

## Electronic Supplementary Information

### Tailoring water stability of cellulose nanopaper by surface functionalization

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#### Optical Microscopy

Avicel PH-10.1 microparticles were observed at different magnifications with a phase contrast microscope (Leica DM III, Leica Microsystems Srl, Milan, Italy); at least 15 digital images per sample were acquired through a CCD camera (Leica DC100, Leica Microsystems, Germany; Meyer Instruments, Houston, TX, USA) at different magnifications. Images were analysed with the Image J image analysis software (National Institute of Health, New York, NY, USA) to evaluate the average diameter.

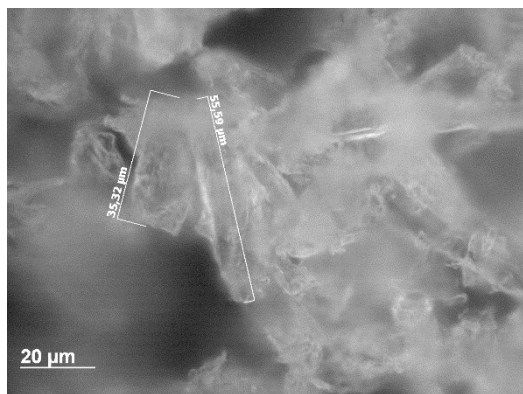
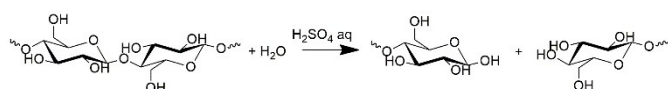


Figure S1. Avicel PH-10.1

#### Acid hydrolysis of Avicel: screening of reaction conditions



**Scheme 1.** Acid hydrolysis of microcrystalline cellulose carried out with aqueous sulfuric acid.

The acid hydrolysis was carried out in H<sub>2</sub>SO<sub>4</sub>: deionized water 1:1 v/v. A temperature and reaction time screening was performed to identify the best reaction conditions leading to maximized yield in CNC4000. The results of this preliminary screening are reported in the Table 1 and Scheme 1 and are in agreement with the previous studies by Loelovich<sup>1</sup> and by Dong<sup>2</sup>.

**Table S1.** Screening of acid hydrolysis conditions

Entry	Reaction Temperature [°C]	Reaction time [min]	Reaction yield <sup>a</sup>
1	40	30	29
2	40	60	42
3	45	60	42
4	45	80	53
5	90	30	0

<sup>a</sup> Reaction yield is referred to the nanocrystals fraction **CNC4000**.

When the reaction was performed at 45°C for 80 minutes, the yield in the CNC4000 fraction was maximized. The results evidence that the parameter having more influence on the yield at moderate temperatures is the reaction time: at 45 °C extension of the reaction time from 60 to 80 minutes increases the yield in the fraction CNC4000 from 42 to 53%. Conversely at much higher temperatures, for instance 90 °C, as in entry 5, the reaction is too fast, and brings to decomposition of the starting material, with formation of a black sludge, that probably originates from acid-activated degradation processes of the crystalline structure.

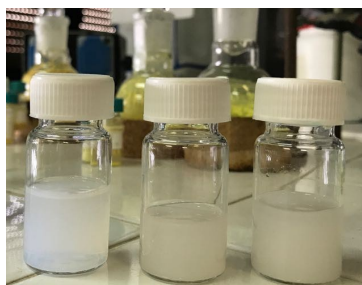


Figure S2. Aspect of CNC4000 (left), CNC3000 (middle) and CNC2000 (right) suspensions.

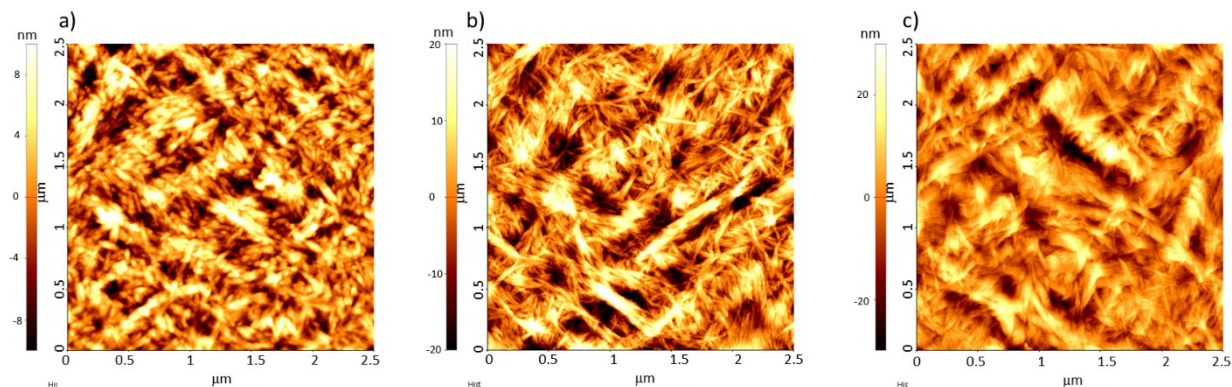


Figure S3. Tapping-mode 2.5x2.5 μm<sup>2</sup> AFM topographies of films of a) CNC4000; b) CNC3000; c) CNC2000 deposited by solution casting from water suspensions on quartz 1x1cm<sup>2</sup> glasses.

