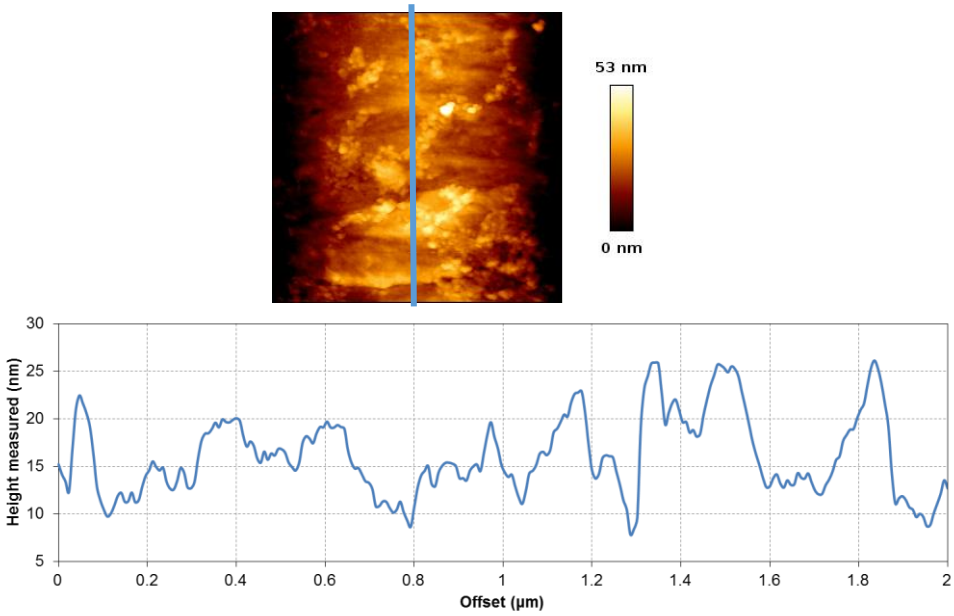
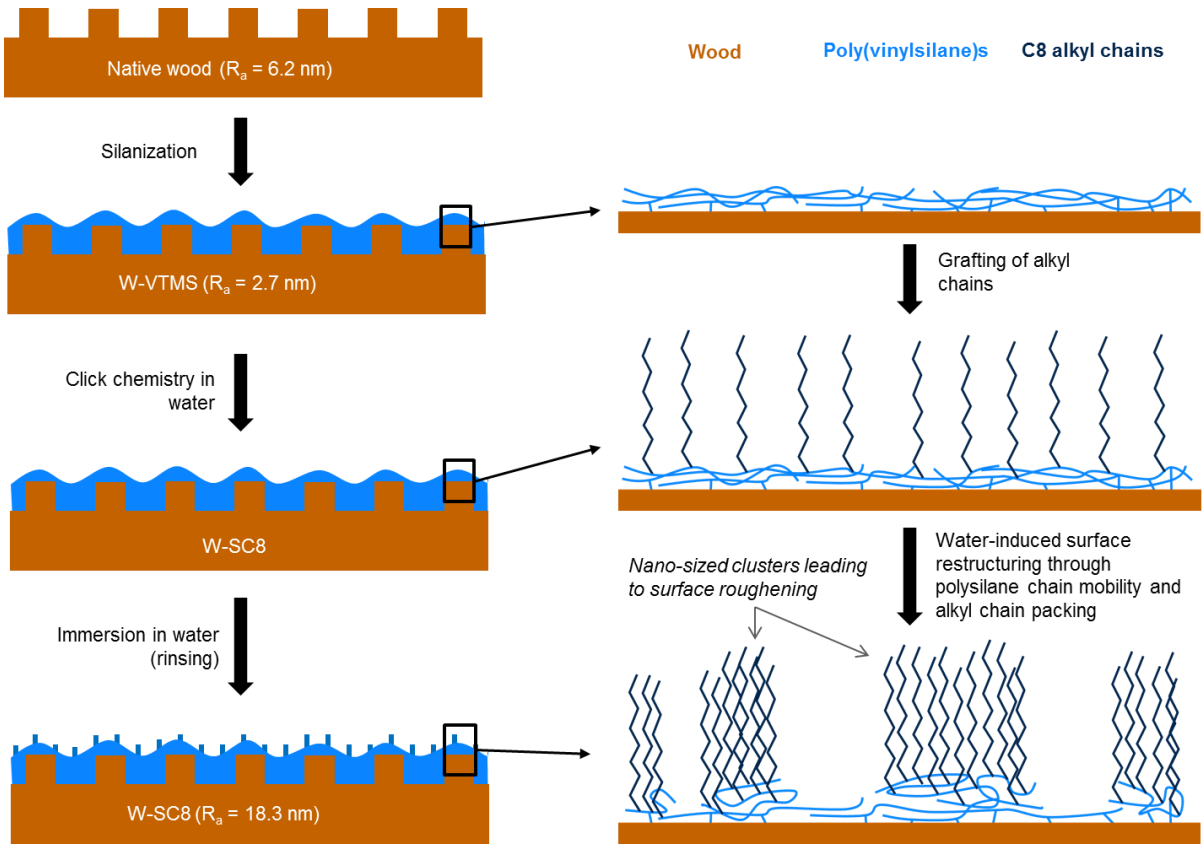


Figure S2: AFM height profiles to better visualize roughness.



Scheme S1: scheme illustrating the hypothesis of a water-induced surface restructuring.

Table S2: contact angle values for abrasion tests after 1, 5 and 10 cycles.

	Test cycles	Water jet test	Scratch test	Scotch tape test
W-VTMS	1	119.1 ± 0.1	115.4 ± 0.3	119.3 ± 0.1
	5	115.5 ± 0.2	112.0 ± 0.3	118.5 ± 0.1
	10	110.4 ± 0.3	96.7 ± 0.3	111.5 ± 0.2
W-SC4	1	125.5 ± 0.2	123.5 ± 0.1	122.5 ± 0.1
	5	124.4 ± 0.1	120.4 ± 0.1	120.4 ± 0.1
	10	123.8 ± 0.1	118.3 ± 0.1	118.5 ± 0.1
W-SC6	1	133.2 ± 0.1	130.6 ± 0.1	135.2 ±0.1
	5	130.1 ± 0.2	128.7 ± 0.1	132.8 ± 0.1
	10	132.5 ± 0.1	125.3 ± 0.1	129.5 ± 0.1
W-SC8	1	162.6 ± 0.1	163.5 ± 0.1	162.8 ± 0.1
	5	162.4 ± 0.1	160.5 ± 0.1	161.6 ± 0.1
	10	162.4 ± 0.1	155.7 ± 0.1	157.4 ± 0.2