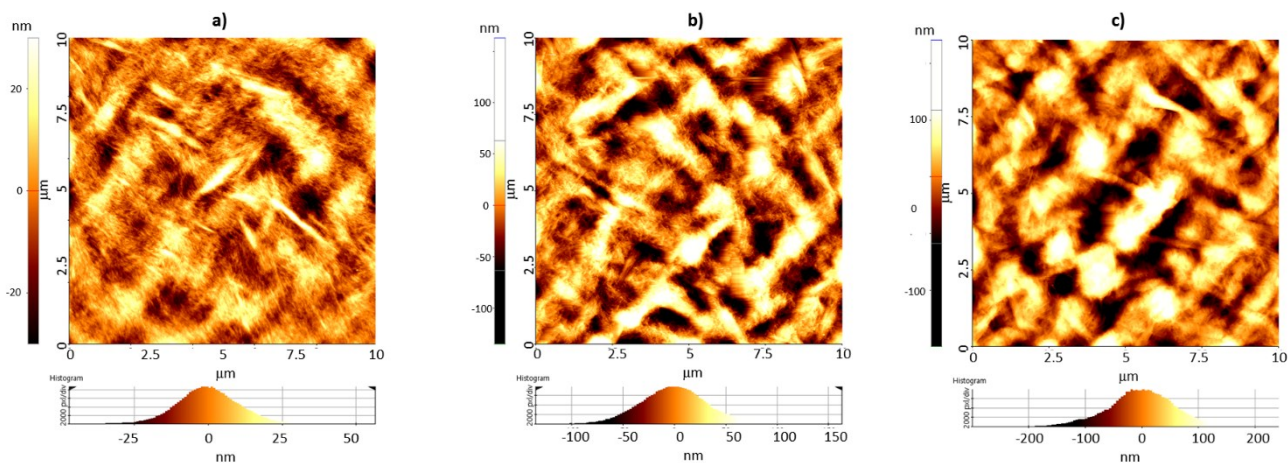


Figure S4. Large area 10x10 μm<sup>2</sup> AFM topographies (top panels) and heights histograms (bottom) on drop cast a) CNC4000, b) CNC3000 and c) CNC2000 fractions.

Table S2. Root mean square roughness of the topographies reported in Figure S3.

Aliquot	RMS [nm]
CNC4000	7.6±1.4
CNC3000	23±9
CNC2000	48±4

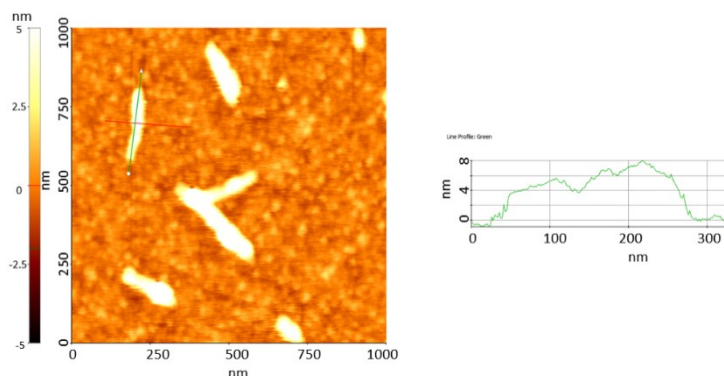


Figure S5. 1000x1000 nm<sup>2</sup> tapping mode AFM topography acquired on CNC4000 fraction deposited on diluted solution on quartz glass (right) and line profile measured on a single nanocrystal (left).



Figure S6. Left: a CNP free-standing film. Right: transmittance spectrum of CNP.

Table S3. Screening of the surface hydrophobization reaction conditions<sup>a</sup>

Entry	Lauroyl Chloride/nanocellulose molar ratio	Pyridine/nanocellulose molar ratio	Reaction time [h]	Notes
1	1.5	140	96	Reaction results in nanopaper brittleness
2	15	140	1	Reaction results in nanopaper brittleness
3	10	15	1	
4	5	7.5	1.30	

<sup>a</sup> All reactions were carried out in a nitrogen filled glove-box with dry reagents, at room temperature and in dichloromethane as solvent. The procedures were all successful from the point of view of functionalization, but the use of a high amount of pyridine apparently compromised the flexibility of nanopaper.

Table S4. Elemental combustion analyses of Avicel and of CNP before and after chemical modification with lauroyl chloride and pyridine, according to the conditions reported in table S3 entry 3, measured at different reaction times: 0, 10, 30, 60 and 120 minutes. Elemental analyses were run twice.

Entry	Reaction time [min]	N [%]	C [%]	H [%]	O [%] <sup>a</sup>	DS <sup>b</sup>
1	Avicel <sup>c</sup>	0.54	41.94	7.66	49.86	0
2	0 <sup>d</sup>	1.00	39.85	8.99	50.16	0
3	10	0.76	40.79	8.92	49.53	0.011
4	30	1.05	41.89	9.01	48.05	0.023
5	60	1.50	42.84	9.18	46.48	0.034
6	120	1.31	41.46	8.92	48.31	0.018

<sup>a</sup> Calculated. <sup>b</sup> Calculated from C [%] attributing the mass increase per gram of CNP with respect to entry 2 to C<sub>12</sub> functionalization. <sup>c</sup> According to the provider, Avicel pH 10.1 has a water content of approximately 5% w/w. In addition, we find nitrogen impurities. These impurities are present in our CNP derivatives as well. <sup>d</sup> In our CNP we calculate a water content of approximately 8% w/w.

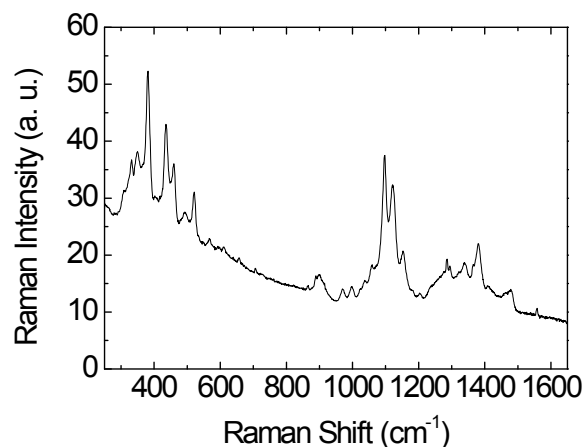


Figure S7. Raman spectrum recorded for Avicel powders. The value of the peak intensities ratio found in this spectrum is  $I_{380}/I_{1096}=1.1$

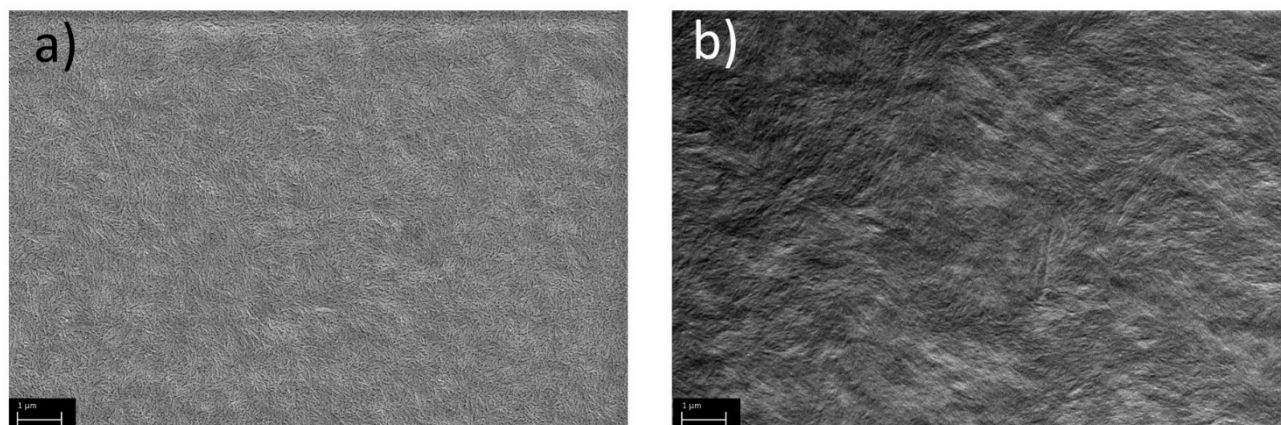


Figure S8. FE-SEM surface micrographs of a) CNP and b) C<sub>12</sub>-CNP (scale bar 1 μm).

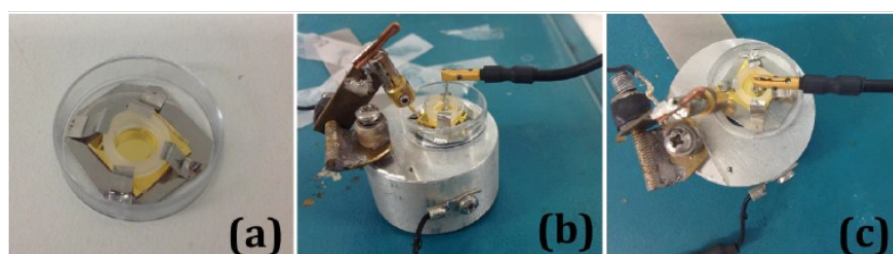


Figure S9. Electrochemical setup used for measuring the resistance of nanopaper to water permeation.

1. M. Ioelovich, *Nanosci. Nanotec.*, 2012, 2, 9.
2. Dong et al. *Cellulose*, 1998, 5, 19.
3. C. Vaca-Garcia, M. E. Borredon, A. Gaseto, *Cellulose*, 2001, 8, 225.